CHAPTER 6

RESIDUAL FUEL OILS

In order of economic importance of major oil products in the world, residual fuel oil is the third most important petroleum product after gasolines and gas oils. Nevertheless, residual fuel oils are largely the by-product of refineries that aim at maximizing the production of light and middle distillates. Material remaining after maximizing light and middle distillate production (i.e., atmospheric or vacuum resids) are blended with a minimum amount of distillates to produce salable fuel oils. Refineries generally aim at minimizing the production of fuel oil, the lowest valued petroleum product, to maximize their refining margins. In the early years of petroleum refining, atmospheric distillation residuum, known as long resid, was sold as residual fuel oil without any further processing. As the cost of crude oil increased, it was realized that the atmospheric residue of crude distillation contained valuable heavy distillate that could be further cracked in fluid catalytic cracking units (FCCUs) and hydrocracker units to make more gasoline and middle distillates and thus further decrease fuel oil production. The average refinery production of fuel oil has come down from 20 vol % (percentage by volume) of the crude oil 20 years ago to approximately 14 vol % at present. In 2005, about 80 million barrels per day crude oil was distilled and processed into petroleum products throughout the world, producing 12 million barrels per day or fuel oil. As a result of the increased conversion of heavy distillates into lighter products in refineries, the quality of the fuel oil produced is decreasing, with a higher concentration of sulfur and impurities, higher density and higher molecular weight.

USES OF RESIDUAL FUELS

Residual fuel oil is a bottom-of-the-barrel product blended from the vacuum residue of crude oil distillation, and the residual products from various refining processes, to make cheapest possible fuel.

It is typically a dark viscous liquid of a complex mixture of hydrocarbons, and its composition can vary a great deal depending on the crude processed and the refinery's complexity. Viscosity ranges from 450 cSt to 180 cSt at 120°F. The flash point is typically above 150°F. Since residual fuel oil is thick and viscous, it must be heated before use to reduce its viscosity for easy combustion.

Residual fuels are widely used in industrial applications requiring heat generation. They are also used as fuel for steam generation in power plants and in the boiler "lighting up" facility in every coal-fired power plant where they initiate the combustion process. Among other uses are open hearth furnaces, soaking pits in the iron and steel industry, rotary kilns in cement and lime industry, and for firing heaters for petroleum refining and the manufacture of petrochemicals. A petroleum refinery may consume 8 to 10 percent of its throughput as liquid refinery fuel depending on the complexity of the process. Residual fuel oils are used in industries such as cement, glass, and paper. It is used as a feedstock in fertilizer manufacture where it generates hydrogen by a partial oxidation process.

The marine industry is the largest single consumer of residual fuels (bunker C fuel), consuming almost 33 percent of the world's total residual fuel oil production. Most of the fuel oil used by the world's merchant fleet and other naval ships is residual fuel oil.

DIESEL ENGINES

Sea transport is an energy efficient means of moving freight and carries 90 percent of the global trade (tons-km). The shipping industry generally uses residual fuel oil for economic reasons. The world's shipping fleet is powered mainly by slow and medium-speed diesel engines. A smaller percentage use marine diesel. It is estimated that more than 95 percent of the world's shipping fleet is powered by slow speed (less than 300 r/min) and medium speed (300 to 1000 r/min) diesel engines. Unlike high speed (more than 1000 r/min) diesel engines that use automotive diesel as fuel, low and medium-speed diesel engines use residual fuel oils. The shipping industry uses lower quality residual fuel oil for economic reasons. A large merchant ship powered by diesel engines may consume 150 tons/day heavy fuel oil and may typically carry 3000 to 4000 ton of fuel oil in tanks. Two-stroke low-speed diesel engines are capable of burning the lowest and cheapest quality commercially available residual fuels. The life of diesel engines is inversely proportional to its speed. Reducing the speed of an engine to half is known to increase engine life four times. Slow-speed diesel engines are capable of attaining efficiencies of more than 50 percent.

STEAM BOILERS

Residual fuels are widely used both in stationary and mobile steam boilers of all sizes. No particular problem is encountered in its burning. However, in high-pressure steam boilers that also operate at high temperatures, the fouling of boiler tubes may be encountered due to the presence of vanadium and other metallic compounds in the fuel oil ash. Power generation companies use slow-speed diesel engines in preference to medium-speed diesel engines and steam turbines because of their better efficiencies and longer engine life.

GAS TURBINES

A gas turbine extracts energy from the flow of hot gases produced by the combustion of gas or fuel oil. It has an upstream air compressor coupled to a downstream turbine and a combustion chamber in between. Compressed air is mixed with fuel and ignited in the combustion chamber. The resulting gases pass over the turbine blades, spinning the turbine and mechanically powering the compressor. Finally, gases pass through the nozzle, generating additional thrust, and pass to the atmosphere. Gas turbines are used on high-speed naval boats, ships, locomotives, and in small power plants. Gas turbines have very high power-to-weight ratio compared with reciprocating engines but have a high initial cost. The inherent simplicity of gas turbines makes this type of power plant attractive for many applications. A simple cycle gas turbine for power generation requires a smaller capital investment and actual construction can take as little as a few weeks, compared with years for base power plants. Gas turbines can be turned off and on within minutes, supplying power during peak demand. However, simple cycle gas turbines are less efficient than combined cycle turbines; they are generally used as peaking power plants.

RESIDUAL FUEL OIL SPECIFICATIONS

Marketing specifications have been established by a number of agencies to assure the satisfactory operation of industrial and marine equipment utilizing heavy fuel oils. These specifications include ISO-8217, ASTM D-396, BS 2869, and CIMAC (Conseil International des Machine a Combutiou). Table 6-1 shows ISO-8217 specifications.

TABLE 6-1 Requirement of Marine Residual Fuel Oils (ISO 8217)

Parameter	Units	Limts	RMA 30	RMB 30	RMD 80	RME 80	RMF 80	RMG 380	RMH 380	RMK 380	RMH 700	RMK 700
Density	kg/m^3	Max.	960	975	980	991	991	991	991	1010	991	1010
Kinematic viscosity	cSt, 50°C	Max.	30	30	80	180	180	380	380	380	700	700
Flash point	°C	Min.	60	60	60	60	60	60	60	60	60	60
Pour point												
Winter quality	°C	Max.	0	24	30	30	30	30	30	30	30	30
Summer quality	°C	Max.	6	24	30	30	30	30	30	30	30	30
Carbon residue	Mass %	Max.	10	10	14	15	20	18	22	22	22	22
Ash	Mass %	Max.	0.1	0.1	0.1	0.1	0.15	0.15	0.15	0.15	0.15	0.15
Water	V/V %	Max.	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	Mass %	Max.	3.5	3.5	4	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Vanadium	mg/kg	Max.	150	150	350	200	500	300	600	600	600	600
Total sediment	Mass %	Max.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Aluminum and silicon	mg/kg	Max.	80	80	80	80	80	80	80	80	80	80

Marine Fuel Oils

There are two basic types of fuel oils; distillate and residual. A third type of fuel oil is a mixture of the two basic types, commonly known as "intermediate" (Table 6-2). Distillate fuel oils are made of diesel fractions of crude oil fractionation, whereas residuals are blended from distillation residue such as atmospheric or vacuum bottoms with diesel boiling range cutter stock to reduce their viscosity to specification. In marine industry, distillate fuels are called gas oil or marine gas oil. For example, as per ISO 8217 specifications, marine fuel grades DMX, DMA, DMB, DMC (Table 6-3) are marine gas oils. Residual fuels are called marine fuel oils or residual fuel oils (Table 6-1). Specifications for marine fuels use the first letter "D," signifying "distillate fuel," or "R," signifying "residual fuels." The second letter "M" signifies "marine fuel." Thus DMA is marine distillate fuel A. Residual fuels are designated by letters A to H, K and L, and a number signifying viscosity limit. For example, RMA -30 is "Residual Marine Fuel A" with a maximum viscosity of 30 cSt at 50°C. One important difference between land-based distillate fuels and marine fuels from an environmental perspective is sulfur content. Land-based fuels are generally required by environmental regulations to have lower sulfur levels than equivalent marine fuels.

DMA is a common fuel for tugboats, fishing boats, crew boats, drilling rugs, and ferry boats. Oceangoing ships that take residual fuel oil bunker also take distillate fuels for use in auxiliary engines and sometimes in port areas. The most common residual fuels are grades with a kinematic viscosity of 180 and 380 cSt at 122°F. All marine fuels for safety and insurance reasons are required to have a minimum flash of 140°F (60°C).

TABLE 6-2 Black Diesel for Industrial and Bunkering Uses

Property	Units	Limiting specification
Gravity	API	28.0–33.5
Carbon residue	Wt %, Max.	2.0
Sulfur	Wt %, Max.	1.6
Viscosity	cSt, 100°F	3.3–9.0

1. No visbroken residuum or cracked cutter may be included in the blend.
2. Normal blending components are straight run vacuum resid and light and heavy diesel.
3. Normal blending is to maximum viscosity and after meeting this requirement to the following specifications; (a) maximum carbon residue and (b) maximum SG × sulfur.

TABLE 6-3 Requirements of Marine Distillate Fuels

Parameter	Units	Limits	DMX	DMA	DMB	DMC
Density, 15°C	kg/m^3	Max.		890	900	920
Kinematic viscosity	cSt, 40°C	Max.	5.5	6.0	11.0	14.0
		Min.	1.4	1.5		
Water	V/V %	Max.			0.3	0.3
Sulfur	Mass %	Max.	1.0	1.5	2.0	2.0
Aluminum and silicon	mg/kg	Max.				25
Flash point	°C	Min.	43	60	60	60
Pour point						
Winter quality	°C	Max.		–6	0	0
Summer quality	°C	Max.		0	6	6
Cloud point	°C	Max.	–16			
Cetane index		Min.	45	40	35	

PROPERTIES OF RESIDUAL FUEL OILS

Typical properties of commercial residual fuel oils used in industry are listed in Table 6-4. By definition, residual fuel oils are the product remaining after the distillates have been removed from the crude oil and as such have high concentration of impurities contained in crude oil such as sulfur and metals.

Viscosity

Viscosity is not a measure of residual fuel oil quality, but it is an important specification from a fuel oil handling point of view. Viscosities of residual fuel oils for marine industry range from 80 to 700 cSt at 122°F. Refineries generally produce two grades of residual fuel oils with viscosities of 180 and 380 cSt at 122°F. Heavy fuel oils are heated to approximately 300°F to reach the correct injection viscosity of 10 to 15 cSt in the case of marine diesel engines. Fuel oil heating is also required for direct burning in boilers, in order to get the proper atomization of fuel.

Sulfur

Sulfur content of the residual fuel depends on the vacuum resid sulfur content, which in turn depends on crude processed and refinery processing configuration. Because resid desulfurization processes

TABLE 6-4 Residual Fuel Oil Specifications

Property	Units	1	2	3	4	5	6
Ash	Mass %, Max.	0.1	0.1	0.1	0.1	0.1	0.25
Carbon residue micro	Mass %	15.0			15.0	15.0	20.0
Density, 15°C	kg/L, Max.	0.980	0.980	0.991	0.990	0.985	0.990
Elements, trace	mg/kg, Max.						
Vanadium		55				550	
Aluminum						30	
Sodium		25					
Explosiveness	Vol %, Max.				50		
Flash point, Penskey Martin							
Closed cup	°C, Min.	66	66	66	66	66	60
Pour point	°C, Max.	24	21	–9	20	12	21
Fluidity			Fluid at 0°C				Fluid at 15°C
Pumpability, viscosity, 9°C	Poise, Max.			20			
Sediment by extraction	Mass %, Max.	0.1	0.12		0.12	0.15	
Stability							
ASTM spot test rating	Max.	2	2	2	2	2	2
Compatibility							
ASTM spot test rating	Max.				2		
Sulfur	Mass %, Max.	2.8	3.5	3.5	3.5	3.5	4.00
Thermal stability rating					No. 1 tube		
Thermal value gross	MJ/kg, min.	43.03					
	Btu/lb					18300	
Total sediment	Mass %, Max.	0.15	0.15	0.15	0.15	0.15	
Viscosity, kinematic, 50°C	cSt, Max.	180	80	75	48	180	380
	cSt, Min.			11.8			
Water by distillation	Vol %, Max.	0.5	0.5	0.5	0.5	0.5	
Water and sediment by Centrifuge	Vol %, Max.						0.6

are expensive, any further processing of resid to reduce sulfur would add to the cost of the residual fuel. Sulfur content of most residual fuel oils is between 3.5 and 4.5 wt % (percentage by weight) due to the high sulfur content of vacuum resids, which typically constitutes 60 to 70 percent of blended fuel oil. However, the sulfur in residual fuel oils pose a serious pollution problem. In many land areas where pollution is critical, regulations are progressively prohibiting the use of high-sulfur fuel oils and lowering the fuel oil sulfur level to 1.5 wt % maximum. In industrial boilers, use of high-sulfur fuel oils can lead to excessive corrosion. In steelmaking operations, a portion of the sulfur present in fuel is absorbed in steel, adversely affecting its quality. Flue gas desulfurization (FGD) has been used since the 1930s in shore-based facilities such as power plants to reduce sulfur emissions. In the FGD process, flue gas is scrubbed with an alkaline medium such as a lime solution to neutralize sulfur oxides. But the process produces large amounts of solid waste such as calcium sulfate, which present a disposal problem.

Sulfur emissions from ships' exhaust constitute a significant proportion of total sulfur global sulfur emissions. To control sulfur emissions from ships, MARPOL (the international convention for prevention of pollution from ships) adopted MARPOL[1] annexe VI, which came into effect on May 19, 2005. This convention includes a global upper limit of 4.5 percent sulfur for fuel oils used as fuel in ships. Annex VI contains provisions allowing for special SOx Emission Control Areas (SECAS) such as the Baltic Sea to be established with more stringent controls on sulfur emissions. In these areas the sulfur content of fuel oil used on board ships must not exceed 1.5 wt %. Alternatively, ships must be equipped with an exhaust gas cleaning system to limit SOx emissions.

Seawater scrubbing is emerging as the process of choice for onboard cleanup of sulfur emissions from engine exhaust gases. It can achieve emission reductions equivalent to using 0.1 percent sulfur diesel oil. Seawater scrubbing also removes soot, ash, and unburned oil.

In seawater scrubbing,[2] the flue gases are washed with seawater. Seawater is alkaline (typical pH, 8.3) due to the presence of bicarbonates of various metals. Sulfur oxides present in exhaust gases are thus neutralized and converted to water-soluble sulfites and sulfates. The effluent scrubbing water is highly acidic (pH 3). It is next processed to remove potentially harmful components, diluted with large quantity of sea water, and discharged back to the sea.

Ash Content

Compared with coal, residual fuel oils have a very low ash content and no ash-handling equipment is required. However, certain elements present in fuel oil ash may cause problems in furnaces where very high temperatures are encountered. Sodium and vanadium are particularly troublesome. The vanadium concentration of residual fuels varies quite widely. Vanadium comes from the vacuum resid component of fuel oil. Table 6-5 shows the vanadium and nickel content of some crude oils. Sodium may be present in crude or may come from seawater contamination of crude oil. Because sodium exists mainly as chloride or other water-soluble salts, it can be easily removed in the desalting operation carried out in the refinery. Sodium can be removed by water washing and centrifuging of fuel oil. Vanadium and sodium can cause corrosion and fouling of superheater tubes in high-pressure boilers, with high operating temperatures of 1200°F or above. Similarly, excessive corrosion and fouling of gas turbine blades may be encountered at temperatures of more than 1200°F. At a temperature below the fusion point of ash, there is relatively little corrosion in either boilers or gas

TABLE 6-5 Properties of Vacuum Resids from Various Crude Oils

Property	Units	Arab light	Arab heavy	Kuwait	Aghajari	Gash saran	Taching
Specific gravity		1.020	1.036	1.020	1.007	1.025	0.925
Carbon residue	Wt %	22.4	23.2	17.4	18.0	19.0	7.5
Asphaltene	Wt %	5.5	10.7	5.1	2.9	9.3	0.35
Sulfur	Wt %	4.1	5.1	5.15	3.56	3.3	0.2
Ni + V	mg/kg	87	190	110	228	430	10

turbines. At low operating temperatures, much of the ash passes out of the stack in the form of fly ash with little or no fouling. Thus where fuels with high vanadium must be used, the turbine or boiler operating temperature is lowered below the fusion temperature of ash, typically 1100 to 1200°F. Vanadium salts are converted to vanadium oxide (V_2O_5) during the combustion process, which deposits on furnace tubes and refractory and causes further problems in the furnace operations such as:

- Severe metallurgical attack as temperature is elevated.
- Refractory attack through formation of eutectic (a low melting inorganic compound) on the surface of refractory, which at a critical temperature can destroy refractory.
- Because V_2O_5 is a catalyst for the conversion of SO_2 to SO_3, it can greatly increase the concentration of SO_3 in the stack gases, thus increasing sulfuric corrosion.

Aluminum and Silicon

Residual fuel oils blending use heavy aromatic cutters such as light and heavy cycle oils, decant oil ex fluid catalytic cracker unit. These cutters may contain suspended catalyst fines. Catalysts used in FCCUs and other cracking units are aluminum and silicon zeolites. The measurement of aluminum and silicon content of fuel oil provides an indication of the catalyst fines in fuel oil. In residual fuel oil, catalyst fines can cause significant abrasive wear of engine components such as fuel pumps, injectors, cylinders, and pistons. The centrifuging of marine residual fuel reduces catalyst fines to a safe levels before use in marine engines.

Total Sediment

Before heavy fuel oil blending can be used in a low-speed diesel engine, an essential condition is that it must be free of sediment. Total sediment is one of the key parameters that fuel oil is tested for to make sure it meets the required specification. Too much sediment can result in a gradual buildup of sludge, resulting in blocked filters, pipes, and purifiers. If this occurs, the fuel will not get through the engine and the ship may be disabled on the high seas with a potentially critical situation. Sediment present in residual fuel oils consists of both hydrocarbons and inorganic material. The hydrocarbon material is typically asphaltenes, which are more prevalent in fuels blended from cracked blend components such as visbroken tar. If sediment reaches the engine in a large quantity, it leads to several problems arising from the slow-burning characteristics of asphaltenes, resulting in delayed ignition. Formation of sludge by flocculation of asphaltenes is a time- and temperature-dependent process. Asphaltene separation does not occur in fuels blended from straight run blend components such as straight run vacuum residuum. Heavy fuel oil is centrifuged to reduce sediment to acceptable levels before its use in marine engines.

Density

Residual fuel oils generally have densities in the range of 985 to 991 kg/m^3 at 60°F. However, a small percentage of residual fuel oils may have density exceeding 991 kg/m^3. High density can affect the operation of centrifuge separators installed to separate water and solid particles. Traditional separators can remove water and solids from residual fuels up to 991 kg/m^3 density. In the case of higher density fuel oils, specially designed separators have to be used and separator feed rate and temperature have to be carefully adjusted to ensure the efficient reduction of water, catalyst fines, sodium, and sediment. In case of an accidental oil spill involving high specific gravity (more than 1.0) residual fuel oils, these oils tend to float low in water, making recovery using skimmers difficult. Also, sunken heavy oils may inflict significant damage to seabed resources, fish, and mariculture activities.

Ignition Quality

The operation of all internal combustion engines depends on the ignition quality of the fuel. For spark-ignited engines, the fuel ignition quality is termed as the octane number. For high-speed diesel engines used in automobiles, the fuel used is distillate fuel and the ignition quality is known as the cetane rating. The cetane rating cannot be used for low-speed diesel engines because these engines were not designed for residual fuels. For residual fuel oils used in low-speed diesel engines, an empirical index calculated Carbon aromaticity Index[3] (CCAI) is used. The CCAI is defined below (Fig. 6-1).

$$\text{CCAI} = D - 81 - 141^{*}\ \text{LOG}\left[\text{LOG}\ (V + 0.85)\right] - 483^{*}\ \text{LOG}\left[\frac{T + 273}{323}\right]$$

Where:

CCAI = Calculated carbon aromaticity index
D = Density of residual fuel oil, kg/m^3
V = Viscosity of fuel cSt at temp T.
T = Temperature of viscosity measurement °C

FIGURE 6-1 Calculated carbon aromaticity index (CCAI).

The CCAI normally has a value between 800 and 880. The lower the value, the better the ignition quality. Fuels with a CCAI value of more than 880 can present problems in engines due to poor ignition quality. Modern medium-speed engines tolerate CCAI values up to 870 to 875. Low-speed engines are more tolerant of higher CCAI values. Limits of viscosity and density in international maritime fuel specifications in them provide control of ignition quality for residual fuel grades. For example a 380 cSt (at 122°F) residual fuel at a maximum specification density of 991 kg/m^3 will have a CCAI of 852, whereas a 180 cSt viscosity (122°F) fuel oil with the same density has a CCAI of 861. Ignition quality improves with increasing viscosity and decreasing density.

Ignition quality of heavy fuel oils can vary a lot depending on its blend components. Low ignition quality can cause problems at engine start and during low load operations, ignition delay, and it may also cause fast pressure rise and very high maximum pressure and engine deposits on the piston top, exhaust valves, and, in the case of turbines, on turbine nozzle ring and blades.

Water

The water content of heavy fuel oils varies widely between 0.5 and 1.0 v/v %. Water may come from several different sources. Also, water can be either fresh or more generally saline. It can also be from condensation in the storage tanks. If the water is salt free and well emulsified in heavy fuel oil, the effective energy content decreases with increasing water content, leading to increasing fuel consumption. If heavy fuel is contaminated with seawater, the chlorine in the salt can cause corrosion in fuel handling and fuel injection equipment. The effect of sodium that originates from salt is in its combination with vanadium metal. During combustion, vanadium sodium salts such as sodium vandate are formed that forms deposits on the exhaust valve and in the exhaust gas system and turbocharger.

Heat of Combustion

In almost every application, fuel oil is burned to produce heat. The heat of combustion is a measure of energy available from the burning of a fixed mass of fuel. Calorific value is the most important property of fuel oils and used for comparing the economics of different fuel oils with alternative fuels such as gas or coal. Fuel oil price in term of dollars per million Btu is often used as a reference price for fixing the price of other forms of energy such as natural gas or coal.

The heat of combustion of liquid fuel can be determined in the laboratory by means of a bomb calorimeter (ASTM D-240). In this method, the heat of combustion is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion with the proper allowance for thermochemical and heat transfer corrections.

Gross Heat of Combustion

The gross heat of combustion of a liquid or solid hydrocarbon at constant volume is the quantity of heat liberated when a unit mass of fuel is burned in oxygen in an enclosure of constant volume, the product of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water with the initial temperature of fuel and oxygen and the final temperature of products at 25°C.

Net Heat of Combustion

The net heat of combustion at constant pressure is the quantity of heat liberated when a unit mass of fuel is burned in oxygen at a constant pressure of one atmosphere; the product of combustion is carbon dioxide, nitrogen, sulfur dioxide, and water, all in the gaseous state, with the initial temperature of fuel and oxygen and the final temperature of product of combustion at 25°C.

The laboratory determination of the heat of combustion is a laborious and time-consuming process. It has been found that the heat of combustion of pure hydrocarbons can be estimated fairly accurately from specific gravity and the hydrogen content of the fuel (Table 6-6) based on empirical correlations presented by Gutherie[4] (Fig. 6-2). Because commercial residual fuel oils contain an appreciable amount of water, sediment, and sulfur, it is necessary to correct the estimated values for the effect of these impurities.

TABLE 6-6 Heat of Combustion of Residual Fuel Oils

				Heat of combustion at constant pressure			
Api gravity	Specific gravity	Density lb/gal	% H_2	kcal/kg	Btu/lb	Btu/gal	mm Btu/bbl
0	1.0760	8.980	9.859	9471	17037	152945	6.424
1	1.0679	8.912	9.981	9501	17091	152278	6.396
2	1.0599	8.845	10.101	9531	17145	151610	6.368
3	1.0520	8.779	10.219	9560	17197	150940	6.339
4	1.0443	8.715	10.336	9588	17248	150270	6.311
5	1.0366	8.651	10.451	9616	17297	149599	6.283
6	1.0291	8.588	10.564	9643	17346	148928	6.255
7	1.0217	8.526	10.675	9669	17393	148257	6.227
8	1.0143	8.465	10.785	9695	17440	147587	6.199
9	1.0071	8.404	10.893	9720	17485	146917	6.171
10	1.0000	8.345	11.000	9745	17529	146248	6.142
11	0.9930	8.287	11.105	9769	17573	145580	6.114
12	0.9861	8.229	11.209	9793	17615	144914	6.086
13	0.9792	8.172	11.311	9816	17656	144249	6.058
14	0.9725	8.116	11.412	9838	17697	143586	6.031
15	0.9659	8.060	11.512	9860	17736	142925	6.003
16	0.9593	8.006	11.610	9882	17775	142266	5.975
17	0.9529	7.952	11.707	9903	17813	141609	5.948
18	0.9465	7.899	11.803	9923	17850	140954	5.920
19	0.9402	7.846	11.897	9943	17886	140302	5.893
20	0.9340	7.794	11.990	9963	17922	139652	5.865

$$Q_V = 12400 - 2100^* D^2$$

$$Q_P = Q_V - 50.45^* H$$

$$H = 26 - 15^* D$$

Where:

Q_V = Total heat of combustion at constant volume, KCAL/Kg

Q_P = Total heat of combustion at constant pressure, KCAL/Kg

D = Specific gravity of fuel at 15°/15°C

H = Hydrogen content, Wt % in hydrocarbon

Or

Heat of combustion (gross) in Btu/lb

$$= 57.9* \text{API} + (17687 - 23\ ^*\text{sulfur}\%)$$

FIGURE 6-2 Heat of combustion of residual fuel oils.

Pour Point (ASTM D 97)

The pour point is the lowest temperature expressed in multiple of 5°F or 3°C at which the movement of oil is observed. In this test, after preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for its flow characteristics. The lowest temperature at which the movement of oil is observed is recorded as the pour point. Most residual fuel oils are blended to have a maximum pour point of 86°F. The pour point requirement of fuel oils is fixed by the ambient condition of storage and handling.

Fluidity

The usefulness of the pour point test in relation to residual fuel oils is open to question, and the tendency to regard pour point as the limiting temperature at which fuel will flow can be misleading. Thus pour point test does not indicate what happens when oil is subjected to considerable pressure such as when flowing out of a storage tank under the gravity head. Failure to flow at pour point is normally attributed to the separation of wax from fuel or due to the effect of viscosity. Also the pour point of residual fuel oil is also influenced by the previous thermal history of oil. The fluidity test is restricted to residual fuel oils. The problem of accurately specifying handling behavior of fuel oils is important because of technical limitations of the pour point test. Various pumpability tests such as ASTM D 3245 have been proposed. The fluidity test[4] covers the determination of the fluidity of a residual fuel oil at a specified temperature. In this test method, the sample as received is cooled at a specified temperature for 30 min in a standard 12.5-mm diameter U tube (Fig. 6-3). The sample is considered fluid if it flows 2 mm in 1 min under a maximum pressure of 152 mm Hg (0.2 atm or 3 lb/in^2). Results are reported as fluid or not fluid at the specified temperature.

Thermal Stability

Most residual fuel oil whether in ships or in industrial applications must be preheated to reduce its viscosity before it enters the burner nozzle or marine engine. Preheating is done in a shell and tube heat exchanger using steam as the heating medium. Preheating may be done to a temperature of 300 to 350°F using medium pressure steam. It has been found that certain fuel oils can cause rapid fouling of the heat exchanger tube, resulting in lowered oil temperatures and necessitating frequent shutdown of the equipment for cleaning. The thermal stability test is designed to predict the fouling characteristics of a given residual fuel oil in preheater equipment.

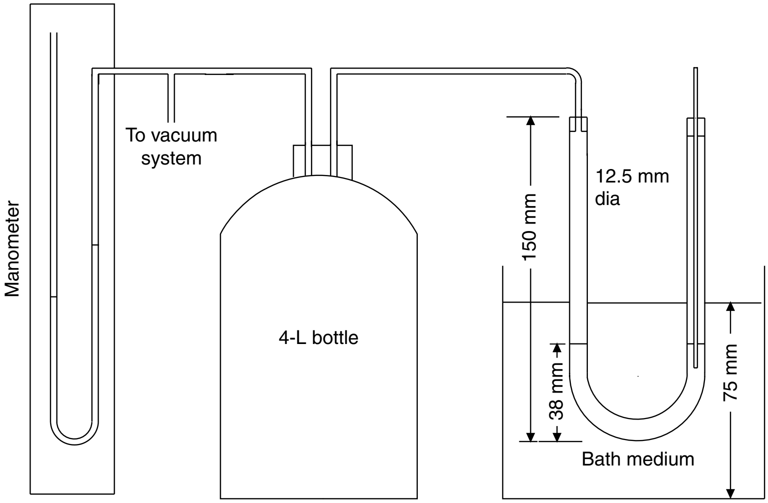

FIGURE 6-3 Fluidity test apparatus.

Thermal Stability Test (ASTM D 1661)

The test apparatus is in the form of a U tube made of heat-resistant glass (Fig. 6-4). A finger air cooler made of glass sealed at one end, about 330 mm long with a 10-mm outside diameter is fitted at one end. A metal thimble consisting of 4-in long seamless mild steel, BWG 16, 0.05 in outside diameter, 1.65-mm wall thickness is reamed to snug fit a heater cartridge and sealed at the other end.

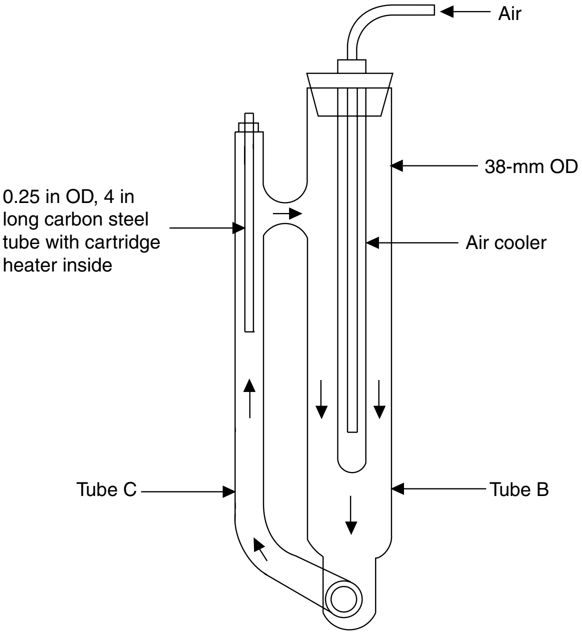

FIGURE 6-4 Apparatus for R.F.O thermal stability test.

The fuel oil (300 cm^3) is preheated to 140 to 160°F and poured into tube B until the oil level is at the top of the short arm connecting tubes B and C. The heater is switched on and power input adjusted so that the thimble temperature is 350°F. Air flow in the cooler is turned on and adjusted to give a temperature of 210°F in tube C.

The fuel oil sample is circulated by thermo-syphon action through the glass apparatus. The fuel oil is in contact with the surface of a steel thimble containing a sheathed heating element. The sample is heated on the hot surface of the steel thimble in the heater chamber, flows up through a riser tube, and then descends in a connecting tube and returns to the heater chamber for recirculation. The temperature of the thimble surface is maintained at 350°F. Heating is continued for 6 h, after which the heater is switched off. At the end of the period, the thimble is removed and examined for sediment formation and discoloration of the surface and compared with reference samples to rate the fuel oil fouling characteristics.

Explosiveness

Residual fuel oils are generally stored in heated tanks at 140 to 170°F. Light hydrocarbon vapor can build up in the head space of the tanks. This can cause flammability and explosion hazards even at temperature below the normal flash point of fuel. Several serious explosions have taken place in fuel oil storage facilities on land and onboard ships. Most explosions occur due to an accumulation of an explosive mixture of gases in the vapor space of fuel oil tanks. The vapor space gases consist predominantly of propane and lighter hydrocarbons with varying proportions of hydrogen sulfide. The light hydrocarbons are believed to be produced because of the delayed decomposition of cracked components such as visbroken tar. Traces of cracking catalysts may aid the process. Hydrogen sulfide may be released from decomposition of high-sulfur stocks. In oil tankers, inert gas blanketing is done to prevent potentially explosive mixtures of hydrocarbon gases and air from forming. Inert gas is obtained by seawater scrubbing of exhaust gases from the tanker boiler plant, which removes all sulfur oxides and particulate matter.

The explosiveness of an atmosphere in tank head space is determined by a device called "Explosimeter." This instrument measures the amount of combustible gas present in a sample drawn from the tank head space. In this instrument, a wire is heated and the sample of gas drawn from the tank is introduced to hot wire, causing combustion. The heat generated increases the resistance of the wire, which is measured by the instrument. The concentration of combustible gas as a percentage of the lower explosive limit is reported as explosiveness[5] of the sample even when the combustible material is unknown.

RESIDUAL FUEL OIL BURNING

The equipment used for burning residual includes storage tanks for storing the fuel oil, pumps for moving the fuel oil to the burner, and a preheater for adjusting the viscosity of the oil fed to the burner. The fuel oil burner is normally a part of the refinery furnace along with the stack and a suitable control system.

Oil Burner

Fuel oil is introduced into furnace through a fuel oil burner. An oil burner is a mechanical device that combines fuel oil with the requisite amount of air before delivering the mixture to the point of combustion. For proper combustion of fuel oil, the oil-air mixture must be well homogenized with a minimum of possible oil droplets. Three types of oil burners are used for residual fuel oil burning

- Mechanical atomizing
- Air atomizing
- Steam atomizing

Mechanical atomizing burners are also known as gun-type burners. Fuel oil is pressurized to a pressure of 100 to 300 lb/in^2 and forced through a nozzle that atomizes it into a fine spray in air and is thus partly evaporated before combustion in the furnace. In rotary nozzle burners, fuel is supplied through the shaft and thrown off a nozzle assembly, rotating at high speed. The fuel is converted into a fine spray. In air-atomized burners, the gravity causes a flow of fuel oil to the burner. Air is supplied through a natural draft or a forced draft using a fan. These types of burners are the most inexpensive and the have lowest operating cost. In steam atomizing systems, atomizing steam is introduced into the burner chamber and comes in contact with the oil stream just before burner tip. The kinetic energy of steam forces the fuel oil into tiny droplets as it leaves the burner. For proper atomization, steam pressure is kept 10 to 15 lb/in^2 higher than fuel oil pressure. Steam consumption is 1.5 to 5 lb/gal oil burned. Dry steam with superheat of 50°F is generally used. Steam consumption is 125 to 200 lb steam per barrel fuel oil.

Fuel Oil System

The purpose of the fuel oil system is to ensure a constant regulated supply of residual fuel oil to the burners of steam boilers and process furnaces. A typical fuel oil system is shown in Fig. 6-5. The system includes facilities for storage, pumping, heating, and distribution of fuel oil at suitable pressure and viscosities so that atomization and burning are possible. Storage is one of the essential needs that must be met with ample provision for availability of at least 5 days' supply at the normal firing rates of furnaces and boilers. If the fuel oil is obtained from more than one source, it may be necessary to blend the stored material, and more than one tank may be required. Oil is delivered to

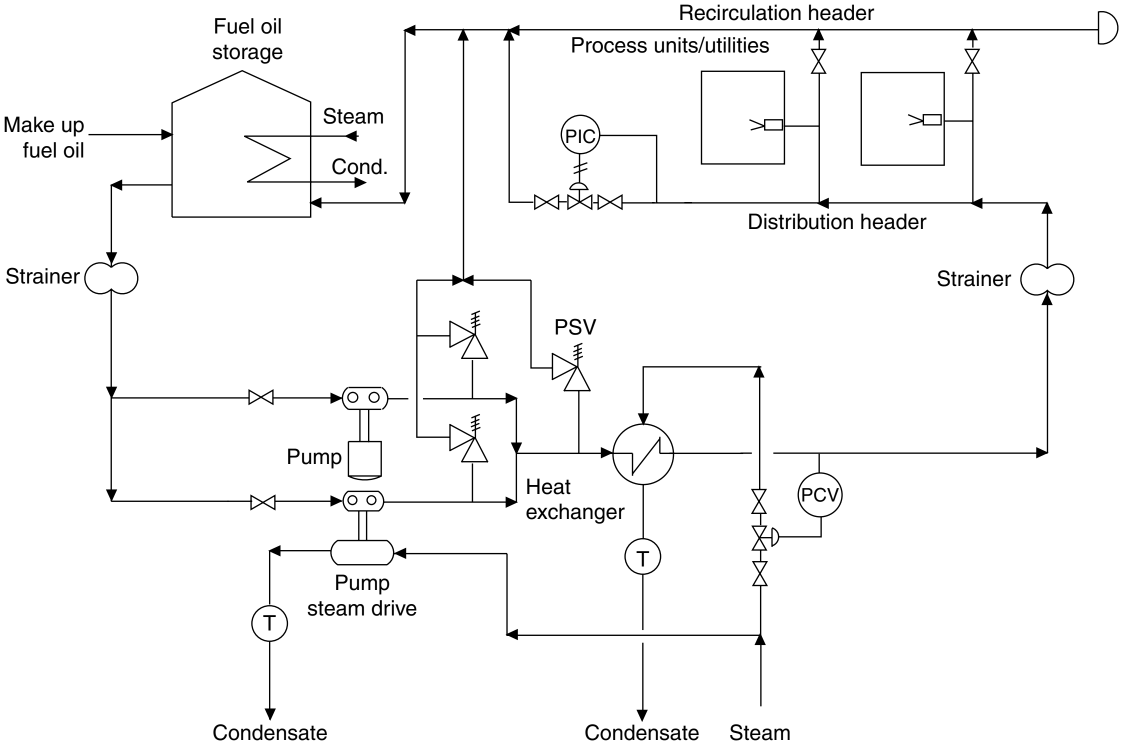

FIGURE 6-5 Residual fuel oil system.

burners at a pressure of approximately 100 lb/in^2 for proper control and atomization. Pump discharge pressure is typically set at 125 to 150 lb/in^2. Pump suction lines from storage tanks are equipped with strainers to intercept dirt and foreign material. Oil is heated in a shell and tube heat exchanger by steam to a temperature sufficient to lower the viscosity of residual fuel oil to 20 to 30 cSt.

Fuel Oil System on Ships

A slightly different fuel oil system is used on ships using residual fuel oil for its propulsion. A typical fuel oil system for use on ships[6] is shown in Fig. 6-6. When using high-viscosity fuels requiring high preheating temperatures, oil from the engine fuel system to the return pipe also has a relatively high temperature. There is a possibility of boiling and foaming in the return pipe in case water is present in the fuel. Also, cavitation in the fuel oil primary suction pump may occur. To circumvent this problem, an additional pump is placed between the service tank and return pipe, which is connected via an automatic deaerating valve to the service tank. With this arrangement, a minimum pressure of 4 bar can be maintained to ensure against boiling.

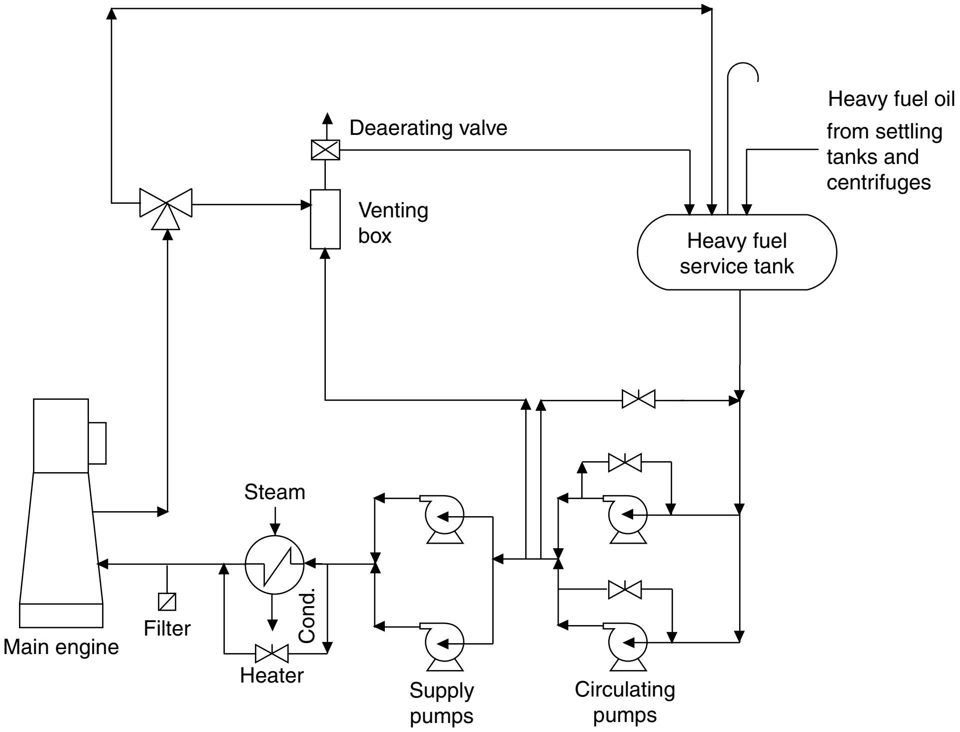

FIGURE 6-6 Merchant ship fuel oil system.

RESIDUAL FUEL OIL BLENDING

Depending on the refinery configuration and process units available, residual fuel oil may be blended from the following refinery streams (Fig. 6-7):

- Atmospheric distillation bottoms (long residue), 650°F+
- Vacuum distillation bottoms (short residue), 1000°F+

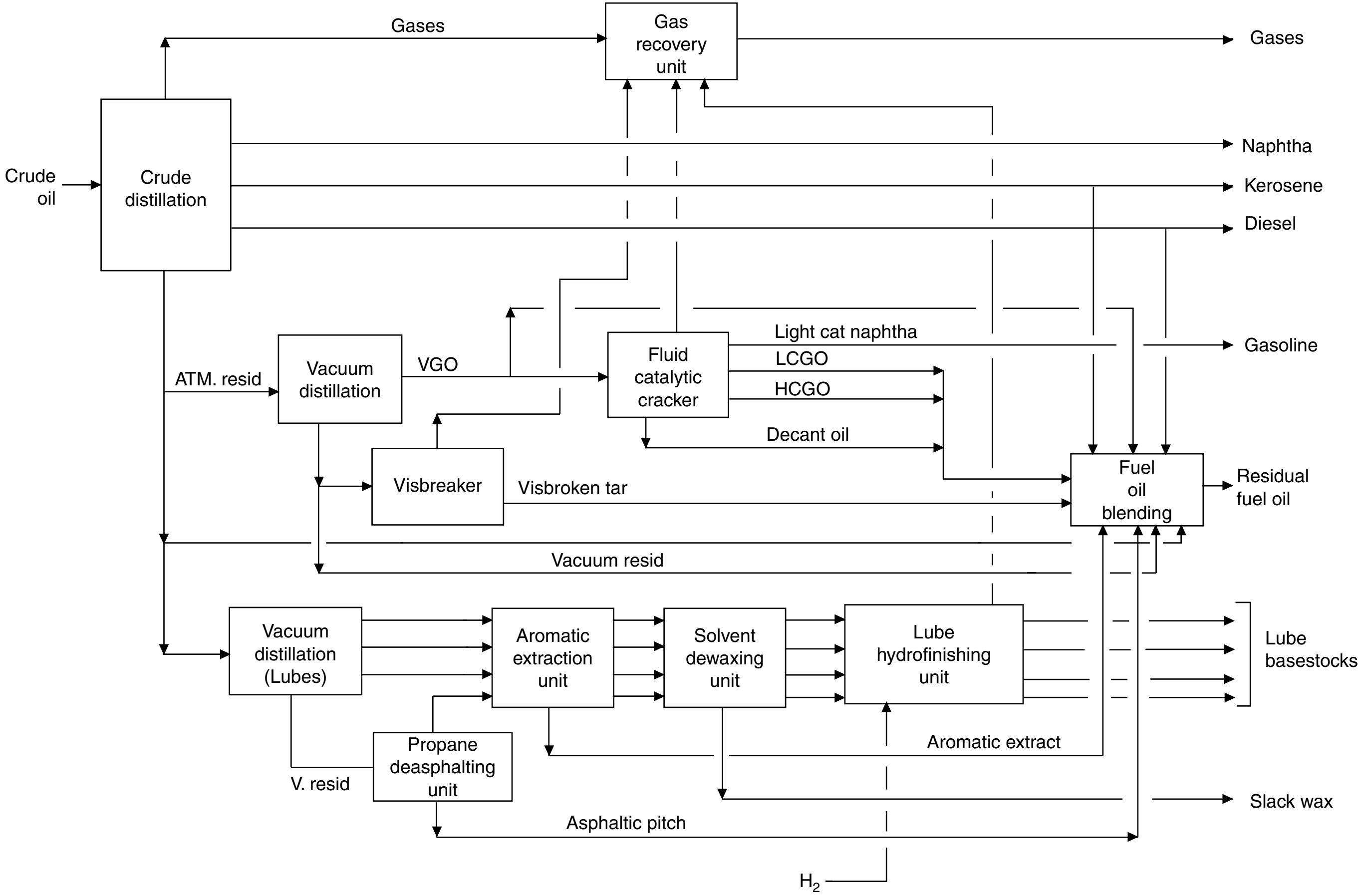

FIGURE 6-7 Refinery residual fuel oil blending.

- Visbroken or thermally cracked long or short residue
- Vacuum residue from resid hydrocracking units such as H oil
- Vacuum resid from resid desulfurization unit
- Cat cracker light cycle oil
- Cat cracker heavy cycle oil
- Cat cracker slurry (clarified) oil
- Gas oil
- Kerosene

Blending is done to make a blend of the available stocks with the least cost to the refinery. Key fuel oil specifications for blending include viscosity, sulfur, and conradson carbon and flash point.

Cracked Fuel Oils

A typical cracked fuel oil may be blended from visbroken vacuum resid and FCCU cutters (light cycle gas oil, medium and heavy cycle gas oils, and decant oils). It is known that fuel oils consisting essentially of thermally cracked hydrocarbons are subject to a stability problem in storage. The quality of the cutter stock is of great importance. Cracked resids have a high concentration of asphaltenes, which must be kept in solution by the use of high aromatic cutter stocks. Use of paraffinic cutter stock can lead to gradual separation of the asphaltenes in fuel oil storage tanks.

Straight Run Fuel Oils

These fuel oils are blended from straight run vacuum resids with straight run diesel and kerosene. Straight run fuel oils do not suffer from the problem of storage stability and do not exhibit the problem of incompatibility if reblended.

Low-Sulfur Fuel Oils

Low sulfur (1.5 to 2.0 percent S) fuel oils can be blended from low-sulfur vacuum resids if crude oil sulfur content is low. However, most export crude has a high sulfur content that produce vacuum resid with 4 to 5 percent sulfur. Fuel oil produced from such resids has a sulfur content of 3.5 to 4 percent. Very few refineries have resid desulfurization or resid hydrocracking units that can produce fuel oils with 1.5 to 2 percent sulfur.

COMPATIBILITY OF RESIDUAL FUEL OILS

One of the major concerns related to compatibility is whether two fuels of different origins can be commingled without having sediment precipitation in the tank. Residual fuel oils blended with thermally cracked residuum and paraffinic distillates may precipitate asphaltenes in storage tanks. Precipitated asphaltenes are also referred to as “hot filtration sediment” or dry sludge. Precipitated asphaltenes contribute to deposits in tankage, to preheater fouling, and to strainer plugging in the fuel-handling system. Asphaltenes can cause overloading in centrifuges installed to remove sediment and particulate matter in marine diesel systems on ships. If asphaltene precipitation occurs during the blending of fuel oil components, the blend components may be termed incompatible. Incompatibility can be determined by making laboratory blends and measuring its stability by the Shell Hot Filtration Test and Spot Test (ASTM D 2781). In this test, equal volumes of residual fuel oil and distillate fuel oils are blended at 149°F. A drop of this blend is allowed to spread on a chromatographic paper of a specified grade at 149°F. The spot thus formed is compared with a series of numbered reference spots. The compatibility of components is rated on the basis of this comparison.

To the extend possible, incompatibility can be prevented by segregating straight run and cracked stocks and avoid putting fuel containing virgin and cracked stocks in the same tank, especially if the straight run fuel is waxy with a high pour point. Usually two cracked fuels, if each is free of sediment, is likely to maintain asphaltene in solution. Also, two fuels of essentially the same viscosity that have the same density can be commingled with a minimum risk of incompatibility.

If the residual component contains only virgin material, it is highly unlikely that intermediates blended from it will be incompatible by themselves. There is no problem in using cracked resids for blending intermediate grades. However, the blend must be tested for stability. Where there is a choice available in the quality of cutter stock to be used in intermediate blends, a cutter with higher density, which also implies higher aromaticity, must be used to improve compatibility.

Whether or not asphaltene precipitation will occur when fuel oil components are blended can be predicted by a procedure developed by Exxon,[7] as follows:

- Estimate the BMCI[8] (Bureau of Mines Correlation Index) of the residual component of blend from its API gravity and mean boiling point (Fig. 6-8). BMCI can also be estimated from API gravity and viscosity. BMCI is indicative of the aromaticity of the stock. Thus the higher the BMCI, the higher the aromaticity. Although the correlation is strictly applicable to distillate stocks, it can be approximated to residual stocks without significant error. BMCI of individual components can be determined by their densities and viscosity or density and mean boiling point. The BMCI of the blend is a linear function of the BMCI of the components.
- Determine the toluene equivalency (TE) of the blend as follows: A sample of residual blend component is dissolved in a mixture of toluene and n-heptane. The mixture is filtered and any undissolved residue is separated and weighed. A number of such mixtures are prepared with increasing toluene concentration until the entire residue is completely dissolved and there is no residue on filtering the solution. The vol % of toluene in the toluene-heptane mixture is the toluene equivalence of the residual blend component. Toluene equivalency (TE) of the blend can be estimated from the TE of the blend component, assuming a component's TE blends in proportion to the amount of asphaltene contributed by each. Thus TE of each component is multiplied by its volume fraction, density, and wt % asphaltenes. The sum of these values is divided by the

Criteria for compatibility

$$\text{BMCI} - \text{TE} \geq K$$

For compatible blends
of cracked resids and conventional
cutters, K should lie between 7 and –14.

Where:
BMCI = Bureau of mines correlation index
TE = Toluene equivalency
K = A constant, applicable to a given set of blend components

BMCI of a blend component is defined as follows;

$$\text{BMCI} = \frac{87552}{\text{VABP}} + 473.7 \times \text{SG} - 456.8$$

Where:
VABP = Volume average boiling point in °R

FIGURE 6-8 Residual fuel oil compatibility.

asphaltene content of the blend to give the TE of the blend. TE is a measure of aromaticity needed to maintain all asphaltenes in solution. A higher TE indicates that a higher percentage of toluene in normal heptane mixture is needed to dissolve the asphaltenes. In a blend of resid and distillate cutter stock, TE of the blend will be TE of resid component.

Criteria for compatibility is presented in Fig. 6-8. For most blends of cracked resids and conventional cutter stocks, BMCI must be greater than TE and a delta between BMCI and TE of blend (K value), in the range of 7 to 14 will ensure that the blend is compatible and the sediment as measured by the hot filtration test (HFS) will be lower than 0.2 percent by weight. The equation indicates that if aromaticity of the blend is higher than the aromaticity needed to keep asphaltenes in solution, the blend will be compatible and no asphaltene precipitation will occur.

REFERENCES

1. Krystallon Sea Water Scrubbing, 27th International Bunker Conference, Gothenburg, Sweden, 2006.
2. G. B. G. Nyman and A. Tokerud, "Sea Water Scrubbing Removes SO_3 from Refinery Flue Gases," *Oil and Gas Journal*, 89 (1991): 52–54.
3. Francisco Arvelo Valencia, Isidro Padron Armas, "Ignition Quality of Residual Fuel Oils" *Journal of Maritime Research*, 2 (3), 2005: 77–96.
4. V. B. Gutherie, *Petroleum Products Handbook* (USA: McGraw Hill Book Company, 1960).
5. ASTM D 97, Appendix, "Test for Fluidity of Residual Fuel Oil at Specified Temperature."
6. U.S. military specifications, MIL-F-859E, FTM 1151.1.
7. O. Gradone, "Fuel Quality, On Board Treatment and Responsive Design of Two Strokes, Low Speed Diesel Engines," Marine Fuels, ASTM STP 878 (C. H. Jones, ed.) (Philadelphia: American Society for Testing and Materials, 1985), pp. 111–128.
8. M. G. Griffith and W. C. Siemoud, "Controlling Stability of Residual Fuel Oils," Marine Fuels Symposium, ASTM STP 878 (C. H. Jones, ed.) (Philadelphia: American Society for Testing and Materials, 1985), pp. 227–247.
9. James G. Speight, *Chemistry and Technology of Petroleum* (New York: Marcel Dekker, 1998).