CHAPTER

9

DISTILLATE FUEL OIL

9.1. INTRODUCTION

Most petroleum products can be used as fuels, but the term fuel oil, if used without qualification, may be interpreted differently depending on the context. However, because fuel oils are complex mixtures of hydrocarbons, they cannot be rigidly classified or defined precisely by chemical formulae or definite physical properties. The arbitrary division or classification of fuel oils is based more on their application than on their chemical or physical properties. However, two broad classifications are generally recognized: (1) distillate fuel oil and (2) residual fuel oil (Gruse and Stevens, 1960; Guthrie, 1967; Kite and Pegg, 1973; Weissermel and Arpe, 1978; Francis and Peters, 1980; Hoffman, 1983; Austin, 1984; Chenier, 1992; Hoffman and McKetta, 1993; Hemighaus, 1998; Warne, 1998; Speight, 1999; Charlot, and Claus, 2000; Heinrich and Duée, 2000). This terminology is used in the present work.

The conventional description of “fuel oil” is generally associated with the black, viscous residual material remaining as the result of refinery distillation of crude oil either alone or as a blend with light components, which is used for steam generation and various industrial processes. The term is sometimes used to refer to the light, amber-colored middle distillates or gas oils that are distinguished from the residual fuel oil by being characterized as distillate fuel oil (ASTM D-396). In this specification the No. 1 grade fuel oil is a kerosene type used in vaporizing pot-type burners whereas the No. 2 fuel is a distillate oil (gas oil) used for general-purpose domestic heating. Kerosene may also be included in this definition, but it is described elsewhere in this text.

Distillate fuel oils are vaporized and condensed during a distillation process and thus have a definite boiling range and do not contain high-boiling oils or asphaltic components. The generally correspond to a light gas oil (Table 9.1, Fig. 9.1), but this correlation is not exact and can vary considerably. A fuel oil that contains any amount of the residue from crude distillation of thermal cracking is a residual fuel oil. The terms distillate fuel oil and residual fuel oil are losing their significance, because fuel oils are now made for specific uses and may be either distillates or residuals or
mixtures of the two. The terms *domestic fuel oil*, *diesel fuel oil*, and *heavy fuel oil* are more indicative of the uses of fuel oils.

Domestic fuel oil is fuel oil that is used primarily in the home. This category of fuel oil includes kerosene, stove oil, and furnace fuel oil; these are distillate fuel oils. Diesel fuel oil is also a distillate fuel oil, but residual oil has been successfully used to power marine diesel engines, and mixtures of distillate fuel oil and residual fuel oil have been used in locomotive diesel engines. Heavy fuel oils include a variety of oils ranging from distillates to residual oils that must be heated to 260°C (500°F) or more before they can be used. In general, heavy fuel oils consist of residual oils blended with distillates to suit specific needs. Included among heavy fuel oils are various industrial oils; when used to fuel ships, heavy fuel oils are called bunker oils.

Because the boiling ranges, sulfur contents, and other properties of even the same fraction vary from crude oil to crude oil and with the way the crude oil is processed, it is difficult to specify which fractions are blended to produce specific fuel oils. In general, however, furnace fuel oil is a blend of straight-run gas oil and cracked gas oil to produce a product boiling in the 175–345°C (350–650°F) range.

Heavy fuel oils usually contain cracked residua, reduced crude, or cracking coil heavy product that is mixed (cut back) to a specified viscosity with cracked gas oils and fractionator bottoms. For some industrial purposes in which flames or flue gases contact the product (ceramics, glass, heat treating, and open-hearth furnaces) fuel oils must be blended to contain

<table>
<thead>
<tr>
<th>Product</th>
<th>Lower Carbon Limit</th>
<th>Upper Carbon Limit</th>
<th>Lower Boiling Point °C</th>
<th>Upper Boiling Point °C</th>
<th>Lower Boiling Point °F</th>
<th>Upper Boiling Point °F</th>
</tr>
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<tr>
<td>Refinery gas</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>–161</td>
<td>–1</td>
<td>–259</td>
<td>31</td>
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<tr>
<td>Liquefied petroleum gas</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>–42</td>
<td>–1</td>
<td>–44</td>
<td>31</td>
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<tr>
<td>Naphtha</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>C&lt;sub&gt;17&lt;/sub&gt;</td>
<td>36</td>
<td>302</td>
<td>97</td>
<td>575</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>–1</td>
<td>216</td>
<td>31</td>
<td>421</td>
</tr>
<tr>
<td>Kerosene/diesel fuel</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>126</td>
<td>258</td>
<td>302</td>
<td>575</td>
</tr>
<tr>
<td>Aviation turbine fuel</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;</td>
<td>126</td>
<td>287</td>
<td>302</td>
<td>548</td>
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<tr>
<td>Fuel oil</td>
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<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>216</td>
<td>421</td>
<td>&gt;343</td>
<td>&gt;649</td>
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<tr>
<td>Lubricating oil</td>
<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
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<tr>
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<td>&gt;C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>302</td>
<td>&gt;343</td>
<td>575</td>
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<tr>
<td>Coke</td>
<td>&gt;C&lt;sub&gt;50&lt;/sub&gt;*</td>
<td>&gt;1000*</td>
<td>&gt;1000*</td>
<td>&gt;1832*</td>
<td>&gt;1832*</td>
<td>&gt;1832*</td>
</tr>
</tbody>
</table>

* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.
minimum sulfur contents, and hence low-sulfur residues are preferable for these fuels.

9.2. PRODUCTION AND PROPERTIES

Distillate fuel oils are petroleum fractions that have been vaporized and condensed. They are produced in the refinery by a distillation process in which petroleum is separated into its fractions according to their boiling range. Distillate fuel oils may be produced not only directly from crude oil (straight run) but also from subsequent refinery processes such as thermal
or catalytic cracking. Domestic heating oils and kerosene are examples of distillate fuel oils.

The manufacture of fuel oils at one time largely involved using what was left after removing desired products from crude petroleum. Now fuel oil manufacture is a complex matter of selecting and blending various petroleum fractions to meet definite specifications, and the production of a homogeneous, stable fuel oil requires experience backed by laboratory control.

The term *domestic heating oil* in the present context is applicable to the middle distillate or gas oil-type product used principally with atomizing burner-heating equipment. This material may consist of the straight-run gas oil from the distillation of the crude oil, which boils within the approximate temperature range of 160–370°C (320–700°F). Straight-run gas oil fraction is usually blended with the appropriate boiling-range material from catalytic cracking processing. The components are suitably treated before final blending, and additives may also be added to further assist in the stabilization of the finished product.

The quality and performance requirements for fuel oils differ widely, although general quality limitations for various fuel grades are used to serve as guides in the manufacture, sale, and purchase of the oils. These quality definitions are often referred to as *specifications* or *classifications*, but more precise specifications of quality requirements such as the vapor pressure (ASTM D-323) and metals content (ASTM D-5184, ASTM D-2788, ASTM D-4951, ASTM D-5185, ASTM D-5708, ASTM D-5863, IP 377) may be required for any given application (ASTM D-396).

### 9.3. TEST METHODS

Fuel oil, therefore, in its various categories has an extensive range of applications, and the choice of a standard procedure to be used for assessing or controlling product quality must, of necessity, depend on both the type of fuel and its ultimate use. But first, as for all petroleum analysis and testing, the importance of correct sampling of the fuel oil cannot be overemphasized, because no proper assessment of quality can be made unless the data are obtained on truly representative samples (ASTM D-270, IP 51).

#### 9.3.1. Acidity

The presence of inorganic acids in distillate fuels, resulting from refinery treatment, is unlikely. However, some specifications for these fuels still include limiting clauses for total acidity and inorganic acidity as a check against possible corrosion of metal equipment in contact with the fuel. Inorganic acidity should in any case be entirely absent.
Acidity is determined through the **acid number**, which is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate a sample in the solvent from its initial meter reading to a meter reading corresponding to a freshly prepared nonaqueous basic buffer solution or a well-defined inflection point as specified in the test method. Test methods include potentiometric titration (ASTM D-66, IP 177) and indicator-indicator titration (ASTM D-974, IP 139) in addition to inorganic acidity (IP 182) and total acidity (IP 1) methods.

One test method (ASTM D-974) resolves constituents into groups having weak acid and strong acid ionization properties. However, oils such as fuel oil that are dark-colored oils, which cannot be analyzed by this test method because of obscurity of the color-indicator end point, should be analyzed by another test method (ASTM D-664, IP 177). This test method is used to determine the presence of those constituents that have weak acid properties and those constituents that have strong acid properties. It may be used to indicate relative changes that occur in an oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil. In the practice of this method, the sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide by using a glass indicating electrode and a calomel reference electrode and the end points are taken at well-defined inflections in the resulting curve.

### 9.3.2. Ash Content

Ash is the organic matter-free (or carbonaceous matter free) residue that remains after combustion of a fuel oil at a specified high temperature (ASTM D-482, IP 4).

Depending on the use of the fuel, ash composition has a considerable bearing on whether or not detrimental effects will occur. However, distillate fuels tend to contain only negligible amounts of ash but pick up ash-forming constituents during transportation from the refinery. Water transportation, in particular, presents many opportunities for fuel oils to be contaminated with ash-forming contaminants (seawater, dirt, and scale rust).

Small amounts of unburnable material are found in fuel oil in the form of soluble metallic soaps and solids, and these materials are designated as ash, although “ash-forming constituents” is a more correct term. In the test for the quantitative determination of ash-forming constituents (ASTM D-482, IP 4), a small sample of fuel oil is burned in a weighed container until all of the combustible matter has been consumed, as indicated by the residue and container attaining a constant weight. The amount of unburnable residue is the ash yield, and it is reported as percent by weight of the sample.
The ash-forming constituents in distillate fuel (ASTM D 2880) are typically so low that they do not adversely affect gas turbine performance, unless such corrosive species as sodium, potassium, lead, or vanadium are present. However, there are recommendations for the storage and handling of these fuels (ASTM D-4418) to minimize potential contamination.

**9.3.3. Calorific Value (Heat of Combustion)**

Because the function of a fuel is to produce heat, the calorific or heating value (ASTM D-240, IP 12) is one of the important fuel properties and a knowledge of this value is necessary in obtaining information regarding the combustion efficiency and performance of all types of oil-burning equipment.

The determination is made in a bomb calorimeter under specified conditions, the oxygen in the bomb being saturated with water vapor before the ignition of the fuel so that the water formed during combustion is condensed. The calorific value so determined will include the latent heat of water at the test temperature and is known as the gross calorific value at constant volume. The corresponding net calorific value at constant pressure is obtained by deducting the latent heat of water formed during the burning of the hydrogen present in the fuel to produce water. The calorific value is usually expressed in British thermal units per pound (Btu/lb) or in calories per gram (c/g). In Europe the net calorific value is more often called for in calculations on burner efficiency because the water formed during combustion passes out as water vapor with the flue gases and hence its latent heat of condensation is not realized as useful heat. In the U.K. the gross calorific value is normally used for this purpose.

An alternative criterion of energy content is the aniline gravity product (AGP), which is related to calorific value (ASTM D-1405, IP 193). The aniline gravity product is the product of the API gravity (ASTM D-287, ASTM D-1298) and the aniline point of the fuel (ASTM D-611, IP 2). The aniline point is the lowest temperature at which the fuel is miscible with an equal volume of aniline and is inversely proportional to the aromatic content. The relationship between the aniline gravity product and the calorific value is given in the method. In another method (ASTM D-3338), the heat of combustion is calculated from the fuel density, the 10%, 50%, and 90% distillation temperatures, and the aromatic content. However, neither method is legally acceptable, and other methods (ASTM D-240, ASTM D-1655, ASTM D-4809) are preferred.

The aniline gravity product is not always suitable for determining the heat of combustion because of the difficulties that can be encountered in determining the aniline point of the fuel (ASTM D-611, IP 2). It is
possible to overcome the issue of color by use of a modification of the test procedure (method B, ASTM D-611, IP 2).

An alternate method of calculation of the calorific value, when an experimental determination is not available or cannot be made conveniently, involves an estimate of this property (ASTM D-6446). In this test method, the net heat of combustion is calculated from the density and sulfur and hydrogen content, but this calculation is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples. Thus the hydrogen content (ASTM D-1018, ASTM D-1217, ASTM D-1298, ASTM D-3701, ASTM D-4052, ASTM D-4808, ASTM D-5291, IP 160, IP 365), density (ASTM D-129, ASTM D-1250, ASTM D-1266, ASTM D-2622, ASTM D-3120, IP 61, IP 107), and sulfur content (ASTM D-2622, ASTM D-3120, ASTM D-3246, ASTM D-4294, ASTM D-5453, ASTM D-5623, IP 336, IP 373) of the sample are determined by experimental test methods, and the net heat of combustion is calculated with the values obtained by these test methods based on reported correlations.

9.3.4. Carbon Residue

The carbon residue of a petroleum product gives an indication of the propensity for that product to form a carbonaceous residue under thermal conditions. The carbonaceous residue is correctly referred to as the carbon residue but is also often referred to as coke or thermal coke.

The use of fuel oil (ASTM No. 2) for heating has resulted in the availability of different types of burners that are classified according to the manner in which the fuel oil is combusted. Any carbonaceous residue formed during the thermal decomposition of the fuel oil that is deposited in, or near, the inlet surface, reduces the fuel oil flow, with resultant loss in burner efficiency. Therefore, fuel oil should have low carbon-forming propensities. Other petroleum products that are lower boiling than distillate fuel oil do not usually reference the carbon residue in the specifications.

Thus assessing the carbon forming tendencies of the fuel oil is carried out with a carbon residue test. The test methods are (1) the Conradson carbon residue (ASTM D-189, IP 13), the Ramsbottom carbon residue (ASTM D-524, IP 14), and the microcarbon carbon residue (ASTM D-4530, IP 398). The data give an indication of the amount of coke that will be formed during thermal processes as well as an indication of the amount of high-boiling constituents in petroleum. For lower-boiling fuel oil, forming low yields of carbonaceous deposits, the carbon residue value is determined
on a residue (10% by weight of the fuel oil) obtained by means of an adap-
tation of the standard distillation procedure for gas oil (ASTM D-8, IP 123),
so that the accuracy of the determination may be improved.

9.3.5. Cloud Point

Distillate fuel oil for heating installations is usually stored in outside
tankage, and a knowledge of the lowest temperature at which the fuel can
be transferred from tank to burner while avoiding line and filter blockage
difficulties is necessary.

An indication of this temperature may be obtained from the cloud point
(ASTM D-2500, ASTM D-5771, ASTM D-5772, ASTM D-5773, IP 219) and
pour point (ASTM D-97, IP 15). These test methods give, respectively, the
temperature at which wax begins to crystallize out of the fuel and the tem-
perature at which the wax structure has built up sufficiently to prevent the
flow of oil. In these installations, a coarse filter is normally sited in the
system near the tank outlet to remove large particles of extraneous matter;
a fine filter is positioned near the burner to protect the pump.

As the temperature continues to decrease below the cloud point, the for-
mation of wax crystals is accelerated. These crystals clog fuel filters and lines
and thus reduce the supply of fuel to the burner. Because the cloud point
is a higher temperature than the pour point (4 to 5°C/7 to 9°F, and even
higher), the cloud point is often considered to be more important than the
pour point in establishing distillate fuel oil specifications for cold weather
usage. The temperature differential between cloud and pour point depends
on the nature of the fuel components, but the use of wax crystal modifiers
or pour depressants tends to accentuate these differences.

9.3.6. Composition

The chemical composition of fuel oil is extremely complex, and an
extremely high number of compounds can be present through the hydro-
carbon types, the range of isomeric hydrocarbons (Table 9.2), and the
various types and isomers of heteroatom constituents. Therefore, it is not
practical to perform individual compound analyses but it is often helpful to
define the compounds present under broad classifications, such as aromat-
ics, paraffins, naphthenes, and olefins.

Thus the first level of compositional information is group type totals as
deduced by adsorption chromatography (ASTM D-1319, ASTM D-2007)
or by emulsion chromatography (ASTM D-2549) to give volume percent
saturates, olefins, and aromatics in materials that boil below 315°C (600°F).
In addition, and depending on the characteristics of the fuel oil, gas chro-
matography can also be used for the quantitative determination of olefins.
Following from the chromatographic separation, compositional analysis of the fractions by a mass spectral Z series in which Z in the empirical formula C_nH_{2n+Z} is a measure of the hydrogen deficiency of the compound is also warranted (ASTM D-2425, ASTM D-2786, ASTM D-3239, ASTM D-6379).

One mass spectrometric method (ASTM D-2425) requires that the sample be separated into saturate and aromatic fractions before mass spectrometric analysis. This separation is standardized (ASTM D-2549). This separation is applicable to fuel only when it is possible to evaporate the solvent used in the separation without also losing the light ends of the jet fuel. Combined gas chromatography-mass spectrometry has been used to give similar group type results to ASTM D-2425 but without preseparation into saturates and aromatics. In addition, this method can give the Z series information by carbon number, showing how the composition changes with boiling point.

The percentage of aromatic hydrogen atoms and aromatic carbon atoms can be determined (ASTM D-5292). Results from this test are not equivalent to mass- or volume-percent aromatics determined by the chromatographic methods. The chromatographic methods determine the mass- or volume-percentage of molecules that have one or more aromatic rings. Any alkyl substituents on the rings contribute to the percentage of aromatics determined by chromatographic techniques. ASTM D-292 gives the mole percent of aromatic hydrogen or carbon atoms.
Correlative methods have long been used as a way of dealing with the complexity of petroleum fractions. Such methods include the use of viscosity-temperature charts (ASTM D-341), calculation of the viscosity index (ASTM D-2270), calculation of the viscosity gravity constant (ASTM D-2501), calculation of the true vapor pressure (ASTM D-2889), and estimation of the heat of combustion (ASTM D-3338).

Organic sulfur compounds (e.g., mercaptans, sulfides, polysulfides, thiophenes) are present in petroleum products to a greater or lesser extent depending on the crude oil origin and the refinery treatment. The sulfur content of fuel oil (ASTM D-396) can be determined by a variety of methods (ASTM D-129, ASTM D-1552, ASTM D-2622, ASTM D-4294, IP 61, IP 63), with mercaptan sulfur in cracked stocks being particularly necessary for evaluation (ASTM D-3227, IP 342).

Corrosion of heating equipment can occur if the sulfur oxides formed on combustion of fuel oil are allowed to condense in the presence of moisture on the cooler parts of the flue system. Corrosion of metal parts of the fuel system may also reflect the presence of corrosive sulfur components in the fuel. The corrosive tendencies of the fuel may be detected by the copper strip test (ASTM D-130, ASTM D-849, IP 154), the effect of these sulfur compounds being indicated by discoloration of the copper strip.

Various standard procedures are available for the determination of the sulfur content of distillate fuels. In the lamp method (ASTM D-126, IP 107), which is widely used, the product is burned completely in a small wick-fed lamp, the gases formed by combustion are absorbed in hydrogen peroxide solution, and the sulfur is subsequently determined as sulfate. Several rapid methods, including X-ray absorption and high-temperature combustion, for the determination of sulfur are also available.

In addition, excessive levels of hydrogen sulfide in the vapor phase above fuel oils in storage tanks may result in corrosion as well as being a health hazard. One method (ASTM D-5705) is available for the determination of hydrogen sulfide but has been criticized because the test conditions do not simulate the vapor phase of a fuel storage tank. A second method (ASTM D-6021) that is believed to be a more accurate simulation of the conditions in a fuel oil storage tank is available. In this method, a sample of the fuel oil is placed in a headspace vial and heated in an oven at 60°C (140°F) for more than 5 min but less than 15 min. The headspace gas is sampled and injected into an apparatus capable of measuring hydrogen sulfide in the gaseous sample either by the lead acetate method (ASTM D-4084, ASTM D-4323) or by the chemiluminescence method (ASTM D-5504).

Nitrogen can be determined by elemental analysis (ASTM D-3228, ASTM D-5291, ASTM D-5762). Nitrogen compounds in middle distillates can be selectively detected by chemiluminescence (ASTM D-4629). Individual nitrogen compounds can be detected down to 100 ppb nitrogen.
9.3.7. Density (Specific Gravity)


The density is the mass (weight in vacuo) of a unit volume of fuel oil at any given temperature (ASTM D-1298, IP 160). On the other hand, the specific gravity of a fuel oil is the ratio of the weight of a given volume of the material at a temperature of 15.6°C (60°F) to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air.

The API gravity (ASTM D-1298, IP 160) is an arbitrary figure related to the specific gravity:

\[ °API = \frac{141.5}{\text{specific gravity @ 60/60°F}}/131.5 \]

9.3.8. Flash Point

The flash point is a measure of the temperature to which fuel oil must be heated to produce an ignitable vapor-air mixture above the liquid fuel when exposed to an open flame. Following from this, the fire point of a fuel is the temperature at which an oil in an open container gives off vapor at a sufficient rate to continue to burn after a flame is applied.

Thus the flash point is used primarily as an index of fire hazards. Consequently, most industry specifications or classifications place limits on the flash point to ensure compliance with fire regulations, insurance, and legal requirements because it is essential that the fuel is safe to transport and store. Generally, because of its distillation characteristics, fuel oil should not contain any volatile or flashable constituents. Nevertheless, the occasion might arise when application of test methods to determine the flash point might be applicable.

The test method for determination of the flash point by Pensky–Martens closed tester (ASTM D-93, IP 34) and the test method for determining flash point by the tag closed tester (ASTM D-56) are employed for fuel oil.

9.3.9. Metallic Constituents

Metals in fuel oil can seriously affect the use and outcome of fuel oil systems. Even trace amounts of metals can be deleterious to fuel oil use. Hence, it is important to have test methods that can determine metals, both at trace levels and at major concentrations. Metallic constituents in fuel oil can be determined by several methods including atomic absorption

Inductively coupled argon plasma emission spectrophotometry (ASTM D-5708) has an advantage over atomic absorption spectrophotometry (ASTM D-4628, ASTM D-5863) because it can provide more complete elemental composition data than the atomic absorption method. Flame emission spectroscopy is often used successfully in conjunction with atomic absorption spectrophotometry (ASTM D-3605). X-ray fluorescence spectrophotometry (ASTM D-4927, ASTM D-6443) is also sometimes used, but matrix effects can be a problem.

The method to be used for the determination of metallic constituents in petroleum is often a matter of individual preference.

### 9.3.10. Pour Point

The *pour point* (ASTM D-97, IP 15) is the lowest temperature at which the fuel oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where a petroleum product, depending on its thermal history, might appear in the liquid as well as the solid state. Pour point data can be used to supplement other measurements of cold flow behavior, and the data are particularly useful for the screening of the effect of wax interaction modifiers on the flow behavior of petroleum. The *pour point* should not be confused with the *freezing point*, which is an index of the lowest temperature at which the crude oil will flow under specified conditions. Test methods (ASTM D-2386, ASTM D-5901, ASTM D-5972, IP 434, IP 435) for the freezing point are not usually applicable to fuel oil but are more applicable to diesel fuel and aviation fuel.

In the original (and still widely used) test for pour point (ASTM D-97, IP 15), a sample is cooled at a specified rate and examined at intervals of 3°C (5.4°F) for flow characteristics. The lowest temperature at which the movement of the oil is observed is recorded as the pour point. A later test method (ASTM D-5853) covers two procedures for the determination of the pour point of petroleum and petroleum products down to –36°C (–33°F). One method provides a measure of the maximum (upper) pour point temperature. The second method measures the minimum (lower) pour point temperature. In these methods, the test specimen is cooled (after preliminary heating) at a specified rate and examined at intervals of 3°C (5.4°F) for flow characteristics. Again, the lowest temperature at which movement of the test specimen is observed is recorded as the pour point.
In any determination of the pour point, petroleum that contains wax produces an irregular flow behavior when the wax begins to separate. Such petroleum possesses viscosity relationships that are difficult to predict in fuel line operations. In addition, some waxy petroleum is sensitive to heat treatment that can also affect the viscosity characteristics. This complex behavior limits the value of viscosity and pour point tests on waxy petroleum. However, laboratory pumpability tests (ASTM D-3245, IP 230) are available that give an estimate of minimum handling temperature and minimum line or storage temperature.

Although the pour point test is still included in many specifications, it is not designated for high-boiling fuel oil (ASTM D 396). In fact, although the failure to flow at the pour point normally is attributed to the separation of wax from the fuel oil (in the case of waxy crude oil precursors), it also can be due to the effect of the viscosity of the fuel oil (in the case of naphthenic crude oil precursors). In addition, the pour point of fuel oil may be influenced by the previous thermal history of the fuel oil. Thus the usefulness of the pour point test in relation to fuel oil, especially residual fuel oil, may be open to question.

Perhaps a more important test is the test the cold filter plugging point. The cold filter plugging point is the lowest temperature at which fuel oil will give trouble-free flow (ASTM D-6371, IP 309). In this test, either a manual or automated apparatus may be used and the sample is cooled under specified conditions, and at intervals of 1°C, is drawn into a pipette under a controlled vacuum through a standardized wire mesh filter. As the sample continues to cool, the procedure is repeated for each 1°C below the first test temperature. The testing is continued until the amount of wax crystals that have separated out of the solution is sufficient to stop or slow down the flow so that the time taken to fill the pipette exceeds 60s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the cold filter plugging point.

Alternatively, in the low-temperature flow test involving determination of the filterability of fuel oil (ASTM D-4539, ASTM D-6426) the results are indicative of the low-temperature flow performance of distillate fuel oil. Both tests are useful for the evaluation of fuel oil containing flow improver additives. In either test method, the temperature of a series of test specimens of fuel is lowered at a prescribed cooling rate. At the commencing temperature and at each 1°C interval thereafter, a separate specimen from the series is filtered through a 17-mm screen until a minimum low-temperature flow test pass temperature is obtained. The minimum low-temperature flow test pass temperature is the lowest temperature, expressed as a multiple of 1°C, at which a test specimen can be filtered in 60s or less.
In another test (ASTM D-2068), the filter plugging tendency of distillate fuel oil can be determined by passing a sample at a constant flow rate (20 ml/min) through a glass fiber filter medium. The pressure drop across the filter is monitored during the passage of a fixed volume of test fuel. If a prescribed maximum pressure drop is reached before the total volume of fuel is filtered, the actual volume of fuel filtered at the time of maximum pressure drop is recorded. The apparatus is required to be calibrated at intervals.

9.3.11. Stability

Fuel oil must be capable of storage for many months without significant change and should not break down to form gum or insoluble sediments or darken in color (ASTM D-156, ASTM D-381, ASTM D-1209, ASTM D-1500, ASTM D-1544, IP 131). In other words, fuel oil must be stable.

The extent of fuel oil oxidation is determined by measurement of the hydroperoxide number (ASTM D-6447) and the peroxide number (ASTM D-3703). Deterioration of fuel oil results in the formation of peroxides as well as other oxygen-containing compounds, and these numbers are indications of the quantity of oxidizing constituents present in the sample as determined by measurement of the compounds that will oxidize potassium iodide.

The determination of hydroperoxide number (ASTM D-6447) does not use the ozone-depleting substance 1,1,2-trichloro-1,2,2-trifluoroethane that is used for determination of the peroxide number (ASTM D-3703). In this method, a quantity of sample is contacted with aqueous potassium iodide (KI) solution in the presence of acid. The hydroperoxides present are reduced by potassium iodide, liberating an equivalent amount of iodine, which is quantified by voltammetric analysis.

The determination of peroxide number (ASTM D-3703) involves dissolution of the sample in 1,1,2-trichloro-1,2,2-trifluoroethane, and the solution is contacted with an aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide, whereupon an equivalent amount of iodine is released that is titrated with standard sodium thiosulfate solution and a starch indicator.

Other tests for storage stability include determination of color formation and sediment (ASTM D-473, ASTM D-2273, ASTM D-3241, ASTM D-4625, ASTM D-4870, ASTM D-5304, IP 53, IP 323), in which reactivity to oxygen at high temperatures is determined by the amount of sediment formation as well as any color changes.

Straight-run fuel oil fractions from the same crude oil normally are stable and mutually compatible. However, fuel oil produced from the thermal cracking and visbreaking operations may be stable by themselves but can be unstable or incompatible if blended with straight-run fuels and vice versa. Furthermore, asphaltic deposition may result from the mixing of (distillate and residual) fuel oils of different origin and treatment, each of which
may be perfectly satisfactory when used alone. Such fuels are said to be incompatible, and a spot test (ASTM D-470) is available for determining the stability and compatibility of fuel oils. Therefore, test procedures are necessary to predict fuel stability and to ensure a satisfactory level of performance by the fuel oil.

In addition, thermal treatment may cause the formation of asphaltene-type material in fuel oil. The asphaltene fraction (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143) is the highest-molecular-weight, most complex fraction in petroleum. The asphaltene content is an indicator of the amount of carbonaceous residue that can be expected during thermal use or further processing (ASTM D-189, ASTM D-524, ASTM D4530, IP 13, IP 14, IP 398) (Speight, 1999; Speight, 2001; Speight and Ozum 2002).

In any of the methods for the determination of the asphaltene content (ASTM D-893, ASTM D-2006, ASTM D-2007, ASTM D-3279, ASTM D-4124, ASTM D-6560, IP 143), the crude oil or product (such as asphalt) is mixed with a large excess (usually >30 volumes hydrocarbon per volume of sample) of low-boiling hydrocarbon such as n-pentane or n-heptane. For an extremely viscous sample a solvent such as toluene may be used before the addition of the low-boiling hydrocarbon, but an additional amount of the hydrocarbon (usually >30 volumes hydrocarbon per volume of solvent) must be added to compensate for the presence of the solvent. After a specified time, the insoluble material (the asphaltene fraction) is separated (by filtration) and dried. The yield is reported as percentage by weight of the original sample.

It must be recognized that, in any of these tests, different hydrocarbons (such as n-pentane or n-heptane) will give different yields of the asphaltene fraction and if the presence of the solvent is not compensated by use of additional hydrocarbon the yield will be erroneous. In addition, if the hydrocarbon is not present in a large excess, the yields of the asphaltene fraction will vary and will be erroneous (Speight, 1999).

The precipitation number is often equated to the asphaltene content, but there are several issues that remain obvious in its rejection for this purpose. For example, the method to determine the precipitation number (ASTM D-91) advocates the use of naphtha for use with black oil or lubricating oil and the amount of insoluble material (as a % v/v of the sample) is the precipitating number. In the test, 10 ml of sample is mixed with 90 ml of ASTM precipitation naphtha (that may or may nor have a constant chemical composition) in a graduated centrifuge cone and centrifuged for 10 min at 600–700 rpm. The volume of material on the bottom of the centrifuge cone is noted until repeat centrifugation gives a value within 0.1 ml (the precipitation number). Obviously, this can be substantially different from the asphaltene content.

Another method, not specifically described as an asphaltene separation method, is designed to remove pentane-insoluble constituents by mem-
brane filtration (ASTM D-4055). In this method, a sample of oil is mixed with pentane in a volumetric flask, and the oil solution is filtered through a 0.8-\(\mu\)m membrane filter. The flask, funnel, and filter are washed with pentane to completely transfer any particulates onto the filter, after which the filter (with particulates) is dried and weighed to give the pentane-insoluble constituents as a percentage by weight of the sample. Particulates can also be determined by membrane filtration (ASTM D-2276, ASTM D-5452, ASTM D-6217, IP 415).

The storage stability of fuel oil may also be influenced by the crude oil origin, hydrocarbon composition, and refinery treatment (especially if unsaturated constituents are present). Fuel oil containing unsaturated hydrocarbons has a greater tendency to form sediment on aging than the straight-run fuel oils. Unsaturated hydrocarbon constituents can be determined by the bromine number. (ASTM D-1159, ASTM D-2710, IP 130).

The bromine number is the number of grams of bromine that will react with 100 g of the sample under the test conditions. The magnitude of the bromine number is an indication of the quantity of bromine-reactive constituents and is not an identification of constituents. It is used as a measure of aliphatic unsaturation in petroleum samples and of the percentage of olefins in petroleum distillates boiling up to approximately 315°C (600°F). In this test, a known weight of the sample dissolved in a specified solvent maintained at 0–5°C (32–41°F) is titrated with standard bromide-bromate solution. Determination of the end point is method- and sample dependent, being influenced by color.

The presence of reactive compounds of sulfur (e.g., thiophenes), nitrogen (pyrroles), and oxygen is also considered to contribute to fuel instability (Mushrush and Speight, 1995; Mushrush and Speight, 1998a; Mushrush and Speight, 1998b; Mushrush et al., 1999).

To ensure a product of satisfactory stability, test procedures are necessary to predict this aspect of quality control. One particular method (ASTM D-2274) uses short-term, high temperature procedures that are generally preferred to long-term, lower-temperature conditions. Although the accuracy of these empirical tests leaves much to be desired they do provide, with some background knowledge of the fuel, useful data relating to the fuel’s storage stability characteristics. And it is not often acknowledged that higher temperatures can, and often do, change the chemistry of the aging process, thereby leaving much open to speculation.

9.3.12. Viscosity

The viscosity of a fluid is a measure of its resistance to flow and is expressed as Saybolt Universal seconds (SUS), Saybolt Furol seconds (SFS), or centistokes (cSt, kinematic viscosity). Viscosity is one of the more important
heating oil characteristics because it is indicative of the rate at which the oil will flow in fuel systems and the ease with which it can be atomized in a given type of burner.

For the determination of the viscosity of petroleum products various procedures, such as Saybolt (ASTM D-88) and Engler, are available and have been in use for many years, all being of an empirical nature, measuring the time taken in seconds for a given volume of fuel to flow through an orifice of specified dimensions.

The use of these empirical procedures is being superseded by the more precise kinematic viscosity method (ASTM D-445, IP 71), in which a fixed volume of fuel flows through the capillary of a calibrated glass capillary viscometer under an accurately reproducible head and at a closely controlled temperature. The result is obtained from the product of the time taken for the fuel to flow between two etched marks on the capillary tube and the calibration factor of the viscometer and is reported in centistokes. Because the viscosity decreases with increasing temperature the temperature of test must also be reported if the viscosity value is to have any significance. For distillate fuel oils the usual test temperature is 38°C (100°F).

The viscosity index (ASTM D-2270, IP 226) is a widely used measure of the variation in kinematic viscosity due to changes in the temperature of petroleum and petroleum products between 40 and 100°C (104 and 212°F). For samples of similar kinematic viscosity, the higher the viscosity index the smaller is the effect of temperature on its kinematic viscosity. The accuracy of the calculated viscosity index is dependent only on the accuracy of the original viscosity determination.

9.3.13. Volatility

The volatility of fuel oil must be uniform, from batch to batch, if too-frequent resetting of burner controls is to be avoided and if maximum performance and efficiency are to be maintained. Information regarding the volatility and the proportion of fuel vaporized at any one temperature may be obtained from the standard distillation procedure (ASTM D-86, IP 123). The distillation test is significant for the distillate fuels because it is essential that the fuels contain sufficient volatile components to ensure that ignition and flame stability can be accomplished easily.

The distillation procedure (ASTM D 86, IP 123) measures the amount of liquid vaporized and subsequently condensed as the temperature of the fuel in the distillation flask is raised at a prescribed rate. A record is made of the volume of distillate collected at specified temperatures or, conversely, the temperature at each increment of volume distilled (usually 10% increments). The temperature at which the first drop of condensate is collected is called the initial boiling point. The end point usually is the highest
temperature recorded as the bottom of the flask becomes dry. If the sample is heated above 370°C (698°F), cracking occurs and the data are erroneous. The test usually is stopped when this point is reached. Some distillations may be run under reduced pressure (10 mmHg) to avoid cracking (ASTM D-1160). Under these conditions, fuel oil constituents may be distilled up to temperatures equivalent to 510°C (950°F) at atmospheric pressure.

Specifications for fuel oil may include limits on the temperatures at which 10% and 90% of the fuel are distilled by the standard procedure (ASTM D-396). For kerosene-type fuel oil (ASTM D-1) these values control the volatility at both ends of the distillation range, whereas for gas oil (ASTM D-1, ASTM D-2), where the front-end volatility is not so critical, only the 90% distillation temperature is normally specified. This ensures that high-boiling-point components, which are less likely to burn and which can cause carbon deposition, are excluded from the fuel.

One particular method is specifically designed for a high-boiling petroleum fraction having an initial boiling point greater than 150°C (300°F) (ASTM D-5236). The method consists of a pot still with a low-pressure drop entrainment separator operated under total takeoff conditions. The maximum achievable temperature, up to 565°C (1050°F), is dependent on the heat tolerance of the charge, but for distillate fuel oil the need to approach the maximum temperature is unnecessary. In this method, a weighed volume of the sample is distilled at pressures between 0.1 and 50 mmHg at specified distillation rates. Fractions are taken at preselected temperatures with records being made of the vapor temperature, the operating pressure, and any other variables deemed necessary. From the mass and density of each fraction distillation, yields by mass and volume can be calculated.

The boiling range distribution of certain fuel oils can be determined by gas chromatography (ASTM D-6352). This test method is applicable to petroleum distillate fractions with an initial boiling point of <700°C (<1292°F) at atmospheric pressure. The test method is not applicable to products containing low-molecular-weight components, for example, naphtha, reformate, gasoline, residuum, and petroleum itself, and should not be used for materials that contain heterogeneous components such as alcohols, ethers, esters, or acids or residue. In the method, a nonpolar open tubular capillary gas chromatographic column is used to elute the hydrocarbon components of the sample in order of increasing boiling point. A sample aliquot diluted with a viscosity-reducing solvent is introduced into the chromatographic system, and the column oven temperature is raised at a specified linear rate to effect separation of the hydrocarbon components. Retention times of known normal paraffin hydrocarbons spanning the scope of the test method are used for normalizing the retention times of the constituents of the fuel oil.
9.3.14. Water and Sediment

Considerable importance is attached to the presence of water or sediment in fuel oil because they lead to difficulties in use such as corrosion of equipment and blockages in fuel lines.

The sediment consists of finely divided solids that may be drilling mud or sand or scale picked up during the transport of the oil or may consist of chlorides derived from evaporation of brine droplets in the oil. The solids may be dispersed in the oil or carried in water droplets. Sediment in petroleum can lead to serious plugging of the equipment, corrosion due to chloride decomposition, and a lowering of residual fuel quality.

In any form, water and sediment are highly undesirable in fuel oil and the relevant tests involving distillation (ASTM D-95, ASTM D-4006, IP 74, IP 358), centrifuging (ASTM D-96, ASTM D-4007), extraction (ASTM D-473, IP 53), and the Karl Fischer titration (ASTM D-4377, ASTM D-4928, IP 356, IP 386, IP 438, IP 439) are regarded as important in examinations of quality.

The Karl Fischer test method (ASTM D-1364, ASTM D-6304) covers the direct determination of water in petroleum products. In the test, the sample injection in the titration vessel can be performed on a volumetric or gravimetric basis. Viscous samples can be analyzed with a water vaporizer accessory that heats the sample in the evaporation chamber, and the vaporized water is carried into the Karl Fischer titration cell by a dry inert carrier gas.

Water and sediment can be determined simultaneously (ASTM D-96, ASTM D-4007, IP 359) by the centrifuge method. Known volumes of the fuel oil and solvent are placed in a centrifuge tube and heated to 60°C (140°F). After centrifugation, the volume of the sediment and water layer at the bottom of the tube is read. For fuel oil that contains wax, a temperature of 71°C (160°F) or higher may be required to completely melt the wax crystals so that they are not measured as sediment.

Sediment is also determined by an extraction method (ASTM D-473, IP 53) or by membrane filtration (ASTM D-4807). In the former method (ASTM D-473, IP 53), an oil sample contained in a refractory thimble is extracted with hot toluene until the residue reaches a constant mass. In the latter test, the sample is dissolved in hot toluene and filtered under vacuum through a 0.45-μm-porosity membrane filter. The filter with residue is washed, dried, and weighed.

REFERENCES


