

# AVIATION FUEL

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## INTRODUCTION

*Aviation fuel*, is a collective term that includes:

- ❖ *aviation gasoline* ,
- ❖ *aviation gas turbine fuel*
- ❖ as well as various types of *jet fuel*.

Aviation fuels consist of **hydrocarbons**, and **sulfur-containing** as well as **oxygen-containing impurities** are limited strictly by specification.

The two basic types of jet fuels in general use are based on: 1-kerosene (kerosene-type jet fuel) and 2-gasoline (naphtha) (gasoline-type jet fuel).

Kerosene-type jet fuel is a modified development of the illuminating kerosene originally used in gas turbine engines and usually has the same distillation characteristics and flashpoint as kerosene (between 150°C and 300°C but not generally above (250°C).

Gasoline-type jet fuel has a wider boiling range and includes some gasoline fractions.

## PRODUCTION AND PROPERTIES

Aviation fuels have a narrower distillation range than motor gasoline, and the octane ratings of aviation gasoline and motor gasoline are not comparable because of the different test methods used to rate the two types of fuels.

In addition, motor gasoline has :

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1–a shorter storage stability lifetime than aviation gasoline.

2–can form gum deposits that can induce poor mixture distribution and valve sticking.

3–the higher aromatics content and the possible presence of oxygenates can induce solvent characteristics that are unsuitable for seals, gaskets, fuel lines, and some fuel tank materials in aircraft.

*Aviation gasoline*, for aviation piston engines, is produced from petroleum distillation fractions containing lower-boiling hydrocarbons that are usually found in straight-run naphtha. These fractions have high contents of *iso*-pentanes and *iso*-hexane and provide needed volatility as well as high octane numbers. Higher-boiling *iso*-paraffins are provided by a stream that consists mostly of branched octanes. Aromatics, such as benzene, toluene, and xylene, are obtained from processes such as catalytic reforming.

*Aviation gasoline* has:

1– an octane number suited to the engine,

2– a freezing point of  $-60^{\circ}\text{C}$ ,

3– and a distillation range usually within the limits of  $30^{\circ}\text{C}$  ( $86^{\circ}\text{F}$ ) and  $180^{\circ}\text{C}$  ( $356^{\circ}\text{F}$ ). Aviation gasoline specifications generally contain three main sections covering suitability, composition, and chemical and physical requirements.

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In addition, *gasoline type jet fuel* includes all light hydrocarbon fractions for use in aviation turbine power units and distills between 100°C (212°F) and 250°C (482°F). It is obtained by blending kerosene and gasoline or naphtha in such a way that the aromatic content does not exceed 25% v/v and the vapor pressure is between 13.7 kPa (2 psi) and 20.6 kPa (3 psi).

*Aviation turbine fuels* are manufactured predominantly from straight-run kerosene or kerosene-naphtha blends in the case of wide-cut fuels that are produced from the atmospheric distillation of crude oil. **Straight-run kerosene** from low-sulfur (sweet) crude oil will meet all the requirements of the jet fuel specification without further refinery processing, but for the majority of feedstocks, the kerosene fraction will contain trace constituents that must be removed by hydro treating or by a chemical sweetening process.

*Jet fuel* has been manufactured only from straight-run components, but in recent years, however, hydrocracking processes have been introduced that produce high quality kerosene fractions ideal for jet fuel blending.

## TEST METHODS

### Acidity

Acidic compounds can also be present in aviation turbine fuels either because of the acid treatment during the refining

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process or because of naturally occurring organic acids. Acidity is an undesirable property because of the possibility of metal corrosion and impairment of water separation characteristics of the fuel.

### Additives

International specifications allow for certain additives to be added to jet fuel, including:

- [Antioxidants](#) to prevent gumming, usually based on [alkylated phenols](#),
- [Antistatic agents](#), to dissipate [static electricity](#),
- [Corrosion inhibitors](#), e.g., [DCI-4A](#) used for civilian and military fuels, and [DCI-6A](#) used for military fuels;
- [Fuel system icing inhibitor](#) (FSII) agents, e.g.,
- [Biocides](#) are to remediate microbial (i.e., bacterial and fungal) growth present in aircraft fuel systems. Currently, two biocides are approved for use by most aircraft and turbine engine [original equipment manufacturers](#) (OEMs); Kathon FP1.5 Microbiocide and Biobor JF.
- [Metal deactivator](#) can be added to remediate the deleterious effects of trace metals on the thermal stability of the fuel. The one allowable additive is N,N'-disalicylidene 1,2-propanediamine.

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### Calorific Value (Heat of Combustion)

The heat of combustion (ASTM D-240, ASTM D-1405, ASTM D-2382, ASTM D-3338, ASTM D-4529, ASTM D-4809, ASTM D-6446, IP 12) is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter.

A simple equation for calculating the heat of combustion is:

$$Q = 12,400 - 2,100d_2 \quad \dots\dots\dots (1)$$

where  $Q$  is the heat of combustion and  $d$  is the specific gravity.

### Density (Specific Gravity)

The density (specific gravity) of a fuel is a measure of the mass per unit volume and can be determined directly with calibrated glass hydrometers.

- Both fuel specific gravity and calorific value vary somewhat according to crude source, paraffinic fuels having a slightly lower specific gravity but higher gravimetric calorific value than those from naphthenic crude oils.
- The volume of fuel that can be carried is limited by tank capacity, and to achieve maximum range a high-density fuel is preferred because this will provide the greatest heating value per gallon (liter) of fuel. The calorific (heating) value per unit weight in kg of fuel

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decreases with increasing density, and when the weight of fuel that can be carried is limited it may be advantageous to use a lower-density fuel, it is more common to specify fuel density in terms of the API gravity (ASTM D-287):

API gravity, degrees =  $[141.5/(\text{specific gravity } 60^\circ/60^\circ\text{F})] - 131.5$

Aviation fuel might be expected to have an API gravity in the range of 57 to 35 (specific gravity: 0.75 to 0.85 respectively).

### Flash point

The flash point test is a guide to the fire hazard associated with the use of the fuel; the flash point can be determined by several test methods.

- The minimum flash point is usually defined by the Abel method (IP 170), except for high-flash kerosene, where the Pensky-Martens method (ASTM D-93, IP 34) is specified.
- For jet fuel the flash point is a guide to the fire hazard associated with the fuel and can be determined by the same test methods as noted above (ASTM D-56, ASTM D-93, ASTM D-3828, IP 34, IP 170, IP 303),
- for high-flash kerosene, where the method (ASTM D-93, IP 34) is specified.

### Freezing Point

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Aviation fuels must have acceptable freezing point and low-temperature **pumpability** characteristics so that adequate fuel flow to the engine is maintained at high altitude; this is a requirement of aviation specifications.

Maximum freezing point values are specified for all types of aviation fuels as a guide to the lowest temperature at which the fuel can be used without risk of the separation of solid hydrocarbons.

The solidified hydrocarbons could lead to clogging of fuel lines or fuel filters and loss in available fuel load due to retention of solidified fuel in the tanks. The freezing point of the fuel (typically in the range  $-40$  to  $-65^{\circ}\text{C}$ ,  $-40$  to  $-85^{\circ}\text{F}$ ) must always be lower than the minimum operational fuel temperature.

### Knock and Antiknock Properties

The various fuel grades are classified by their *antiknock* quality characteristics as determined in single-cylinder laboratory engines.

- ✓ Knock, or detonation, in an engine is a form of abnormal combustion where the air/fuel charge in the cylinder ignites spontaneously in a localized area instead of being consumed progressively by the spark-initiated flame front.

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- ✓ Such knocking combustion can damage the engine and give serious power loss if allowed to persist, the antiknock ratings of aviation gasoline are determined in standard laboratory engines by matching their performance against reference blends of pure *iso*-octane and *n*-heptane. Fuels of higher performance than *iso*-octane (100 ON) are tested against blends of *iso*-octane with various amounts of antiknock additive.

The antiknock rating of fuel varies according to the air-fuel mixture strength used, and this fact is used in defining the performance requirements of the higher-grade aviation fuels. As mixture strength is increased, the additional fuel acts as an internal coolant and suppresses knocking combustion, thus permitting a higher power rating to be obtained.

Because maximum power output is the prime requirement of an engine under rich takeoff conditions, the *rich mixture performance* of a fuel is determined in a special supercharged single-cylinder engine (ASTM D-909, *weak mixture performance* is also determined (ASTM D 2700, IP 236).



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### Pour Point

The lowest temperature at which the movement of the oil is observed is recorded as the pour point. Determination of the pour point, a petroleum product that contains wax produces an irregular flow behavior when the wax begins to separate.

This type of product petroleum possesses viscosity relationships that are difficult to predict in operating conditions. This complex behavior may limit the value of pour point data, but laboratory pumpability tests (ASTM D-3245, IP 230) are available that, with the freezing point (ASTM D-2386, ASTM D-5901, ASTM D-5972, IP 16, IP 434, IP 435), give an estimate of minimum handling temperature and minimum line or storage temperature.

### Storage Stability

Aviation fuel must retain its required properties for long periods of storage in all kinds of climates.

- ✓ Unstable fuels oxidize and form oxidation products that remain as a resinous solid or gum on induction manifolds, carburetors, and valves as the fuel is evaporated. Hence, there is a limitation of olefins in the fuel; they are extremely reactive and form resinous products readily.
- ✓ Other tests for storage stability include determination of color formation and sediment

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(ASTM D-4625, ASTM D-5304) in which reactivity tooxygen at high temperatures is determined by the amount of sediment formationas well as any color change.

### Thermal Stability

Although the conventional (storage) stability of aviation fuel has long beendefined and controlled by the existent and accelerated gum tests,

### Water

Because of their higher density and viscosity, jet fuels tend to retain fineparticulate matter and water droplets in suspension for a much longer timethan aviation gasoline.

Jet fuels can also vary considerably in their tendency to pick up andretain water droplets or to hold fine water hazes in suspension dependingon the presence of trace surface-active impurities (surfactants). Some ofthese materials (such as sulfonic and naphthenic acids and their sodiumsalts) may originate from the crude source or from certain refinery treatingprocesses, whereas others may be picked up by contact with other productsduring transportation to the airfield, particularly in multiproductpipelines.

These latter materials may be natural contaminants from otherless highly refined products (e.g., burning oils) or may

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consist of additives from motor gasoline (such as glycol type anti-icing agents).

# COKE

## INTRODUCTION

Coke is a gray to black solid carbonaceous residue that is produced from petroleum during thermal processing; characterized by having a high carbon content (95%+ by weight) and a honeycomb type of appearance, and insoluble in organic solvents. (ASTM D-121)

Coke consists mainly of carbon (90–95%) and has a low mineral matter content (determined as ash residue). Coke is used as a feedstock in coke ovens for the steel industry, for heating purposes, for electrode manufacture, and for production of chemicals. The two most important categories are *green coke* and *calcinated coke*.

## TEST METHODS

The test methods for coke are necessary for defining the coke as a fuel (for internal use in a refinery) or for other uses, particularly those test methods in which prior sale of the coke is involved. Specifications are often dictated by environmental regulations, if not by the purchaser of the coke.

### Ash

The ash content (that is, the ash yield, which is related to the mineral matter content) is one of the properties used to evaluate coke; it indicates the amount of undesirable residue present. Some samples of coke may be declared to have an acceptable ash content, but this varies with the intended use of the coke.

## COKE

Ashing procedures can be used as a preliminary step for determination of the trace elements in coke and, by inference, in the higher boiling fractions of the crude oil. Among the techniques used for trace element determinations are:

1. flameless and flame atomic absorption (AA)
2. spectrophotometry (ASTM D-2788, ASTM D-5863)
3. and inductively coupled argon plasma (ICP) spectrophotometry (ASTM D-5708).

### Calorific Value (Heat of Combustion)

The calorific value (heat of combustion) is an important property, particularly for the petroleum products that are used for burning, heating, or similar usage. Knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

Heat of combustion per unit of mass of coke is a critical property of coke intended for use as a fuel. Other methods using an adiabatic bomb calorimeter (ASTM D-2015, ASTM D-5865) are also available

### Density

The *density (specific gravity)* of coke has a strong influence on its future use and can affect the characteristics of products such as carbon and graphite.

The density (specific gravity) of coke can be conveniently measured by use of a pycnometer.

## **COKE**

### **Proximate Analysis**

In contrast to the elemental analysis, the proximate analysis of coke is the determination of:

- the amount of mineral ash (ASTM D-3174),
- volatile matter (ASTM D-3175),
- water (moisture) (ASTM D-3173), and
- Fixed carbon. The fixed carbon is a calculated value and is the result of the summation of mineral ash (% by weight), volatile matter (% by weight), and water (% by weight) subtracted from 100.

### **Sulfur**

In addition to metallic constituents, coke also contains considerable amounts of sulfur (ASTM D-1552, ASTM D-3177, ASTM D-4239) that must be determined before sale or use.

### **Volatile Matter**

The volatile matter in coke affects the density of coke particles and can affect artifacts produced from further processing of the coke. The volatile matter can be used in estimating the calorific value of coke. The volatile matter of a moisture-free petroleum coke sample is determined by measuring the mass loss of the coke when heated under the exact conditions of the test method (ASTM D-6374).

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There are two sources of interferences in this test method—moisture and particle size. Moisture increases the mass loss, the moisture-free sample weight is decreased by the amount of moisture actually present in the test sample, and the particle size range of the analysis sample affects the volatile matter.

## **Water**

Water (or moisture) in coke adds weight to coke, and knowledge of the water in the coke is important in the purchase and sale of green coke.

GOOD LUCK

مع تمنياتي لكم بالنجاح

# **DIESEL FUEL**

## **INTRODUCTION**

Kerosene, diesel fuel, and aviation turbine fuel (jet fuel) are members of the class of petroleum products known (middle distillates). These products are higher boiling than gasoline but lower boiling than gas oil. Middle distillates cover the boiling range from approximately 175 to 375°C (350–700°F) and the carbon number range from about C<sub>8</sub> to C<sub>24</sub>.

## **PRODUCTION AND PROPERTIES**

Diesel fuels originally were straight-run products obtained from the distillation of crude oil. The boiling range of diesel fuel is approximately 125–328°C (302–575°F) (Table 8.1). In terms of carbon number and boiling range, diesel fuel occurs predominantly in the kerosene range.

Diesel fuel depends on:

1. the nature of the original crude oil,
2. the refining processes by which the fuel is produced,
3. the additive (if any) used, such as the solvent red dye (ASTM D-6258).

One of the most widely used specifications (ASTM D-975) covers three grades of diesel fuel oils,

1. No. 1-D,
2. No. 2-D
3. No. 4-D.



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**Table 8.1. General Summary of Product Types and Distillation Range**

| Product                 | Lower<br>Carbon<br>Limit | Upper<br>Carbon<br>Limit | Lower<br>Boiling<br>Point<br>°C | Upper<br>Boiling<br>Point<br>°C | Lower<br>Boiling<br>Point<br>°F | Upper<br>Boiling<br>Point<br>°F |
|-------------------------|--------------------------|--------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Refinery gas            | C <sub>1</sub>           | C <sub>4</sub>           | -161                            | -1                              | -259                            | 31                              |
| Liquefied petroleum gas | C <sub>3</sub>           | C <sub>4</sub>           | -42                             | -1                              | -44                             | 31                              |
| Naphtha                 | C <sub>5</sub>           | C <sub>17</sub>          | 36                              | 302                             | 97                              | 575                             |
| Gasoline                | C <sub>4</sub>           | C <sub>12</sub>          | -1                              | 216                             | 31                              | 421                             |
| Kerosene/diesel fuel    | C <sub>8</sub>           | C <sub>18</sub>          | 126                             | 258                             | 302                             | 575                             |
| Aviation turbine fuel   | C <sub>8</sub>           | C <sub>16</sub>          | 126                             | 287                             | 302                             | 548                             |
| Fuel oil                | C <sub>12</sub>          | >C <sub>20</sub>         | 216                             | 421                             | >343                            | >649                            |
| Lubricating oil         | >C <sub>20</sub>         |                          | >343                            |                                 | >649                            |                                 |
| Wax                     | C <sub>17</sub>          | >C <sub>20</sub>         | 302                             | >343                            | 575                             | >649                            |
| Asphalt                 | >C <sub>20</sub>         |                          | >343                            |                                 | >649                            |                                 |
| Coke                    | >C <sub>50</sub> *       |                          | >1000*                          |                                 | >1832*                          |                                 |

\*Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.

Grades No. 1-D and 2-D are distillate fuels (ASTM D-975), the types most commonly used in high-speed engines of the mobile type, in medium speed stationary engines, and in railroad engines.

Grade 4-D covers the class of more viscous distillates and, at times, blends of these distillates with residual fuel oils. The marine fuel specifications (ASTM D-2069) have four categories of distillate fuels and fifteen categories of fuels containing residual components. Additives may be used to improve the fuel performance, and additives such as alkyl nitrates and nitrites (ASTM D-1839, ASTM D-4046) can improve ignition quality.

## **DIESEL FUEL**

Pour point depressants can improve lowtemperatureperformance. Antismoke additives reduce exhaust smoke ,which is of growing concern as more and more attention is paid to atmospheric pollution.

Antioxidant and sludge dispersants may also be used, particularlywith fuels formulated with cracked components, to prevent theformation of insoluble compounds that could cause line and filter plugging (ASTM D-2068, ASTM D-6371, IP 309).

### **TEST METHODS**

#### **1-Acidity**

The *acid number* is a measure of the amount of acidic substances in the product under the conditions of the test. There are three other test methods for thedetermination of acid numbers (ASTM D-974, ASTM D-3339, ASTM D-4739) that are used to measure the inorganic and total acidity of the fuel and indicate its tendency to corrode metals that it may contact.

#### **2-Appearance and Odor**

*appearance*, or *color*, of diesel fuel is a useful indicator against contamination by residual (higher boiling) constituents, water, or fine solid particles. Therefore, it is necessary to make a visual inspection that clearfuel is being delivered (ASTM D-4176). In some cases the color may serve as an indication of the degree of refinement of the material. Several color scales are used for determination(ASTM D-156, ASTM D-1209, ASTM D-1500, ASTM D-1544, IP196). Typically the methods require a visual determination of color withcolored glass disks or reference materials.

Similarly, acceptance is important with regard to *odor*, and it is usually required that diesel fuel is reasonably free of contaminants, such as mercaptans, which impart unpleasant odors to the fuel (ASTM D-4952, IP 30).

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### Ash

Small amounts of unburnable material are found in diesel fuel 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.

The ash-forming constituents in diesel 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. The ash-forming constituents in diesel 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.

- Vanadium can form low-melting compounds such as vanadium pentoxide, which melts at 691°C (1275°F) and causes severe corrosive attack on all of the high-temperature alloys used for gas-turbine blades and diesel engine valves. If there is sufficient magnesium in the fuel, it will combine with the vanadium to form compounds with higher melting points and thus reduce the corrosion rate to an acceptable level. The resulting ash will form deposits in the turbine, but the deposits are self-spalling when the turbine is shut down.
- Sodium and potassium can combine with vanadium to form eutectics, which melt at temperatures as low as 565°C (1050°F), and with sulfur in the fuel to yield sulfates with melting points in the operating range of the gas turbine. These compounds produce severe corrosion for turbines operating at gas inlet temperatures above 649°C (1200°F).

Thus the amount of sodium plus potassium must be limited.

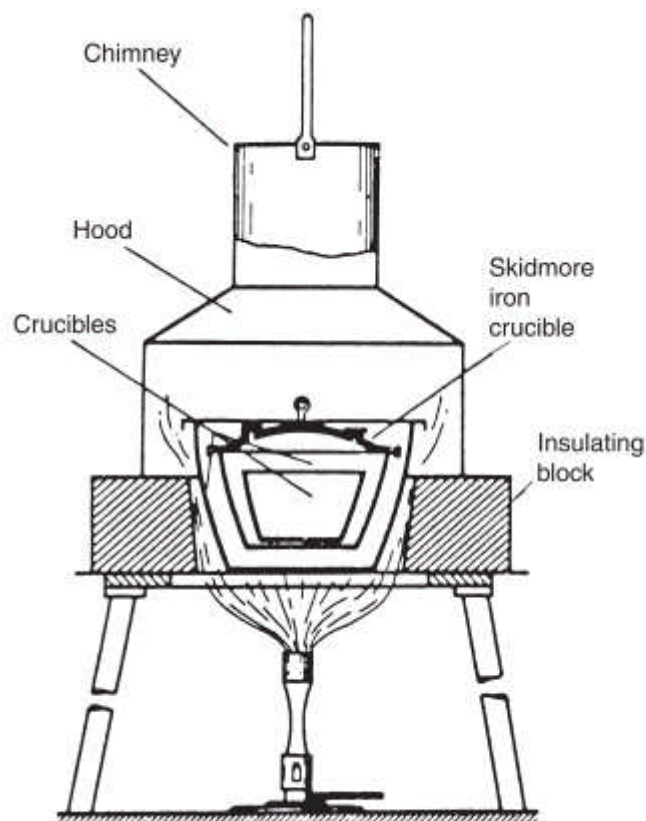
- For gas turbines operating below 649°C (1200°F), the corrosion due to sodium compounds is of lesser importance and can be further reduced by silicon-base additive. Calcium is not as harmful and may even serve to inhibit the corrosive action of vanadium. However, the presence of calcium can lead to deposits that are not self-spalling when the gas turbine is shut down and not readily removed by water washing of the turbine. Lead can cause corrosion, and it can spoil the beneficial inhibiting effect of magnesium additives on vanadium corrosion.

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- lead is only found rarely in significant quantities in crude oils, its presence in the fuel oil is primarily the result of contamination during processing or transportation.

### Carbon Residue

The carbon residue of a petroleum product serves as an indication of the propensity of the sample to form carbonaceous deposits (thermal coke) under the influence of heat. Tests for Conradson carbon residue (ASTM D-189, IP 13) (Fig. 8.1), the Ramsbottom carbon residue (ASTM D-524, IP 14), and the micro carbon carbon residue (ASTM D-4530, IP 398) are often included in specification data for diesel fuel. 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.



Apparatus for the determination of the Conradson carbon residue (ASTM 3)

## DIESEL FUEL

### Cetane Number and Cetane Index

The cetane number is an important property of diesel fuel. In the majority of diesel engines, the ignition delay period is shorter than the duration of injection. Under such circumstances, the total combustion period can be considered to be divided into the following four stages:

- (1) ignition delay,
- (2) rapid pressure rise
- (3) constant pressure or controlled pressure rise
- (4) burning on the expansion stroke.

To establish the cetane number scale, two reference fuels were selected. One, normal cetane, has excellent ignition qualities and, consequently, a very short ignition delay. A cetane number of 100 was arbitrarily assigned to this fuel. The second fuel, 1-methylnaphthalene, has poor ignition qualities and was assigned a cetane number of 0. To determine the cetane number of any fuel, its ignition delay is compared in a standard test engine with a blend of reference fuels (ASTM D-613, IP 41).

The cetane number of a diesel fuel is defined as the whole number nearest to the value determined by calculation from the percentage by volume of normal cetane (cetane No. 100) in a blend with heptamethylnonane (cetane No. = 15) which matches the ignition quality of the test fuel when compared by this method. The matching blend percentages to the first decimal are inserted in the following equation to obtain the cetane number:

$$\text{cetane number} = \% n\text{-cetane} + 0.15 (\% \text{ heptamethylnonane})$$

The shorter the ignition delay period, the higher the cetane number of the fuel and the smaller the amount of fuel in the combustion chamber when the fuel ignites. Consequently, high-cetane-number fuels generally cause lower rates of pressure rise and lower peak pressures, both of which tend to lessen combustion noise and to permit improved control of combustion, resulting in increased engine efficiency and power output.

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In addition to the above, higher-cetane-number fuels tend to result in easier starting, particularly in cold weather, and faster warm-up. The higher-cetane-number fuels also usually form softer and hence more readily purged combustion chamber deposits and result in reduced exhaust smoke and odor. High-speed diesel engines normally are supplied with fuels in the range of 45–55 cetane number.

### **Cloud Point**

Under low-temperature conditions, paraffinic constituents of diesel fuel may be precipitated as a wax. This settles out and blocks the fuel system lines and filters, causing malfunctioning or stalling of the engine. The temperature at which the precipitation occurs depends on the origin, type, and boiling range of the fuel. The more paraffinic the fuel, the higher the precipitation temperature and the less suitable the fuel for low-temperature operation.

The cloud point of a diesel fuel is a guide to the temperature at which it may clog filter systems and restrict flow. Cloud point is becoming increasingly important for fuels used in high-speed diesel engines, especially because of the tendency to equip such engines with finer filters. The finer the filter, the more readily it will become clogged by small quantities of precipitated wax. Larger fuel lines and filters of greater capacity reduce the effect of deposits from the fuel and therefore widen the cloud point range of fuels that can be used.

### **Diesel Index**

The diesel index is derived from the API gravity and aniline point (ASTM D-611, IP 2), the lowest temperature at which the fuel is completely miscible with an equal volume of aniline:

$$\text{diesel index} = \text{aniline point (}^{\circ}\text{F)} \times \text{API gravity} / 100$$

The above equation is seldom used because the results can be misleading.

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### **Pour Point**

Pour points often occur 8–10°F below the cloud points, and differences of 15–20°F are not uncommon.

Fuels, and in particular those fuels that contain wax, will in some circumstances flow below their tested pour point. However, the pour point does give a useful guide to the lowest temperature to which a fuel can be cooled without setting.

### **Viscosity**

Viscosity (ASTM D-445, IP 71) is a measure of the resistance to flow by a liquid and usually is measured by recording the time required for a given volume of fuel at a constant temperature to flow through a small orifice of standard dimensions. The viscosity of diesel fuel is important primarily because of its effect on the handling of the fuel by the pump and injection system.

Fuel viscosity also exerts a strong influence on the shape of the fuel spray insofar as a high viscosity can result in poor atomization, large droplets, and high spray jet penetration.

Fuel viscosities for high-speed engines range from (2 cSt to 6 cSt) at 37.8°C (100°F). Usually the lower viscosity limit is established to prevent leakage in worn fuel injection equipment as well as to supply lubrication for injection system components in certain types of engines. During operation at low atmospheric temperature, the viscosity limit sometimes is reduced to (4 cSt) at 100°F to obtain increased volatility and sufficiently low pour point. Fuels having viscosities greater than (6 cSt) usually are limited in application to the slower-speed engines. The very viscous fuels, such as are often used in large stationary and marine engines, usually require preheating for proper pumping, injection, and atomization.

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### **Volatility**

Distillation (or volatility) characteristics of a diesel fuel exert a great influence on its performance, particularly in medium- and high-speed engines. Distillation characteristics are measured with a procedure (ASTM D-86, IP123) in which a sample of the fuel is distilled and the vapor temperatures are recorded for the percentages of evaporation or distillation throughout the range.

The volatility requirement of diesel fuel varies with

- engine speed,
- size
- design

However, fuels having too low volatility tend to reduce power output and fuel economy through poor atomization, and those having too high volatility may reduce power output and fuel economy through vapor lock in the fuel system or inadequate droplet penetration from the nozzle.

In general, the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content, or viscosity of the fuel. If the 10% point is too high, poor starting may result. An excessive boiling range from 10% to 50% evaporated may increase warm up time. A low 50% point is desirable in preventing smoke and odor. Low 90% and end points tend to ensure low carbon residuals and minimum crankcase dilution.

### **Water and Sediment**

Water can contribute to filter blocking and cause corrosion of the injection system components. In addition to clogging of the filters, sediment can cause wear and create deposits both in the injection system and in the engine itself. Thus one of the most important characteristics of a diesel fuel, the water and sediment content (ASTM D-1796, IP 75), is the result of handling and storage practices from the time the fuel leaves the refinery until the time it is delivered to the engine injection system.



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Instability and resultant degradation of the fuel in contact with air contribute to the formation of organic sediment, particularly during storage and handling at elevated temperatures. Sediment generally consists of carbonaceous material, metals, or other inorganic matter. There are several causes of this type of contamination:

- (1) rust or dirt present in tanks and lines,
- (2) dirt introduced through careless handling practices,
- (3) dirt present in the air breathed into the storage facilities with fluctuating atmospheric temperature.

# DISTILLATE FUEL OIL

## INTRODUCTION

Fuel oils are complex mixtures of hydrocarbons, they cannot be rigidly classified or defined precisely by chemical formulae or definite physical properties , two broad classifications are generally recognized:

(1) *distillate fuel oil*

(2) *residual fuel oil*.

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.

**Table 9.1. General Summary of Product Types and Distillation Range**

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

\* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.

## DISTILLATE FUEL OIL

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.

*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.

## TEST METHODS

### Acidity

The presence of inorganic acids in distillate fuels, resulting from refinery treatment, is unlikely.

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.

### 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.

## DISTILLATE FUEL OIL

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 288) 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.

### 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 is usually expressed in British thermal units per pound (Btu/lb) or in calories per gram (c/g).

### 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*.

## **DISTILLATE FUEL OIL**

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.

The test methods are:

- (1) the Conradson carbon residue (ASTM D-189, IP 13),
- (2) the Ramsbottom carbon residue (ASTM D-524, IP 14),
- (3) 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 adaptation of the standard distillation procedure for gas oil (ASTM D-8, IP 123), so that the accuracy of the determination may be improved.

### **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 temperature 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 formation 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

## DISTILLATE FUEL OIL

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.

### 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.

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 flashpoint by the tag closed tester (ASTM D-56) are employed for fuel oil.

### 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

## **DISTILLATE FUEL OIL**

usually applicable to fuel oil but are more applicable to diesel fuel and aviation fuel. 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.

### **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.

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.

A sphaltic 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.

## DISTILLATE 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)

### 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.

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.

### Volatility

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. 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).

Fuel oil constituents may be distilled up to temperatures equivalent to 510°C (950°F) at atmospheric pressure. 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



## **DISTILLATE FUEL OIL**

with an initial boiling point of  $<700^{\circ}\text{C}$  ( $<1292^{\circ}\text{F}$ ) 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.

### **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.

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),
- 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.

## **GASOLINE**

Gasoline (also referred to as motor gasoline) is a mixture of volatile, flammable liquid hydrocarbons derived from petroleum that is used as fuel for internal combustion engines such as occur in motor vehicle.

The boiling range of motor gasoline falls between  $-1^{\circ}\text{C}$  ( $30^{\circ}\text{F}$ ) and  $216^{\circ}\text{C}$  ( $421^{\circ}\text{F}$ ) and has the potential to contain several hundred isomers of the various hydrocarbons (Tables 5.1 and 5.2).

The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms in their molecular structure and fall into three general types:

- (1) paraffins (including the cycloparaffins and branched materials),
- (2) olefins,
- (3) aromatics.

Gasoline boils at about the same range as naphtha) but below kerosene.

**Table 5.1. General Summary of Product Types and Distillation Range**

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

**Table 5.2. Increase in the number of Isomers with Carbon Number**

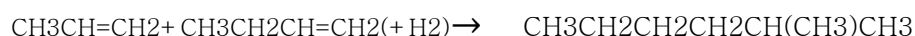
| Carbon Atoms | Number of Isomers  |
|--------------|--------------------|
| 1            | 1                  |
| 2            | 1                  |
| 3            | 1                  |
| 4            | 2                  |
| 5            | 3                  |
| 6            | 5                  |
| 7            | 9                  |
| 8            | 18                 |
| 9            | 35                 |
| 10           | 75                 |
| 15           | 4,347              |
| 20           | 366,319            |
| 25           | 36,797,588         |
| 30           | 4,111,846,763      |
| 40           | 62,491,178,805,831 |

## PRODUCTION AND PROPERTIES

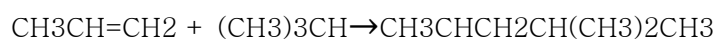
Gasoline was at first produced by distillation, simply separating the volatile, more valuable fractions of crude petroleum, later processes, designed to raise the yield of gasoline from crude oil, split higher-molecular-weight constituents into lower-molecular-weight products by processes known as *cracking* several processes produce the blending stocks for gasoline.

Some of these processes:

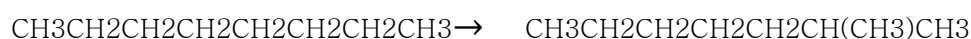
1. *Polymerization* is the conversion of gaseous olefins such as propylene and butylene into larger molecules in the gasoline range.



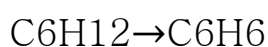
2. *Alkylation* is a process combining an olefin and a paraffin (such as *iso*-butane).



3. *Isomerization* is the conversion of straight-chain hydrocarbons to branched-chain hydrocarbons).



4. *Reforming* is the use of either heat or a catalyst to rearrange the molecular structure.



benzene

The hydrocarbons produced by modern refining techniques (distillation, cracking, reforming, alkylation, isomerization, and polymerization) provide blending components for gasoline production.

Gasoline consists of a very large number of different hydrocarbons so the composition of gasoline is best expressed in terms of hydrocarbon types (saturates, olefins,

## TEST METHODS

The properties of gasoline are quite diverse, and the principal properties affecting the performance of gasoline are volatility and combustion characteristics.

### 1. Additives

*Additives* are chemical compounds intended to improve some specific properties of gasoline or other petroleum products and can be monofunctional or multifunctional (Table 5.4; ASTM D-2669).

**Table 5.4. Additives for Gasoline**

| Class and Function   | Additive Type  |
|--|--|
| Oxidation Inhibitors—minimize oxidation and gum formation  | Aromatic amines and hindered phenols                         |
| Corrosion Inhibitors—inhibit ferrous corrosion in pipelines, storage tanks, and vehicle fuel systems                                       | Carboxylic acids and carboxylates                            |
| Metal Deactivators—inhibit oxidation and gum formation catalyzed by ions of copper and other metals  | Chelating agent  |
| Carburetor/Injector Detergents—prevent and remove deposits in carburetors and port fuel injectors  | Amines, amides, and amine carboxylates                       |
| Deposit Control Additives—remove and prevent deposits throughout fuel injectors, carburetors, intake ports and valves, and intake manifold | Polybutene amines and polyether amines                       |
| Demulsifiers—minimize emulsion formation by improving water separation   | Polyglycol derivatives                                       |
| Anti-Icing Additives—minimize engine stalling and starting problems by preventing ice formation in the carburetor and fuel system          | Surfactants, alcohols, and glycols                           |
| Antiknock Compounds—improve octane quality of gasoline   | Lead alkyls and methylcyclopentadienyl manganese tricarbonyl |
| Dyes—Identification of gasoline  | Oil-soluble solid and liquid dyes                            |

Thus certain substances added to gasoline, notably the lead alkyls, have a profound effect on antiknock properties and inhibit the precombustion oxidation chain that is known to promote knocking.

Tetraethyl lead (TEL) was the preferred compound, but more recently, tetramethyl lead (TML) has been shown to have advantages with certain modern types of gasoline because of its lower boiling point (110°C/230°F as against 200°C/392°F for tetraethyl lead) and therefore its higher vapor pressure, which enables it to be more evenly distributed among the engine cylinders with the more volatile components of the gasoline.

“scavengers” such as dibromoethane, alone or in admixture with dichloroethane, are added to the lead alkyl and combine with the lead during the combustion process to form volatile compounds that pass harmlessly from the engine. The amount of lead alkyl compounds used in gasoline is normally expressed in terms of equivalent grams of metallic lead per gallon or per liter.

The total lead in gasoline may be determined by:

- atomic absorption spectrometry (ASTM D-3237, IP 428),
- the iodine chloride method (ASTM D-3341, IP 270),
- inductively coupled plasma atomic emission spectrometry (ASTM D-5185),
- X-ray fluorescence (ASTM D-5059).

Other additives used in gasoline include:

- antioxidants and metal deactivators for inhibiting gum formation
- surface-active agents and freezing point depressants for preventing carburetor icing,
- deposit modifiers for reducing spark plug fouling and surface ignition,
- rust inhibitors (ASTM D-665, IP 135) for preventing the rusting of steel tanks and pipe work by the traces of water carried in gasoline.

For their estimation specialized procedures involving chemical tests and physical techniques such as spectroscopy and chromatography have been used successfully.

## **Combustion Characteristics**

Combustion in the spark ignition engine depends on

- engine design

- gasoline quality.

The various types of hydrocarbons in gasoline behave differently in :

- their pre-flame reactions and thus,
- their tendency to knock.

It is difficult to find any precise relationship between chemical structure and antiknock performance in an engine. Members of the same hydrocarbon series may show very different *antiknock* effects,

- aromatic hydrocarbons (e.g., benzene and toluene),
- highly branched *iso*-paraffins (e.g., *iso*-octane),
- and olefins

have high antiknock values.

In an intermediate position are *iso*-paraffins with little branching and naphthenic hydrocarbons (e.g., cyclohexane), the normal paraffins (e.g., normal heptane) are of low antiknock value

**Octane number** : is the percentage by volume of *iso*-octane (octane number 100) in admixture with normal heptane (octane number 0) that has the same knock characteristics as the gasoline being assessed.

Gasoline is normally rated by using two sets of conditions of differing severity:

☒ the research method (ASTM D-2699, IP 237), gives a rating applicable to mild operating conditions, that is, low inlet mixture temperature and relatively low engine loading such as would be experienced generally in passenger cars and light-duty commercial vehicles.

☒ The other is the motor method (ASTM D-2700, ASTM D-2885, IP 236), which represents more severe



operating conditions, that is, relatively high inletmixture temperature and high engine loading. The relationship between the octane number scaleabove 100 and the performance number scale is:

$$\text{Octane number} = 100 + (\text{performance number} - 100)/3$$

The **heat of combustion**(ASTM D-240, ASTM D-2382, IP 12) is a directmeasure of gasoline energy content and is determined as the quantityof heat liberated by the combustion of a unit quantity of gasoline withoxygen in a standard bomb calorimeter.

### **Corrosiveness**

Corrosiveness is usually due to the presence of:

- ☒ free sulfur and sulfurcompounds that burn to form sulfur dioxide (SO<sub>2</sub>), which combines withwater vapor formed by the combustion of the gasoline to produce sulfurousacid (H<sub>2</sub>SO<sub>3</sub>). Sulfurous acid can, in turn, oxidize to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>),and both acids are corrosive toward iron and steel. The total sulfur content of gasoline is very low, and knowledge of its magnitudeis of chief interest to the refiner who must produce a product thatconforms to a stringent specification.

- ☒ Mercaptan sulfur (R-SH) and hydrogen sulfide (H<sub>2</sub>S) (ASTM D-1219, IP 103, IP 104) are undesirable contaminants because, apart from their corrosiveness, they possess an extremely unpleasant odor.

Such compounds should have been removed completely during refining. Total sulfur is determined by combustion in a bomb calorimeter (ASTM D-129, IP 61) and is often carried out with the determination of calorific value.

### Density (Specific Gravity

- ☒ Density (the mass of liquid per unit volume at 15°C) and the related terms
- ☒ *specific gravity* (the ratio of the mass of a given volume of liquid at 15°C to the mass of an equal volume of pure water at the same temperature.) and
- ☒ *relative density* (same as *specific gravity*) are important properties of petroleum and petroleum products. Usually a hydrometer, pycnometer, or digital density meter is used for the determination in all these standards.

### Flash Point and Fire Point

The *Flash point* is the lowest temperature at atmospheric pressure (760 mmHg, 101.3 kPa) at which application of a test flame will cause the vapor of a sample to ignite under specified test conditions.

☒ Flash point data can also indicate the possible presence of highly volatile, in a relatively nonvolatile or nonflammable material.

☒ Flash point data are used in shipping and safety regulations to define *flammable* and *combustible* materials

The flash point of a petroleum product is also used to detect contamination.

1- The most common method of determining the flash point confines the vapor (closed cup method) until the instant the flame is applied (ASTM D-56, ASTM D-93, ASTM D-3828, 6450, IP 34, IP 94, IP 303).

2- An alternate method that does not confine the vapor (open cup method) (ASTM D-92, ASTM D-1310, IP 36) gives slightly higher values of the flash point.

☒ The Pensky-Marten apparatus using a closed or open system (ASTM D-93, IP 34, IP 35) is the standard instrument for flash points above 50°C (122°F),

☒ the Abel apparatus (IP 170) is used for more volatile oils, with flash points below 50°C (122°F).

The **Fire point** is the temperature to which the product must be heated under the prescribed conditions of the method to burn continuously when the mixture of vapor and air is ignited by a specified flame (ASTM D-92, IP 36).

### **Oxygenate blending**

Blends of gasoline with oxygenates are common (reduces the amount of [carbon monoxide](#) and [unburned fuel](#) in the exhaust gas) consist primarily of:

- ❖ gasoline with substantial amounts of oxygenates, which are oxygen-containing, ashless, organic compounds such as alcohols and ethers.

the most common oxygenate are:

- ethanol
- methyl-*t*-butyl ether (MTBE)
- with lesser attention focused on ethyl-*t*-butyl ether (ETBE),
- *t*-amyl methyl ether (TAME),
- and di-*iso*-propyl ether (DIPE).

The test methods for determining:

- distillation temperatures,
- lead content,
- sulfur content,

- copper corrosion,
- existent gum,
- and oxidation stability can be used for both gasoline and gasoline-oxygenate blends. Some of the test methods for vapor pressure and vapor-liquid ratio are sensitive to the presence of oxygenates in the gasoline and must be acknowledged accordingly.

## Stability and Instability

- The unsaturated hydrocarbon content and the heteroatom content appear to represent the greatest influence of the instability.
- The sulfur and nitrogen content of crude oil is an important parameter in respect of the processing methods that must be used to produce gasoline of specification sulfur concentrations.

There could well be a relation between nitrogen and sulfur content and crude oil (or product) stability; higher-nitrogen and—sulfur crude oils often exhibit higher sludge-forming tendencies.

Gasoline manufactured by cracking processes contains unsaturated components that may oxidize during storage and form undesirable oxidation products.

- An unstable gasoline will undergo oxidation and polymerization under such conditions, forming gum, a resinous material, which in the early stages of chain

reaction is initiated by the formation of peroxides and catalyzed by the presence of metals.

The *incompatibility* refers to the formation of a precipitate (or sediment) or phase separation when two liquids are mixed. Tests should also be carried out for sediment if the gasoline has been subjected to events (such as oxidation) that could lead to sediment formation and instability of the gasoline and the resulting products.

Test methods are available for the determination of sediment by :

- 1-extraction (ASTM D-473, IP 285)
- 2-membrane filtration (ASTM D-4807, IP 286)
- 3-the determination of sediment simultaneously with water by centrifugation (ASTM D-96, ASTM D-1796, ASTM D-2709, ASTM D-4007, IP 373, IP 374).

*Instability* occurs because of a low resistance of the product to environmental (in use) influences during storage and/or other degradative processes.

**Gum formation** (ASTM D-525, IP 40) alludes to the formation of soluble organic material, whereas *sediment* is insoluble organic material.

**Existent gum** is the name given to the nonvolatile residue present in the gasoline as received for test (ASTM D-381, IP 131).

potential gum is determined by the *accelerated gum test* (ASTM D-873, IP 138), which is used as a safeguard of storage stability and can be used to predict the potential for gum formation during prolonged storage.

## Volatility

The volatility of gasoline affects the performance of the engine in a number of ways,

1. ease of starting,
2. rate of warm-up,
3. vapor lock,
4. carburetor icing
5. crankcase dilution (the dilution of the engine lubricating oil with the higher-boiling constituents of the gasoline).

. The volatility of petroleum and petroleum products is an important aspect of safety and quality. It would be unsafe to attempt to store highly volatile materials in the open sunlight or in an enclosed space where temperature can rise to be in excess of 37.8°C (100°F).

The *vapor pressure* of petroleum or a petroleum product is the force exerted on the walls of a closed container by the vaporized portion of a liquid. Gasoline vapor pressure depends critically on its butane content, and in the refinery the final adjustment of vapor pressure of a gasoline to meet the specification is often made by butane injection.

The Reid vapor pressure (ASTM D-323, IP 69, IP 402) is a measure of the vapor pressure of petroleum or a petroleum product at 37.8°C (100°F) expressed as millimeters of mercury.

Distillation involves the general procedure of vaporizing the petroleum liquid in a suitable flask either at *atmospheric*

*pressure* (ASTM D-86) or at *reduced pressure* (ASTM D-1160).

The distillation tests are planned so that the data are reported:

in terms of one or more of the following items:

1. *Initial boiling point*. This reading is materially affected by a number of test conditions, namely, room temperature, rate of heating, and condenser temperature.

2. *Distillation temperatures*.

3. *End point or maximum temperature* is the highest thermometer reading observed during distillation.

4. *Dry point* is the thermometer reading at the instant the flask becomes dry

5. *Recovery* is the total volume of distillate recovered in the graduated receiver, and *residue* is the liquid material

6. *Total recovery* is the sum of the liquid recovery and residue; *distillation loss* is determined by subtracting the total recovery from 100%.

7. *Percentage evaporated* is the percentage recovered at a specific thermometer reading or other distillation temperatures,

## Water and Sediment

All water must be removed because the presence of more than 0.5% water in test samples of crude can cause several

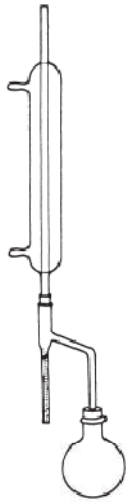


problems during distillation procedures. Water has a high heat of vaporization, necessitating the application of additional thermal energy to the distillation flask. Centrifugation can be used to remove water (and sediment) if the sample is not a tight emulsion. Other methods that are used to remove water include:

1. Heating in a pressure vessel to control loss of light ends,
2. Addition of calcium chloride as recommended in ASTM D-1160,
3. Addition of an azeotroping agent such as *iso*-propanol or *n*-butanol,
4. Removal of water in a preliminary low-efficiency or flash distillation followed by reblending the hydrocarbon that codistills with the water into the sample (IP 74), and
5. Separation of the water from the hydrocarbon distillate by freezing.

Water is a contaminant in gasoline and should be measured with :

- 1-By the **Karl Fischer method** (ASTM E-203, ASTM D-1364, ASTM D-1744, ASTM D-4377, ASTM D-4928, ASTM D-6304),
- 2-by distillation using a Dean and Stark condenser (ASTM D-4006)
- 3-By **centrifuging** (ASTM D-96).



Dean and Stark adaptor on the bottom of a condenser

- ☒ Test methods are available for the determination of sediment:
- 1- by extraction (ASTM D-473, IP 285)
  - 2- by membrane filtration (ASTM D-4807, IP 286).

# KEROSENE

*Kerosene* (*kerosine*), also called paraffin or paraffin oil, is a flammable pale yellow or colorless oily liquid with a characteristic odor intermediate in volatility between gasoline and gas/diesel oil that distills between 125°C (257°F) and 260°C (500°F) (Table 1).

Kerosene has a flash point about 25°C (77°F) and is suitable for use as an illuminant when burned in a wide lamp.

**Table 7.1. General Summary of Product Types and Distillation Range**

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

- Kerosene was first manufactured in the 1850s from coal tar, hence the name *coal oil* as often applied to kerosene, but petroleum became the major source after 1859.

## **KEROSENE**

- From that time, the kerosene fraction was, and has remained, a distillation fraction of petroleum and quality vary with the type of crude oil, and although some crude oils yield excellent kerosene quite simply, others produce kerosene that require substantial refining.
- Kerosene is less volatile than gasoline (boiling range approximately 140°C/285°F to 320°C/610°F) and is obtained by fractional distillation of Petroleum.
- To decrease smoke generation, paraffinic stocks are used normally in the manufacture of kerosene for lighting and heating, for the same reason, aromatic stocks and cracked components are avoided.
- Some crude oils, especially the paraffinic crude oils, contain kerosene fractions of very high quality, but other crude oils, such as those having an asphalt base, must be thoroughly refined to remove aromatics and sulfur compounds before a satisfactory kerosene fraction can be obtained.

## **KEROSENE**

Cracking the less volatile constituents of petroleum is now a major process for kerosene production.

Kerosene from naphthenic oil or high-sulfur crude oil requires :

- ✓ hydrotreating,
- ✓ acid treatment and water wash, or extraction with a solvent and caustic wash and clay brightening to remove undesirable aromatics or sulfur compounds.
- ✓ objectionable odors (mercaptans) are present (ASTM D-3227, IP 342), and these are removed by caustic washing or converted to odorless compounds by sweetening processes.

After treatment, the kerosene streams are blended to meet specifications and the finished product is ready for marketing. Chemically, kerosene is a mixture of hydrocarbons, and the constituents include *n*-dodecane (*n*-C<sub>12</sub>H<sub>26</sub>), alkyl benzenes, and naphthalene and its derivatives (ASTM D-1840).

## **KEROSENE**

The chemical composition depends on its source and has a high number ( $>100,000$ ) of isomers that are possible .

The actual number of compounds in kerosene is much lower, and there are claims to less than 100 constituents but that, again, is source- and process-dependent.

Kerosene, because of its use as burning oil, must be free of aromatic and unsaturated hydrocarbons as well as free of the more obnoxious sulfur compounds.

The desirable constituents of kerosene are saturated hydrocarbons, and it is for this reason that kerosene is manufactured as a straight-run fraction, not by a cracking process.

## **TEST METHODS**

Acids can be present in kerosene aviation turbine fuels because of acid treatment during refining.

These trace acid quantities are undesirable because of:

- the possibility of metal corrosion
- impairment of the burning characteristics and other properties of the kerosene.

## **KEROSENE**

The potential for metals in kerosene is less than it is for aviation fuels, but several of these tests can be applied.

### **Burning Characteristics**

The ability of kerosene to burn steadily and cleanly over an extended period (ASTM D-187, IP 10) is an important property and gives some indication of the purity or composition of the product.

The quality of a kerosene as a burning oil is related to its burning characteristics and is dependent on such factors as :

1. its composition
2. volatility,
3. viscosity,
4. calorific value,
5. sulfur content,
6. freedom from corrosive substances or contaminants.

This test method covers the qualitative determination of the burning properties of kerosene to be used for illuminating purposes.

## **KEROSENE**

The smoke point test (ASTM D-1319, ASTM D-1322, IP 57, IP 156) enables this property to be measured.

In this test the oil is burned in a standard wick-fed lamp in which flame height can be varied against a background of a graduated scale. The maximum flame height in millimeters at which the oil burns without smoking under the standard conditions is termed the smoke point.

The considerable effect on char-forming tendency of even traces of highboiling contaminants is demonstrated by the fact that the addition of 0.01% of a heavy lubricating oil to a kerosene of a char value of 103 mg/kg (the char value) can result in doubling that char value.

### **Calorific Value (Heat of Combustion)**

Heat of Combustion is a direct measure of fuel energy content and is determined as the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. A high calorific value is obviously desirable in oil used for heating purposes. Calorific value does not, however, vary greatly in the range of paraffinic-type kerosene (ASTM D-240, IP 12).

Equation that can be used to calculate the heat of combustion is based on the specific gravity of the kerosene:

$$Q = 12,400 - 2,100d^2$$

where  $Q$  is the heat of combustion and  $d$  is the specific gravity.



## KEROSENE

However, the accuracy of any method used to calculate such a property is not guaranteed and can only be used as a guide to or approximation of the measured value.

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 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.

### Density (Specific Gravity)

- Density (specific gravity) is an important property of petroleum products and is often part of product specifications (Table 7.2).

Materials are usually bought and sold on this basis or, if on a volume basis, then converted to a mass basis via density measurements.

This property is almost synonymously termed as density (mass of liquid per unit volume), specific gravity (the ratio of the mass of a given volume of liquid to the mass of an equal volume of pure water at the same temperature), and relative density (same as specific).

# KEROSENE

**Table 7.4. Specific Gravity and API Gravity of Crude Oil and Selected Products**

| Material                    | Specific Gravity<br>60°/60°F | API Gravity,<br>deg |
|-----------------------------|------------------------------|---------------------|
| Crude oils                  | 0.65–1.06                    | 87–2                |
| Casinghead liquid           | 0.62–0.70                    | 97–70               |
| Gasoline                    | 0.70–0.77                    | 70–52               |
| Kerosene                    | 0.77–0.82                    | 52–40               |
| Lubricating oil             | 0.88–0.98                    | 29–13               |
| Residua and cracked residua | 0.88–1.06                    | 29–2                |

Usually a hydrometer, pycnometer, or digital density meter is used in these standards .

Specific gravity has no relation to burning quality but is a useful aid in checking consistency of production of a particular grade. The specific gravity of kerosene can be determined very conveniently by the hydrometer method (ASTM D-1298, IP 160).

## Flash Point.

- The flash point is a guide to the fire hazard associated with the use of kerosene; it can be determined by several test methods, and the results are not always strictly comparable.
- Generally, the flash point of kerosene is specified as being in excess of 38°C (100°F) because of production as well as safety considerations.
- The minimum flash point is usually defined by the Abel method (IP 170), except for high-flash kerosene, where the Pensky-Martens method (ASTM D-93, IP 34) is specified.

## Freezing Point

## KEROSENE

The freezing point of kerosene is not of the same importance as the freezing point of aviation fuel.

Three test methods are available for determination of the freezing point: the first test (ASTM D-2386, IP 16)

the second test (ASTM D-5901, IP 434), the third method (ASTM D-5972, IP 435),

### Pour Point

The *pour point* is an index of the lowest temperature at which the crude oil will flow under specified conditions. The maximum and minimum pour point temperatures provide a temperature window where petroleum, 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 screening of the effect of wax interaction modifiers on the flow behavior of petroleum.

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. 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

pipeline 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

## **KEROSENE**

available that give an estimate of minimum handling temperature and minimum line or storage temperature.

### **Smoke Point**

The smoke point test adequately reflects the essential feature of hydrocarbon type composition in relation to burning characteristics, as already indicated, and consequently no analysis for composition is necessary in the normal evaluation of burning oils. Kerosene can vary widely in its burning quality as measured by carbon deposition, smoke formation, and flame radiation. This is a function of hydrocarbon composition—paraffins have excellent burning properties, in contrast to those of the aromatics (particularly the polynuclear aromatic hydrocarbons). As a control measure the smoke point test (ASTM D-1322, IP 57) gives the maximum smokeless flame height in millimeters at which the fuel will burn in a wick-fed lamp under prescribed conditions. The combustion performance of wide-cut fuels correlates well with smoke point when a fuel volatility factor is included, because carbon formation tends to increase with boiling point. A minimum smoke volatility index (SVI) value is specified and is defined as:

## **KEROSENE**

SVI = smoke point + 0.42 (percent distilled below 204°C/400°F).

### **Viscosity**

The kinematic viscosity of many petroleum fuels is important for their proper use, for example, flow of fuels through pipelines, injection nozzles, and orifices, and the determination of the temperature range for proper operation of the fuel in burners. Viscosity (ASTM D-445, IP 71) is more significant in this respect than surface tension, because it varies more in magnitude than the latter with different kerosenes and with change of temperature.

### **Volatility**

An abnormally high final boiling point and percentage residue of a kerosene may indicate contamination with higher-boiling constituents, although the presence of trace quantities of very heavy oils sufficient to cause high char values might not necessarily be revealed by these features. Thus the boiling range of kerosene is an important aspect of kerosene properties. The nature of the distillation range (ASTM D-86, IP 123) is of significance with regard to burning characteristics. It can control the flash point and viscosity, the effect of which has already been mentioned. The initial boiling point and the 10%

## **KEROSENE**

point chiefly affect the flash point and ease of ignition, whereas the midboiling point is more relevant to the viscosity. Contamination of kerosene with heavy oil may also be revealed by the test method that is used to determine the amount of residue left by evaporation (ASTM D-381, IP 131), although this depends on the relative volatility of the contaminant. The vapor pressure of petroleum products at various vapor-to-liquid ratios is an important physical property for shipping and storage. Although determining the volatility of kerosene is usually accomplished through a boiling range distribution (ASTM D-86, IP 123), determination of the Reid vapor pressure (ASTM D-323, IP 69) can also be used along with several other methods (ASTM D-5190, ASTM D-5482, ASTM D-6378).

### **Water and Sediment**

Kerosene, because of its higher density and viscosity, tends to retain fine particulate matter and water droplets in suspension for a much longer time than gasoline. Free water in kerosene can be detected by the use of a Dean and Stark adaptor (ASTM D-4006, IP 358) (Fig. 7.3), by the Karl Fischer titration method (ASTM D-1744, ASTM D-6304), by the distillation method (ASTM D-95, IP 74),

# LUBRICATING OIL

## INTRODUCTION

*Lubricating oil* is used to reduce friction and wear between bearing metallic surfaces that are moving with respect to each other by separating the metallic surfaces with a film of the oil. Lubricating oil is distinguished from other fractions of crude oil by a high ( $>400^{\circ}\text{C}/>750^{\circ}\text{F}$ ) boiling point (Table.1). In the early days of petroleum refining, kerosene was the major product, followed by paraffin wax wanted for the manufacture of candles. Lubricating oils were at first by-products of paraffin wax manufacture.

The preferred lubricants in the 1860s were lard oil, sperm oil, and tallow, but as the trend to heavier industry increased, the demand for mineral lubricating oils increased, and after the 1890s petroleum displaced animal and vegetable oils as the source of lubricants for most purposes.

## PRODUCTION AND PROPERTIES

Lubricating oil is a mixture that is produced by distillation, after which chemical changes may be required to produce the desired properties in the product. One such property requires that the oil adhere to metal surfaces and ensure protection of moving parts by preventing metal-metal contact (ASTM D-2510).

Petroleum base lubricating oils are present in the atmospheric residuum (boiling above  $370^{\circ}\text{C}/698^{\circ}\text{F}$ ) of selected paraffinic and naphthenic crude oils. The production of lubricating oils is well established and consists of five basic procedures:

1. Distillation and deasphalting to remove the lighter constituents of the feedstock.

## LUBRICATING OIL

2. Solvent refining and/or hydrogen treatment to remove the non-hydrocarbon constituents and to improve the feedstock quality.
3. Dewaxing to remove the wax constituents and improve the low temperature properties.
4. Clay treatment or hydrogen treatment to prevent instability of the product.

**Table 12.1. General Summary of Product Types and Distillation Range**

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

\* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.

### Acidity and Alkalinity

The acid number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. The *acid number* is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample in this solvent to a green/green-brown end point with *p*-naphtholbenzene indicator solution (ASTM D-974, IP 139). The base number is used as a guide in the quality control of oil formulation and is also used as a measure of oil degradation in service.

The *neutralization number*, expressed as the *base number*, is a measure of this amount of basic substance in the oil, always under the



## LUBRICATING OIL

conditions of the test. The neutralization number is used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service;

### Ash

The ash formed by the combustion of lubricating oil (ASTM D-482, ASTM D-2415, IP 4) is, as defined for other products, the inorganic residue, free from carbonaceous matter, remaining after ignition in air of the residual fuel oil at fairly high temperatures. The ash content is not directly equated to mineral content but can be converted to mineral matter content by the use of appropriate formulae.

### Asphaltene Content (Insoluble Constituents)

The asphaltene fraction (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. Insofar as the asphaltene content gives an indication of the amount of coke that can be expected during exposure to thermal conditions. Use of the oil under stressful conditions where heat is generated may introduce the need to determine the amount of insoluble constituents precipitated by the addition of a low-boiling hydrocarbon liquid to mineral oil.

### Carbon Residue

The tests that are applied to determine the carbon-forming propensity of fuel oil (and other petroleum products) are also available for application to lubricating oil should the occasion arise.

Thus the tests for:

1. the Conradson carbon residue (ASTM D-189, IP 13),
2. the Ramsbottom carbon residue (ASTM D-524, IP 14),

## LUBRICATING OIL

3. and the microcarboncarbon residue (ASTM D4530, IP 398) are often included in inspectiondata for fuel oil.

### Cloud Point

The *cloud point* is the temperature at which a cloud of wax crystal firstappears in a liquid when it is cooled under conditions prescribed in the testmethod. The cloud point is an indicator of the lowest temperature of theutility of an oil for certain applications and it is usually higher than the pourpoint .The cloud point (ASTM D-2500, IP 219) of lubricating oil is the temperatureat which paraffinic wax, and other components that readily solidify,begin to crystallize out and separate from the oil under prescribed testconditions. It is of importance to know when narrow clearances might berestricted by accumulation of solid material (for example, oil feed lines orfilters).

### Density (Specific Gravity)

Density (specific gravity) and API gravity measurements are used as manufacturing control tests and, in conjunction with other tests, are alsoused for characterizing unknown oils because they correlate approximatelywith hydrocarbon composition and, therefore, with the nature of the crudesource of the oil (ASTM D-1298, IP 160).

### Flash Point and Fire Point

- ☒ The Cleveland open cup method (ASTM D-92, IP36) can be used to determine both flash and fire points of lubricating oils,
- ☒ The Pensky–Martens closed (ASTM D-93, IP 34) and open (IP 35) flashpoints are also widely used.
- ☒ The flash and fire points are significant in cases where high-temperatureoperations are incountered, not only because of the hazard of fire but alsoas an indication of the volatility of an oil. In the case of used oils, the flashpoint is used to indicate the extent of contamination with more volatile oilsor with fuels such as gasoline (ASTM D-3607). The flash point can also beused to assist

## LUBRICATING OIL

in the identification of different types of base oil blend.

For used automotive engine oils that can be contaminated by a variety of materials, the presence of diesel fuel constituents can be approximately estimated from measurements of the flash point of the oil (ASTM D-92, IP36) that is appreciably lowered by small quantities of fuel. The presence of gasoline constituents can be measured by :

- distillation (ASTM D-322, IP 23)
- infrared spectroscopy.

### Oxidation Stability

Oxidation results in the development of

- acidic products that can lead to corrosion .
- Oxidation can also lead to an increase in viscosity
- the formation of sludge that can restrict oil paths, thus impairing circulation of the oil and interfering with the function of governors and oil relays.

Correctly formulated turbine oils have excellent resistance to oxidation and will function satisfactorily for long periods without changing the system charge. Although systems are usually designed to avoid entrainment of air in the oil, it is not always possible to prevent this, and the formation of stable foam increases the surface area of the oil that is exposed to small bubbles of air, thus assisting oxidation.

Defoaming agents are usually incorporated in turbine oils to decrease their foaming tendency, and this can be measured (ASTM D-892, IP 146).

Air release is also an important property, and

## LUBRICATING OIL

a careful choice of type and amount of defoaming agents is necessary to provide the correct balance of foam protection and air release properties.

### Pour Point

The pour point of wax-containing oils can be reduced by the use of special additives known as pour point depressants that inhibit the growth of wax crystals, thus preventing the formation of a solid structure. It is a recognized property of oil of this type that previous thermal history may affect the measured pour point. The test procedure (ASTM D-97, IP 15) also permits some measurement of the effect of thermal conditions on waxy oils.

The importance of the pour point to the user of lubricants is limited to applications where low temperatures are likely to influence oil flow. Obvious examples are refrigerator lubricants and automotive engine oils in cold climates. Any pump installed in outside locations where temperatures periodically fall below freezing should utilize lubricants with a pour point below those temperatures or the borderline pumping temperature can be determined by a designated test method (ASTM D-3829).

### Viscosity

The rate of flow of the oil through a pipe or capillary tube is directly proportional to the pressure applied. This property is measured for most practical purposes by timing the flow of a fixed amount of oil through a calibrated glass capillary tube under gravitational force at a standard temperature and is known as the kinematic viscosity of the oil (ASTM D-445, IP 71). The unit of viscosity used in

## LUBRICATING OIL

conjunction with this method is the centistoke (cSt), but this may be converted into the other viscosity systems (Saybolt, Redwood, Engler) by means of conversion formulae. At very high pressures, the viscosity of mineral oils increases considerably with increase in pressure, the extent depending on the crude source of the oil and on the molecular weight (ASTM D-2502, ASTM D-2878) of the constituent components.

Because the main objective of lubrication is to provide a film between load-bearing surfaces, the selection of the correct viscosity for the oil is aimed at a balance between a viscosity high enough to prevent the lubricated surfaces from contacting and low enough to minimize energy losses through excessive heat generation caused by having too viscous a lubricant (ASTM D-2422, BS-4231). The viscosity of automotive engine oil is the main controlling property for manufacture and for selection to meet the particular service condition using the American Society of Automotive Engineers (SAE) viscosity classification.

The higher-viscosity oils are standardized at 210°F (99°C), and the lighter oils that are intended for use in cold weather conditions are standardized at 0°F (−18°C). The viscosity index is important in applications in which an appreciable change in temperature of the lubricating oil could affect the operating characteristics of the equipment. Automatic transmissions for passenger vehicles are an example of this, where high-viscosity-index oils with improvers are used to minimize differences between a viscosity low enough to permit a sufficiently rapid gear shift when starting under cold conditions and a viscosity adequate at the higher temperatures encountered in normal running.

Paraffinic oils have the lowest rate of change of viscosity with temperature

## LUBRICATING OIL

(highest viscosity index), whereas the naphthenic/aromatic oils have the highest rate of change (lowest viscosity index) (ASTM D-567, ASTM D-2270, IP 73, IP 226). The viscosity index of multigrade automotive engine oils is typically in the range of 130–190, whereas monograde oils are usually between 85 and 105. The improved viscosity–temperature characteristics of multigrade oils enables, for example, an SAE 20W/50 oil to be formulated that spans SAE 20W viscosity characteristics at low temperatures and SAE 40 to 50 characteristics at the working temperature.

### Water and Sediment

Knowledge of the water content of petroleum products is important in refining, purchase and sale, and transfer of products and is useful in predicting the quality and performance characteristics of the products. The Karl Fischer test method (ASTM D-6304) can be applied to the direct determination of water in lubricating oil. Sediment in lubricating oil can lead to system malfunction in critical applications, and determination of the amount of sediment is a necessity. Insoluble material may form in lubricating oil in oxidizing conditions, and a test method is available (ASTM D-4310) to evaluate the tendency of lubricating oil to corrode copper catalyst metal and to form sludge during oxidation in the presence of oxygen, water, and copper and iron metals at an elevated temperature.

# WAX

## INTRODUCTION

Paraffin (petroleum) wax consists of the solid hydrocarbon residues remaining at the end of the refining process. Paraffin waxes consist mainly of straight-chain alkanes (also called normal alkanes), with small amounts (3–15%) of branched-chain alkanes (or *iso*alkanes), cycloalkanes, and aromatics.

Microcrystalline waxes contain high levels of branched-chain alkanes (up to 50%) and cycloalkanes, particularly in the upper end of the molecular weight distribution. Paraffin waxes contain alkanes up to a molecular mass of approximately 600 amu, whereas microcrystalline waxes can contain alkanes up to a molecular mass of approximately 1100 amu. Wax provides improved strength, moisture proofing, and low cost for the food packaging industry, the largest consumer of waxes today.

The coating of corrugated board with hot melts is of increasing importance to the wax industry. Other uses include the coating of fruit and cheese, the lining of cans and barrels, and the manufacture of anticorrosive.

## PRODUCTION AND PROPERTIES

Chemically, paraffin wax is a mixture of saturated aliphatic hydrocarbons (with the general formula  $C_nH_{2n+2}$ ). Wax is the residue extracted when lubricant oils are dewaxed and it has a crystalline structure with a carbon number greater than 12.

The main characteristics of wax are:

(1) absence of color,

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- (2) absence of odor,
- (3) translucence,
- (4) a melting point above 45°C (113°F).

Petroleum wax is of two general types,

- ❖ the paraffin waxes in petroleum distillates
- ❖ the microcrystalline waxes in petroleum residua.

The melting point of wax is not directly related to its boiling point, because waxes contain hydrocarbons of different chemical nature. Nevertheless, waxes are graded according to their melting point (ASTM D-87, IP 55) and oil content (ASTM D-721, IP 158)

### Appearance

Waxed coatings provide protection for packaged goods, and the high gloss characteristics provide improved appearance. Both the nature of the wax and the coating process contribute to the final gloss characteristics. *Specular gloss* (ASTM D-1834) is the capacity of a surface to simulate a mirror in its ability to reflect an incident light beam

### Barrier Properties

The ability of wax to prevent the transfer of moisture vapor is of primary concern in the food packaging industry. To maintain the freshness of dry foods, moisture must be kept out of the product, but to maintain the quality of frozen foods the moisture must be kept in the product.

This results in two criteria for barrier properties: moisture vapor transmission rates

- (A) at elevated temperatures and high relative humidity and



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(B) at low temperatures and low relative humidity, for frozen foods.

### Color

Paraffin wax is generally white in color, whereas microcrystalline wax and petrolatum range from white to almost black. A fully refined wax should be virtually colorless (*water-white*) when examined in the molten state.

### Hardness

Hardness is a measure of resistance to deformation or damage; hence it is an important criterion for many wax applications. It is indirectly related to blocking tendency and gloss. Hard, narrow-cut waxes have higher blocking points and better gloss than waxes of the same average molecular weight.

### Melting Point

The *melting point* is one of the most widely used tests to determine the quality and type of wax because wax is, more often than not, sold on the basis of the melting point range (ASTM D-87, ASTM D-4419, IP 55).

Petroleum wax, unlike the individual hydrocarbons (Table 14.1) does not melt at sharply defined temperatures because it is a mixture of hydrocarbons with different melting points but usually has a narrow melting range but wider molecular weight range.

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### **Molecular Weight**

The molecular weight of various waxes may differ according to (1) the source of the wax (whether it originated in lighter- or heavier-grade lubricating oils) .

(2) the processing of the wax (the closeness of the distillation cut or the fractionation by crystallization).

An increase in molecular weight increases viscosity and melting point. However, many of the other physical and functional properties are more related to the hydrocarbon types and distribution than to the average molecular weight.

### **Slip Properties**

Friction is an indication of the resistance to sliding exhibited by two surfaces in contact with one another. The intended application determines the degree of slip desired. Coatings for packages that require stacking should have a high coefficient of friction to prevent slippage in the stacks.

Folding box coatings should have a low coefficient of friction to allow the boxes to slide easily from a stack of blanks being fed to the forming and filling equipment.

### **Storage Stability**

The presence of peroxides or similar oxy-compounds is usually the result of oxidation and deterioration of waxes either in use or storage. Antioxidants, such as butylated hydroxyanisole, may be used to retard oxidation.

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### Viscosity

Viscosity of molten wax (ASTM D-3236) is of importance in applications involving coating or dipping processes because it influences the quality of coating obtained. Examples of such applications are paper converting, hot dip anticorrosion coatings, and taper manufacturing.

Paraffin waxes do not differ much in viscosity, a typical viscosity being  $\pm 0.5$  cSt at 99°C (210°F). Microcrystalline wax is considerably more viscous and varies over a wide range, 10–20 cSt at 99°C (210°F). Some hot melt viscosities exceed 20,000 cSt at 177°C (350°F).

### Volatility

The boiling point distribution of paraffin wax provides an estimate of hydrocarbon molecular weight distribution that influences many of the physical and functional properties of petroleum wax. To a lesser extent, distillation characteristics also are influenced by the distribution of various molecular types; that is, *n*-paraffins, branched, or cyclic structures. In the case of the paraffin waxes that are predominantly straight chain, the distillation curve reflects the molecular size distribution.