FOSSIL FUELS

Background

The three general classes of fossil fuels are coal, oil and natural gas. Other fuels, such as shale oil (bitümlü şist), tar-sand oil (ziftli kum) and other fossil-fuel derivatives are somewhat different, but they are still considered to be fossil fuels and are commonly lumped under one of the three common fossil-fuel categories.

All of the fossil fuels were produced from the fossilization of carbohydrate compounds. These compounds with a general chemical formula of $C_n(H_2O)_y$, were produced by living plants in the photosynthesis process as the plants converted direct solar energy into chemical energy. Most of the fossil fuels were produced during the Carboniferous Period of the Paleozoic Era—some 325 million years ago. After the plants died, the carbohydrates were converted, by pressure and heat, in the absence of oxygen, into hydrocarbon compounds with a general chemical formula of $C_nH_m$. Since all fossil fuels are composed of hydrocarbon compounds, a brief, general review of hydrocarbon chemistry would appear to be warranted.

Hydrocarbon Chemistry

Although hydrocarbon compounds are composed of only carbon and hydrogen atoms, in some of the more complex molecules the same number of carbon and hydrogen atoms can be arranged in different structures to produce compounds with strikingly different chemical and physical properties.

There are three major groups of hydrocarbon compounds—the aliphatic hydrocarbons, the alicyclic hydrocarbons, and the aromatic hydrocarbons. The aliphatic hydrocarbons are compounds which are composed of carbon-atom "chains" and most of the fossil-fuel compounds fall into this major group. The other two major hydrocarbon groups are "ring" hydrocarbons. The adjectives "saturated" and "unsaturated" are sometimes applied to hydrocarbon compounds. Saturated hydrocarbons are those compounds in which there are only single bonds between any two carbon atoms. Unsaturated hydrocarbons have at least two carbon atoms that share multiple bonds.

The aliphatic or chain hydrocarbons are further divided into three subgroups—the alkane, the alkene, and the alkyne hydrocarbons. The alkane hydrocarbons, also called the paraffin series, are the saturated group of chain hydrocarbons. The general chemical formula for this group is $C_nH_{2n+2}$. Many of the common fuel compounds fall into this subgroup and some of the typical compounds are listed below with their chemical formulas:

| Methane, CH$_4$ | Pentane, C$_5$H$_{12}$ | Nonane, C$_9$H$_{20}$ |
| Ethane, C$_2$H$_6$ | Hexane, C$_6$H$_{14}$ | Decane, C$_{10}$H$_{22}$ |
| Propane, C$_3$H$_8$ | Heptane, C$_7$H$_{16}$ | Octane, C$_8$H$_{18}$ |
| Butane, C$_4$H$_{10}$ | Octadecane, C$_{16}$H$_{34}$ |

Some of the compounds listed above are readily recognizable as the prime components of some of the common fossil fuels. Methane and ethane comprise most of the natural gases. Propane and butane make up liquefied petroleum gas (LPG), and octane is a common compound used in gasoline. As the number of atoms in the alkane molecules increase, the hydrogen fraction decreases and the hydrocarbons become less volatile. The first four compounds are gases at room temperature and atmospheric pressure (STP), while the balance of those listed are liquids at those conditions. The very long-chained molecules are solids.
The exact structure of the hydrocarbon molecule strongly influences its chemical and physical properties. If the prefix \( n \)-, which stands for "normal" appears in front of the hydrocarbon name, it means that all of the carbon atoms are connected in one long chain. The prefix \( iso \) in front of the name means that there are carbon-atom branches, usually methyl groups \((\text{CH}_3)\) connected to the main chain. The \( n \)-octane and isooctane (called as 2,2,4-trimethylpentane) molecules are:

\[
\text{n-Octane} \\
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

\[
\text{Isooctane} \\
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

If one of the hydrogen atoms in an alkane hydrocarbon is replaced with an OH\(^-\) radical, the compound is an alcohol. These compounds are also used as fuels. Some of the more common alcohols are methyl alcohol or methanol \((\text{CH}_3\text{OH})\), ethyl alcohol or ethanol \((\text{C}_2\text{H}_5\text{OH})\), and propyl alcohol or propanol \((\text{C}_3\text{H}_7\text{OH})\).

The alkene and alkyne subgroups of aliphatic hydrocarbons are unsaturated hydrocarbon compounds. The alkene hydrocarbons, also called the olefin series, have one double bond between two of the carbon atoms in the chain. The general formula for this group is \( \text{C}_n\text{H}_{2n} \), and some of the typical compounds are ethylene \((\text{C}_2\text{H}_4)\), propylene \((\text{C}_3\text{H}_6)\), butene \((\text{C}_4\text{H}_8)\), pentene \((\text{C}_5\text{H}_{10})\), and hexene \((\text{C}_6\text{H}_{12})\). The alkyne hydrocarbons, also called the acetylene series, have one triple carbon-atom bond in the hydrocarbon chain. The general formula for this series is \( \text{C}_n\text{H}_{2n-2} \), and some typical compounds are acetylene \((\text{C}_2\text{H}_2)\) and ethylacetylene \((\text{C}_4\text{H}_6)\). Two unsaturated aliphatic hydrocarbons are as follows:

\[
\text{Propylene} \\
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \equiv \text{C} \equiv \text{C} \\
\text{H} \\
\text{H} \\
\end{array}
\]

\[
\text{Ethylacetylene} \\
\begin{array}{c}
\text{H} \\
\text{C} \equiv \text{C} \equiv \text{C} \\
\text{H} \\
\text{H} \\
\end{array}
\]

The other two major hydrocarbon groups, the alicyclic and the aromatic compounds, are "ring" hydrocarbons because the molecules are composed of carbon-atom rings. The alicyclic hydrocarbons (naftenler) are composed of saturated carbon-atom rings and have a general formula that is identical to that of the alkene subgroup of aliphatic hydrocarbons, i.e., \( \text{C}_n\text{H}_{2n} \). The names of the alicyclic compounds are simply the names of the alkane group preceded by
the prefix "cyclo." Thus, there is cyclopropane ($C_3H_6$), cyclobutane ($C_4H_8$), cyclopentane ($C_5H_{10}$), etc. A typical alicyclic compound is shown, as follows:

![Cyclobutane](image)

The aromatic hydrocarbons are composed of the basic benzene ring or rings. This ring is a six-atom carbon ring with double bonds between every other carbon atom (three double bonds in the simple ring). The general chemical formula for single-ring molecules is $C_nH_{2n-6}$ and for double-ring molecules is $C_nH_{2n-12}$. Some of the typical aromatic compounds are benzene ($C_6H_6$), toluene ($C_7H_8$), xylene ($C_8H_{10}$), and naphthalene ($C_{10}H_8$). These compounds are made by adding methyl groups to the basic ring or rings. The two basic rings are shown as follows:

![Benzene and Naphthalene](image)

**Standard Fuels**

There are a number of basic hydrocarbon compounds that are used as standards for internal combustion engine fuels. Spark-ignition, internal combustion engine fuels are rated according to the *octane number*. Compression-ignition, internal combustion engine fuels are rated according to the *cetane number*.

The 100-octane fuel standard is 2,2,4-trimethylpentane, $C_8H_{18}$ while the 0-octane fuel standard is n-heptane, $C_7H_{16}$. The octane number of an unknown fuel is determined in a cooperative fuels research engine (CFR engine). This engine is a single-cylinder engine with a compression ratio that can be adjusted from about 4:1 to about 14:1. The unknown fuel is burned in the engine and the compression ratio is slowly increased until a certain "knock" or detonation reading is obtained from a vibration detector. Blends of the standard fuels are then burned at the same compression ratio until approximately the same "knock" reading is obtained. The percent by volume of 2,2,4-trimethylpentane in a blend of 2,2,4-trimethylpentane and n-heptane is the octane number of the unknown fuel. The octane ratings of most "regular" gasolines range from 85 to 95.

Some premium gasolines have octane numbers greater than 100. Octane numbers in excess of 100 can be achieved by using lighter hydrocarbons and alcohols and/or by putting additives, such as tetraethyl lead (TEL), in the basic fuel.
The 100-cetane fuel standard for compression ignition or diesel fuels is n-hexadecane (C\textsubscript{16}H\textsubscript{34}), which is sometimes called \textit{n-cetane}. The 0-cetane fuel standard is alpha-methylnaphthalene (C\textsubscript{11}H\textsubscript{10}). The cetane rating of an unknown diesel fuel is equal to the percent by volume of n-hexadecane in a mixture of the standard fuels that has the same combustion characteristics in a CFR diesel engine as that of the unknown fuel. The cetane ratings of most diesel fuels range between 30 and 60.

\textbf{Composition Crude Oil}

The proportion of hydrocarbons in the mixture is highly variable and ranges from as much as 97\% by weight in the lighter oils to as little as 50\% in the heavier oils and bitumens.

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits as follows:

<table>
<thead>
<tr>
<th>Element</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>83-87%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10-14%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.1-2%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.1-1.5%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.5-6%</td>
</tr>
<tr>
<td>Metals</td>
<td>&lt;1000 ppm</td>
</tr>
</tbody>
</table>

The proportion of hydrocarbons in the mixture
Industrial Fractional Distillation

Fractional distillation is used in oil refineries to separate crude oil into useful substances, (or fractions) having different hydrocarbons of different boiling points, by heating them to a temperature at which several fractions of the compound will evaporate. The crude oil fractions with higher boiling points:

- have more carbon atoms
- have higher molecular weights
- are darker in color
- are more viscous
- are more difficult to ignite and to burn

In order to separate the different length chains in the crude mix, it is heated to a very high temperature. The temperature is set so that all those fractions with a Carbon chain length of 20 and below are evaporated from the crude mix. The temperature cannot be set higher than this as there is a risk that the lighter fractions will ignite.

The remaining liquid, which is composed of only the heavier fractions, passes to a second location where it is heated to a similar temperature, but at lower pressure. This has the effect of making the heavy hydrocarbon fractions more likely to evaporate.
How the Distillation Tower Works

The way the distillation tower works is by becoming progressively cooler from the base to the top. All the hydrocarbon fractions start off in gas form, as they have been heated to that point. The gases then rise up the tower. The gas mixture then encounters a barrier through which there are only openings into the bubble caps. The gas mixture is then forced to go through a liquid before continuing upwards. The liquid in the first tray is at a cool enough temperature to get the heaviest gas fractions to condense into liquid form, while the lighter fractions stay gaseous. In this way the heaviest hydrocarbon fractions are separated out from the mixed gas. The remaining gas continues its journey up the tower until it reaches another barrier. Here the bubble cap process is repeated but at a lower temperature than before, which then filters out the next lightest set of fractions.

The separation of the heavier elements in the second tower follows exactly the same process but at lower pressure.
Cracking
In petroleum geology and chemistry, cracking is the process whereby complex organic molecules such as heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors. The rate of cracking and the end products are strongly dependent on the temperature and presence of any catalysts.

Reforming
Catalytic reforming is a chemical process used to convert petroleum refinery naphthas, typically having low octane ratings, into high-octane liquid products called reformates which are components of high-octane gasoline. Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstocks as well as breaking some of the molecules into smaller molecules. The overall effect is that the product reformate contains hydrocarbons with more complex molecular shapes having higher octane values than the hydrocarbons in the naphtha feedstock.

Alkylation
The alkylation process in petroleum refining combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with isobutene in the presence of a catalyst, either sulfuric acid or hydrofluoric acid. The product is called alkylate and is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons.

Coking
A coker or coker unit is an oil refinery processing unit that converts the residual oil from the vacuum distillation column or the atmospheric distillation column into low molecular weight hydrocarbon gases, naphtha, light and heavy gas oils, and petroleum coke. The process thermally cracks the long chain hydrocarbon molecules in the residual oil feed into shorter chain molecules.
LABORATORY TESTS
Flash Point Test

Flash point for a hydrocarbon or a fuel is the minimum temperature at which vapor pressure of the hydrocarbon is sufficient to produce the vapor needed for spontaneous ignition of the hydrocarbon with the air in the presence of an external source, i.e., spark or flame. From this definition, it is clear that hydrocarbons with higher vapor pressures (lighter compounds) have lower flash points. Generally flash point increases with an increase in boiling point.

Significance and use

- Flash point is an important parameter for safety considerations, especially during storage and transportation of volatile petroleum products (i.e., LPG, light naphtha, gasoline) in a high-temperature environment.
- Flash point is used as an indication of the fire and explosion potential of a petroleum product.

There are two methods used for determining the flash point of an intermediate and finished petroleum product. These are the ASTM D56 The Tag Closed Cup method (commonly known as the ABEL flash point) and the ASTM D93 The Pensky Marten Closed Cup method.

Test Method

A brass test cup is filled to an inside mark with the test specimen. A cover is fitted of specified dimensions, see Figure 1. The specimen is heated and stirred at specified rates. An ignition source in the form of a small flame is directed into the cup at regular intervals. When the specimen is seen to flash, the temperature of the specimen is noted as the flash point of the sample.

Figure 1
**Viscosity Test**

The viscosity of a fuel is a measure of its resistance to internal flow and is an indication of its lubricating qualities. The common viscometer instruments are the Saybolt, Kinematic, Oswald, Engler and Redwood. In the oil industry it is usual to quote viscosities either in centistokes (which is the unit for kinematic viscosity), seconds Saybolt universal, seconds Saybolt furol, or seconds Redwood. These units have been correlated and such correlations can be found in most data books.

**Significance and use**

- Kinematic viscosity is a useful characterization parameter for heavy fractions in which boiling point data are not available due to thermal decomposition during distillation.
- Not only is viscosity an important physical property, but it is a parameter that can be used to estimate other physical properties as well as the composition and quality of undefined petroleum fractions.
- Kinematic viscosity affects injector lubrication and fuel atomization. Higher viscosity levels tend to form larger droplets on injection which can cause poor combustion and increased exhaust smoke. Extremely low viscosities may not provide sufficient lubrication for the closely-fit pumps and injector plungers. They can promote abnormal wear and cause injector leakage and dribbling leading to loss of power and smoke problems.

Since viscosity varies with temperature, values of viscosity must be reported with specified temperature. Generally, kinematic viscosity of petroleum fractions are measured at standard temperatures of 37.8°C (100°F) and 98.9°C (210°F) However, for very heavy fractions viscosity is reported at temperatures above 38°C i.e., 50°C (122°F or 60°C (140°F).

Viscosity (absolute viscosity) shown by $\mu$ has the dimension in the SI system the unit of viscosity is Pa- s (N. m$^{-2}$.s). In the cgs system the unit of viscosity is in g/cm.s that is called poise (p) and its hundredth is called centipoises (cp), which is equivalent to milli-Pa, s (mPa.s).

The ratio of viscosity to density is known as kinematic viscosity ($\nu$) and has the dimension of in the cgs system, the unit of kinematic viscosity is cm$^2$/s also called stoke (St) and its hundredth is centistoke (cSt).

Another unit to express kinematic viscosity of liquids is Saybolt universal seconds (SUS), which is the unit for the Saybolt universal viscosity as shown in Fig. 2.

**Test Method**

Determines the time required for 60mL of sample to flow through a calibrated orifice under precisely controlled conditions. Saybolt Universal Seconds (SUS) is the standard measurement for lubricants, insulating oils, and lighter fuel grades, and Saybolt Furol Seconds (SFS) is used for heavier oils and bitumens (zift).
Pour and Cloud point Tests

The pour point of a petroleum fraction is the lowest temperature at which the oil will pour or flow when it is cooled without stirring under standard cooling conditions. Pour point represents the lowest temperature at which an oil can be stored and still capable of flowing under gravity. Pour point is one of low temperature characteristics of heavy fractions.

Significance and use

- When temperature is less than pour point of a petroleum product it cannot be stored or transferred through a pipeline.

The cloud point is the lowest temperature at which wax (mum) crystals begin to form by a gradual cooling under standard conditions. At this temperature the oil becomes cloudy and the first particles of wax crystals are observed. As temperature decreases below the cloud point, formation of wax crystals is accelerated. Therefore, low cloud point products are desirable under low-temperature conditions.

Significance and use

- Wax crystals can plug the fuel system lines and filters, which could lead to stalling aircraft and diesel engines under cold conditions.

Test Method

The apparatus used to determine pour point (and cloud point) consists of a cylindrical glass jar with a flat bottom a coke stopper at it’s top as shown in Fig. 4. A thermometer is inserted through the coke stopper so that the bulb is immersed up to 3 mm of the capillary in the specimen. The sample is inserted into the jar up to a prescribed level.

![Figure 4](image)
Cold Filter Plugging Point Test (CFPP) - [or Low Temperature Filterability Test (LTFT)]

The temperature at which a fuel will cause a fuel filter to plug due to fuel components, which have begun to crystallize or gel.

**Significance and use**

- The CFPP of a fuel is suitable for estimating the lowest temperature at which a fuel will give trouble-free flow in certain fuel systems.
- In cold temperate countries; a high cold filter plugging point will clog up vehicle engines more easily.

**Test Method**

A specimen of the sample is cooled under specified conditions and, at intervals of 1°C, is drawn into a pipet under a controlled vacuum through a standardized wire mesh filter. The procedure is repeated, as the specimen continues to cool, for each 1°C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipet exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1°C. The indicated temperature at which the last filtration was commenced is recorded as the CFPP.

![Figure 5](image-url)


**Vapor Pressure Test (Reid VP)**

Reid vapor pressure is the absolute pressure exerted by a mixture at 37.8°C at a vapor-to-liquid volume ratio of 4. The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space. The RVP is one of the important properties of gasolines and jet fuels and it is used as a criterion for blending of products. This test is the standard test for low boiling point distillates. It is used for naphthas, gasolines, light cracked distillates and aviation gasolines. The RVP and boiling range of gasoline governs ease of starting, engine warm-up, mileage economy, and tendency toward **vapor lock**.

**Significance and use**

- RVP is a useful parameter for estimation of losses from storage tanks during filling or draining.

**Vapor lock**: Another important property of gasoline is its volatility. The gasoline must be volatile enough to provide the engine capable of starting at the lowest temperature expected in its service. At too low volatility the engine would have difficulty starting and would be prone to stalling in service. On the other hand too high a volatility would cause excessive vapor which in turn would cause vapor lock in pipes and pumps, etc. and prevent the flow of gasoline.

![Figure 6](image)

**Test Method**

In the above diagram A represents the vapor chamber which has a length of 254 mm and a diameter of 51 mm. The ratio of the volume of the vapor chamber A to the liquid chamber B shall be between 3.8 and 4.2. The diameters of both the vapor chamber and the liquid chamber shall be the same. The liquid test sample is placed in the liquid chamber to fill the vessel. The liquid chamber is then connected to the vapor chamber and the pressure gage inserted as shown in the diagram. The assembled apparatus is then immersed vertically in a water bath up to a level of 190 mm of the vapor chamber. The water bath is kept at a temperature of 100°F for 30 min and then removed tilted once or twice and replaced for a further 15 min. At the end of this time the vapor pressure of the test sample is read from the pressure gage to the nearest 0.2 psi.
Distillation Test

The basic test method of determining the boiling range of a petroleum product by performing a simple batch distillation has been in use as long as the petroleum industry has existed. Pure compounds have a single value for the boiling point; however, for mixtures the temperature at which vaporization occurs varies from the boiling point of the most volatile component to the boiling point of the least volatile component. Therefore, boiling point of a defined mixture can be represented by a number of boiling points for the components existing in the mixture with respect to their composition. For a petroleum fraction of unknown composition, the boiling point may be presented by a curve of temperature versus vol% (or fraction) of mixture vaporized. Different mixtures have different boiling point curves as shown in Fig. 7 for a gas oil petroleum product. The curves indicate the vaporization temperature after a certain amount of liquid mixture vaporized based on 100 units of volume. The boiling point of the lightest component in a petroleum mixture is called initial boiling point (IBP) and the boiling point of the heaviest compound is called the final boiling point (FBP). In some references the FBP is also called the end point.

- The distillation (volatility) characteristics of hydrocarbons have an important effect on their safety and performance, especially in the case of fuels and solvents. The boiling range gives information on the composition, the properties, and the behavior of the fuel during storage and use. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors.
- The distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting, warm-up, and tendency to vapor lock at high operating temperature or at high altitude, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits.
- Distillation limits are often included in petroleum product specifications, in commercial contract agreements, process refinery/control applications, and for compliance to regulatory rules.

Figure 7
Test Method

The diagram in Figure 8 is the apparatus used for ASTM D86 distillations. Only the apparatus item sizes will change and the temperature levels in the condenser bath. The measured sample is introduced into an Engler glass flask (A) at 100 ml for the D86 test. The liquid fills about two thirds of the flask leaving the space above the liquid to the cork in the vessel neck as vapor space. About half way along the neck of the flask there is a vapor offtake tube. The open end of this tube is connected to the condenser tube which is routed through the condenser bath (B). This condenser tube emerges from the Bath’ and the open end is directed into a measuring cylinder. For the lighter boiling range samples (i.e. naphthas) this cylinder is placed in a cold water (slightly below room temperature) bath. The Engler flask rests on an asbestos or similar plate (F) which has a hole 1’ in diameter exposing the bottom of the flask to the heat source. In this case the heat source is shown as a Bunsen burner (C). A thermometer is introduced into the top of the flask and is positioned so that the bulb is directly in line with the vapor offtake. The condenser bath is filled with water and ice and allowed to reach 32°F before heat is applied to the sample flask and the test begun. The temperature of the sample is increased slowly until the liquid begins to boil. The initial boiling point is read as the temperature measured by the thermometer located in the flask when the first condensate drop enters the receiving cylinder (D) at the end of the condensate bath (B). For light boiling point samples (i.e. naphthas) this receiver is cooled in a water bath (E). For kerosenes the water bath (E) is not required. The test is allowed to proceed at a constant rate and temperature readings are taken at predetermined recovery levels of condensate. (usually these temperatures will be at 10 vol% recovered, 30, 50, and 90 vol % recovered). When the flask (A) has been boiled apparently dry, the temperature shown by the thermometer will rise sharply and then begin to fall. The highest temperature observed in this rise and fall is the final boiling point of the sample.
Effect of Fuel Volatility on Vehicle Performance

A fuel's ability to vaporize or change from liquid to vapor is referred to as its volatility. Volatility is an extremely important characteristic of gasoline which affects many vehicle performance parameters.

For example, if the volatility curve in Figure 10 moves down in the initial range of up to 30% evaporated, then more fuel would vaporize at lower temperatures and it may cause poor hot starting and vapor lock problems. If the curve moves upwards then vehicles may encounter poor cold starting problems.

The 10% evaporated temperature must be low enough to provide easy cold starting but high enough to minimize vapor lock and hot drivability problems. The 50% evaporated temperature must be low enough to provide good warm up and cold weather drivability without being so low as to contribute to hot drivability and vapor lock problems. The mid boiling range of gasoline also affects short trip fuel economy. The 90% and end point evaporation temperatures must be low enough to minimize crankcase and combustion chamber deposits as well as spark plug fouling and dilution of engine oil.

![Figure 10](image-url)
Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test

The corrosion test serves to indicate the presence or absence of materials that could corrode copper, brass, and bronze components of the fuel system.

Significance and use

- Crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petroleum product, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content. The effect can vary according to the chemical types of sulfur compounds present. The copper strip corrosion test is designed to assess the relative degree of corrosivity of a petroleum product.

Figure 11
<table>
<thead>
<tr>
<th>Classification</th>
<th>Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshly polished strip</td>
<td>...</td>
<td></td>
</tr>
</tbody>
</table>
| 1                      | slight tarnish | a. Light orange, almost the same as freshly polished strip        
|                        |              | b. Dark orange                                                              |
| 2                      | moderate tarnish | a. Claret red                                      
|                        |              | b. Lavender                                                  
|                        |              | c. Multicolored with lavender blue or silver, or both, overlaid on claret red |
|                        |              | d. Silvery                                           
|                        |              | e. Brassy or gold                                              |
| 3                      | dark tarnish  | a. Magenta overcast on brassy strip                                             
|                        |              | b. Multicolored with red and green showing (peacock), but no grey             |
| 4                      | corrosion    | a. Transparent black, dark gray or brown with peacock green barely showing     
|                        |              | b. Graphite or lusterless black                                              
|                        |              | c. Glossy or jet black                                                       |

*The ASTM Copper Strip Corrosion Standard is a colored reproduction of strips characteristic of these descriptions.

*The freshly polished strip is included in the series only as an indication of the appearance of a properly polished strip before a test run; it is not possible to duplicate this appearance after a test even with a completely noncorrosive sample.
Water and Sediment in Fuel Oils by the Centrifuge Method Test

This test method covers the laboratory test for determination of water and sediment in fuel oils by using the centrifuge method in the range from 0 to 30 % volume.

Significance and use

- The water and sediment content of fuel oil is significant because it can cause corrosion of equipment and problems in processing. Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of the fuel-handling facilities and to give trouble in the fuel system of a burner or engine. An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to the combustor.

Test Method

Equal volumes of fuel oil and water saturated toluene are placed in each of two cone-shaped centrifuge tubes. After centrifugation, the volume of the higher gravity water and sediment layer at the bottom of the tube is read.

Figure 13
Determination of Water in Petroleum Products, Lubricating Oils and Additives by Coulometric Karl Fisher Titration Test

This test method covers the direct determination of water in the range of 10 to 25 000 mg/kg entrained water in petroleum products and hydrocarbons using automated instrumentation.

Significance and use

- The presence of moisture could lead to premature corrosion and wear, an increase in the debris load resulting in diminished lubrication and premature plugging of filters, impedance in the effect of additives, and undesirable support of deleterious bacterial growth.

Test Method

An aliquot is injected into the titration vessel of a coulometric Karl Fisher apparatus in which iodine for the Karl Fisher reaction is generated coulometrically at the anode. When all of the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated. Based on the stoichiometry of the reaction, 1 mol of iodine reacts with 1 mol of water; thus, the quantity of water is proportional to the total integrated current according to Faraday’s Law. The sample injection can be done either by mass or volume.

Figure 14
Sulfur Content Test

Sulfur content is one of the most important property in petroleum products. Sulfur is mostly compounded with heavy hydrocarbons in crude oil and for this reason; it is included much more in the petroleum which obtained from near the bottom side of the refining tower. For instance, sulfur content in diesel is higher than gasoline and kerosene.

Significance and use

- The quality of many petroleum products is related to the amount of sulfur present. Knowledge of sulfur concentration is necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in some fuels. This test method provides a means of determining whether the sulfur content of petroleum or a petroleum product meets specification or regulatory limits.
- The dew point of water vapor in exhaust gases of sulfur-free petroleum is approximately 40°C. In other words, the water vapor in the exhaust gases will not condense as long as exhaust gases decrease to this temperature. Such a low temperature is not encountered normally in an engine so that wearing problem due to water does not constitute any trouble.
- Petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO₂ forms sulfur trioxide (SO₃). Among these gases, SO₂ is not very dangerous but combining with water forms sulfurous acid \( \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \) which decomposes again SO₂ and H₂O at 100°C. The temperatures that near 100°C are not encountered in an engine will not constitute any problem for this reason. However, combining SO₃ with water forms sulfuric acid \( \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \) that has very abrasive property and it increases the dew point temperature to 150°C which also leads to wear of the engine elements.
Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter Method

When a hydrocarbon, \( \text{C}_x \text{H}_y \) is burned, the only products are \( \text{H}_2\text{O} \) and \( \text{CO}_2 \). Combustion is a reaction in which the enthalpy of products is less than enthalpy of reactants and as a result the heat of reaction (enthalpy of products - enthalpy of reactants) is always negative.

Amount of heat released by burning one unit mass of a fuel is called heating value or calorific value and has the unit of kJ/kg or Btu/lb. The heating value depends on the phase of the \( \text{H}_2\text{O} \) in the products. The heating value is called the higher heating value (HHV) when the \( \text{H}_2\text{O} \) in the products is in the liquid form, and it is called the lower heating value (LHV) when the \( \text{H}_2\text{O} \) in the products is in the vapor form (Fig. 16). The two heating values are related by

\[
HHV = LHV + (mh_{f\ell})_{\text{H}_2\text{O}} \quad (\text{kJ/kg fuel})
\]

where \( m \) is the mass of \( \text{H}_2\text{O} \) in the products per unit mass of fuel and \( h_{f\ell} \) is the enthalpy of vaporization of water at the specified temperature. Higher and lower heating values of common fuels are given in Table 2.

**Figure 16**

| Fuel         | HHV (MJ/kg) | LHV (MJ/kg) | HHV/LHV
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>34.1</td>
<td>33.3</td>
<td>1.024</td>
</tr>
<tr>
<td>CO</td>
<td>10.9</td>
<td>10.9</td>
<td>1.000</td>
</tr>
<tr>
<td>Methane</td>
<td>55.5</td>
<td>50.1</td>
<td>1.108</td>
</tr>
<tr>
<td>Natural gas</td>
<td>42.5</td>
<td>38.1</td>
<td>1.115</td>
</tr>
<tr>
<td>Propane</td>
<td>48.9</td>
<td>45.8</td>
<td>1.068</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.7</td>
<td>42.5</td>
<td>1.099</td>
</tr>
<tr>
<td>Diesel</td>
<td>45.9</td>
<td>43.0</td>
<td>1.067</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>141.9</td>
<td>120.1</td>
<td>1.182</td>
</tr>
</tbody>
</table>
Orsat Analysis Test

The orsat apparatus is a relatively simple and compact portable gas analyzer that is specifically designed to measure the concentration of three of the gas compounds found in the combustion products. A typical orsat gas analyzer is shown in Fig. 17, and is used to determine the volumetric or molar fractions of carbon dioxide, oxygen, and carbon monoxide in the dry exhaust gas.

Significance and use

- The actual air-fuel ratio for a given combustion process is normally estimated from an experimental measurement of the gaseous components of the exhaust gas.

Test Method

A 100 cm³ sample of exhaust gas is taken at room temperature in the burette by using the leveling water bottle to collect and transfer the gas sample. Since the gas is collected at room temperature over water, it is usually assumed that any water vapor in the exhaust gas will have condensed and that any sulfur dioxide in the exhaust gas will have reacted with the water in the exhaust gas and in the collecting bottle. Consequently, it is assumed that the resulting "dry" gas sample is composed of carbon dioxide, oxygen, carbon monoxide, and nitrogen.

Once the gas sample has been obtained, it is then sequentially passed through three chemical reactors in the device. The first chemical-reactor contains an aqueous solution of potassium hydroxide (KOH) that preferentially removes any carbon dioxide in the gas sample. The second chemical reactor contains a solution of pyrogallic acid in potassium hydroxide and water, and this solution preferentially removes any oxygen in the sample. The final chemical reactor contains a solution of cuprous chloride in ammonia, and this solution absorbs any carbon monoxide present in the gas. By carefully measuring the decrease in sample volume as the gas is passed through each chemical reactor, in series, and dividing each decrease by the original gas volume (100 cm³), the volume or mole fractions of carbon dioxide, oxygen and carbon monoxide in the dry exhaust gas are obtained. Any gas remaining after the sample has been passed through all three reactors (usually around 80 percent) is assumed to be nitrogen.
Figure 17

Figure 18
ASTM Color of Petroleum Product Test

Significance and use

- Determination of the color of petroleum products is used mainly for manufacturing control purposes and is an important quality characteristic since color is readily observed by the user of the product. In some cases the color may serve as an indication of the degree of refinement of the material. When the color range of a particular product is known, a variation outside the established range may indicate possible contamination with another product. However, color is not always a reliable guide to product quality and should not be used indiscriminately in product specifications.

Test Method

Using a standard light source, a liquid sample is placed in the test container and compared with colored glass disks ranging in value from 0.5 to 8.0. When an exact match is not found and the sample color falls between two standard colors, the higher of the two colors is reported.

![Figure 19](image_url)
REFERENCES

[5]. ASTM Petroleum Product Standards
[6]. Petrol Ofisi teknik el kitabi: Yağlar ve Yakıtlar
[7]. Shell Petrol Şirketi Teknik Servis kitap notları: Yakıtlar Yağlar ve Yağlama
[8]. Modern Marvels Documentary - Gasolines
[9]. http://www.google.com
[12]. http://www.eoearth.org/
[14]. http://www.koehlerinstrument.com
**FUEL-OIL**

<table>
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<tr>
<th></th>
<th>Fuel oil 3</th>
<th>Fuel oil 4</th>
<th>Fuel oil 5</th>
<th>Fuel oil 6</th>
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<tbody>
<tr>
<td>Kükürt (%m/m, en çok)</td>
<td>1.0</td>
<td>2.0</td>
<td>2.8</td>
<td>3.5</td>
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<tr>
<td>Kinematik viskozite (mm²/s, 100 ºC, en çok)</td>
<td>40</td>
<td>10</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Parlama Noktası (ºC, en az)</td>
<td>66</td>
<td>56</td>
<td>66</td>
<td>66</td>
</tr>
<tr>
<td>Yoğunluk (kg/m³, en çok)</td>
<td>998</td>
<td>950</td>
<td>998</td>
<td></td>
</tr>
<tr>
<td>Su (%v/v, en çok)</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Toplam tortu (%m/m, en çok)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Akma noktası (ºC, en çok)</td>
<td>+38</td>
<td>+10</td>
<td>+38</td>
<td>+38</td>
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<tr>
<td>Görunüş</td>
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<td></td>
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</tr>
</tbody>
</table>

1) Yaz: 1 Nisan-30 Eylül (± 15 gün)
2) Kış: 1 Ekim-31 Mart (± 15 gün)

**KURŞUNSUZ BENZİN**

<table>
<thead>
<tr>
<th>Yapılan Testler</th>
<th>TS EN-228</th>
<th>Deney</th>
</tr>
</thead>
<tbody>
<tr>
<td>Özellik</td>
<td>Yaz Tipi</td>
<td>Kış Tipi</td>
</tr>
<tr>
<td>Yoğunluk (kg/m³, 15.6ºC’de)</td>
<td>720-775</td>
<td>720-775</td>
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<tr>
<td>Reid buhar basıncı, kPa</td>
<td>45 – 60</td>
<td>60 – 90</td>
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<tr>
<td>Damıtma</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70ºC’de buharlaşma, %(v/v)</td>
<td>20 – 48</td>
<td>22 – 50</td>
</tr>
<tr>
<td>100ºC’de buharlaşma, %(v/v)</td>
<td>46 – 71</td>
<td>46 – 71</td>
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<tr>
<td>150ºC’de buharlaşma, %(v/v)</td>
<td>75 en az</td>
<td>75 en az</td>
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<tr>
<td>Kaynama noktası sonu ºC, (En çok)</td>
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<td>210</td>
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<tr>
<td>Damıtma kalıntısı (% v/v) en fazla</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Korozyon:Bakır şerit, (3 saat, 50 ºC da), (En çok)</td>
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<td>No:1</td>
</tr>
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* Yaz ayları: 1 Nisan-31 Ekim (±4 Hafta)
Kiş ayları: 1 Kasım-31 Mart (±4 Hafta)
## MOTORİN

<table>
<thead>
<tr>
<th>Yapılan Deneyler</th>
<th>TS 3082-EN590</th>
<th>Deney Sonuçları</th>
</tr>
</thead>
<tbody>
<tr>
<td>Renk (En çok)</td>
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<tr>
<td>Yoğunluk, (g/cm³) 15 °C’de</td>
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<tr>
<td>Parlama Noktası (En az)</td>
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<td>Kinematik Viskozite (mm²/s) 40°C’de</td>
<td>2 – 4.5</td>
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<tr>
<td>Kükürt Muhtevası (mg/kg), (En çok)</td>
<td>Motorin 7000⁴</td>
<td>7000</td>
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<tr>
<td></td>
<td>Motorin 50⁵</td>
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<tr>
<td>Su Muhtevası (mg/kg), (En çok)</td>
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<td>Korozyon, Bıçak serit, (3 saat, 50 °C da)</td>
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<tr>
<td>SFTN³ (En çok)</td>
<td>Yaz¹</td>
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<td>Kısa² tipi</td>
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### Destilasyon Standart Değerleri (TS 3082-EN590)

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<thead>
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<th>Sıcaklık(°C)</th>
<th>Miktar(%v/v)</th>
<th>Sıcaklık(°C)</th>
<th>Miktar(%v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C’de</td>
<td>Hacimce en çok %65</td>
<td>350 °C’de</td>
<td>Hacimce en az %85</td>
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<tr>
<td>En çok 360°C</td>
<td>Hacimce % 95’de</td>
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<td></td>
</tr>
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</table>

### İndiüler

1) Yaz : 1 Nisan-30 Eylül (± 15 gün)
2) Kısa : 1 Kasım-31 Mart (± 15 gün)
3) SFTN: Soğuk Filtre Tıkanma Noktası
4) Motorin 7000: 2002 tarihi TSE 3082 EN 590 standartına uygun piyasaya arz edilen motorindir.
5) Motorin 50: Kükürt oranı azaltılmış, yürürlükteki TSE 3082 EN 590 standarına uygun motorindir.