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Criteria for the Quality Assessment of Engine Fuels in Storage and Operating Conditions

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Additional information is available at the end of the chapter

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1. Introduction

Plenty of literature exists on research and findings relating to changes in the performance characteristics of conventional fuels concerning their oxidation (ageing) processes. These processes affect a majority of the functional properties of fuels and cause them in many cases to exceed the values stated in applicable standards. However, the proper fuel storage time, that is, duration of the effect of many different factors on the process kinetics of low-temperature oxidation of fuels, is yet not clearly defined. The process kinetics is affected by a number of factors (including random ones), namely the following:

- fractional composition of fuels;
- structural-group composition;
- volume;
- surface area of the fuel mirror;
- free volume over the fuel mirror;
- type of tank;
- type of tank roof;
- tank foundation;
- type of tank layer material in contact with fuel;
- multiplicity of warehouse operations;
- tank breathing system;

- weather conditions.

Regardless of the above mentioned statements, fuels, being compositions of many types of hydrocarbons and their oxygen derivatives, may differ from one another in respect of structural-group composition within the various product lots of the same fuel grade, therefore, they are subject to ageing at different rates.

In light of the above, the correct organization and functioning of a fuel quality control system during storage is one of the criteria that enable fuel storage.

The fuel quality surveillance system should specify in particular:

- conditions of acceptance of the respective deliveries of product lots;
- scope and methodology for the quality control of the accepted product lots;
- duration of safe storage of fuels, pre-determined from the results of assessment of selected parameters, which are significantly affected by the anticipated conditions of storage;
- the duration and scope of control analyses (full, short, basic) and their definitions;
- how to deal with products of which the properties are outside the ranges referred to in the appropriate standard specifications;
- a list of documents required, and templates;
- authorizations and responsibilities of the staff with regard to maintaining the quality of stored fuels.

As the requirements relating to fuels quality may change and progress in their manufacturing technology may be observed, assessment of the criteria of fuel quality during storage may be modified accordingly. Hence, it is necessary to review such assessment criteria and amend them as necessary, so as to enable the assessment of changes in the quality of fuels on a regular basis, since the results are meant to help take decisions on how to handle the fuel stored.

The choice of criteria for assessing the quality of fuels should, therefore, be dictated by the requirement to determine at certain time intervals only those parameters of which the values may change due to the low-temperature oxidation of fuels, which occurs during their storage. The right choice of such parameters will be possible after analyzing the changes observed in the properties of standard fuels during storage and, as a result of such analysis, determination of the proper hierarchy of assessment criteria and their weights and measures; these issues are going to be discussed later in this chapter.

Evaluation of the usefulness of fuel delivered for storage and forecasting the maximum duration of safe storage in specific storage capacities are an important element of the effective operation of the Quality Assessment System. Therefore, a full analysis of the received product is required, in addition to a certificate from the fuel supplier's laboratory. The certificate typically includes the results of fuel quality assessment made by the manufacturer at the time of manufacturing. The time that elapses between the production of a fuel lot and its intermediate storage and distribution processes may result in significant changes in the quality of

fuel, affecting the process of its storage, all the more so as fuel handling habits may not always be appropriate.

If the full analysis results show limiting values, in particular those which may be subject to change due to the storage process (e.g.: vapor pressure, resin content, oxygen content, fractional composition for diesel fuels, flash-point, solids, etc.), the available options include the refusal to accept such fuel for storage, or its acceptance on the supplier's responsibility.

In order to ensure compliance with the relevant fuel storage procedure, in the case of fuels intended for long-term storage, a reserve in the range of properties that can be affected in the normal execution of the process should be provided. Hence, as in some countries, a proper fuel storage standard should be prepared and implemented. The standard should take into account a "quality reserve" with regard to those parameters which are particularly sensitive to low-temperature oxidation.

2. Criteria for an assessment of the quality of gasoline in storage and distribution conditions

In the classification of combustion engines, spark-ignition engines are in the group of engines with external preparation of the fuel mixture. These engines are forced-ignition engines and the fuel mixture is prepared outside the combustion chamber; this means that the necessary condition is to generate a mixture of fuel vapor and air. Evaporation is defined as the passage of liquid into the gaseous state. Evaporation occurs practically at any temperature in liquids having a free surface. Evaporation is of the free type (without any factors forcing the motion of particles, i.e., into a motionless medium) and of the forced type, i.e., into a moving medium.

The molecule of a liquid passes into the gaseous state after overcoming the forces of intermolecular cohesion – therefore, it does a certain work (E). The kinetic energy of the molecule must be greater than the work, hence:

$$\frac{m u^2}{2} \geq E$$

where:

m-mass of the molecule;

u – velocity component, perpendicular to the liquid surface.

The movement of molecules takes place in both directions, i.e., the molecules also pass from the gaseous into the liquid state. Depending on the number of particles passing into the vapor state (n) and into the liquid state (m), the following phenomena may occur:

n> m-evaporation;

n=m-saturated vapor state;

n <m>condensation

The condition in which surface evaporation takes place in addition to volumetric evaporation is important for the evaporation process. In this case, gas bubbles are produced throughout the liquid volume and are directed towards the liquid surface. This rapid evaporation is called “boiling” and, for a homogeneous liquid, is characterized by a constant temperature from the beginning of boiling till the whole liquid has evaporated. Gasoline, a mixture of many components, is characterized by a boiling range which depends on the concentration and boiling points of its individual components.

The rate of evaporation is affected by a number of different factors, including external ones, such as the following:

- *temperature* – increase in temperature causes a rise in the kinetic energy of molecules, and therefore an increase in temperature causes an increase in the intensity of evaporation, up to the boiling condition;
- *pressure* – the lower the pressure in the medium into which the liquid evaporates, the higher the intensity of the evaporation process taking place. The phenomenon is used in combustion engines, where the suction stroke in the cylinder generates partial vacuum which, in turn, facilitates fuel evaporation. Thus, reduction in pressure causes a decrease in the boiling range of the liquid; this is used in vacuum distillation.
- *concentration difference* – removal of the vapors, accumulated above the liquid surface increases the gradient of concentration and accelerates evaporation of the liquid;
- *diffusion coefficient* – specifies the amount of mass transferred in a defined unit of time per unit of area; thus, the higher the diffusion coefficient, the more intense evaporation of the liquid will occur;
- *surface area of the liquid*.

Vapors from above the liquid surface can be removed by diffusion. The phenomenon consists in that the solute (solved in any solvent) tends to be evenly distributed in the entire volume of the solvent. In this case, the volume of air (which is limited by the size of the combustion chamber or an open space in the case of free evaporation) is the solvent for the fuel vapor. Therefore, fuel vapors perform in the process of diffusion a series of thermally excited, small transitions. The process of diffusion is determined using Fick's first law:

$$\frac{dn}{dt} = -Ds \frac{dc}{dx}$$

where:

n – number of moles of molecules which diffuse in time “t”

s – distribution area surface

D – diffusion coefficient

$\frac{dc}{dx}$ -concentration gradient in the direction of diffusion

The rate of diffusion depends on temperature, pressure, and other factors.

From Fick's formula, after conversion, changes in the mass of the diffusing substance can be found from the following relationship:

$$\Delta M = -D \left(\frac{dc}{dx} \right) ds dt$$

The diffusion process is characterized by the diffusion coefficient, which is equal to the number of moles of gas (fuel vapor) passing across 1 m² of the interface per second, when concentration – in the perpendicular direction to the interface – changes by one unit per 1 meter of the distance. Hence, the amount of mass moving during a unit of time across a unit of area depends on the value of the diffusion coefficient for the substance. Assuming that the diffusing particles have the shape of spheres – with the radius r – the relationship between the diffusion coefficient and viscosity is described by the formula:

$$D = k \frac{T}{6\pi r\eta}$$

where:

k -Boltzmann constant

T -temperature

η -dynamic viscosity

Taking into account the approximate relationship between the diffusion coefficient and viscosities on the one hand and the average velocity of vapor particles u_a and free path length τ on the other, we have:

$$D = \frac{1}{3} \tau u_a$$

and

$$\eta = \frac{1}{3} d u_a \tau$$

where:

d -density

it is possible to determine the estimated value of the diffusion coefficient D at a given temperature from a known viscosity and density, using the formula:

$$D = \frac{\eta}{d}$$

In addition to the factors mentioned above, fuel evaporation is affected by some internal factors, resulting from the chemical structure of fuels, among which volatility and heat of evaporation are the most important ones.

Heat of evaporation is defined as the amount of heat required to convert one unit of mass or one unit of volume of a liquid into the vapor state in specified temperature and pressure conditions. As the temperature changes into the critical point (CP), heat of evaporation gradually decreases, assuming the value of zero at that point. The heat of evaporation depends on the chemical structure (molecular mass) of the liquid and on the interaction forces (association) between the particles. Heavier fuels have higher heats of evaporation and tend to be evaporated with more difficulty, therefore, the use of conditions in which forced liquid evaporation takes place is required to obtain the appropriate composition of the fuel mixture.

In spark-ignition engines, intense evaporation of the fuel begins as the fuel leaves the nozzle. The fuel drops get disaggregated, forming tiny drops in the air jet stream. The phenomenon is called fuel atomization.

Fuel drops, which are suspended in the air and move around, evaporate gradually. As mentioned before, the rate of evaporation depends on pressure, temperature, flow rate of air, volatility, evaporation heat, diffusion coefficient, and the fuel drop surface. A portion of the fuel drops settle on the suction duct walls and gradually evaporate from there. In this case, intensity of evaporation largely depends on fuel drops' wettability, as compared with the suction duct material, expressed by the wetting angle. The larger is the wetting angle, the quicker the fuel's evaporation. However, at the same time, some of the fuel that settled on the walls in the form of liquid will be stripped mechanically by the steam of air and carried (in a non-evaporated form) into the combustion chamber. The phenomenon is applicable to the heavier components of fuels, also called the phlegm. The presence of the phlegm in the combustion chamber is an undesirable phenomenon, which affects the process of fuel combustion.

Roughly a half of the fuel evaporates in the suction duct, therefore, the composition of the fuel mixture in multi-cylinder engines is different in each cylinder. The differences in the blend composition can be up to a dozen or so per cent. Differences are seen not only in the fuel share but also in the chemical composition of the vapors and the non-evaporated stage in each cylinder. For obvious reasons, this affects the combustion process as well as the engine power and fuel consumption.

Part of the fuel gets into the combustion chamber in liquid form. Such fuel settles on the walls of the combustion chamber and piston head, and evaporates – mostly during the intake stroke and partly during the compression stroke. The least volatile components can evaporate as early as during combustion. If the fuel has a content of high-boiling components, they can decompose thermally instead of vaporizing, despite the high combustion process temperature; this leads to an immensely high contamination of exhaust gases, and to the formation of carbon

deposits (solid decomposition products) on the chamber walls and piston head. For high rates of the suction/compression/work processes, part of the fuel can also be removed from the chamber in liquid form, washing the lubricating oil from the walls, thus accelerating the wear-and-tear of the piston-crankshaft system. In that case, the fuel is removed from the combustion system along with the exhaust gas.

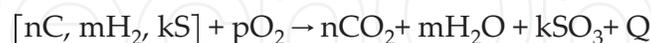
The elementary carburetor does not assure the correct supply of fuel to the engine when a fuel-rich mixture is required. Therefore, a series of devices were introduced to ensure a desirable composition over a wide range of operating conditions; they include starting devices, accelerating devices, and so-called "fuel savers". Unfortunately, these devices tend to complicate the carburetor's design, affecting its reliability and causing the need to adjust the carburetor as necessary.

Gasoline-fuelled engines with direct fuel injection by means of an injection pump do not have the above mentioned disadvantages in the carburetor system. This is because the mixture is evenly distributed into the respective cylinders and the adverse effect of the phlegm is also eliminated. However, technologically, direct injection is a much more complex system which requires extreme precision of workmanship and highly specialized repairs.

As a result, volatility is a very important operating parameter of fuels; it is estimated from their fractional compositions and vapor pressures.

Combustion is described as violent oxidation during which a high amount of heat is generated in addition to gaseous reaction products which create a flame. Combustion is one of oxidation reactions even though it does not require the presence of pure oxygen. Oxygen is the oxidizing agent in most combustion processes, other ones include HNO_3 , H_2O_2 , or F_2 . The mechanism and the effect of combustion of hydrocarbons are identical regardless of the type of oxidizer. There are a wide range of compounds with a potential as fuels, however, most fuels are organic substances and their mixtures, containing mainly carbon, hydrogen and smaller quantities of nitrogen, sulfur and oxygen.

The complete combustion of a hydrocarbon fuel can be described by means of the following simplified reaction:



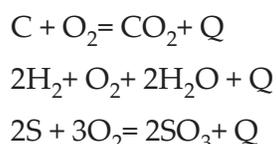
Usually, the nitrogen content of fuels is not reactive. Incomplete oxidation may give CO and SO_2 as additional combustion products. Heat energy (Q) is generated as the bonds between atoms in fuel particles are broken and bonds in the reaction products are created. The higher the bonds in the combustion reaction products, compared with the bonds in the reactants, the higher is the energy effect of the reaction.

The temperature of the combustion process is influenced by dissociation of combustion product particles, which has a major role at temperatures above 2500°C .

Combustion is an exothermal reaction during which heat is generated. Activation energy (usually provided by heating) is needed to initiate combustion. The energy generated by the

system is higher than the energy used for breaking bonds in the reactants. In engines having a carburetor, the energy needed for initiating combustion (also called "ignition energy") is provided by the ignition plug discharge and heating of the combustion chamber walls. In gasoline-fuelled engines, the ignition energy should be as low as possible, since such conditions lead to higher reaction heat effects.

After a flammable mixture is introduced into the combustion chamber but before it is ignited there elapses a period of time, called ignition delay. It is needed for the evaporation of gasoline particles getting into the combustion chamber in the liquid form and for their thorough mixing with air (practical delay), as well as for the initial, flameless oxidation of the gasoline vapors in the air so as to enable the formation of intermediate oxidation products which facilitate combustion of the mixture at a stable rate (chemical delay). The intermediate oxidation products include such compounds as: alcohols, aldehydes, ketones, acids and hydroxyacids. The initial oxidation process is called low-temperature combustion. In fuels with higher oxidation stabilities, fewer components participate in low-temperature combustion. According to Hess's law, the thermal effect of a chemical reaction depends on the initial and final states, rather than on transformation path. Although numerous intermediate combustion products are made in fuel combustion, it is safe to assume for the purposes of thermochemical balance that the initial state is: carbon and hydrogen, while the final combustion products are: H_2O , CO_2 , SO_3 . The general equation of the fuel combustion process can be formulated as follows:



The above reactions take place in theoretical conditions. However, practically, oxygen is not used entirely: some of it is wasted with exhaust gas. Therefore, what occurs is an incomplete combustion, connected with evaporation of the fuel and formation of its mixture with air, as mentioned above.

In practice, the quantity of oxygen introduced into the combustion chamber together with air is larger than its stoichiometrically indispensable quantity. The ratio between the actually introduced quantity of air and the stoichiometric (or theoretically required) quantity is called "excess-air ratio", α . For $\alpha < 1$, the fuel-air mixture is lean; for $\alpha = 1$, the mixture is stoichiometric, and for $\alpha > 1$, the mixture is rich.

For fuels which contain sulfur (which is the case in some diesel fuels and heating oils), an additional amount of oxygen is needed for oxidation of that element, and it is determined accordingly.

Reduction of the combustion product vapor volumes, as compared with the gaseous reactants, is called chemical contraction; when combined with physical contraction resulting from reduction of product volumes due to steam condensation, it is called "total contraction".

Depending on temperature range, fuel oxidation comprises three stages:

- slow oxidation at temperatures up to 200°C;
- low-temperature oxidation – slow, in gaseous phase at temperatures in the range (200...600)°C;
- fast oxidation in flame.

Although the first step has no major role in the engine technology, it does matter in determining the permissible duration of storage of fuels.

At low temperatures, particles have low kinetic energy so the number of fuel particles colliding with oxygen particles is small, therefore, oxidation process is very slow. At temperatures higher than 200°C some fractions in light fuels evaporate while the probability of collision between the evaporated fuel and oxygen particles is higher, which leads to the formation of low-temperature oxidation products (alcohols, aldehydes, ketones, acids and hydroxyacids in what is called “the first stage of oxidation”, and peroxides, of which the structure comprises an oxygen bridge made of two oxygen atoms bonded together). Intermediate oxidation products have different kinetics of their further reactions with oxygen. The oxidation products mentioned above (except peroxides) have similar combustion kinetics. Their formation enhances the heat effect and the fuel combustion process rate, leading in effect to what is called “normal course of combustion” where the flame front moves away from the ignition source at a speed of (15...30) m/sec.

Fuels are multicomponent mixtures, in which paraffins are the hydrocarbon components having the lowest oxidation stabilities (the lower, the longer are their backbones and the lower are their isomerization degrees). Compared with paraffins, naphthenes have better oxidation stabilities because of their cyclic structure, and aromatic hydrocarbons have the highest oxidation stability. In the case of aromatic hydrocarbons with side chains, oxidation leads primarily to the breaking of these side chains whereby oxygen hydrocarbon derivatives are formed, after that the ring is broken and carbon oxides and water are generated.

In all the three hydrocarbon groups, during oxidation there may also appear intermediate combustion products which comprise an oxygen bridge-O-O-(peroxides). At lower oxidation temperatures, the duration of low-temperature oxidation is longer and, therefore, the amount of peroxides formed is higher. In high-temperature oxidation conditions, no peroxides were detected, because they are highly unstable and readily decompose. Hence, if low-temperature oxidation does not lead to the formation of peroxides, combustion is considered as a normal combustion reaction which proceeds gradually. Any intermediate oxidation products that may be formed and are in “first stage of oxidation” because of their higher stability, do not usually lead to the formation of peroxides.

The peroxides formed during low-temperature oxidation are highly reactive. The oxygen bridge in their structure may be present in the chain or form a bypass.

Having such structure, the compounds are very strong oxidants. Hydrogen peroxide is the simplest peroxide. Nitric acid(V) (HNO_3) is also a very strong oxidant. The content of active

oxygen in their molecules is sufficient to initiate ignition or even combustion in the absence of atmospheric oxygen. Peroxides, which are formed during oxidation of hydrocarbons, being active particles, are able to initiate a combustion chain reaction. In such type of reactions, each active particle initiates another reaction, leading to new particles, initiating "n" subsequent reactions.

The combustion reaction accelerates violently till the process is complete. In that case, the whole fuel-air mixture is combusted violently in practically one moment. Such combustion process leads to very high values of temperature and pressure in the engine combustion chamber. It generates a shock wave which travels at a speed of (1500...2500) m/sec and, when colliding with the combustion chamber walls, causes the metallic knocking effect with sound frequencies of around 3000 Hz. This type of combustion is highly disadvantageous and is termed "detonation combustion".

Detonation combustion occurs around 0.6° crankshaft rotation (while the position of the flame front, developed by the initiated, ignition hardly changes at all). Interference of waves being created by the various detonation sites is observed: the waves amplify or dampen at the nodes. After such combustion, new mixture portions are introduced into the overheated combustion chamber during the consecutive intake cycles. Low-temperature oxidation is accelerated while the ignition delay remains the same. This increases the probability that new active particles will be formed and will initiate the detonations. Moreover, at too high temperatures, the fuel getting through in its liquid form is unable to evaporate fast enough and is thermally decomposed, which generates an immense amount of gaseous decomposition products and layers of carbon deposit on the walls (they have a thermally-insulating effect and reduce the capacity of the combustion chamber).

The sum of these phenomena very much improves the possibility that a significant number of detonation sites will soon develop. The subsequent strokes, which are performed at high speeds, can lead to the incomplete removal of combustion products from the chamber – these products have then enough time for being oxidized into the form of active particles. Therefore, detonation combustion can be intensified very rapidly and lead – in extreme cases – even to engine damage or destruction. However, not every case of active particle formation leads to a chain reaction or avalanche effect because the reaction tends to slow down as the peroxides develop. This is caused by the formation of final products of the combustion of carbon oxides and water as well as its intermediate products, such as alcohols, aldehydes etc. The combustion chamber walls also tend to deactivate the active particles being formed.

Group composition has a decisive influence on the nature of combustion of fuels because the respective hydrocarbon groups have different oxidation tendencies. Intensity of oxidation, resulting in the formation of active particles, decreases in the following order: alkanes (paraffins) > alkenes (olefins) > alkadienes (diolefins) > cycloalkanes (naphthenes) > arenes (aromatic hydrocarbons). Depending on their isomerization degree, higher branched isoparaffins show higher resistance to detonation combustion. Thus, e.g., 2,3-dimethylpentene has a detonation combustion resistance similar to that of benzene, while that of 2,2,3-trimethylpentane is much higher. Apart from initial oxidation products, which are directly responsible

for detonation combustion, there exist a number of direct and indirect factors increasing the possibility of peroxides being formed in the combustion chamber.

Indirect factors include:

- design factors;
- operating factors;
- physico-chemical properties of fuels;
- chemical composition of fuels.

Direct factors include

- temperature;
- pressure;
- duration of contact with oxygen.

Further, these factors can be grouped as follows:

Design factors:

- compression ratio;
- pressure charging;
- size and shape of the combustion chamber;
- material of construction of the combustion chamber;
- quantity and distribution of sparking plugs.

Operating factors:

- ignition advance angle;
- composition of the fuel mixture;
- motor load;
- RPM;
- performance of the cooling system.

Compression ratio is one of the most important factors affecting the type of combustion. At what is called the "critical compression ratio", detonation combustion takes place due to an increase in pressure and temperature. The compression ratio (ϵ) is the ratio between the total capacity of the combustion chamber (defined as the sum of engine displacement and combustion chamber capacity) to the combustion chamber capacity.

In order to prevent detonation combustion at high compression ratios, it is necessary to use fuels with high oxidation stabilities. The value of critical compression ratio is also the measure of a given fuel resistance to detonation combustion.

An increase in the pressure of the air entering the combustion chamber, which is usually carried out by so-called pressure charging, increases the fuel's tendency for detonation combustion. This leads to higher temperatures during the compression stroke, thus intensifying oxidation of the fuel vapor which causes the formation of active particles.

The size and shape of the combustion chamber have an effect on the reaction rate, the amount of heat generated, and on the pressure increase; therefore, the fuel's tendency for detonation combustion increases with the cylinder capacity. The more complex the combustion chamber is, the greater the fuel's tendency for detonation because, after the flame front passage, there may remain some unburnt fuel particles which continue to react with oxygen and, at elevated temperatures, they may react, forming active forms which initiate detonation.

The probability that detonation sites will be formed is lower for less intense removal of heat from the combustion chamber; such intensity is provided by an efficient cooling system and good thermal conductivity of the chamber construction material. For example, an aluminum combustion chamber, due to the material's higher thermal conductivity, allows the use of higher compression ratios, compared with that of a cast iron chamber. A kind of catalytic effect of the construction metals on the course of initial fuel oxidation is observed, but the effect is not fully understood.

The probability that detonation sites will be formed is lower for smaller cylinder diameters and increased quantities of sparking plugs. Additional, properly distributed sparking plugs reduce the path length of the flames spreading from the ignition point to the end of the combustion chamber, thereby reducing the duration of contact between the fuel particles and oxygen. Gasoline-fuelled aircraft engines have two sparking plugs, arranged as follows: one near the intake valves and the other near the exhaust valves.

Design factors affecting the combustion process should be taken into account in engine designing and in selecting the proper fuel for them. But the operating factors, discussed below, which influence the course of fuel combustion ought to be adjusted accordingly during the operation of motors. Correct maintenance should help almost completely eliminate their adverse effect.

Thus, the higher the ignition advance angle, the higher (and correlated with an increase in the maximum combustion pressure) is the fuel's tendency for a detonation combustion. During early ignition, temperatures of the head and of the combustion chamber walls will rise; however, if the ignition is too late, the temperature growth is observed in the exhaust valve and the exhaust pipe. Hence, very often, when knocking is heard, normal combustion can be achieved by delaying ignition.

Another operating factor which influences the formation of peroxides is the fuel mixture's composition, the associated contamination of the mixture with exhaust gases, and the characteristics of the intake air. The most pronounced tendency is exhibited by mixtures of which the composition is similar to the stoichiometric one. This is connected with the highest burning rates being attained for excess-air ratios in the range of 0.95...1.05.

Throttling the suction process reduces the degree of filling, thus, it reduced the amount of heat being released during the process, which in turn reduces the fuel's tendency for detonation

combustion. The fuel's tendency for detonation combustion increases at full engine loads and low rotational speeds. Throttling causes increased contamination of the mixture by exhaust gases which, by isolating the vapors with inert combustion products, increases resistance to detonation combustion, thus reducing the necessary activation energy in the particles.

The higher the atmospheric pressure, the higher is the probability of formation, in the pre-oxidation process, of active particles which initiate detonation combustion. If this happens, pressure at the end of the suction process will increase, resulting in a more accurate filling of the combustion chamber with the fuel mixture. The temperature rise due to the large mixture volume enhances oxidation in that portion of the mixture where combustion is not yet taking place.

In gasoline aircraft engines, the composition of the air varies with altitude so that the content of oxygen is lower and that of nitrogen is higher at higher altitudes. The mixture becomes leaner in oxygen, and the inert nitrogen has an isolating effect and reduces the activation energy, thus reducing the tendency for detonation combustion.

As the temperature of the air entering the fuel increases, so does its evaporation rate (and a more homogeneous mixture is obtained, although the fuel's tendency for detonation combustion is higher, too).

Higher air humidities lead to lower temperatures and pressures of the gas in the cylinder, while the dissociated steam (having better anti-knocking properties in comparison with inert gases) accelerates combustion, and a lesser amount of heat evolves from the wet mixture. The tendency for detonation combustion grows with the number of revolutions (RPM) because of the shorter residence time of the fuel in the high temperature zone, where it is pre-oxidized from the moment of ignition. The ability to form active particles is then reduced, the combustion process is accelerated and heat exchange between the fuel mixture and the heated walls of the combustion chamber is intensified.

The increased engine loads lead to higher temperatures which, in turn, cause detonation combustion.

The performance of the cooling system and the resulting intensity of the cooling process have a significant effect on the combustion process. Insufficient cooling may lead to oil burning on the cylinder bearing surface, seizing of piston rings, pre-ignition, and detonation combustion due to the temperature increase in the combustion chamber.

During combustion, thermal decomposition of the hydrocarbons may occur, causing settling of a carbon deposit on the combustion chamber walls which, in turn, leads to higher compression ratios and accelerated oxidation. Air cooled engines require fuels with a higher detonation resistance, compared with liquid-cooled engines. However, it should be kept in mind that engine overcooling leads to lower power outputs and has other consequences.

Physicochemical properties of fuels, such as degree of evaporation, volatility, boiling range, heat of evaporation, and chemical composition, have been discussed earlier in this chapter. From an analysis of the above, it follows that other indirect factors, for instance, temperature, pressure, and duration of contact with oxygen, also have an effect on the nature of combustion.

However, it should be kept in mind that detonation combustion is directly caused by the formation of active particles having the structure of peroxides and acting as detonation combustion initiators. External signs of detonation combustion include a yellow flame and smoke in the exhaust pipe.

Engine operation is rough and jerky, with its output getting lower and lower. This causes rapid wear of the piston-crank assembly, valve burnout and deformation, burnout of piston heads, damage to gaskets and sparking plug insulations which, in intense detonation combustion conditions, lead altogether to engine destruction.

In some engines (particularly in aircraft engines), detonation combustion is prevented by injecting water or other liquids with low freezing points (such as ethyl-, methyl-, or isobutyl alcohols). The high heat of evaporation of the injected fluid reduces temperature of both the mixture and the combustion chamber walls, which impedes the detonation combustion. Moreover, steam being an inert gas interrupts the chain reaction and reduces the amount of carbon deposit. Another method to prevent detonation combustion is to use a mixture of water with the above mentioned alcohols.

2.1. Fractional composition

In fractional composition determination by the so-called normal distillation method, the highest temperature obtained before the exhaust appear in the flask is assumed to be the final boiling point. It will drop slightly in the next steps of the process, then grow rapidly. The drop is observed because, after the light components have evaporated, the distillation residue is so heavy that the kinetic energy of the particles is too low to enable them to leave the liquid medium. Therefore, the liquid particles do not pass into vapor phase even though the flask is heated continuously and, therefore, no heat is carried to the thermometer. The rapid rise in temperature, as indicated by the thermometer, is caused by the thermal decomposition of the residue, leading to the formation of gaseous products of decomposition. In advanced measurement sets, the initial and final boiling points are determined by means of suitable, automatic sensors.

The starting capability of a fuel is assessed from the values of its initial boiling point and distillation 10% point. The lowest ambient temperature (t_o) which enables engine start is determined from the empirical relationship:

$$t_o = \frac{1}{2}t_{10\%} - 50.5 + \frac{1}{3}(t_p - 50)$$

where:

$t_{10\%}$ -distillation 10% point for gasoline;

t_o -initial boiling point.

Temperature $t_{10\%}$ should be a maximum of 80°C. If the initial boiling point is lower than 40°C, the risk of so-called vapor locks being formed in the supply system exists. The vapor locks,

which consist of gasoline vapors having too high volatility, air bubbles, and heavier liquid components, tend to disturb the flow, leading to the fuel mixture rapidly becoming lean, and even to engine stoppages. The ambient temperature at which the vapor locks can be formed (t_{o1}), is found from the following relationship:

$$t_{o1} = 2t_{10\%} - 93$$

Because of the possibility of vapor locks formation, ambient temperature must not be higher than 76°C when the temperature under the hood is 60°C, and not more than 46°C for 0°C under the hood. Distillation 50% point for gasoline describes the fuel's average volatility and its average ability of evaporation and fuel mixture formation.

The values of distillation 90% and 97% points as well as the final boiling point characterize the fuels in terms of their content of heavy cuts. Such values should not be very high, otherwise, part of gasoline components would not be burned and the engine power output would be reduced for too-high fuel consumptions. Thermal decomposition of the fuel would be taking place in the combustion chamber, leading to overheating of the chamber walls, accumulation of too much coke and carbon deposits, resulting in an undesirable course of the fuel combustion process.

2.2. Vapor pressure

Vapor pressure is the pressure exerted by the vapors of a liquid in a closed vessel onto its walls at a predetermined temperature. In hydrocarbon mixtures, such as gasoline, the parameter depends on the proportion of light components in the mixture. According to Dalton's law, the measured value of gasoline vapor pressure is the sum of the partial pressures of its individual components. It is not a constant value at a given temperature, since it depends on the concentration of its individual components in the test liquid and on the ratio between the volumes of the gaseous phase and the liquid phase. The higher the ratio, the lower the vapor pressure of the mixture.

The starting properties of gasoline are determined largely by its vapor pressure, which has a effect also on the formation of gas locks in the pipes (especially in aircraft engines at high altitudes). Therefore, saturated vapor pressure for aviation gasoline should be in the range from 0.03 MPa to 0.05 MPa.

The ambient temperature (t_{o1}) at which the gas locks can be formed, is found from the value of vapor pressure:

$$t_{o1} = 260 - 77.8 \log p$$

where:

p -vapor pressure of gasoline, as determined in Reid bomb.

The time it takes for the engine to start is dictated by volatility of gasoline and by ambient temperature. These relationships can also be illustrated using a suitable nomogram. These effects are also associated with fuel consumption, as shown in Table 1.

Air temperature [°C]	Engine starting time [sec] for gasoline		Fuel consumption [cm ³] during engine starting time [sec] for gasoline	
	$t_{10\%} = 79^{\circ}\text{C}$	$t_{10\%} = 72^{\circ}\text{C}$	$t_{10\%} = 79^{\circ}\text{C}$	$t_{10\%} = 72^{\circ}\text{C}$
	0	10.5	9.4	10.0
-6	45.0	29.0	480	70,0
-16	515.0	225.0	678,0	309,0

Table 1. Influence of ambient temperature on consumption of gasoline and engine starting time for a passenger car

2.3. Resistance to detonation combustion

Critical compression ratio was the first criterion used for fuel assessment in the aspect of detonation combustion. The parameter was assumed to be the highest ratio at which combustion was normal. The value, however, depends on a number of subjective factors as well as on the engine condition and measurement conditions. So called “fuel equivalent methods” (using aniline, benzene or toluene) were also used. They compare combustion conditions for the test fuel solutions in reference gasoline with those of the same amount of fuel equivalent dissolved in the same kind of gasoline. The quantity of the fuel equivalent introduced indicated the fuel’s resistance to detonation combustion. The study was carried out in a single-cylinder laboratory engine with variable compression ratio. However, the fuel equivalent methods were burdened with large errors associated with the resistance of the test solution (not pure fuel) to combustion detonation. In addition, the reference gasoline used showed different properties, depending on its origin and method of preparation.

In 1927, a criterion for the assessment of resistance to detonation combustion was developed and was adopted by the Standard Committees in most countries all over the world. The criterion is called the octane number or octane rating of fuels, and it measures their resistance to detonation. The octane number is determined using the octane number scale, based on the following, conventionally adopted, reference fuels:

- n-heptane (critical compression ratio=2.8; conventionally assumed octane number=0 units);
- 2,2,4-trimethylpentane – one of isoctanes (critical compression ratio=7.7; conventionally assumed octane number=100 units).

The adopted values are associated with the structure of the individual substances identified as reference fuels and with their resistance to detonation combustion. The adopted reference fuels have the physical properties of hydrocarbon components of gasoline.

The octane number is an absolute number, an integer equal to the percentage of 2,2,4-trimethylpentane in n-heptane in such a composition that the mixture, as prepared in the standar-

dized motor in standardized conditions burns with the same detonation resistance as the test fuel.

To determine the octane number of fuels, the Cooperative Fuel Research designed and built a standard CFR engine. Other countries developed their own design, in accordance with the CFR engine requirements.

The test engines, designed for octane number determination, are single-cylinder, overhead-valve engines with a movable cylinder, cast as a whole with the head, having sensors (called "Midgley detonation needles") mounted in it, which enable evaluation of the intensity of detonation using the pressure-based method. As the cylinder is brought closer to or farther from the piston-connecting rod assembly through the worm gear system, the compression ratio of the engine during operation is changed.

A synchronous electric motor acts as a starter but also, after engine start, it receives the generated power by means of a belt drive. The reference engine is equipped with three fuel tanks and is fuelled through a carburetor having three float chambers which enable the engine to be supplied with a fuel mixture having different compositions of the reference fuels. Stable engine operating conditions are maintained by keeping stable temperatures of air, oil, and cooling water, and the optimum ignition advance angle for each compression ratio.

Depending on the measurement method, the engine can be provided with additional devices and measurements are made at the suitable rotational speeds. Conditions for octane number determination using the standardized motor according to various methods are listed in Table 2.

Only the so-called Army Method uses a different design of the combustion chamber. The method provides octane number values which are higher by 3 to 5 units, in comparison with the motor method. However, the Army Method has not become very popular and has been replaced by temperature-based methods.

Because of differences in engine rotational speeds between the research method (RM) and motor method (MM), some differences appear in the values of the octane numbers provided by the methods. RON is mainly used to determine the detonation combustion resistance of fuels, as used in passenger cars operated in the city or in field conditions at partial engine loads. RON shows generally higher values, compared with MON. The difference between RON and MON is defined as the fuel's sensitivity to the method of measurement. Out of two gasoline types having same MON but different RON values, the one with the higher RON is more sensitive, therefore, more useful. Similarly, among two gasoline types with same RON and different MON values, the one with the higher MON is more useful in operation.

Sensitivity of fuel as expressed by octane number values, can be as high as a dozen or so units. The lowest, sometimes negative, sensitivity is shown by paraffins (for example: pentane=-0.2, 3-methyl-hexane=-4.2). Higher sensitivities are shown by naphthenes (such as: ethyl cyclopentane=6.0, propyl cyclopentane=3.1) and the highest sensitivities characterize olefins (such as: butane-1=16.0, pentene-1=13.8) and aromatic hydrocarbons (toluene=12.0, propylbenzene=9.8).

Although olefins are highly resistant to detonation combustion, their presence in gasoline is not preferred because they tend to form resins during storage and sludge during fuel combustion in engines. However, for reasons of economy, they are used as additives to gasoline in amounts of about 30%.

MON is most commonly used for assessing the behavior of fuels in vehicles operated on longer routes (when the engine is exposed to more strenuous operating conditions, works in stable high-load conditions, at higher speeds and higher temperatures). MON is also used to evaluate resistance to detonation in less strenuous operating conditions for aircraft engines.

Test-stand methods for octane number assessment were found inadequate for determination of desired octane number values of fuels used in newly-manufactured cars with modified engines. Therefore, another method was developed for measurement of DON (road Octane Number). DON is determined in accordance with Uniontown and Borderline methods. In both of them, the fuel's behavior is tested while driving a car equipped with additional accessories on a road section of 1 km in standard conditions (such as surface, rectilinearity, wind power, etc.). The test car is provided with at least five tanks filled with fuels having different known RON values and is equipped with a device enabling measurement of the intensity of detonation, amount of fuel charge, linear velocity, rotational velocity, as well as measurement and change of the ignition advance angle.

In the Uniontown procedure, for each subsequent run 2° before TDC, every 2° , the car is made to run at a constant ignition advance angle until weak knocking for the given gasoline is observed. For the huge population of vehicles for which the test is carried out, it is possible to determine the ignition advance angle for the particular gasoline. The DON value as found by this method is usually lower than that of RON. The smaller the difference, the better the fuel's resistance to detonation combustion in operating conditions.

In contrast, the Borderline method estimates engine's rotational speed at which detonation ceases for a given fuel and for a given value of ignition advance angle. In the subsequent starting runs of a car, for gasoline having a known RON, the velocity is found for which detonation ceases at a pre-determined ignition advance angle which is varied in accordance with the characteristics recommended by the manufacturer. The detonation combustion region comprises part of the plot area limited by the characteristics of the ignition advance angle controller and part of sections in a pencil of curves.

The approximate value of DON can be determined also from the octane index, which is the arithmetic mean of RON and MON.

For aviation gasoline with octane values of more than 100 units, ON measurements are carried out by 1-C and 3-C temperature methods. The methods are based on the cylinder wall heating-up with the higher intensity, the more intense detonation combustion occurs. A thermocouple is placed inside the cylinder head of the CFR engine with an aluminum piston, to determine the temperature rise gradient. The detonation temperature calibration line is found before starting the measurements. The composition of the fuel-air mixture is selected so that the

Parameters of motor operation	Method:				
	Research method (automotive gasoline)	Motor method (automotive and aviation gasoline)	Army Method	Temperature method 1-C (aviation gasoline)	Temperature method 3-C (aviation gasoline)
RPM (revolutions per minute)	600	900	1200	1200	1800
Coolant type	water	water	ethylene glycol	ethylene glycol	ethylene glycol
Coolant temperature [°C]	100	100	160	190	190
Air temperature [°C]	-	38	-	52	107
Oil temperature [°C]	55	55	70 - 80	65	74
Mixture temperature [°C]	-	150	-	107	-
Ignition advance angle (degrees before TDC)	26	22.6	30	35	45
Cylinder diameter [mm]	82.6	82.6	66.7	82.6	82.6
Piston stroke [mm]	114.0	114.0	112.0	114.0	114.0
Detonation/knocking indicator	pressure	pressure	Thermo-element	Thermo-element	-

Table 2. Operating conditions for a reference engine in determination of octane numbers by different methods

thermocouple shows the highest temperature, and the compression ratio is selected in a manner that enabled the maximum temperature to be found in the reference temperature line.

In the case of aircraft engines with direct fuel injection and air-compressor turbocharging, the 1-C method is insufficient for determination of the correct octane number. Therefore, the 3-C temperature-based method was developed, whereby the octane number measurements are carried out by means of a seriously modified reference engine which is equipped with a compressor and an apparatus for measuring power outputs, fuel consumption, and air flows. Determination of fuel resistance to detonation combustion is based on finding the relationship between the mean indicated pressure (proportional to power output) and the mixture composition for the engine running with a slight detonation. Leading to detonation combustion is effected by increasing the supercharging pressure. The measurement starts with a lean mixture, and then the mixture is gradually enriched, the indicated pressure increases to a maximum and then drops. The plotted curve for mean indicated pressure vs. mixture composition is applied against comparable curves obtained for the reference fuels, thus determining the value of what is so-called "performance number".

Empirically, the performance number can be determined from the indicated pressure (P_i) according to the formula:

$$LW = 276 - \frac{29650}{P_i}$$

The quality of gasoline at the time of engine start and engine acceleration are characterized by the fuel's octane segregation index (R_{100} or R_{75}). Segregation index is the difference between RON for the test gasoline and for the fraction of the same gasoline boiling to 100°C (ΔR_{100}) or evaporating to 75% by volume (ΔR_{75}). The smaller the value of the segregation octane index, the more homogeneous is the gasoline. Such gasoline shows stable resistance to detonation combustion regardless of how much of it has evaporated.

The phlegm which is formed in the process of gasoline evaporation may lead to a non-homogeneous fuel (with different fractional compositions) being distributed into the cylinders and this will result in different resistances of the fuel to detonation combustion. The phenomenon is assessed by means of FON ("front octane number", formerly "distribution octane number"), measured by means of a reference engine, equipped with device called dephlegmator.

Dephlegmator is a water cooler for the flowing fuel vapors, with the cooling water temperature of 4.4°C. It is mounted between the carburetor and the inlet of the cylinder. The temperature of the mixture from the dephlegmator is in the range 17 to 22°C. Heavier components of the fuel are condensed in the dephlegmator fall to the bottom and are then sent to the measuring vessel; part of them (5... 7)% (V/V) is entrained into the combustion chamber. The fed mixture is slightly richer during the measurements for FON, compared with RON. FON will be much lower than RON in the case of phlegm formation in winter operating conditions in engines with carburetors (especially during the cold start).

Gasoline is a hydrocarbon mixture of about 100 different compounds obtained by straight-run or destructive processing. Table 3 summarizes the basic group compositions of most light distillate fuels.

With regard to the desired combustion method, gasoline should preferably have a relatively high content of aromatic hydrocarbons, most of which are obtained by reforming while some by pyrolysis. Very important components, especially in aviation gasoline, are mixtures of hydrocarbons produced in isomerization and alkylation processes, also called "isoparaffins". They have the advantage of high knock resistance, in addition to high calorific value.

Hydrocarbons	Limits [% (V/V)]
Paraffins	40...65
Naphthenes	20...35
Aromatics	8...20

Table 3. Group composition of light distillates

All the necessary ingredients for gasoline blending are obtained from different refinery processes and then handled in the blending unit, in accordance with the respective technological requirements for a particular gasoline grade, as discussed earlier in Chapter 1.

2.4. Ignition properties of fuels (flash-point, self-ignition temperature and fire-point)

The respective fuel ignition limits depend on many factors, including: chemical composition of the fuel, temperature, and pressure of the mixture, ignition sites, etc. The problem applies to all motor fuels, from the engine gasoline, diesel fuel, heating oil, aviation fuel and biofuel. The essence of changes in these properties and, therefore, the criterion for measurement and the assessment of its weight and measure, depend mainly on the group-and structural composition for a given fuel. Therefore, general considerations about these properties are provided in the section concerning the first group of fuels, that is, gasoline.

The fuel mixture can be ignited when its composition falls within flammability limits and the temperature, called flash-point, is high enough (vapors are formed above the liquid surface at a concentration above the lower flammability limit).

Flash-point depends on the volatility of the liquid, in the first place. Light liquids with low densities (e.g., gasoline) have low flash-points although the value rises for liquids with higher densities. Flash-points of fuels are measured mainly by two types of methods: open cup – Marcusson, Cleveland or Brenken method or, depending on the type of fuel, using the closed cup: as in Abel-Pensky or Pensky-Martens method.

In closed cups, within the vapor space enclosed by the structure, the resulting mixture is unable to interact with the atmosphere so it will reach and exceed its lower flammability limit sooner (at a lower temperature) and ignite, if provided with the appropriate ignition energy by the initiator (such as a small gas burner). That is why closed cup testers are used mostly for determination of flash-points for light fuels.

Flash-point values obtained for a same fuel by a closed-cup method will be lower than those obtained by open-cup methods. Heavier fuels, having lower diffusion coefficients, in conditions of unlimited contact of vapors with the atmosphere above the liquid surface will make a suitable rich mixture much easier.

In the Marcusson method, correction for the flash-point reading is required because of the difference between the ambient pressure at which the measurement was carried out and normal pressure.

In the Marcusson and Brenken method if, after an initiated successful ignition, the fuel continues to burn for at least 5 seconds then the temperature of the heated fuel is called the fire point. At that temperature, the amount of heat supplied to the fuel is so large that, in the process of burning of the fuel vapor above the liquid surface, a sufficiently large number of particles evaporate therefrom to sustain the condition of the resulting mixture above its lower flammability limit. Therefore, fire point is higher than flash-point, at which the accumulated vapors will burn but the flame will not be sustained.

Self-ignition temperatures of fuels are higher than their fire points. In laboratory conditions, the values of self-ignition temperature of fuels are determined by the dynamic method, by dripping fuel droplets from the burette into the airstream flowing by a heated chamber.

The higher the fuel's density, the lower its self-ignition temperature. Self-ignition of fuels is associated with what is called their low-temperature oxidation, which is intensive for more complex particles with lower stability.

The qualitative requirements and test methods applicable to gasoline in the EU ought to be conformable with the said standard EN 228 in which fuels are categorized into volatility grades. The currently applicable division of gasoline into volatility grades in the EU countries is shown in Table 4.

Properties	Units	Range						Test methods ^a
		grade A	grade B	grade C/C1	grade D/D1	grade E/E1	grade F/F1	
Vapor pressure (VP)	kPa, min	45.0	45.0	50.0	60.0	65.0	70.0	EN 13016-1 ^b
	kPa, max	60.0	70.0	80.0	90.0	95.0	100.0	
% of evaporation to 70°C, E70	% (V/V), min	20.0	20.0	22.0	22.0	22.0	22.0	EN ISO 3405
	% (V/V), max	48.0	48.0	50.0	50.0	50.0	50.0	
% of evaporation to 100°C, E100	% (V/V), min	46.0	46.0	46.0	46.0	46.0	46.0	EN ISO 3405
	% (V/V), max	71.0	71.0	71.0	71.0	71.0	71.0	
% of evaporation to 150°C, E150	% (V/V), min	75.0	75.0	75.0	75.0	75.0	75.0	EN ISO 3405
Final boiling point (FBP)	°C, max	210	210	210	210	210	210	EN ISO 3405
Distillation residue	% (V/V), max	2	2	2	2	2	2	EN ISO 3405
Vapor Lock Index (VLI) (10VP+E70)	index, max	-	-	C	D	E	F	
Vapor Lock Index (VLI) (10VP+E70)	index, max			C1	D1	E1	F1	
				1050	1150	1200	1250	

NOTE: The requirements printed in bold type refer to the European Directive 98/70/EC, as amended by 2003/17/EC.

a) See also 5.8.1.

b) The value of dry vapor pressure equivalent (DVPE) should be provided.

Table 4. Volatility grades of gasoline

It follows, from the above considerations, that the following types of analysis are required in the assessment and maintenance of the quality of gasoline during storage:

1. Full analysis for conformity with the applicable standard specifications – to be performed when accepting the product for storage.
2. Short analysis – to be performed at least once in 24 months, to assess the following parameters:
 - appearance;
 - density;
 - vapor pressure;
 - fractional composition;
 - content of inherent resins;
 - optionally, content of oxygen compounds.
3. Control analysis – to be performed at least once in 6 months, to assess the following parameters:
 - appearance (visually);
 - water content (visually);
 - impurities (visually);
 - density.

According to NATO standards, the permissible safe time of storage of gasoline is 36 months.

If the short or control analysis of the fuel parameters indicates limit values for the fuels, as shown in the applicable standard specifications, or the results are dangerously close to the limit values, then a full analysis is required and its findings will show how to deal with the stored fuel.

A control analysis ought to be carried out after any technical procedure was performed with regard to the storage tank with the fuel in it, and a short analysis is applicable after any procedure was performed with regard to the fuel being stored in the tank.

Whenever the whole fuel batch is released, the short analysis should essentially be sufficient subject to acceptance from the recipient but even so, full analysis is the recommended solution to prevent any complaints.

3. Criteria for the assessment of the quality of diesel fuels in storage and operating conditions

Diesel fuels are mixtures of liquid hydrocarbons having boiling ranges (180...380)°C, with a content of improvers and they are used as fuels for engines with spontaneous-ignition (diesel,

or self-ignition engines). Diesel fuels are obtained by blending the appropriate products of crude oil distillation and other refinery processes.

Differences in the diesel fuels of to-day are found, first of all, in their having different cold filter plugging points (CFPP), freezing points, and viscosities. Many users still tend to believe that diesel fuels are a residual, poor quality product. Generally though rather wrongly, diesel fuels are regarded by such users as a deteriorated fuel with low requirements concerning quality, production methods, storage, and performance in operating conditions. Another prevailing conviction is that most diesel engines can be fuelled with poor-quality fuels, an example of which diesel fuels are believed to be. However, all the requirements relating to advanced engine designs, to the complex advanced methods for the obtaining of diesel fuels, as well as the ever more stringent environmental protection requirements are ignored in this approach.

Existing diesel fuels are fuels with high qualitative requirements and sophisticated testing methodology. This results from certain radical changes in the design of self-ignition engines, as well as more stringent requirements concerning the various consumable fluids used in such engines. Not only are such requirements rather essentially connected with the design of engine fuel distribution and combustion systems but also with environmental impact issues and severe control of harmful emissions.

3.1. Low-temperature properties of diesel fuels

Rheological properties of diesel fuels, especially in low-temperature conditions, have a significant impact on the performance of fuel and combustion systems in diesel engines. They determine the possibility of delivering sufficient amounts of oil into the combustion chamber. This is especially important when starting the engine at low ambient temperatures because crystallization of some of the components of diesel fuels may occur in such conditions. Paraffin hydrocarbons (waxes), otherwise a desirable component of diesel fuels because of their self-ignition properties, tend to crystallize at the highest temperatures.

Crystallization of hydrocarbons in the fuel leads to filter plugging, which causes significant flow resistance, thus reducing fuel delivery. Intensified crystallization may cause complete plugging and stop the fuel from flowing through the filter: this occurs after a more than 3 mm thick deposit of crystals has accumulated on the filter. The temperature at which the phenomenon occurs is called the cold filter plugging point (CFPP), or critical filterability temperature, and is a very important criterion in analyses intended to check the quality of diesel fuels in the aspect of approval for use.

CFPP is determined by the Hagenmann and Hammerich method by measuring the highest temperature at which a diesel fuel stops flowing through a standard filtration system in standardized conditions, or the flow of 20 cm³ of the diesel fuel takes more than 60 sec. CFPP is about (10...15)°C higher than the freeze point of a diesel fuel, defined as the temperature at which the mobility of the diesel fuel sample is reduced so that its meniscus in a tilted test tube at an angle of 45° does not move within less than 60 sec. The cloud point of diesel fuels, as defined in standard specifications, is above the freeze point. The value of crystallization point is also stated in some sources. Both these temperature values characterize the same physical

phenomenon, though it is visualized in different ways. When measuring the cloud point, the standardized sample becomes cloudy; in crystallization temperature measurements, single crystals which are visible to the naked eye start forming in the sample as it is cooled down.

The above values, especially CFPP, are very much affected by the sample's contamination, water content, and duration of storage in storage tanks, in addition to fractional composition. Mechanical impurities (solids) will deposit on the filters, thus accelerating filter plugging. In addition, dust microparticles and impurities tend to attract wax particles and favor their crystallization. While the content of water has a highly undesirable effect on the low-temperature properties of diesel fuels, during their long-term storage, resinous ageing products may form in them, which disturb their flow through the filter and accelerate crystallization.

According to European requirements for the temperate climate for the various diesel fuel grades, the following CFPP values are permissible: from 5°C max. for grade "A"; followed by 0,-5,-10,-15°C for the consecutive grades, with -20°C for grade "F". For the so-called arctic oils category, the CFPP values for grades 0 to 4 are -20,-26,-38,-44°C, respectively. The cloud point values "tolerated" in applicable standards are 10°C higher for each oil grade.

Table 5 shows applicable requirements, according to the European standard, concerning the most important low-temperature properties of diesel fuels, intended for use in so-called arctic climate conditions.

Property	Range					Test method
	0	1	2	3	4	
Oil grade	0	1	2	3	4	-
Freezing point in °C max.	-10	-16	-22	-28	-34	EN 23015
CFPP in °C max.	-20	-26	-32	-38	-44	EN 116

Table 5. Low-temperature properties of diesel fuels intended for use in arctic climate conditions, according to EN 590:2013

3.2. Requirements connected with the evaporation of diesel fuels

Evaporation of diesel fuel in a self-ignition engine, as a process, has essentially two phases.

The first phase takes place from the start of fuel injection to the time self-ignition; it takes place at the cost of the heat contained in the compressed-air combustion chamber. During that phase, the evaporating hydrocarbons are preliminarily oxidized while evaporation is accelerated and intensified by the heat of exothermal oxidation reactions. This step is also called self-ignition delay and, as explained later in this chapter, it occurs at the same time as the first step of combustion.

The second phase of evaporation takes place from the time of self-ignition to the completion of fuel injection. Evaporation of the fuel, in this case, takes place at the same time as combustion, at the cost of the heat being generated during the combustion of the previously evaporated portions of fuel.

In engines equipped with pre-combustion chambers, evaporation starts at the time the fuel is injected into the pre-combustion chamber. The rich mixture formed in it has a composition which enables self-ignition. This occurs at sufficiently high temperatures; part of the mixture is combusted. The rapid evaporation of a portion of non-evaporated fuel causes a pressure increase, whereby the fuel during combustion is forced into the main combustion chamber and the fuel combustion process is continued.

The fuel's delivery and evaporation is much affected by the viscosity of diesel fuel. At 20°C, the viscosity of diesel fuels for high-speed diesel engines is typically between (2.8...8.0) mm²/sec.

For every type of engine, there is a limit to the fuel viscosity which, for a given design of the fuel system, makes impossible normal power delivery because flow resistance is too high, leading to flow disturbances. Viscosity of diesel fuels decreases as the temperature increases, this affects the conditions of flow. The least observable changes in viscosity, with temperature variations, are shown by the paraffin fractions of diesel fuels. If present in excess in the oil, the paraffin fractions will improve its spontaneous-ignition properties but its low-temperature properties will be much worse (higher cloud point and CFPP values).

With a decrease in the oil viscosity, the fuel stream's atomization and evaporation are lower though the fuel stream can reach farther, therefore, the fuel tends to settle on piston heads and chamber walls, leading to the formation of carbon deposits. Too low viscosities will affect lubrication of the injection pump pistons and reach of the fuel stream, vary the distribution of the fuel droplets in the combustion chamber, lead to incomplete combustion and to the presence of local hot spots in locally overheated walls of the combustion chamber. Low viscosities may result in fuel leakages from precision pairs of components and in reduced fuel dosage.

A fuel stream, delivered by the injection pump through the injectors, is composed of several million droplets of fuel, the size between (3...5) μm and (100...150) μm. The fuel spraying quality is characterized by its droplet size and quantity or, to be more precise, by the degree and uniformity of spraying, the range of the fuel stream, and angle of spraying cone.

The degree of spraying is defined as the average size of the fuel droplets going out of the injector. Stream uniformity is to be understood as the ratio between the number of average-size fuel droplets to the total number of fuel droplets.

The quality of spraying depends on the following properties of diesel fuels, in addition to the injector nozzle design:

- viscosity (discussed earlier);
- density;
- fractional composition;
- vapor pressure;
- surface tension;
- heat of evaporation;

- heat of combustion.

Evaporation of diesel fuel is easier at higher values of spraying degree and uniformity. Like the fuel's viscosity, its density affects mainly the range of the fuel stream in the combustion chamber. Moreover, lower densities of diesel fuel lead to reduced emissions of solids to a linear course but also, in certain instances, may lead to reduced emissions of NO_x. Lower density of diesel fuel is connected with its lower calorific value – this is of importance to engine performance. In this case, inhibition of engine output reduction by increasing the fuel dosage leads to higher fuel consumption levels, eliminating the solids emission-reducing effect. Reduction of density may also result in a degree of reduction of CO₂ emissions by a maximum of 1%. Therefore, the density of diesel fuels should be suitably low and vary over a small range only. According to applicable European standards, the permissible density of diesel fuels is (820...860) kg/m³ at a temperature of 15°C, though its upper limit is expected to be lowered to 845 kg/m³.

Uniformity of fuel spraying is proportional to its surface tension which, in turn, depends on the presence in the oil molecules of polar links. Along with the increase in fuel density, surface tension grows and, at the air-oil interface, is in the range (27•10⁻⁷...30•10⁻⁷) J/cm² and getting lower as the temperature increases: this is favorable for fuel spraying. Paraffin-naphthene fractions in the fuels have much lower surface tensions, compared with aromatic hydrocarbons.

Fuel evaporation depends also on its fractional composition which is determined by means of normal distillation. The drip point has an effect on the engine start characteristics. The distillation 50% point correlates with the viscosity and density of fuels, affecting the degree and uniformity of spraying, as well as on the stable course of evaporation and combustion processes and on the easy engine start. The distillation 90 and 95% points as well as the final boiling point have a significant impact on toxic emissions. According to the applicable EU Directive, the maximum distillation 95% point for diesel fuels is 370°C, and is to be lowered to 360°C. If the evaporation of light fuel fractions is fast enough, then the time required for making a homogeneous combustible mixture is short. On the other hand, there takes place a rapid pressure build-up, leading – after self-ignition of the mixture – to rough engine operation, which is undesirable. Heavy fractions in diesel fuels may lead to the incomplete combustion of the fuel, causing thermal decomposition of non-evaporated fuel droplets, which is accompanied by the formation of large amounts of soot in the exhaust gases and carbon deposits on injector tips. Moreover, the non-combusted fuel flowing down the combustion chamber walls may wash down the lubricating oil, thus accelerating the wear and tear of cylinder sleeves.

The heat of evaporation of fuels, though not determined in applicable standards is taken into account in the processes of collection of diesel fuel cuts from the distillation column. The value of heat of evaporation determines how readily a combustible mixture is formed in cold engine start conditions. As stated earlier in this chapter, such properties may also be determined by means of drip point and distillation 50% point for diesel fuel.

According to European requirements, the volumes of distilled diesel fuel are established for operation in arctic climate conditions for temperatures 180°C and 340°C, as shown in Table 6.

Property	Range					Test method
	0	1	2	3	4	
Oil grade						-
Density at 15 °C in kg/m ³	800...845		800...840			EN ISO 3675 EN ISO 12185
Viscosity at 40 °C in mm ² /sec	1.50...4.00		1,40...4.00	1.20...4.00		EN ISO 3104
Fractional composition:						ISO 3405
%(v/v) distill. to 180°C max.	10					
%(v/v) distill. to 340°C min.	95					

Table 6. Properties of diesel fuels for use in arctic climate conditions, connected with evaporation, according to EN 590:2013

3.3. Requirements connected with diesel fuel combustion

Diesel fuel combustion, which takes place in self-ignition engines, is a three-phase process.

Phase 1 is the time of self-ignition delay, in other words, the time of preoxidation of the fuel. It starts at the time of fuel injection, at (20...30)° of crankshaft rotation before TDC (Top Dead Center) and takes about 0.0007sec, that is, until self-ignition. Phase 1 overlaps entirely with the first step of evaporation of fuel. If the fuel preoxidation is more intensified (which happens at higher temperatures and pressures in the combustion chamber), then the duration of the self-ignition delay is shorter and the engine operation is smoother. The duration of the first phase of combustion depends predominantly on the fuel's chemical composition.

Phase 2 of the process is the actual combustion of the fuel that was accumulated and prepared for combustion in phase 1. What occurs here is a fast combustion and intensified pressure buildup in the combustion chamber. A flame appears in many spots in the combustion chamber; it originates from the respective self-ignition sites, created by active radicals. The duration of phase 2 depends on the evaporated amount of fuel and the homogeneity of its mixtures with air. A rapid pressure buildup in the second phase of combustion may generate effects which are comparable to a detonation combustion in spark-ignition engines. Its duration determines the operation of a compression-ignition engine. With short self-ignition delays, pressure increments are rather mild and the engine operation is smooth. Long-lasting self-ignition delays may lead to a number of undesirable phenomena.

Rapid pressure and temperature increments lead to the formation of too much carbon deposit due to thermal decomposition of the fuel. Moreover, loads acting upon the piston, connecting rod and bearings can be too high, engine output and its efficiency are low. Exhaust gases are contaminated by soot and toxic fuel decomposition products, smoke level is higher and metallic knocking is heard in the cylinders. The engine operation in such conditions is termed "rough".

Phase 3 is a step of delayed, controlled combustion during which the fuel rapidly evaporates and is combusted as it is injected until the injection process is complete. For normal engine

operation, settings and fuel choice, the pressure increase rate is not expected to be higher than approx. 588 kPa/sec.

Among the components of diesel fuels, the best self-ignition properties are shown by long-chain paraffins. The isomerization degree for those hydrocarbons determines for the duration of the self-ignition delay. Unsaturated hydrocarbons, or alkenes, have self-ignition delays close to those of their respective paraffins and isoparaffins. Naphthenes have better oxidation stabilities, compared with paraffins. The side-chain in paraffins usually extends the self-ignition delay in naphthenes.

The longest self-ignition delays are observed in aromatic hydrocarbons: they are proportional to the number of rings per molecule. The presence of a side chain reduces the self-ignition delay for aromatic hydrocarbons, especially in the case of unbranched chains.

Generally, the higher the boiling point for the hydrocarbons in diesel fuels, the better their self-ignition properties. The self-ignition tendency of diesel fuels is defined in standard specifications by means of cetane number and cetane index.

The cetane number (CN) of diesel fuels, which measures their self-ignition tendency, is defined as a non-denominated integer which expresses the percentage by volume of the standard fuel n-cetane ($C_{16}H_{34}$) of which the cetane number is assumed to be 100 units, contained in a mixture with the standard fuel α -methyl-naphthalene of which the cetane number is assumed to be 0 units, so that the resulting mixture in standard conditions in a standard engine is combusted showing the same self-ignition tendency as the test fuel.

The measurement of CN is a complex procedure which requires special test engines, depending on their settings, and is carried out by delayed self-ignition methods, when the fuel injection is set at 10° of crankshaft rotation before TDC and self-ignition is effected by varying the compression ratio, 1° of crankshaft rotation after TDC, or by synchronization of fuel injection, by analogy: fuel injection 13° of crankshaft rotation before TDC, self-ignition at TDC.

Too low CN values of less than 45 units lead to deteriorated engine operation and the self-ignition delay is too long. This may cause excessive temperature increase and pressure buildup in the combustion chamber, leading to rough engine operation which causes a premature wear and tear of engine components and makes difficult the cold engine start.

The combustion of fuels with CN values of more than 70 units will also lead to deteriorated course of the combustion process because the fuel combustion is incomplete and the self-ignition delay is very short, causing too high smoke levels in the exhaust gases and inefficient engine operation.

According to the applicable European requirements, the permissible minimum value of CN is 51 units. For fuel grades intended for use in arctic climate conditions, the minimum CN values, according to the same European standard, are somewhat lower, especially for higher fuel grade numbers.

Because the CN measurement procedure is so complex, the notion of cetane index (CI, CCI) has been introduced in standard specifications for diesel fuels. It characterizes the self-ignition

properties of diesel fuels as well, although it can be calculated from their densities and the course of their normal distillation.

According to ASTM D976-80, the value of CI is calculated as follows:

$$CI=454.74-1641.416D+774D^2-0.554B+97.803(\lg B)^2$$

where:

D – fuel density at a temperature of 15°C;

B – the temperature at which 50% vol. of the fuel has distilled (distillation 50 point, °C).

Another method to obtain the Calculated Cetane Index (CCI), in accordance with ASTM D4737-87, is more complicated and requires the knowledge of the fuel density and distillation 10, 50 and 90% points of fuel: CCI is calculated from the following relationship:

$$CCI=45.2+(0.0892)(T_{10N})+[0.13]+(0.901)(B)(T_{50N})+[0.0523-(0.0420)(B)][T_{90N}]+$$

$$+[0.00049][(T_{10N})^2-(T_{90N})^2]+(107)(B)+(60)(B)^2$$

where:

$$B=[e^{(-3.5)(DN)}]-1;$$

$$DN=D-0.85;$$

D – fuel density at 15°C;

T₁₀ – the temperature at which 10% vol. of the fuel has distilled (distillation 10 point, °C);

$$T_{10N}=T_{10}-215;$$

T₅₀ – the temperature at which 50% vol. of the fuel has distilled (distillation 50 point, °C)

$$T_{50N}=T_{50}-260;$$

T₉₀ – the temperature at which 90% vol. of the fuel has distilled (distillation 90 point, °C);

$$T_{90N}=T_{90}-310.$$

The latter method to calculate the cetane index (CCI) is currently adopted as applicable in standards. The difference between the cetane index and cetane number values is 1...4 units, and the former is usually lower. The minimum value of cetane index for diesel fuels intended for use in temperate climate conditions is set to be 46 units.

The flash point value for diesel fuels is also established in standard specifications. According to European requirements, its minimum value is higher than 55°C; the value applies to diesel fuels for both the temperate and arctic climate conditions (Table 7).

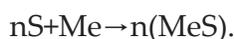
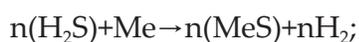
Property	Range					Test method
	0	1	2	3	4	
Oil grade	0	1	2	3	4	-
Flash point °C	"/>55					EN 22719
Cetane number, min.	47.0		45.0			EN ISO 5165
Cetane index, min.	46.0		43.0			EN ISO 4264

Table 7. Properties of diesel fuels intended for use in arctic climate conditions, relating to the combustion process, according to EN 590:2013

3.4. Environmental impact requirements for diesel fuels

The presence of sulfur in diesel fuels and their aromatic hydrocarbon content is extremely important, in addition to the above-mentioned correlations between the normative properties of diesel fuels and the environmental impact of such fuels.

Sulfur and its compounds – which are hard to remove from diesel fuel during its production process – may have a direct corrosive effect on engine construction materials, as shown by the following reaction:



The corrosive effect of elementary sulfur is observed at as low concentrations as 1mg per 100 ml of fuel.

During the diesel fuel combustion process, their sulfur content is oxidized to form sulfur trioxide and dioxide which combine with steam forming, respectively, solutions of sulfuric(VI) acid and sulfuric(IV) acid, which – owing to their presence in the exhaust gases – have a strong corrosive and acidifying effect on the environment. A certain amount of sulfur (1..2) %(m/m) reacts to form insoluble sulfates which are emitted in the form of solids with the exhaust. Their emissions may be high in the case of vehicles equipped with oxidation catalysts. Moreover, sulfur has a destructive effect on reduction catalysts, which may result in worse NO_x conversions into N₂.

In addition to their adverse effect on the self-ignition properties of diesel fuels, aromatic hydrocarbons lead to increased emissions of solids, lower reduction of NO_x emissions, and direct pollution by toxic emissions of cancerogenic hydrocarbons, especially multi-ring aromatic hydrocarbons.

3.5. Other performance requirements for diesel fuels

There are a category of properties of diesel fuels (and they are characterized in applicable standards), which have an indirect effect on all of their performance parameters: on the course of evaporation and combustion but also on environmental hazard. Such properties include the following;

- water content;
- solids content;
- ash residue after incineration;
- carbon residue in 10% distillation residue;
- oxidation stability;
- lubricity.

Lubricity was implemented in EN 590 in the year 1998. The requirement of its determination for diesel fuels is justified by the need to prevent any unnecessary wear and tear, particularly with regard to precision pairs of components in the fuel distribution system. This is especially important in view of the low-sulfur content standards which are applicable to diesel fuels, because some sulfur compounds appear to have good wear and tear properties. Advanced compression-ignition engines are characterized by low tolerance, very high machining precision of components, and their structural materials are frequently modified.

The effect of the other above-listed properties of diesel fuels on the essential engine operation parameters and on the toxicity of exhaust gases was discussed earlier in this chapter. Water content and solids disturb the process of fuel transport and distribution in the fuel system; at near 0°C temperatures, they favor clouding (crystallization) and freezing processes and increase the value of CFPP.

Oxidation stability is a property which may determine the permissible duration of storage of diesel fuels, and may affect the course of combustion of such fuels. Very high values of oxidation stability will extend the permissible duration of storage of diesel fuels but they also affect combustion, for instance, by extending the self-ignition delay; this may lead to rough engine operation and its further undesirable consequences. There are good reasons to believe that the value of oxidation stability according to the applicable European standard is not essentially going to change in the near future, unless the standard related to the test method has been amended.

The coking number of diesel fuels indicates their tendency to form carbon deposits and is found from 10% of distillation residue. The phenomenon may change the thermal conditions prevailing in the combustion chamber, and lead to a deteriorated course of the combustion process, formation of local temperature gradients and, consequently, also high stresses in construction materials. The phenomenon, combined with the value of ash residue after incineration, may indicate the possible emission of solids with the exhaust gases. According to the requirements of the respective environmental protection agencies, such emissions are going to be more and more strictly limited. Emission level depends on the type and amount of improvers being added to diesel fuels. The limit on the coking number, as set out in the applicable European standard, ought to be maintained by fuel manufacturers before they choose to use of any additives that are known to increase the value of CN. If such an additive is detected in a commercial fuel by means of a test referred to in EN ISO 13759 concerning the presence of nitrate additives, then the limiting coking number as set out in that standard is not applicable.

As regards the essential properties of diesel fuels, in the assessment of their quality and performance in accordance with applicable standards, it is not necessary to determine their foaming tendency. Silicone-based foam inhibitors are used in diesel fuels in many countries except for the USA, where the material has not been approved by the EPA. Antifoaming properties of diesel fuels are of importance to the storage, distribution, and engine fuelling processes. The parameter ought to be included in the surveillance of the quality of diesel fuels, as indicated by laboratory tests and engine tests with respect to the evaluation of the anti-foaming properties of diesel fuels, their correlations, and impact on selected performance parameters of vehicles.

Considering the above, the full analysis of diesel fuels, which is due before storage, ought to comprise tests of conformity with the requirements of applicable standard specifications, and be carried out in accordance with the principles described earlier for gasoline.

The short analyses of diesel fuels with a zero content of biocomponents ought to be performed at least once in 24 months, assessing the following parameters:

- color and appearance;
- density;
- fractional composition;
- flash point;
- coking number.

The control analyses of diesel fuels, to be performed at least once in 12 months, are intended to assess the following:

- color and appearance;
- density;
- flash point.

In carrying out the respective analyses, the rules discussed earlier in this chapter for gasoline apply.

4. Criteria for the assessment of the quality of heating oils in distribution, storage, and operating conditions

Heating systems and devices are specific in terms of their designs and requirements with respect to heating oils. A definite majority of such systems, especially those with lower capacities, as well as their fuel storage tanks or reservoirs, are located underground and in lower floors of the buildings or facilities they provide heat for. Heating oils are kept in suitable storage tanks which are supplemented once or twice a year, therefore, they must not have any content of flammable or explosive or malodorous material. Flammability is limited by the flash

point (not lower than 55°C). In this aspect, favorable materials include vegetable oils (flash points higher than 295°C) and spent oils.

Compared with light petroleum oils, products of thermal destruction of spent oils and vegetable oils are characterized by much lower flash points. Alcohols have even lower flash points, which definitely limits their usefulness as fuels or fuel components.

There are no commonly used methods for the assessment of liquid fuels, especially alternative fuels. The concentration of those substances or groups in heating oils which are accountable for their noxious smell is determined instrumentally (by chromatography) though, as a rule, such assessment is carried out organoleptically. Petroleum based heating oils usually have rather low volatilities and moderately noxious smell. A definitely undesired odor is observed in spent oils, products of their thermal destruction, and some hydrocarbon waste. The most desirable odor (very low vapor volatility) is shown by fresh vegetable oils and their methanolysis products but this may change after lengthy storage.

Because fuel storage tanks are located in unheated rooms indoors, or outdoors (which is obvious for fire safety reasons), liquid heating fuels are required to have a specific low-temperature profile. It defines their fluidity, therefore, the possibility to transport the materials to storage tanks and then deliver them to the burners. If a given liquid heating fuel has unfavorable low-temperature properties, it is necessary to use depressants or heating devices. Compared with petroleum oils, worse low-temperature properties are shown by vegetable oils and their esters. A definitely optimum low-temperature profile is that of alcohols.

Long-term storage of heating fuels, especially when combined with their low chemical stability, favors sedimentation of all kinds of deposit and water. Sludge at the tank bottom may cause corrosion and eventually plug the fuel system. This leads to problems with repairing and cleaning the heating systems. Therefore, liquid heating fuels should be kept clean and stable, although the issue is frequently very much underestimated.

Heating systems running on oils are typically equipped with automatic control systems, therefore, they are started periodically, depending on heat demand. Especially in the heating season, boiler operating conditions favor the emissions of soot or other products of incomplete combustion of the fuel components. Particular attention is required in the case of aromatic hydrocarbons and heterocyclic compounds, especially chloroderivatives because all of them are hazardous compounds. Such conditions, as well as too low furnace temperatures, may promote the formation of polyaromatic compounds and dioxins.

That is why heating oils must not have a content of substances which cause this kind of phenomena, even though this is not directly stated in standard specifications. Particular attention is required in the case of flue gases resulting from the combustion of liquid heating fuels based on spent oils, even though a specific heating system may be adapted to such fuels.

Also important in selecting potential components for heating oils is the factor of their local availability and pricing. The distribution of petroleum heating oils is typically the domain of private businesses which follow the Western solution of offering domestically made heating oils or, if purchased abroad, delivering them to onsite using motor transport. The distribution

of refineries or major heating oil stations or storage facilities is highly varied over the territory of Poland. Under the circumstances, heating oils supplies are unduly inexpensive because they have to be transported over long distances. What is more, Poland having no domestic petroleum resources depends on imports and on any disturbances in the petroleum market that may occur. Therefore, satisfying the demand on heating oils is becoming a major economic issue and determines the further growth of the heating industry based on heating oils. In view of the above, any potential components of liquid heating fuels, as safe and affordable substitutes for heating oils, ought to be considered also in the aspect of rational economics.

4.1. Key requirements for the quality of heating oils

A heating fuel is expected, first of all, to provide inexpensive heat energy as a result of its combustion in an environmentally-friendly process. Conventional petroleum-based heating oils are mixtures of hydrocarbons having various chemical compositions (carbon-to-hydrocarbon ratios) and structures. Consequently, their combustion may have different kinetics and results. Controlling the quality of heating oils is understood as the optimum blending of their chemical composition. The presence in heating oils of any other ingredients, in addition to carbon and hydrogen, is an unnecessary burden, which affects their quality.

In design works, selection of equipment and fuels as well as in the correct operation of heating systems based on liquid fuels, the knowledge of physico-chemical parameters of heating oils is a must. Most of such parameters – though only for heating oils – are set out in standard specifications for the respective fuel brands and ought to be confirmed in commercial product quality certificates.

Some of the essential properties of heating oils, of which the knowledge is indispensable in their production process, in designing heating systems, as well as in their sale and operation are the following:

- **heat of combustion;** Combustion is a chemical process in which heat energy is generated. The reaction takes place in a gas phase, in the presence of oxygen, at a temperature above the fuel's flash point value. The levels of hydrogen, carbon, and sulfur in the fuel are taken into account in calculating the generated amounts of heat and flue gases. Experimental determination of the heat of combustion (upper and lower values) is carried out in a bomb calorimeter. In practice, the lower heat of combustion, usually referred to as its "calorific value", has more practical use. The difference between the upper and lower values of heat of combustion is the value of the heat of evaporation of the water contained in the fuel and formed during its combustion. The lower heat of combustion, for instance, for light heating oils, is in the range (41...42) MJ/kg.
- **specific heat;** Its value is necessary for calculating the heat demand required to heat a liquid heating fuel. The parameter is expressed in [kJ/kg K], and can be calculated from Crag's empirical formula:

$$C_{Dt} = \frac{I}{\sqrt{\rho}}(0,403 + 0,00081t)$$

where:

ρ – specific density of fuel, kg/m³

t – temperature of fuel, K.

On average, specific heats for liquid heating fuels at temperatures in the range (273...473)K are (1.7...2.0) kJ/kg K.

- **heat of evaporation;** Heating oils are complex mixtures, comprising a variety of hydrocarbons having different boiling ranges, and it is not possible to state an exact value of heat of evaporation. Therefore, its value is determined using empirical formulae (such as Trouton's): it is in the range (209...230) kJ/kg for light heating oils, (189...209) kJ/kg for medium heating oils, and (147...189) kJ/kg for heavy heating oils.
- **heat conduction;** This value is required for designing heating systems. It depends on the chemical composition and phase composition of heating oils, as well as on temperature and pressure. For light heating oils, heat conduction is 0.116 W/mK.
- **viscosity;** Viscosity is essential for the correct spraying of fuel, it determines the quality of the combustion process. The value of viscosity of a heating oil has an effect on its droplet size during spraying. Spraying is effected by means of dedicated sprayers (burner nozzles). Every nozzle will release a jet of optimum fine droplets of a heating oil for its specific viscosities only. Heating oils during spraying should, preferably, have viscosities in the range (3...30) mm²/sec. Some nozzle designs are capable of spraying liquids with viscosities up to 45 mm²/sec. A majority of heating oils have much higher viscosities at ambient temperatures, therefore, their pre-heating is required. All standard specifications concerning heating oils relate to the maximum permissible values of viscosity. They are preferably determined at 40, 50, 80, and 100°C. The range is very wide: typically from 20 to 190 mm²/sec at 50°C (standards PN, GOST, BDS, TGL).

Assuming that the correct viscosity of heating oil (in mm²/sec) for different types of spraying devices is as stated below:

- low-pressure air burner (12.5... 18.5)
- medium-pressure air burner (15.5...24.0)
- vapor burners (21.0...29.0)
- pressure burners (15.5...24.0)
- centrifugal burners (21.0...34.0)
- injectors in self-ignition engines (12.5...24.0),

then heavy heating oils (with high viscosities) need heating to high temperatures. For instance, a heating oil of which the viscosity is 100 mm²/sec at 50 °C requires heating to 102, 92 and 79°C to have viscosities of 15, 20 and 30 mm²/sec, respectively.

- **density;** It is useful in establishing the category and origin of heating oils, their combustion and spraying efficiency. It is essential in settlements of delivery-acceptance operations.

Density of heating oils is expressed in different units and at different temperatures: this complicates the comparison of fuels in this aspect. For instance, in the standards PN, CNS, GOST, TGL and BD, density is stated at 20°C (and is in the range (0.910...1.015) g/cm³); in DIN – at 15°C (0.860...1.20) g/cm³, in ASTM in OAPI (30...35 range of values).

- **flash point;** It determines fire safety in the aspect of storage and use of heating oils and their heating limit. The minimum flash point of heating oils is stated in all standard specifications. Its values are in the range 65-85°C (PN, GOST, CNS, TGL, BS, ASTM, DIN). The lowest flash points of heating oils are stated in standards applicable in Western countries (ASTM: (38...60°C); BS: 38, 56 and 66°C; DIN: 55, 65 and 85°C; JIS: 60 and 70°C, depending on grade). Some manufacturers provide different values for different heating oil types: light, medium, or heavy oil.
- **fire point;** It is the lowest temperature at which product vapors continue burning for some time after being set on fire in open cup (Marcusson method). The lighter the oil, the larger the difference between the fire point and the flash point.
- **self-ignition temperature;** The lowest temperature at which the vapors of a heated heating oil will ignite spontaneously after being contacted with air. Self-ignition temperature of light heating oils is expected to be in the range (600...630)K. The parameter is essential for the safety of boiler rooms where liquid fuels are used, especially in conditions of incomplete combustion, which is a potential cause of fire.
- **freeze point;** The parameter determines the transport and storage conditions for heating oils. It depends on the group composition of such oils and is frequently connected with the type of feedstock. Heating oils and hydrocarbon fractions obtained from high-wax diesel fuel as well as heavy heating oils have high freeze points. The value for fuel fractions of high-wax diesel fuel is 10...15°C higher than that for low-wax diesel fuel. In relevant standards in the West, freeze point is stated only for light and medium heating oils. The value of the parameter is in the range from -8 to 0°C for light heating oils and to +40°C for heavy heating oils.
- **fractional composition;** It is very important for the combustion of light liquid heating fuels because it reduces the content of the fractions which evaporate to a specified temperature, breaks flame continuity and leads to generation of soot. As the boiling range of a liquid heating fuel increases, a higher level of aromatic hydrocarbons is observed (as well as that of sulfur compounds and resinous compounds with the tendency to generate soot and to undergo coking). For the course of the combustion process to be correct, heavy liquid heating fuels must have a content of flammable fractions which provide energy for disintegration of the large droplets of heavy fractions. Fractional composition is only specified for light heating oils. In practice, values are measured only for the percentage by volume of those fractions which distill to a specified temperature or for the boiling range for a specific percentage of a liquid heating fuel.
- **sulfur content;** The possibility of high sulfur content in liquid heating fuels is directly related to the origin of their components and their purification and blending technologies. In boiler fuelling systems based on liquid fuels, the presence of sulfur has no harmful effect, although

its oxidation to form SO_2 leads to corrosion in flue discharge systems and to environmental pollution. Therefore, sulfur content in liquid heating fuels ought to be kept consistently low. Sulfur content in top-quality liquid heating fuels must be a max. 0.3% (m/m). For fuel blends based on crude oil distillation products with low and medium sulfur levels, the value is in the range (0.5...1.0)% (m/m). Heavy fuels based on medium-and high-sulfur fractions have a sulfur content in the range (5...7)% (m/m), which leads to sulfur compound emissions into the atmosphere – to a larger extent than in the combustion of high-sulfur coal.

- **ash content;** Liquid heating fuels, especially heavy ones, have a – usually low – content of dissolved, bound chemical elements (organometallic compounds), which form ash on burning. Some of its components (for instance, vanadium pentoxide) may lead to high-temperature corrosion of boiler parts. Ash particles, as they are carried into the atmosphere, tend to intensify solid emissions. Therefore, the parameter is limited in standard specifications to 0.1% (m/m).
- **content of foreign solids;** Liquid heating fuels may have a content of solids originating from the production process or penetrating during distribution and storage. Sedimentation of the solids is a very slow process because the fuels are highly viscous substances. Therefore, it is necessary to remove the solids by filtering or centrifuging the fuels after heating but before delivering them to the burner, sprayer or injector. Since these are laborious and energy-consuming steps, it is more advisable to limit the content of mechanical impurities in liquid heating fuels. The maximum permissible values of that parameter are stated in all standards for heating oils. In liquid materials, such values should be different depending on its grade and application. The permissible content of solids is in the range (0.01...0.1)% (m/m) for light heating oils and (0.2...0.5)% (m/m) for other ones.
- **water content;** Water in liquid heating fuels may also appear in production processes, during distribution, and storage: either dissolved, or in the form of emulsion, or free water. Its presence in fuels leads to sludge formation processes and, consequently, to disturbances in the work of the boiler fuelling systems. The total content of free water (including emulsions) is determined by the distillation method.
- **vanadium content;** Vanadium content is determined because of the potential risk of high-temperature corrosion of furnace systems in boilers fuelled with liquid heating fuels of which the initial boiling range is above 300°C , originating from the blending of heavy waste hydrocarbon fractions. The lighter range of liquid heating fuels and mixtures of non-refinery raw materials have a negligibly low vanadium content so there is no need to assess the value in them.
- **tendency to form carbon deposit;** It characterizes fuel's ability to form solid residues after liquid-phase evaporation in the absence of air. The phenomenon potentially occurs if the stoichiometry of the combustion process is disturbed (incorrect spraying and evaporation of fuel, locally absence of oxygen). An increased tendency to form carbon deposits is observed when switching from lighter to heavier liquid hydrocarbons. The parameter is assessed by measuring the carbon residue.

For the full analysis of heating oils, the same rules as those provided in standard specifications for the other fuels may be applied. The short analysis ought to be performed at least once in 12 months to assess the following parameters:

- flash point;
- density;
- water content;
- viscosity;
- flowability or freeze point.

The control analysis ought to be performed at least once in 6 months, to assess the following parameters:

- flash point;
- density;
- water content.

The same rules of procedure as those set out for the other fuel types should be followed for the respective types of analysis.

5. The quality of fuels, as illustrated in requirements of combustion engine manufacturers

Developments and modifications relating to the propulsion systems of the present-day engines depend, among other things, on technological progress in the area of suitable fuels for such propulsion systems. It is necessary to ensure compliance with applicable requirements connected with such processes as fuelling, evaporation, combustion, and dealing with exhaust gases, as well as those connected with environmental protection, transport, storage, and fuel distribution. Therefore, fuels must be in conformity with requirements concerning fuel combustion devices. The requirements are set out by design engineers and vehicle manufacturers, to guarantee sturdy and reliable engines, running on the suitable types of fuels.

The World-Wide Fuel Charter (WWFC) was established by major global vehicle manufacturers to assure the appropriate quality of fuels for spark-ignition and self-ignition engines and their conformity with combustion engine design requirements and environmental protection laws.

The most recent, Fifth Edition of WWFC, came into force in September 2013. It classifies fuels into five categories, both in the spark-ignition and self-ignition engine fuel categories.

Category 1 comprises requirements applicable to fuels used in markets with no or minimum requirements (US Tier 0, EURO 1) on the control of harmful emissions in exhaust gases; such fuels comply, first of all, with the essential requirements for engines and vehicles.

Category 2 comprises fuels being used in markets with more severe general and environmental-protection requirements, including those conformable with US Tier 1, EURO 2/II, EURO 3/III or equivalent requirements relating to toxic emissions in exhaust gases.

Category 3 comprises fuels for use in markets with severe general requirements and those relating to the control of toxic emissions in exhaust gases, conformable with US LEV, California LEV, ULEV, EURO 4/IV and P 2005 or equivalent, with regard to toxic emissions in exhaust gases.

Category 4 comprises fuels with more severe quality requirements, especially with regard to emissions, inclusive of advanced methods to reduce NO_x and solids in exhaust gases. Category 4 fuels are in conformity with US Tier 2, US Tier 3 (pending), US 2007/2009 Heavy Duty On-Highway, US Non-Road Tier 4, California LEV II, EURO 4/IV, EURO 5/V, EURO 6/VI and JP 2009 requirements or equivalent standards; in addition to requirements relating to fuel consumption reduction.

The Fifth Edition of WWFC, introduced a new category of fuels, Category 5, which comprises those conformable with highly advanced requirements for emissions control and fuel efficiency, including US 2017 light duty fuel economy, US heavy duty fuel economy, California LEV III or equivalent standards, including those applicable to Category 4.

The WWFC requirements apply to a finished product, therefore, if a fuel is conformable with such requirements, no extra requirements or methods for intermediate or internal control are necessary or should be introduced.

Those WWFC provisions which are applicable to spark-ignition engines indicate the following essential tendencies in the development of such fuels, in connection with requirements applicable to engines and vehicles:

- Reduction of sulfur level in fuels, because its combustion products have a toxic effect on the environment, and sulfur tends to poison the catalytic converter, thus limiting the possibility to reduce the amount of hydrocarbons NO_x in the exhaust gases. In addition to that, sulfur affects the efficacy of elimination of NO_x in prospective solutions based on combustion of lean blends (fuel economy).
- Elimination of the content of lead compounds;
- Elimination of additives which may promote ash formation;
- Elimination of the content of octane-enhancing, organometallic compounds such as methylcyclopentadienyl manganese tricarbonyl (MMT) or (iron-based) ferrocenes. Studies are in progress to establish the effect of manganese compounds on the efficiency of catalytic converters. It is assumed that manganese compounds are comparable with iron compounds in that they tend to form deposits on the surface of catalytic converters, thus increasing the content of toxic components in exhaust gases;
- Elimination of silicon and silicon compounds, which may be introduced into fuels by blending them with various spent solvents, causing failure of the oxygen sensors and catalytic converters;

- Limitation of the introduction into gasoline of oxygenates such as ethers or ethanol and higher alcohols and exclusion of methanol from fuels. The limitation results from the degraded driveability and inefficient reduction of NO_x emissions in engines fuelled with lean blends. Moreover, tests of combustion of gasoline blended with 10% ethanol have shown that toxic emissions were 2% lower and carbon emissions were 10% lower, compared with a gasoline blended with 11% MTBE, although NO_x emission was 14% higher, hydrocarbons 10% higher, and the ozone forming potential was 9% higher. This indicates that ethers are not permitted as an additional component, when blending gasoline with alcohols. Methanol is not permitted because of its potential to cause corrosion of metal components and degrade elastomer and other plastic components;
- Limitation of the use of olefins (unsaturated hydrocarbons), in spite of their octane-enhancing effect; this is justified by their potential to form resins and precipitate deposits and increase emissions of reactive hydrocarbons potentially leading to the formation of ozone and toxic compounds;
- Limitation of the content of aromatic hydrocarbons which favor the formation of deposits on engine components and lead to higher emissions of exhaust gases, including carbon dioxide;
- Limitation of the content of benzene because of its strongly carcinogenic effect;
- Formulation of a relationship between evaporation temperatures of 10%, 50%, 90% of fuel in normal distillation (T₁₀, T₅₀ and T₉₀, respectively) and the percentage of oxygenates in the fuel (%OXY) to obtain Distillation Index (DI) as follows: $DI = 1.5 T_{10} + 3 T_{50} + T_{90} + 11 \%OXY$. The ASTM standard also specifies the Driveability Index (DI) for gasoline containing ethanol according to the relationship: $DI = 1.5 + 3.0 T_{10} T_{50} T_{90} + 1.0 + 1.33 \text{ } ^\circ\text{C} (2.4 \text{ } ^\circ\text{F}) \times \text{Ethanol Volume } \%$. DI values above the range 550...570 degrade driveability and hydrocarbon emissions are also higher. As seen, both of these indexes depend on the volatility and the content of oxygen derivatives.

As regards fuels for self-ignition engines, engine manufacturers indicate the following tendencies in the research works being made to improve the fuels quality:

- A minimum differential between the cetane number CN and calculated cetane index CCI is set, to avoid the excessive use of cetane-enhancers;
- A density range is set for each fuel category, as indicated by studies intended to find a correlation between the effect of lower densities and lower emissions of solids and NO_x from high duty engines, with the accompanying lower engine power output and higher fuel consumption;
- A fuel viscosity range is established, as indicated by studies on the fuel injection process and fuel tank filling, which depends on that value, with the accompanying exponential decrease in viscosity due to the temperature increase;
- The permissible sulfur content is very much reduced in fuels for advanced engines because the presence of sulfur in fuels leads to higher solids emissions, stimulates low-temperature

corrosion, and poisons NO_x adsorbers, in addition to forming sulfur oxide during combustion;

- The content of polycyclic aromatic hydrocarbons (PAH) in fuels is reduced, even though their cetane numbers are low. This is due to their effect of increasing solids emissions (smoke level) and the presence of PAH in exhaust gases, while leading to an increased rough-engine operation tendency;
- Optimum values of distillation temperature for 90 or 95% (V/V) of fuel are established, as indicated by tests, because lower values cause lower emissions of NO_x and higher emissions of hydrocarbons in the exhaust gases from high-duty engines, as well as a reduced emission of solids and higher emissions of NO_x for light-duty engines;
- If low-temperature properties of self-ignition engine fuels are set from cloud points (CP) or from the Low Temperature Flow Test (LTFT) which is applicable in the USA and Canada, then the value of that parameter ought to be above the minimum expected ambient temperature. For the purposes of determination of Cold Flow Plugging Point (CFPP), then maximum value of CFPP ought to be equal to or below the lowest expected ambient temperature, except that the value should not be more than 10°C above the set value of CFPP for the specific fuel category according to WWFC;
- The content of vegetable-derived esters, especially FAME (fatty acid methyl esters) in diesel fuels is limited because of their poor low-temperature properties, hygroscopic nature, higher tendency to form deposits, and aggressive effect on rubber seals and some other components in fuel systems. Oxidation stability of diesel fuels is established by Method 1 referred to in ISO 12205 and ASTM D 2274, although additional methods apply for fuels with more than 2 % (v/v) FAME, namely: Method 2a (modified Rancimat) according to EN 15751, Method 2b (Δ TAN) according to ASTM D 664, and modified ASTM D 2274 and Method 2c (PetroOxy) according to EN 16091;
- Injector fouling is controlled; the parameter depends on the amount and types of detergents being used as additives to improve fuel atomization, among other things;
- Lubricity of fuels is determined in order to ensure the appropriate operation of the injection pump while eliminating sulfur from the exhaust gases. Its value is established, at 60°C, using the High Frequency Reciprocating Rig (HFRR) testing device.

6. Military tests applicable to fuel storage in the NATO member states

The fuel quality assessment criteria that are applicable in the military technology of NATO member-states are based on long-standing experience. They are highly rigorous, therefore, they provide the most reliable criteria that guarantee the desirable quality of petroleum products in the contemporary military technology. The currently applicable standard is STANAG 3149 SILCEP (Edition 8) "Minimum Quality Surveillance of Petroleum Product" and was introduced in September 2002.

In STANAG 3149 SILCEP, all the applicable analytical tests were categorized as follows:

1. Test A: An exact specification of all relevant parameters according to the standard. Applicable before product acceptance from supplier. Required for all storage tanks (with the exclusion of airfields) after filling them for a first time, for storage tanks after fuel replacement, and for storage tanks after cleaning.
2. Test B-1: Applicable on completion of product reloading (transfer) using a non-segregating system such as multi-product tankers, or a pipeline system, or a common loading system.
3. Test B-2: Applicable in fuel quality assessment after a pre-defined period of storage.
4. Test B-3: Applicable before starting the transfer/flow of next product batches through the system in which they are not separated, before combining product batches, and in tanks which hold mixtures from pipelines before repumping.
5. Test C: Visual test, intended to make sure no visible changes have occurred in product. Applicable mainly for the routine assessment of fuels' quality (storage tanks, pipelines, tank trucks, railway tankers).

The scope of determination applicable to each test for the respective fuel types is shown in Tables 8, 9, and 10.

Characteristics	test			
	B-1	B-2	B-3	C
Appearance	X	X	X	X
Content of water and solids	X	X	X	X
Color	X	X	X	X
Density	X	X	X	X
Fractional composition	X	X	X	-
Vapor pressure	X	X	-	-
Corrosion on copper	-	X	X	-
Inherent resin content	-	X	X	-
Oxidation stability	-	X	-	-

Table 8. Scope of determination in tests for gasoline

Characteristics	test			
	B-1	B-2	B-3	C
Appearance	X	X	X	X
Color	X	X	X	X
Density	X	X	X	X
Fractional composition	X	X	-	-
Flash point	X	X	X	X
Coking value	X	X	-	-

Table 9. Scope of determination in tests for diesel fuels

Characteristics	test			
	B-1	B-2	B-3	C
Flash point	X	X	X	X
Density	X	X	X	X
Water content	X	X	X	X
Viscosity	X	X	-	-
Flowability, or freeze point	-	X	-	-

Table 10. Scope of determination in tests for heating oils

7. Conclusions

A Fuel Quality Assessment System is indispensable in the aspect of correct management of fuel storage, and its consistent application is required to prevent measurable losses. Improvements in the system ought to be made by eliminating redundant determinations of those qualitative parameters of fuels which do not change in storage conditions which are correct in the aspect of technology and performance. It is obvious that the parameters ought to be established by way of analyses, and be unambiguous. The currently applicable methodology of testing the quality of fuels during storage is based on measurements of a number of parameters which are indicated in the applicable standard specifications: this requires the development and use of a suitable procedure for sample collecting and their analysis in accredited laboratories. The frequency of sampling and the sample sizes were established based on previous experience in fuel storage. As shown in Chapter 1, fuel blends are subject to changes resulting from technological progress in the manufacturing of the respective components, specifically, in the area of technological processes based on the use of novel processing methods for handling heavy ends and residues in order to obtain fuel cuts or components. The use of new fuel components may change their oxidation kinetics, thereby

changing the scope of quality surveillance which is indispensable in establishing the permissible duration of fuel storage. Therefore, in order to improve the cost-effectiveness and complexity of existing quality surveillance systems, storage facilities may be equipped with rapid on-line analysis kits enabling surveillance of the quality of (a number of parameters of) engine fuels, so that control analyses can be carried out; the findings would then be an early warning, indicating tendencies of changes in the quality of the fuels during storage but would also, in undisputable cases, suggest the necessity to determine certain parameters using more sophisticated, laboratory methodology, or to carry out a full analysis – this, altogether, could improve the cost-effectiveness of the Fuel Quality Assessment System.

Chances are that the course of oxidation of such mixtures will be changed entirely by the introduction of biofuels as additives to conventional fuels. Although so called “drop-in biofuels”, which are compositions of hydrocarbons obtained by biomass or waste material processing in BtL (Biomass-to-Liquid) or WtL (Waste-to-Liquid) processes, have no significant effect on the kinetics of oxidation reactions, the course of oxidation of fuels which have a content of fatty acid alkyl esters (FAME, FAEE) as well as alcohols and ethers used as engine fuel components is changed entirely by such additives. Hence, considerations described in this monograph refer to an analysis of the findings of tests intended to develop and construct a system enabling the continuous monitoring of the engine fuel ageing process, including fuels with a content of biocomponents such as ester and other hydrocarbon derivatives. The project to implement the system is intended to enable on-line control of the operating usefulness of engine fuels during storage.

The above notwithstanding, it is advisable to develop and adopt applicable standard specifications for fuels which are intended for medium-or long-term storage.

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