Storage Stability of Fuels

Edited by Krzysztof Biernat

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Preface

This book presents an analysis of the results of studies of motor fuels ageing, conducted in laboratory and model conditions, in terms of building a system operating on-line, allowing continuous assessment of the operational usability of gasoline and diesel fuels, including those containing the addition of ethanol and FAME, respectively.

This research was carried out in the framework of the project: "A system for the continuous control of the degree and rate of the liquid fuels ageing process during storage, which received co-funding from the European Regional Development Fund under the Operational Programme "Innovative Economy".

The book presents an evaluation of the impact of fuel production processes on its stability and an analysis of changes in normative parameters of fuels during their storage and use.

The book presents also the results of tests on the corrosive effects of fuels during storage processes.

Chapter 1

The Influence of Engine Fuel Manufacturing Processes on Their Performance Properties in Operating Conditions

Krzysztof Biernat

Additional information is available at the end of the chapter

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1. Introduction

1.1. Straight-run processing of petroleum

Straight-run processing of petroleum (or crude oil) is the kind of processing where the material is distilled after being purified and is separated into fractions (or cuts), based on boiling range differences between its respective components, without modifying the chemical structure of its constituent compounds. Fractional distillation is typically carried out in two steps: under normal pressure and under reduced pressure. Figure 1 shows a simplified diagram for straight-run processing of petroleum.

Before processing, petroleum has a content of solid contaminants (up to 1.5 %) and water (up to 0.3 %). Part of insoluble contaminants and water are removed from petroleum by being left to stand (sedimentation). The process simply involves storage of petroleum in storage tanks for a certain length of time, during which the solids and part of its water content migrate to the bottom while the other solids dissolve in the water, forming a brine, which it is rather hard to remove. In that emulsion, the petroleum is the dispersion medium while water with salts is the disperse phase. Existing emulsion breaking methods are categorized into three groups:

- mechanical methods – involve sedimentation, centrifugation, and filtration of fresh emulsions;
- chemical methods – involving first of all the use of deemulsifiers, which are supposed to dissolve the adsorption film at the water interface;
- electrical methods – involving the use of electrohydrators.

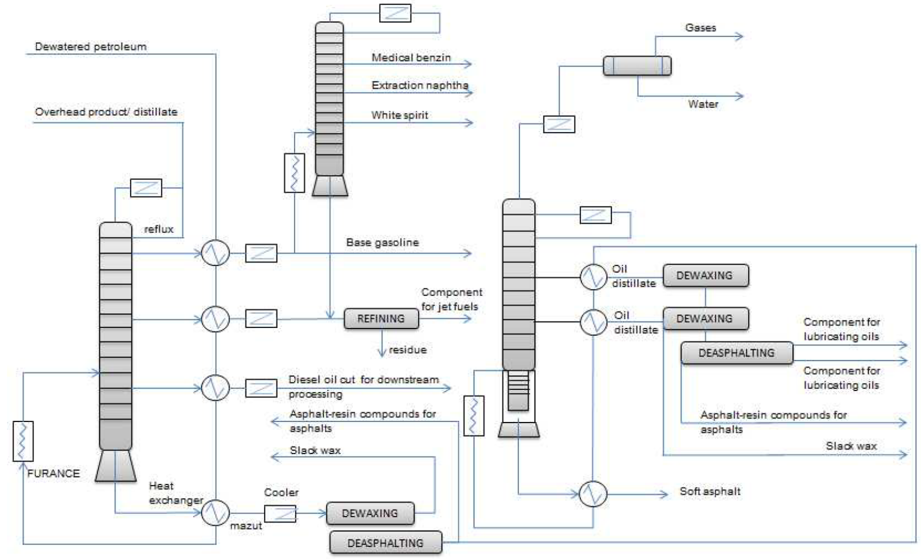


Figure 1. Straight-run processing of petroleum – simplified diagram

In all such groups, deemulsification involves the combining of small disperse water drops by overcoming surface tensions forces at the interface, to form drops big enough to be able to fall down the tank by gravitation. In industry, electrical methods are typically used, where the reactor has two flat electrodes installed in it, between which there is a voltage of about 30 kV. The water molecules move towards the respective electrodes and, as the electrode symbol changes, the molecules lose their electrical orientation and collide with one another, forming suitably large drops which fall down the tank. The resulting dewatered petroleum is taken at the top of the reactor. Electrohydration is carried out at an elevated temperature in a continuous manner.

The purified and degassed petroleum is made to flow into a tubular furnace to be heated to a temperature not higher than 370°C and then to the base of a first distillation tower (atmospheric column). The distillation tower is approximately 40 m high and comprises a number of so-called trays. Their shape depends on the rectification process parameters, the typical tray designs include: bubble cap, sieve, wave, West, cascade, Venturi, ejector, valve, and combinations of the above. The rectification process in the atmospheric tower is carried out at nearly-atmospheric pressures. After flowing into the tower, the hot petroleum is divided into fractions as follows: the consecutive fractions (in terms of density) evaporate and then condense on the respective tray groups, are then taken to heat exchangers (where their heat is transferred to the petroleum flowing into the furnace) and sent downstream.

Inside the column, there circulates a so-called “reflux", which may be of the hot (water or, less frequently, feedstock), cold, or circulating type. The reflux is supposed to keep sufficient temperatures, especially in the top regions of the column.

The products obtained in the atmospheric distillation tower include:

1. overhead fraction (which also functions as the circulating reflux;
2. side fractions (their amount and boiling ranges depend on the process parameters and design of column); typically, they include:
   - light gasoline fraction;
   - naphtha fraction;
   - kerosine fraction (jet fuels);
   - diesel fuel fraction;
   - spindle oil fraction.
3. distillation residue, also called mazut.

For a better fractionation of the gasoline fraction (to obtain medical benzin, extraction naphtha, painter's naphtha), it is possible to re-rectify a portion on it in a separate atmospheric tower. Its design and processing regime are the same as described earlier. Distillation residue from that column is combined with the kerosine fraction. Rectification in each atmospheric tower takes place above the feed point for the gas phase but below the feed point for the liquid phase. In order to ensure appropriate rectification of the liquid phase, it is necessary to provide additional heat or another evaporating agent. Rectification in atmospheric towers is a continuous process.

A vacuum tower is another major component of a straight-run petroleum processing plant. It serves for distillation of the high-boiling distillation residue from the atmospheric tower, after heating it to 430°C in deep-vacuum conditions. In the vacuum towers of to-day, pressures in the evaporation region are in the range (1.99...2.27) kPa, compared with 0.66 kPa at the vapor outlet point. Atmospheric towers are 15-30 m high, their diameter is a max. of 12 m. The column is filled with bubble cap or sieve or valve-type trays; depending on the kind of product made in the vacuum column, the number of trays varies between 8...14 (if the product is used for catalytic cracking) and 38...42 (if the distillate is used for oil production).

Mazut, which flows into the column typically above tray 6, is combined with foam reducers (for instance, silicones at a concentration of 0.75 mg/dm^3 of feedstock). Lower pressure, which is reduced by means of a system of so-called ejectors and condensers, leads to lower boiling ranges, enabling rectification of heavy mazut without decomposing it.

The vacuum tower products include: between one and three side fractions, a gas overhead fraction and the distillation residue called soft asphalt. After further straight-run or destructive processing, the side fractions are an important component for various engine oils and heating oils.

In addition, straight-run processing comprises a number of auxiliary treatments, enabling the various components to be separated from the distillation products. Such treatments include: crystallization and filtration, refining with the use of H_2SO_4 and selective solvent, dewaxing with the use of selective solvents and de-asphalting with propane.

Crystallization and filtration are intended to separate paraffins from the distillation cuts. The crystallized paraffins are then filtered off using a pressure press and filtration cloth. After the removal of paraffins, the oil fraction is further processed and the crude paraffin that results is used for making insulation materials, maintenance materials, or candles (after refining). Refining of the post-distillation fractions is intended to remove asphalts and resinous compounds, which are undesirable in further processing.

1.2. Chemical refining

In order to remove acid oxygen-based compounds or some sulfur compounds, the petroleum products are subjected to refining by means of lye: it reacts with acidic compounds, forming respective water-soluble salts. Part of the compounds remain in the refined product and can only be removed therefrom by washing with water. The oils are refined using weak sodium hydroxide solutions. The process is carried out at elevated temperatures to prevent the formation of emulsions which it would otherwise be hard to break.

In the process of neutralization of the oil distillates with lye, the napthene acid content of the distillate initially reacts with sodium hydroxide to form soaps, which dissolve in aqueous lye solutions whereby they are removed from the distillate; the emulsions formed then are usually not very stable. Stable emulsions are formed after another water-washing operation. This is due to the presence in the oil of resinous products which, in a dispersed form, are hydrophobic emulsifiers. Owing to the presence of high levels of hydrophilic emulsifiers, their activity as hydrophilic emulsifiers is not manifested during neutralization; on the other hand, when washing with water, the hydrophobic emulsifiers are not separated from the oil along with the waste lye and their effect shows very well. The phenomenon is observed when refining oils having a high content of tars and asphalts and a high content of oxidation products. The hydrophobic emulsions formed then may be separated by heating the distillates to high temperatures, by adding a solution of hydrophilic naphthene soaps, or by treatment with the use of weak solutions of mineral acids, which destroy the emulsifier’s interface films.

1.3. Refining with the use of selective solvents

Refining the kerosine fractions with solvents is based on the choice of a suitable solvent which is able to dissolve in different ways the desirable and the undesirable components of the refined product. Selective solvents are expected to be able to readily dissolve, to be selective and stable, to form readily separating extract and raffinate phases, to be easily regenerated, to resists corrosion in operating conditions, and to have non-toxic properties.

The essential parameters which determine the level of refining include temperature and the solvent-to-material ratio. The choice of temperature for the refining process depends on the critical temperature of solubility for a given mixture. Refining with the use of selective solvents is feasible in those temperature ranges where a two-phase system exists: the raffinate solution (containing a trace amount of solvent) and the extract solution (comprising mainly the solvent and the undesirable components of the starting raw material which are dissolved in the solvent). The critical solubility temperature depends on the structure of hydrocarbon molecules: their critical solubility temperature is lower (and going down rapidly) for higher numbers of rings in the hydrocarbons but is lower for longer alkyl lengths. Naphthenes with five-member molecules will better reduce the critical temperature of solubility, compared with six-member molecules. In the case of aromatic hydrocarbons and naphthenes with same structures, for same solvent, critical temperature of solubility of aromatic hydrocarbons is much lower than that of naphthenes. Naphthene-aromatic hydrocarbons have lower critical temperatures of solubility, compared with naphthene hydrocarbons having a similar structure. Normal paraffins have the highest critical temperature of solubility. The value of critical temperature of solubility and kerosine fractions in a solvent is affected also by the solvent's properties: for instance, critical temperature of solubility of hydrocarbons in nitrobenzene is much lower than that in phenol, but is lower in phenol compared with that in furfurol.

Solubility of substances in solvents depends on attractive forces between the molecules of the solvent and the solute. Attraction between molecules takes place due to the Van der Waals forces and hydrogen bonds. In view of the fact that kerosine fractions comprise mainly nonpolar hydrocarbons, selective extraction of undesirable components is only possible in the case of Deby's effect, that is, co-operation of induced dipols which are formed in non-polar molecules under the effect of the electric field of polar solvent's molecules. The highest polarizability is shown by aromatic hydrocarbons, the lowest by naphthenes and paraffins. Therefore, aromatic hydrocarbons readily submit to the action of the electric field of solvents, which leads to the formation in their molecules of an induced dipol moment, resulting in their readily dissolving in polar solvents.

In addition to the refining temperature and type of solvent, the degree of extraction of undesirable components depends also on its amount that is indispensable for extraction. On the other hand, the amount of solvent depends on its properties, chemical composition of the starting material, the desirable refining degree, and on the extraction method.

Selective refining by means of furfurol is a method for removing aromatic hydrocarbons from vacuum petroleum distillates, and is used as a base oil production step. Furfurol is a polar substance with a high dipol moment. It is able to selectively dissolve hydrocarbons by inducing the dipol moment in the hydrocarbon molecules which are contacted with furfurol. It is useful as a solvent in selective refining processes because of the following advantages:

- high density and lack of tendency to form foams or emulsions; these properties facilitates phase separation between the raffinate extract solutions;
- low freeze point: therefore, its mixtures are easier to handle at low temperatures, requiring no extra care or devices;
- large difference between the critical temperatures of solubility for paraffinic and aromatic compounds.

On the other hand, furfural has the following disadvantages:

- low resistance to oxidation at high temperatures, both in alkaline and acidic environments,
- formation of acidic oxidation products and high-molecular products of polycondensation;

- high toxicity.

In the process of selective refining with furfurol, aromatic compounds are removed from the oil more readily than paraffins, compounds with high viscosity. Hence, a more aromatic compound requires less solvent and lower temperatures to be entirely dissolved. Therefore, by selecting suitable extraction temperatures and solvent-to-material ratio, it is possible to remove either only aromatic compounds from the raw material or – after modification of extraction conditions – to remove mixed compounds as well.

1.4. Refining by adsorption

Adsorption as a refining process is currently used, first of all, in the finishing of light kerosine cuts, lubricating oils, specialty oils, and paraffins.

The role of adsorption in the refining of petroleum products is in the adsorption of asphaltenes, resins, diolefins, acids, etc. on the adsorbent surface, consequently providing a finished product with improved color and odor, and stable physico-chemical and performance properties.

The adsorption refining process is carried out either by the cold or hot method, using percolation (where adsorbent pellets are used) or by the contact method, using so-called decolorizing earths (adsorbents in the pulverized form, obtained from natural aluminosilicates).

The following materials are used in the refining process:

- sorbents, obtained by thermal or thermal-chemical modification of natural mineral raw materials (aluminosilicates);
- synthetic sorbents, such as: silica gel or alumina;
- active carbon.

When selecting s suitable sorbent, care is taken not only about the efficiency of regeneration, connected with improving the properties of oil, but also about the cost-efficiency of the process. To select the most suitable sorbent, it is necessary to consider some of its properties, first of all, its refining capacity, selectivity, chemical properties, mechanical strength, costs, availability, possible reactivation, and disposal.

2. Destructive processing of petroleum

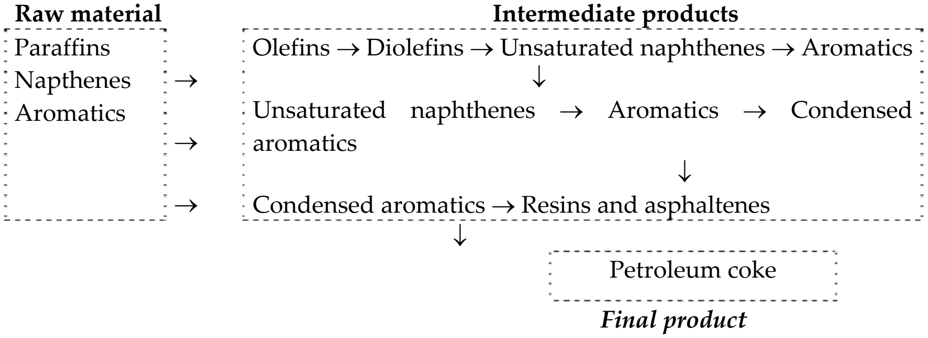
Destructive processing of petroleum involves modification of the structure of hydrocarbons contained in the fractions obtained from the straight-run processing of petroleum. Such modification is intended to improve intermediates for use in final product blending. Destructive processing cannot be carried out with the omission of straight-run processing. The essential process groups included in destructive processing of petroleum are discussed below.

2.1. Thermal cracking

Thermal cracking is a process in which large hydrocarbon molecules are broken to form light unsaturated hydrocarbons in high-temperature conditions.

Thermal cracking comprises three groups of processes:

- Cracking of liquid raw materials at high pressures (1961.3...6864.6) kPa in the temperature range (470...540)°C to obtain gasoline. The process is intended to obtain a higher amount of fuels at the cost of oil fractions. Gasoline can be obtained from the post-distillation side-fractions in atmospheric and vacuum towers, while heating oils can be obtained from the distillation residue (soft asphalt) in a vacuum tower. The process to obtain heating oils, carried out in mild conditions, is called *visbreaking*;
- Low-pressure cracking – also called coking, or destructive distillation. The process is carried out at temperatures in the range (450...550)°C. It is intended to provide light-colored products with a high hydrogen content, such as gasoline, diesel fuels or gases, as a result of decarbonization (concentrating asphalts and resins into so-called "petroleum coke"). The coke product is often a target product, intended for making, for instance, coatings for electrodes. The coking process is carried out as shown in the diagram below and may be interrupted or slowed down at any time by injection of an extra amount of cold raw material.



- Thermal cracking in the most severe conditions: pyrolysis. The process is carried out at temperatures in the range (670...800)°C (though the process temperature may be as high as 1200°C). The process is intended mainly to provide unsaturated gases, usually ethylene, for use in petrochemical syntheses. The process also provides aromatic hydrocarbons such as benzene, toluene, xylenes, or naphthalene, and so-called post-pyrolytic gasoline which is a component for automotive gasoline, though they are only to be considered as side products.

In addition to the above, there exist a number of intermediate thermal cracking processes, for instance, vapor phase cracking in low pressure conditions at a temperature of 600°C to produce gasoline, or coking of the residue in severe conditions in order to increase the amount of gas and aromatization of liquid products.

2.2. Catalytic cracking

Catalytic or thermocatalytic cracking processes are carried out at high temperatures in the presence of catalysts. They are intended to provide light products with good quality at the cost of heavy products (mainly gasoline and diesel fuels) or to improve the quality of other distillation products.

Gasoline and diesel fuels, obtained at temperatures in the range (450...500)°C in the presence of an aluminosilicate catalyst, are characterized by high resistance to decomposition and oxidation processes (mainly gasoline) and high purity. The mechanism of catalytic cracking is reverse to that of thermal cracking and leads to highly saturated hydrocarbons.

Gasoline reforming has been isolated from the catalytic cracking and is a separate process, intended to improve the gasoline fractions by their aromatization and purification to remove sulfur compounds therefrom. Pure aromatic hydrocarbons such as benzene, toluene, xylenes, can be obtained from the aromatized gasoline for petrochemical synthesis after its suitable separation. Moreover, reforming provides hydrogen for hydrogen processes. Depending on its variant, the reforming process uses a number of catalysts (Co, Ni, Mo, Pt, Fe), usually aluminosilicates. The process temperature is around 550°C. The essential reactions taking place during gasoline reforming include dehydrogenation of cycloalkanes (naphthenes), dehydroisomerization of naphthenes, and dehydrocyclization of alkanes (paraffins). These reactions are accompanied by isomerization and hydrocracking of paraffins. The essential reactions generate free hydrogen, therefore, such reactions as desulfurization and saturation of alkenes take place as well.

2.3. Fluidized-Bed Catalytic Cracking

Fluidized-Bed Catalytic Cracking (FBCC) of de-asphalted vacuum and heavy petroleum cuts, in the presence of aluminosilicate catalysts (typically zeolites), is one of the major methods for deep processing of petroleum that are used in advanced refineries. The process is highly complex in terms of equipment and, accordingly, involves relatively high investment costs. On the other hand, the use of the process unit is justified in economic terms, since on average, only about 50 % (m/m) of petroleum is distilled-off at an atmospheric pressure. The petroleum fraction that results from vacuum distillation, having a boiling range of (350...500)°C and constituting typically 25 % of its weight, is a perfect feedstock for the FBCC plant, for making valuable components of engine fuels and light olefins for use in synthetic plastics (polyethylene, polypropylene, rubbers, etc).

Cracking of high-molecular hydrocarbons causes breaking of intermolecular bonds, which is accompanied by dehydrogenation and hydrogenation, comprising hydrogen transfer reactions. The bonds between carbon atoms are broken in irreversible reactions. Out of a great variety of bonds between the atoms, those with the lowest energy are the easiest to break. The elementary energy of C-C bonds in paraffins is 265 kJ/mol, for C-H bonds it is 360 kJ/mol, and that of C-C bonds in aromatic compounds is (500...610) kJ/mol, therefore, paraffins are most frequently subjected to cracking. Hydrogen transfer reactions contribute to the formation of gasoline compounds as saturated compounds, though at the cost of formation of those with a low hydrogen content, including coke. During the cracking process, owing to thermodynamic conditions, polymerization of olefins – though only insignificant – is the first phase in the formation of aromatic compounds and coke.

The essential reaction leading to the formation of coke is the condensation of aromatic hydrocarbons with olefins. Therefore, naphthenes and naphthene-paraffin compounds are the most preferable raw materials for fluidized-bed cracking. On the other hand, aromatic feedstock hinders the cracking process, favoring the formation of coke.

During the cracking process, primary reactions are accompanied by a number of secondary ones which become more and more intensified: such processes include polymerization, aromatization, isomerization, alkylation and dealkylation. Catalytic cracking takes place at lower temperatures, compared with thermal cracking but the amount of coke being formed in it is much more limited. The aluminosilicate catalysts used in the process accelerate the most desirable reactions: the rate of cracking of paraffins is 10 times as high, compared with that in a purely thermal process, conversion of naphthenes is 1000 times as fast, and that of side-chain aromatics is 10,000 times as fast.

The cracking feedstock contains more or less of metals (mainly vanadium, nickel, and iron), sulfur and nitrogen, in addition to oxygen. Organometallic links are broken and their metals accumulate on the catalyst, leading to its deactivation, accelerated formation of coke, and higher amount of gaseous hydrocarbons.

Cracking of aromatic feedstock is characterized by an increased efficiency of the formation of aromatic hydrocarbons with a considerable admixture of olefins, in addition to the higher amount of coke. A naphthene feedstock produces a top quality gasoline as the result of isomerization and aromatization reactions.

A fluidized-bed catalytic cracking plant is composed essentially of a vertical-tube reactor, raising the catalyst and raw material (the basic process zone) and a regenerator with pipes carrying a spent and regenerated aluminum-silicon oxide system. At the bottom of the vertical tube, the strongly pulverized catalyst is mixed with the – nearly entirely evaporated – heavy hydrocarbon feed; cracking takes place as the feed flows upwards at the rate of (4...12) m/sec at a pressure in the range (0.8...1;5) bar, at a temperature typically in the range (480...530)°C. The cracking of heavy petroleum feedstocks is accompanied by the formation of coke: it accumulates on the catalyst, blocking its active sites. In such conditions, it is gravitationally carried into a regenerator to remove the coke by burning, typically at temperatures in the range (635...650)°C.

The naphtha cut from the FBCC plant is the main source of sulfur being carried into the final gasoline products during the blending process. In the global refinery industry, the level of sulfur in nahptha obtained by FBCC is reduced by the following methods:

- pre-treatment of the FBCC feedstock using a hydrogen-catalyst method for the removal of the entrained sulfur;
- increasing the conversion of organic sulfur compounds into hydrogen sulfide during FBCC;
- processing the FBCC product by distillation with absorption.

The highest percentage of sulfur is concentrated in the highest-boiling gasoline fraction from FBCC. Therefore, lowering the final boiling range of that fraction is the obvious method to reduce its sulfur content. The available techniques include the following:

- dropping part of naphtha into light diesel fuel; on the other hand, rejecting part of naphtha leads to higher quantities of light oil being collected but reduces its boiling range, changes the heat load of the light oil (part of which is recirculated within the main rectifying column) and degrades part of the naphtha to the medium distillate range;
- collecting separately the heavier naphtha cut as part of the overall distillation of FBCC products; however, this changes product proportions, operation of the major fractionating column, and operation of the gas absorption system.

2.4. Hydrogen-based processes

Hydrogen-based processes are thermo-catalytic processes, carried out at free-hydrogen pressure conditions. There are three different variants of hydrogen-based processes, depending on the degree of conversion; only those relating to the production of fuel components will be discussed later in this chapter.

2.4.1. Hydrodesulfurization of the cracking feedstock

A hydrocracking plant usually comprises the following units: hydrocracking of vacuum distillates, hydrogen generation, and hydrogen recovery from post-production gas. The process is intended to handle vacuum distillates from the pipe-tower distillation system with a boiling range (330...575)°C and provide desulfurized products having lower molecular weights and lower boiling ranges.

The process of technology in the plant is divided into the following steps: hydrodesulfurization, hydrocracking, and fractionation of hydrocracking products. Hydrodesulfurization and hydrocracking take place in the presence of catalysts at elevated temperatures (340...450)°C, at a hydrogen pressure of about 15 MPa. The hydrodesulfurization reaction is accompanied by the removal of other contaminants from the feedstock (including nitrogen, chlorine, oxygen, metals), hydrogenation of olefins, and part of aromatic compounds. The main reason why the metals are removed is to protect the catalyst from irreversible deactivation taking place as metal compounds accumulate on the catalyst's surface.

The mechanisms of hydrocracking include two basic conversions: cracking of hydrocarbons, and hydrogenation of the products of catalytic cracking, typically in the presence of an aluminosilicate-based nickel-tungsten catalyst. The post-reaction mixture provides the following fractions: liquid gas, light gasoline, middle gasoline, aviation fuel, light diesel fuel, heavy diesel fuel, and a desulfurized but non-cracked vacuum oil fraction which is a feedstock to the fluidized-bed catalytic cracking (FBCC) plant.

Hydrocracking has the essential advantage of providing top quality products which, unlike similar products obtained by catalytic cracking, have a better stability because they contain no olefins or dienes. Moreover, the content of sulfur and nitrogen in the gasoline and diesel fuel products obtained is low enough to enable them to be used directly in obtaining environmentally-friendly blends of final products.

2.4.2. Destructive hydrogenation

Destructive hydrogenation is a process in which a solid and a liquid feedstock is cracked under a hydrogen pressure in the range (29419.8...68646.2) kPa at a temperature in the range (420...500)°C in the presence of catalysts (Fe, W, Mo, Ni). The process is intended to produce gasoline products, but sometimes also diesel fuels from coal, bituminous shale, tar and soft asphalt.

2.5. Catalytic processing of gases and light gasoline fractions

The processing of light fractions and gases is intended to provide saturated components of fuels or products for petrochemical syntheses. The process includes the following reactions, running in the presence of suitable catalysts:

- polymerization of gaseous alkenes;
- alkylation of gaseous and liquid isoparaffins with alkenes;
- alkylation of aromatic compounds with alkenes;
- dehydrogenation of butane and pentane fractions;
- isomerization of butane and light hydrocarbons from gasoline fractions.

Although rather energy-consuming, the catalytic processing of these gases enables elimination of distillation losses, that is, flare combustion of gases while increasing the obtained amounts of gasoline.

2.6. Efficient processing of soft asphalt

Soft-asphalt utilization technology includes thermal methods (mainly coking and *visbreaking*), extraction, hydrogen-based methods (such as hydrodesulfurization and hydrocracking), and gasification.

Among these methods, hydrogen-based processes and gasification are believed to have the highest potential and be most environmentally-friendly, although they require the highest investment costs.

Lurgi offers a Multi Purpose Gasification (MPG) technology for gasification of hydrocarbon feedstock. Its main advantages include the possibility to handle low-quality/high-viscosity heavy fractions, also with a content of sludge, mud, and waste coke, and the possibility to handle raw materials with a high sulfur content. The oxygen-steam feedstock gasification unit comprises a burner and a reactor, gas cooling section, and a system for the removal of ash, metals, soot, and liquid waste.

Gasification is an autothermal process, controlled by the oxygen-to-steam ratio, running according to the following reaction:

$$2CH_n + O_2 \rightarrow 2CO + nH_2$$
$$CH_n + H_2O \rightarrow CO + (n/2 + 1)\ H_2$$

The ratio of CO and H_2 generated in syngas depends on the composition of raw materials, oxygen-to-steam ratio, and parameters of gasification. Non-catalytic semi-combustion of hydrocarbons in the MPG technology takes place in an empty reactor lined with a refractory material, selected for a load resulting from the ash content in the feedstock. The material is fed into the reactor through the burner at the top of the reactor. The burner accepts liquid feeds with the highest viscosities as well as emulsions and sludge with particles the size of several millimeters. The feed and an oxidizer are heated and mixed with steam as a moderator before the burner. The burner and the reactor are "fine-tuned", or adapted, to each other by dynamic simulation to entirely mix the reactants in as small a volume as possible and, in this way gasification of the raw materials is complete. The hot crude gas from the reactor is quenched with water originating from the ash and soot removal unit. The water is injected in a radial arrangement into the quenching-ring zone, where it is quenched, or cooled down rapidly, into the form of glassy beads the size of (1...2) mm. The beads accumulate at the bottom of the separator and are discharged through a hopper. The glassy slag carries a majority of heavy metal content and water-insoluble components. Further cooling takes place in a medium-pressure steam boiler, generating steam in the range (1.5...3.0) MPa. Final cooling takes place in a water cooler, then the gas is sent to the acid gas removal unit.

The crude syngas portion which is intended for use in hydrogen generator, passing by the steam boiler, is sent straight into the CO catalytic conversion unit, working according to the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Carbon dioxide is removed by means of cooled methanol.

The syngas, generated during gasification of hydrocarbons, contains a certain amount of free carbon (soot), typically about 0.8 % (m/m) on the feedstock basis. The soot particles are removed from the gas together with ash, mainly in the Venturi gas srubber, located after the quenching section. Sludge with a content of soot is collected together with condensates from the steam boiler and from the cooler-gas scrubber, and is sent to the ash (and metals) removal section. The sludge, with soot from gasification, is depressured batchwise to an atmospheric pressure in the sludge tank before being filtered.

The German refinery PCK Schwedt and Toyo Engineering Corporation from Japan developed one of the most advanced processes of technology for processing the residue from vacuum distillation of petroleum: HSC-DESUS (*HSC-High Conversion Soaker Cracking*). Compared with conventional visbreaking, it is characterized by a very high conversion and the residue has a stable quality. A variety of intermediate products can be used as a feedstock with a high content of sulfur and heavy metals (including heavy oil and bitumens from oil sands as well as residues from the production of lubricating oil). Post-cracking distillates from that technology are usually light or heavy gas oils having a lower content of unsaturated compounds than that in distillates from coking processes.

In the HSC technology, the feedstock is heated to a temperature in the range 440…460°C, depending on the desired conversion in the soaking drum. Cracking in the furnace is minimized by using high flow rates. A reactant stream from the furnace is made to flow into the soaking drum in which the residence time is long enough to provide desired conversions. The soaking drum operates at an atmospheric pressure, and its bottom section is filled with stripping steam. In the soaking drum, the raw material flows downward, through perforated plates. Steam along with cracking gas and distillate vapor flow through the perforated plates upward; their flow is countercurrent, compared with that of the raw material. The temperature in the soaking drum is highest at the top and becomes lower in its lower sections due to the adiabatic cracking reaction and stripping of the cracked substrate. The liquid from the bottom is pumped out and quenched in the heat exchanger to a temperature of less than 350°C. Vapor from the soaking drum flows into the rectifying column in which desirable intermediate fractions are formed, including heavy vacuum oil.

The soaking drum contains a stable homogeneous dispersion of asphaltenes in the residue, even at much higher conversions than in conventional visbreaking.

Distillates from conventional visbreaking, which is regarded as a first step in the processing of soft asphalt, and from the second step (the HSC plant) are then subjected to hydrogen treatment in the DESUS plant. The feed, after a multi-step heat exchange and after being mixed with hydrogen, is made to flow through the furnace and into a fixed-bed reactor. This is the hydrofining reactor, where sulfur, nitrogen, and oxygen are removed from the liquid reactants and hydrocracking takes place, with conversions of around 30 % (m/m). The post-reaction mixture flows through heat exchangers first into the hot separator, then the vapor and gas flow through a heat exchanger and two-step coolers into a cold separator for the separation of the liquid/gas phases. Liquid products are sent downstream to rectification, except that light fractions are subjected to stabilization.

3. Manufacturing of synthetic liquid fuels

The process to make synthetic fuels from syngas is known as the Fischer-Tropsch synthesis and was first used commercially in the 1940's. The process to make engine fuels from a gas which contains a mixture of carbon monoxide and hydrogen, in the presence of cobalt and iron catalysts runs according to the following reaction:

the cobalt catalyst

$$(2n+1)\,H_2 + n\,CO \rightarrow C_nH_{2n+2} + nH_2O$$
$$2n\,H_2 + n\,CO \rightarrow C_nH_{2n} + n\,H_2O$$

the iron catalyst

$$(n+1)\ H_2 + 2n\ CO \rightarrow C_nH_{2n+2} + n\ CO_2$$
$$n\ H_2 + 2n\ CO \rightarrow C_nH_{2n} + n\ CO_2$$

The process comprises:

- syngas production by oxygen-steam gasification of coal, or by the catalytic semi-combustion or catalytic reforming (or both processes) of natural gas in the presence of steam;
- removal of sulfur and carbon dioxide;
- catalytic synthesis of carbon monoxide and hydrogen to form hydrocarbons;
- distillation and treatment of the resulting intermediate products to obtain: liquefied gas, gasoline, jet fuels, diesel fuel, and paraffins.

The first American plant using the Fischer-Tropsch technology was built, in 1951, in Brownsville, Texas, by Carthage Hydrocol Company. It was based on a desulfurized natural gas. The plant was composed of two reactors (diameter 5.1 m, height 24 m), packed with 200 Mg of a fluid-bed iron catalyst each. A simplified diagram of the process is shown in Fig. 2. The oxygen generating plant supplied 1800 Mg O_2 per day into the generator of catalytic semi-combustion of methane. The whole process was carried out at 3 MPa. Carbon dioxide was removed from syngas using a water jet.

Water, as a coolant, was made to flow through coolers located in the catalyst bed. Heat, generated during the reaction, was used for making steam. Gas and synthesis products were collected at the top of the reactor, carrying along the fine dust of the catalyst after removing it downstream by means of cyclones. The condensing portion of hydrocarbons and oxygen compounds was chilled and washed out with water. Lighter hydrocarbons were removed using an absorption-desorption system. C_3 and C_4 olefins were polymerized catalytically, obtaining gasoline which was then refined.

The resulting liquid products were composed of 25 % oxygen compounds and 75 % hydrocarbons. Gasoline after final treatment had a high olefin content and its octane number was 85.

In 1955, in Sasolburg, South Africa, a coal-based plant using the Fischer-Tropsch synthesis was started. The raw material, named SASOL, is a poorly-sintering type of coal, containing about 25 % ash and 10 % water, its heat of combustion is 23,000 kJ/kg. Fig. 3 shows a general diagram of the process to obtain synthetic fuels in the Sasolburg plant.

Coal is crushed into finer pieces and then divided into three categories. The smallest pieces are used in the power station in four boilers, each of a capacity of 160 tons of steam per hour. After purification, the gas at a pressure 2.5 MPa is separated into two streams: one stream is sent to the synthesis unit which is equipped with revamped fixed-bed cylindrical reactors (each has a heat exchanger, cooler and blower enabling the gas to be recirculated). The other gas stream is made to flow to fluidized-bed reactors which are supplied with the gas obtained from conversion of the C_1 and C_2 hydrocarbons being made at the same plant. Each reactor in the

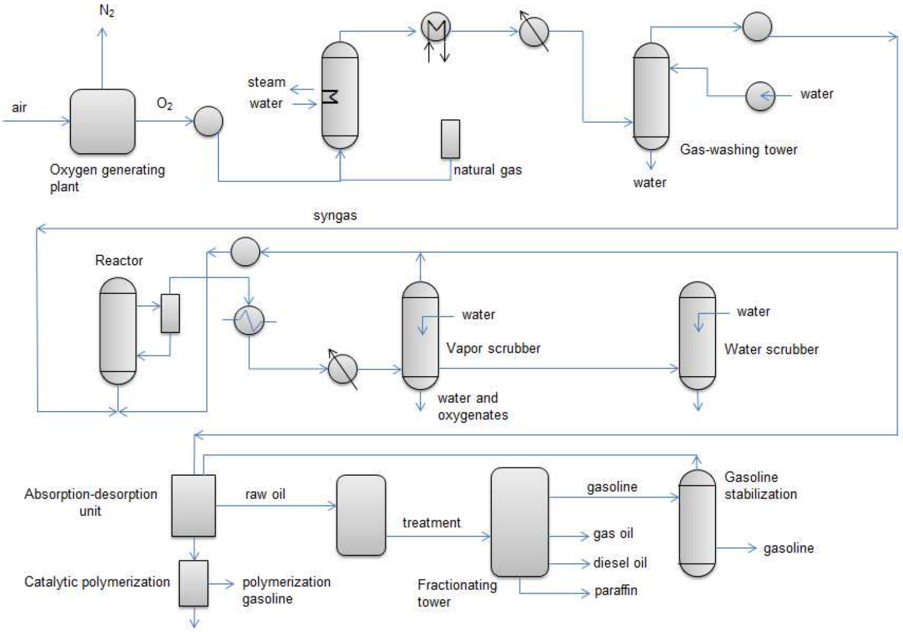


Figure 2. Simplified diagram of the Hydrocol plant.

synthesis plant is provided with approx. 20,000 m^3 of syngas per hour. The gas conversion is in the range (50...60) %.

A majority of the products obtained in the synthetic plant are high-boiling hydrocarbons. The fluidized-bed reactors produce mainly gasoline.

3.1. Methanol as a starting material for making liquid fuels and petrochemical products

At present, the synthesis of methanol is carried out globally starting from a mixture of carbon monoxide and dioxide and hydrogen in the presence of catalysts which typically contain Cu-Zn-Al or Cu-Zn-Cr at a pressure in the range (5...10) MPa at a temperature in the range 240…275°C, according to the following reaction:

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^0 = -92 \text{ kJ/mol}$$

and, in part:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^0 = -50 \text{ kJ/mol}$$

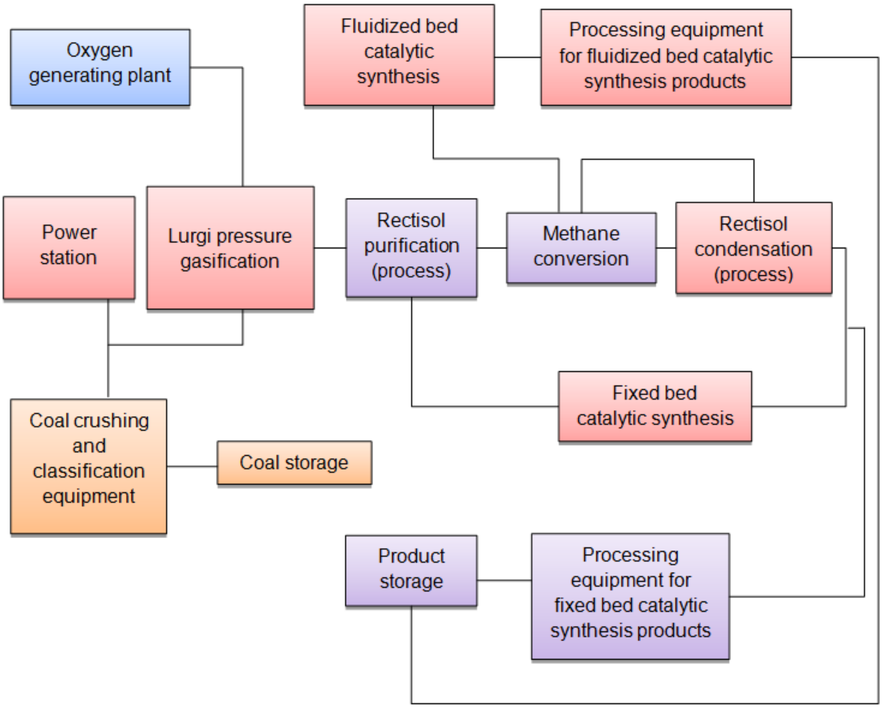


Figure 3. A block diagram of the synthetic fuel plant in Sasolburg (source: own elaboration on the basis of company materials)

The process selectivity is enormously high, therefore, only a maximum of 0.5 % (m/m) of side products (in addition to water) is made.

A diagram of the complete methanol plant, based on natural gas or biogas from a municipal waste dump or anaerobic biomass fermentation tanks, is shown in Fig. 4. The methane or biogas is heated in the central furnace to approx. 420°C and made to flow into a desulfurization reactor which is packed with zinc oxide beads ($ZnO+H_2S \rightarrow ZnS+H_2O$). From the reactor, the gas flows into the saturator (scrubber) to be saturated with steam. The saturator is supplied with a mixture of hot water from the distillation section and from the process condensate tank. Methane is heated in the respective apparatuses to about 800°C after being saturated with more steam (live steam) to form the desired mixture, and then directed into the reforming unit I° for the endothermal reaction $CH_4+H_2O \rightarrow CO+3H_2$ to take place on the $Ni/\gamma\text{-}Al_2O_3$ catalyst. If a biogas with 60 % CH_4 and 40 % CO_2 is used for the synthesis of methanol, then the reaction $CH_4+CO_2 \rightarrow 2CO+2H_2$ takes place additionally. Approximately 10 % (v/v) of methane is not converted, therefore, the reaction mixture is sent into the reactor II° for a strongly exothermal semi-combustion of CH_4 to take place with participation of a strictly measured amount of oxygen on a nickel catalyst, according to the reaction:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

A syngas at nearly 900°C is then made to flow through a boiler which generates compressed steam for the methanol plant, and is combined with hydrogen, separated from fuel gas (post-production gas) by Pressure Swing Adsorption (PSA).

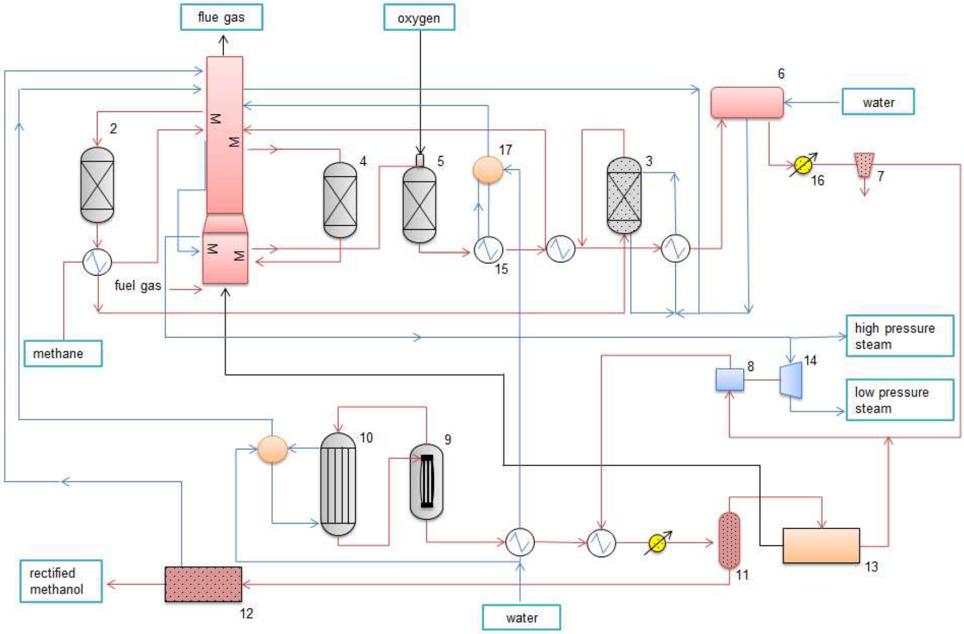


Figure 4. A diagram of the methanol plant based on natural gas or biogas at Lurgi Ől-Gas (source: own elaboration on the basis of company materials) **1** – central gas-fired heater, **2** – methane desulfurization reactor with a ZnO catalyst, **3** – saturator, **4** – stage 1 reactor for methane steam reforming over a Ni catalyst, **5** – stage 2 reactor for methane reforming with the use of oxygen, **6** – water evaporator, **7** – water separator, **8** – turbocompressor, **9** – stage 1 reactor for methanol synthesis, **10** – stage 2 reactor for methanol synthesis, **11** – methanol recovery from unreacted syngas, **12** – 3-column distillation of raw methanol, **13** – hydrogen recovery from waste gases, PSA method, **14** – steam turbine which drives the turbocompressors of syngas and recycle gas, **15** – heat exchanger, **16** – cooler, **17** – water-steam separator

Then, it is sent into the turbo-compressor to obtain a pressure in the range (5...10) MPa and is combined with the unreacted reactant being recirculated from the methanol separator, and sent to two serially-connected methanol synthesis reactors. After the second synthesis reactor, the post-reaction mixture flows through the heat exchanger and water-cooled methanol condenser into the product separator. From the bottom part of the product separator, a crude methanol flows through pressure reduction valves and into three serially-connected rectifying columns. After the last rectifying column in the series, the purity of the methanol product is a minimum of 99.99 %. A portion of the unconverted post-process gas is recirculated for another synthesis of CH_3OH, while another portion is sent through the PSA system (for recovery of hydrogen) into the fuel gas network and then into the central furnace. Bleeding a portion of the unconverted post-process gas continuously enables the inert content in circulation (N_2+CH_4) to be kept at a stable level of approximately 15 % (v/v).The first step, in which a crude methanol is neutralized using an aqueous soda lye solution, is followed by oxidation of aldehydes and iron cabonyls using an aqueous potassium permanganate solution. This results in the formation of a sludge which comprises manganese dioxide and other solids and is removed by filtration. The crude methanol is refined by distillation in two or three rectifying columns. For a two-column system, two process variants are possible: either both columns operate at an atmospheric pressure, or one operates at an atmospheric pressure while the other does at an elevated pressure.

The components of crude methanol are divided into three essential groups: light components, ethanol, and higher alcohols. Low-boiling compounds, having boiling points lower than or close to that of methanol, are removed along with the dissolved gases from the synthesis plant (H_2, CO, CO_2, CH_4 etc.) in the first column. It is also referred to as the extraction column, with water being the extraction agent, which differentiates the liquid phase activity coefficients of the major components. The scope of changes in the activities of the respective components is determined by the quantity of the solvent required.

The crude feed is pre-treated with chemicals (NaOH, $KMnO_4$), then heated to a boiling range and made to flow into the middle section of the extraction column. Extraction water, which is recirculated from the bottom section of the second rectifying column, is fed to the top of the extraction column. When extracting, the water is cooled down in the heat exchanger by the flowing crude methanol feed. Vapors from the extraction column, flowing upwards, carry along all the volatiles and a small amount of methanol vapor with water. Most of the methanol, water, and of less volatile components are condensed in the condenser and recirculated as the reflux through the separator and into the extraction column, the other ones escape to the fuel gas network or to the flare.

After extraction distillation, the crude methanol from the column bottom contains roughly 50% (m/m) CH_3OH. The volume of the extractant to be added depends on the amount of contaminants as actually found in the crude feed and as shown in product specifications.

The second rectifying column is called the refining column: its main function is to separate water and high-boiling compounds from methanol being the principal product. Higher alcohols have a maximum concentration at the bottom of the column, below the feed point. Therefore, that part of the column comprises alternative points for carrying out higher alcohols from the system. The higher alcohols, if being carried out with the vapor stream, must be cooled down, condensed and sent into the separator. In addition to the higher alcohols and high-boiling components, the stream has a content of methanol, water, and small amounts of ethanol. If the stream is carried out from the lower trays of the stripping section or as a “liquid blow”, it may have a significant water content and is likely to become separated into two phases if allowed to stand. The light phase (or the organic phase) is a quite valuable fuel and may be used as a fuel for a furnace (methane reforming reactor, or steam boiler). The aqueous phase may be drained and disposed of as a chemical liquid waste.

In a two-column process system, the pure methanol is collected at the top of the refining column. Typically, it is collected between trays number 4 and 6, counting from the top down. That section has 4 to 6 trays at the top (pasteurization section) and is designed to concentrate low-boiling components, which penetrate through the bottom of the extraction column. A small volume of the total condensate, which is obtained at the top, is intentionally “blown out" or recirculated into the first column for such trace amounts of minor contaminants to be finally taken to the top of the system and out.

With the second column operating as a pressure column, part of the vapor being collected at the top may be used to provide heat to the first distillation column. However, at higher pressures, the difference between relative volatilities for the respective components is lower, therefore, for same product purities and same heat loads in the evaporator, the pressure column needs more trays.

In a three-column methanol rectification system, the third column is designed to separate methanol from ethanol. One of the methods to remove ethanol is by “blowing out" a small stream above the feed tray in the refining column, or by collecting an ethanol-methanol mixture at the top of the refining column, followed by separation of the two components in the third column. The feed to that column contains nearly all of the ethanol present in the feedstock (crude methanol) plus the methanol product. Water and trace amounts of higher alcohols are removed from the column together with ethanol while pure methanol is collected overhead. The pasteurization section is located above the product collection point.

4. Production of gasoline

Gasoline is a hydrocarbon mixture of roughly 100 of various compounds, obtained by the straight-run and destructive processing of petroleum. The fractions, found in gasoline, include the paraffin fraction (40...65)% (V/V), naphthene fraction (20...35)% (V/V) and aromatic fraction: (8...20)% (V/V).

Taking into account the desirable method of combustion, gasoline should preferably contain large amounts of aromatic hydrocarbons, obtained mainly by reforming and partly by pyrolysis. Very important components – especially in aviation fuels – are mixtures of hydrocarbons obtained in isomerization and alkylation processes (isoparaffins). Highly resistant to knocking combustion, they have the added advantage of a sufficiently high calorific value.

All the components that are required for gasoline blending are obtained in the respective types of refining processes and are combined in the blending unit in accordance with process requirements for the specific gasoline types. Major components of gasoline are listed in Table 1. The respective components are blended so as to obtain a final product (commercial gasoline) which complies with the requirements of applicable standards.

Most of those qualitative parameters of fuels are only approximate because their fractional and chemical composition is very complex. Numerical values for the respective qualitative parameters are selected in a manner which, in as far as possible, enables compliance with performance requirements, resulting from the design and mode of operation of spontaneous-ignition engines fuelled by such blends.

Component	Boiling point/range [°C]	RON	Function or use
Base cut from distillation	45 ÷ 195	40 ÷ 54	Essential component of gasoline
Butane	0	95	Facilitates cold engine start, component of automotive gasoline
Pentane-hexane fraction	27 ÷ 65	45 ÷ 93	Enables continuous combustion during startup, when present in automotive and aviation gasoline types
Light distillate	65 ÷ 90	-	same as above
Reforming product: - complete	-	-	Major component of automotive and aviation gasoline types, resistant to detonation combustion
- de-aromatized	45 ÷ 200	92÷ 101	
- de-xylenated	-	-	
- refined reformate	-	-	
Hydrocracking fraction	40 ÷ 200	72 ÷ 85	Component of automotive and aviation gasoline types with good anti-detonation properties and low sulfur content
Catalytic cracking fractions	40 - 200	91 – 93	Widely used as a component of high-octane gasoline
Hydrogenated pyrolysis gasoline	60 ÷ 200	96 ÷ 99	Used in smaller amounts, especially for automotive gasoline
Polymerization gasoline	60 ÷ 200	94 ÷ 96	Less important, high-octane component of gasoline
Isooctane (2,2,4-trimethylpentane)	111	100	High-octane component of aviation fuels
Various alkylates	40 ÷ 150	93 ÷ 96	Widely used in blends of aviation gasoline (usually), and automotive gasoline (less frequently)
Various isomerisates	40 ÷ 70	82 ÷ 85	Desirable as components of gasoline types for high-duty applications
Additives	-	-	Component which improves lubrication and resistance to detonation combustion, depending on its essential composition

Table 1. Characteristics of gasoline components

The quality or properties of fuels affect a number of processes, connected with their use in a wide sense. The impact of the most significant qualitative parameters of fuels for spark-ignition engines on the various performance processes has been established in a number of tests. The criteria are shown in Table 2.

	Requirements relating to gasoline			
	Storage, distribution, fuelling	**Formation of fuel-air mixture**	**Optimum combustion**	**Environmental impact**
Properties of fuels	Density	Chemical composition	Chemical composition	Formation of toxic components of emissions
	Chemical stability	Fractional composition	Fractional composition	
	Corrosive effect	Vapor pressure	Calorific value	
	Level of contamination	Heat of evaporation	Resistance to detonation combustion	
	Low-temperature properties	Washing properties		Biodegradability
	Electrostatic properties	Density		
	Fire safety	Viscosity		

Table 2. Qualitative criteria of gasoline in their performance processes

5. Obtaining of diesel fuels

Diesel fuels are made by blending fractions having boiling ranges from 190°C to 350°C, obtained from petroleum processing in the following technologies:

- an oil fraction from atmospheric distillation (base fraction) of which the properties depend on the chemical nature of petroleum;
- an oil component obtained by thermal cracking; it has a low cetane number, low stability, and a considerable content of unsaturated hydrocarbons;
- an oil component obtained by catalytic cracking, which has a rather low cetane number (CN=40…60) because of a content of aromatic hydrocarbons;
- an oil component obtained by hydrocracking, used for reducing the corrosive effect of diesel fuels by decomposing sulfur compounds in the process; the amount of the hydrocracking product component which is present in the finished diesel fuel determines the oil category in respect of its content of sulfur links;
- an oil component obtained by dewaxing; it deteriorates spontaneous-ignition properties of oils while much improving their low-temperature properties;
- a light oil fraction obtained by vacuum distillation (depending on the grade of petroleum being processed) which increases the amount of oil product thus reducing its volatility and increasing its viscosity and density.
- Depending on the intended use, diesel fuels are blended essentially in two groups:
- diesel fuels for high-speed engines;
- diesel fuels for medium-and low-speed engines; another type of blends comprises so-called heating oils which are intended for use in steam boilers for marine or land applications, industrial furnaces (in rolling mills, glass works etc.), firing up coal dust-fired steam boilers, and for technological reasons.

- The following improvers can be added to diesel fuels, depending on their intended application:
- pro-detonators – to increase the cetane number of diesel fuels;
- corrosion inhibitors – to reduce the corrosive effect of diesel fuels and their combustion products;
- oxidation inhibitors – to improve diesel fuels in terms of stability, enable longer storage;
- depressants – to lower the freezing point of diesel fuels;
- additives which reduce the smoke level in exhaust gases by improving the combustion process.

Those fuels for spontaneous-ignition engines (diesel fuels) which have the desirable composition are expected to show the following characteristics:

- ensure the correct functioning of the fuel system, especially the injection assembly;
- ensure a correct and energy-efficient combustion;
- ensure reduction of toxic components and solid emissions;
- guarantee chemical stability in the storage process.

The qualitative criteria for diesel fuels which are important for the whole area of their application are shown in Table 3.

	Requirements relating to diesel fuels			
	Storage and distribution	**Functioning of fuel distribution system**	**Atomization, evaporation, and combustion**	**Environmental impact**
Properties of fuels	Density	Density	Viscosity	Formation of toxic components of emissions
	Chemical stability	Viscosity	Surface tension	
	Low-temperature properties	Low-temperature properties	Spontaneous ignition properties	
	Corrosive effect	Lubrication	Spontaneous ignition properties	
	Resistance to microbial contamination	Level of solid contaminants and water		Biodegradability
	Electrostatic properties		Calorific value	
	Foaming			
	Fire safety.		Washing properties	

Table 3. Qualitative criteria of diesel fuels in their performance processes

Regardless of standard fuels, for which applicable standards and approved testing methodologies exist, a number of alternative fuels are known, including biofuels, which can be applied as propulsion materials. Such fuels are used in typical spontaneous-combustion engines, of which the designs are adapted to the properties of conventional (standard) fuels. Therefore, taking into consideration engine requirements, the scope of the respective evaluation criteria ought to correspond to those which apply to conventional fuels. Existing alternative fuels for spontaneous-combustion engines for various applications are listed in Table 4.

<table>
<tr><th colspan="4">Alternative fuels for use in engines</th></tr>
<tr><th>Form</th><th>For spark-ignition engines</th><th>For spontaneous-ignition engines</th><th>For stationary engines</th></tr>
<tr><td rowspan="12">Liquid</td><td colspan="3">methanol</td></tr>
<tr><td colspan="3">ethanol</td></tr>
<tr><td colspan="3">butanol</td></tr>
<tr><td>other alcohols (<i>tert</i>-butyl TBA, <i>sec</i>-butyl SBA, isopropyl IPA, neopentyl-NPA);</td><td colspan="2">fatty acid esters (FAME, FAEE) from transesterification of rapeseed, soy, sunflower oils</td></tr>
<tr><td>ethers (ethyl-<i>tert</i>-amyl TAEE, ethyl-<i>tert</i>-butyl ETBE, methyl-<i>tert</i>-amyl TAME, methyl-<i>tert</i>-butyl MTBE, diisopropyl DIPE);</td><td></td><td>tall fuels (TPO-tall pitch oils) obtained by esterification with ethyl / methyl alcohols of tall oils obtained from gums/resins of coniferous trees (side products in sulfate cellulose production processes and low-temperature dry distillation of wood);</td></tr>
<tr><td colspan="3">hydrogen-based synthetic fuels (including BG, FT, HTU processes)</td></tr>
<tr><td colspan="3">liquefied petroleum gas (LPG)</td></tr>
<tr><td rowspan="2">dimethylofuran (DMF)</td><td colspan="2">fuel-water emulsions (aquasols)</td></tr>
<tr><td colspan="2">pure vegetable oils</td></tr>
<tr><td colspan="3">liquefied natural gas (LNG)</td></tr>
<tr><td rowspan="5">Gaseous</td><td colspan="3">compressed natural gas (CNG)</td></tr>
<tr><td rowspan="3"></td><td>biomethane from biogas</td><td>biogas</td></tr>
<tr><td colspan="2">dimethyl ether (DME) and (contemplated) diethyl ether (DEE);</td></tr>
<tr><td colspan="2">gaseous fuels from CtG processes</td></tr>
<tr><td colspan="3">hydrogen</td></tr>
</table>

Table 4. Alternative fuels for use in engines

In view of the above data, for a rational assessment of the quality of fuels and their usefulness, especially after storage processes, in engine operation it is necessary to chose applicable assessment criteria and methodology, enabling a relatively fast analysis of changes in the parameter values. The choice of such criteria ought to result from the sensitivity of the respective criteria to fuels' oxidation and contamination, potentially causing the accepted and recognized limiting values to be exceeded both in respect of their measure and weight.

Experience in using engine fuels indicates that their quality may change, mainly in storage and distribution processes. This causes the necessity to establish the scope and frequency of the quality surveillance of fuels. Some of the generally adopted types, scopes, and frequencies of control of the quality of fuels in their distribution chain are shown in Table 5.

Fuel type and scope of control	Fuel distribution step
Full – comprising assessment of the values of all quality parameters of fuels, as described in the standard ON-EN 228 for gasoline and PN-EN 590 for diesel fuels	• Refinery – before delivering a fuel lot for distribution; • Storage facilities – after acceptance of fuel for storage and on its release, or periodically, every 6 months of storage
Control – comprising assessment of selected parameters, usually appearance, density, fractional composition, and vapor pressure – for gasoline, or flash point and cold filter plugging point – for diesel fuels.	• Storage facilities – periodically, during storage; • Fuel station – random analysis, for instance every 3 to 4 deliveries, after acceptance of fuel for storage.
Short – comprising determination of density, fractional composition, content of water and contaminants – for diesel fuels, or appearance, color, density – for gasoline.	• Fuel station – before acceptance of fuel for storage; • Storage facilities – before unloading tankers.

Table 5. Fuel types and scopes of analysis in the distribution chain

6. Conclusion

The growing demand on liquid fuels necessitates maximization of production output, especially those fuel components which originate from destructive processing. Even though in straight-run processing of petroleum, processes may be conducted which are intended to expand the limits of fractions of base gasoline, kerosine and diesel fuels fractions, yet the main focus is on secondary processing, providing increased numbers and amounts of components of diesel fuels, also by means of thermal and thermocatalytic processes, in the presence or absence of hydrogen.

Owing to the growing number of spontaneous-ignition engines in Europe, the supply of diesel fuels is insufficient while that of gasoline is excessive. As a result, technological processes are carried out which provide the maximum yield of propellant cuts and the residues are processed to provide components which are useful for diesel fuel blending processes.

Experiments were made in which fractions resulting from depolymerization of plastics (KTSF fraction) were “sunk” in petroleum or components which result from re-refining of spent lubricating oils were utilized.

In the production of gasoline, if correct process conditions are maintained, components obtained in isomerization processes, catalytic reforming, full hydrocracking, alkylation (using isobutane) and fluidized-bed cracking (FBCC) are not expected to affect the stability of gasoline during long-term storage.

As regards the motors spirits manufacturing and blending technologies, the following fractions, which originate from the processes of technology discussed above, may very much reduce the duration of safe storage of such fuels:

- the gasoline fraction obtained by thermal cracking of the vacuum column residue, which was not hydrogenated;
- alternately, the non-hydrogenated fraction of pyrolysis gasoline;
- fractions from synthesis of gaseous hydrocarbons;
- ethanol as a biocomponent.

The contemporary diesel fuel blending techniques are typically based on the combining of components derived from the following major process unit:

- distillation in a tube-tower distillation system
- hydrocracking;
- fluidized-bed cracking (FBCC);
- hydrodesulfurization of soft asphalt;
- thermal processing of residue.

The stability of diesel fuels can be much affected by the following factors:

- components from thermal processes;
- biocomponents (FAAE);
- components from WtL processes (KTSF fraction) and re-refining products of the processing of spent lubricant oils.

Some refineries offer co-hydrogenation of petroleum fractions and vegetable oils. The solution carries a potential risk to the blend stability because the process mechanism, connected with the presence in such oils of heterogenic compounds, is not very well known.

Generally, the stability of fuel blends is the lower, the more unsaturated bonds such as those in alkenes (or olefins) they contain.

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References

[1] K. Biernat, „Kierunki rozwoju układów zasilania i spalania oraz źródeł energii we współczesnych silnikach spalinowych", [*Trends in the development of fuelling and combustion systems and energy sources in contemporary internal combustion engines*], „Przemysł Chemiczny" December 2006;

[2] K. Biernat „Prognoza rozwoju paliw" [*A forecast for the development of fuels*], „Studia Ecologiae et Bioethicae" No. 3/2005;

[3] K. Biernat, A. Kulczycki „Prognoza rozwoju biopaliw w Polsce", Krajowa Konferencja „Rynek biopaliw w Polsce – szanse i zagrożenia", [*A forecast for the development of biofuels in Poland,* National Conference *The biofuels market in Poland – opportunities and risks*], Warsaw, 26.04.2006;

[4] K. Biernat, A. Kulczycki, M. Rogulska: „Development of Alternative Fuels in Poland", conference proceedings: „Expert Workshop on Biofuels Support in Baltic States, Nordic Countries and Poland", Tallin, Estonia 14.02.2007.

[5] J.M. Maćkowski, The EU Directives on Fuels Quality: a look beyond year 2000", conference proceedings: Mat. II Międzynarodowej Konferencji pt: "Rozwój technologii paliw w świetle Dyrektyw Europejskich i Narodowych Uregulowań Normatywnych" [2nd International Conference: The development of fuel technology in the light of European Directives and national normative regulations] Warsaw 1999

[6] J. Gronowicz „Ochrona środowiska w transporcie lądowym" [Environmental protection in land transport], ITE Radom 2004.

[7] J. M. Maćkowski, „ Paliwa samochodowe początku XXI wieku" [Automotive fuels of early 21st century], Wyd. Centrum Badawczo-Szkoleniowe Diagnostyki Pojazdów Samochodowych", Katowice 2002

[8] K. Biernat "Materiały Pędne i Smary" [Propellants and lubricants], WAT, Warsaw 1983

[9] K. Biernat, Z. Karasz "Paliwa płynne i ich użytkowanie" [Liquid fuels and their use], SIMP, Warsaw 1997.

[10] K. Baczewski, T. Kałdoński, „Paliwa do silników o zapłonie samoczynnym" [Fuels for self-ignition engines], WKiŁ, Warsaw 2004.

[11] K. Baczewski, T. Kałdoński, „Paliwa do silników o zapłonie iskrowym" [Fuels for spark-ignition engines], WKiŁ, Warsaw 2005.

[12] A. Podniało, „Paliwa, oleje i smary w ekologicznej eksploatacji" [Fuels, oils, and lubricants in their environmentally-friendly operation], WKiŁ, Warsaw 2002.

[13] D. Singh, „Meeting diesel specifications at sustained production", Hydrocarbon processing No. 4. 2011.

[14] W. Kotowski "Maksymalizacja produkcji paliwa dieslowskiego w rafinerii przerobu ropy" [Maximization of production of diesel fuels in a petroleum refinery]. Paliwa Płynne No. 4 and No. 5. 2012.

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:

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

The diffusion process is characterized by the diffusion coefficient, which is equal to the number of moles of gas (fuel vapor) passing across 1 m^2 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:

$$[\mathrm{nC, mH_2, kS}] + \mathrm{pO_2} \rightarrow \mathrm{nCO_2} + \mathrm{mH_2O} + \mathrm{kSO_3} + \mathrm{Q}$$

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, its 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:

$$C + O_2 = CO_2 + Q$$

$$2H_2 + O_2 + 2H_2O + Q$$

$$2S + 3O_2 = 2SO_3 + Q$$

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:

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

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 [cm³] during engine starting time [sec] for gasoline**	
	$t_{10\%}$ **= 79°C**	$t_{10\%}$ **= 72°C**	$t_{10\%}$ **= 79°C**	$t_{10\%}$ **= 72°C**
0	10.5	9.4	10.0	8,7
-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 isooctanes (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 standardized 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 (Pi) 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 1050	D1 1150	E1 1200	F1 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 cm^3 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**
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) mm^2/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 abut also, in certain instances, may lead to reduced emissions of NOx. 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 CO_2 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/m^3 at a temperature of 15°C, though its upper limit is expected to be lowered to 845 kg/m^3.

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 ($27\bullet10^{-7}$...$30\bullet10^{-}7$) J/cm^2 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**
Oil grade	0	1	2	3	4	-
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: %(v/v) distill. to 180°C max. %(v/v) distill. to 340°C min.	10 95					ISO 3405

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-methylnaphthalene 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;

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

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

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

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

T_{90} – 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
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:

$n(R\text{-}SH)+Me \rightarrow (R\text{-}S)_n+nH_2$;

$n(H_2S)+Me \rightarrow n(MeS)+nH_2$;

$nS+Me \rightarrow n(MeS)$.

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 N_2.

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 NOx 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 55ºC). In this aspect, favorable materials include vegetable oils (flash points higher than 295ºC) 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/m^3

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) mm^2/sec. Some nozzle designs are capable of spraying liquids with viscosities up to 45 mm^2/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 mm^2/sec at 50°C (standards PN, GOST, BDS, TGL).

Assuming that the correct viscosity of heating oil (in mm^2/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 mm^2/sec at 50 °C requires heating to 102, 92 and 79°C to have viscosities of 15, 20 and 30 mm^2/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 20^0C (and is in the range (0.910...1.015) g/cm^3); in DIN – at 15^0C (0.860...1.20) g/cm^3, in ASTM in 0API (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 66^0C; DIN: 55, 65 and 85^0C; JIS: 60 and 70^0C, 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 300^0C, 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 NOx 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 ad 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 NOx in the exhaust gases. In addition to that, sulfur affects the efficacy of elimination of NOx 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 NOx 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 NOx 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 T10+3 T50+T90+11 %OXY. The ASTM standard also specifies the Driveability Index (DI) for gasoline containing ethanol according to the relationship: DI=1.5+3.0 T10 T50 T90+1.0+1.33 ° C (2.4 ° F) × 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 NOx 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 NOx 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 NOx 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 NOx 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 10^0C 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 60^0C, 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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References

[1] K.Biernat „Prognoza rozwoju paliw” [A forecast for the development of fuels] „Studia Ecologiae et Bioethicae” No. 3/2005;

[2] K.Biernat, A.Kulczycki „Prognoza dla Polski” [A forecast for Poland] „Nowe Życie Gospodarcze” special supplement of 26 April 2006;

[3] K.Biernat, „Kierunki rozwoju układów zasilania i spalania oraz źródeł energii we współczesnych silnikach spalinowych” [Trends in the development of fuelling and combustion systems and energy sources in contemporary internal combustion engines], „Przemysł Chemiczny” December 2006;

[4] J.Merkisz „Ekologiczne aspekty stosowania silników spalinowych” [Environmental aspects of the use of combustion engines], Wyd. Politechniki Poznańskiej, Poznań 1994.

[5] J.M. Maćkowski, The EU Directives on Fuels Quality: a look beyond year 2000”, conference proceedings: Mat. II Międzynarodowej Konferencji pt: “Rozwój technologii paliw w świetle Dyrektyw Europejskich i Narodowych Uregulowań Normatywnych” [2nd International Conference: The development of fuel technology in the light of European Directives and national normative regulations] Warsaw 1999

[6] J.Gronowicz „Ochrona środowiska w transporcie lądowym” [Environmental protection in land transport], ITE Radom 2004.

[7] L.J.Sitnik „Ekopaliwa silnikowe” [Environmentally-friendly engine fuels]. Oficyna Wydawnicza Politechniki Wrocławskiej. Wrocław, 2004.

[8] K.Biernat, A.Łuksa „Węglowodory i tłuszcze odpadowe jako ciecze opałowe” [Hydrocarbons and fat waste as liquid heating fuels], „Sozologia” No. 1/2003.

[9] J.M Maćkowski, „ Paliwa samochodowe początku XXI wieku” [Automotive fuels of early 21st century], Wyd. Centrum Badawczo-Szkoleniowe Diagnostyki Pojazdów Samochodowych”, Katowice 2002.

[10] Gray C., Webster G.: A Study of Dimethyl Ether (DME) as an Alternative Fuel for Diesel Engine Applications. Advanced Engine Technology Ltd. Report TP 13788E; Canada, May 2001;

[11] Gronowicz J. „Ochrona środowiska w transporcie lądowym” [Environmental protection in land transport], Instytut Technologii Eksploatacji, Poznań-Radom 2004

[12] K. Biernat „Materiały Pędne i Smary” [Propellants and lubricants], WAT, Warsaw 1983

[13] K. Biernat, Z. Karasz „Paliwa płynne i ich użytkowanie” [Liquid fuels and their use], SIMP, Warsaw 1997.

[14] K.Baczewski, T.Kałdoński, „Paliwa do silników o zapłonie samoczynnym” [Fuels for self-ignition engines], WKiŁ, Warsaw 2004.

[15] K.Baczewski, T.Kałdoński, „Paliwa do silników o zapłonie iskrowym” [Fuels for spark-ignition engines], WKiŁ, Warsaw 2005.

[16] A.Podniało, „Paliwa, oleje i smary w ekologicznej eksploatacji" [Fuels, oils, and lubricants in their environmentally-friendly operation], WKiŁ, Warsaw 2002.

[17] Worldwide Fuel Charter, Fifth Edition, September 2013;

[18] STANAG 3149 SILCEP (Edition 8) „Minimum Quality Surveillance of Petroleum Product"

[19] K.Biernat, A.Malinowski, J.Czarnocka: Chapter No18 in Monograph Editor: Zhen Fang, Title: „Biofuels-Feedstock, Production and Application", Editions by "InTech", December 2012: „An analysis of physico-chemical properties of the next generation biofuels and their correlation with the requirements of Diesel engines".

Chapter 3

Biofuels in Storage and Operating Conditions

Krzysztof Biernat

Additional information is available at the end of the chapter

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1. Introduction

In most countries, the term “biofuels” tends to be reduced only to fatty acid methyl esters (FAME), which are derived from rapeseed oil. “Biofuels” also include mixtures of FAME with diesel oil which are generally, though incorrectly, termed “biodiesel”, and ethyl alcohol, termed “bioethanol”, which is added to motor spirits. Biofuels are also generally and completely wrongly considered to emit no carbon dioxide (CO_2) from the combustion process into the atmosphere. When evaluating the environmental hazards which may result from the use of biofuels, one should take into consideration total emissions along the whole train: starting from plant growing, through the production of fertilizers and fertilization, use of agricultural machines and equipment, transportation, processing and, finally, combustion processes taking place in engines. That train of processes is defined as “well to wheel” (WtW). It is a sum of WtT (“well to tank”) and TtW (“tank to wheel”) components, hence it is possible to evaluate the values of WtW. It should be kept in mind at the same time that carbon is the basic energy-carrying element which is present in chemical compounds of biofuels. Therefore, when examining CO_2 emissions in the WtW cycle and comparing them with the amounts of CO_2 absorbed in the photosynthesis process by the plants which make feedstocks for the production of biofuels, the energy balance of the currently available biofuels turns out to be unfavorable. As regards the production of bioethanol, large volumes of CO_2 obtained in fermentation processes should be considered as well. Apart from that, the WtW cycle may also release other compounds into the environment, for instance, nitrogen and sulfur compounds, and the production of biofuels from plants which are cultivated for human/animal consumption may reduce the pool of available foodstuffs and consequently increase the prices of food produce. Excessive exploitation of forest resources, leading to the complete deforestation to obtain arable land for the cultivation of other energy plants with a definitely lower CO_2 assimilation potential, may pose another environmental hazard.

Requirements concerning motor spirits according to currently applicable standards in 150 countries worldwide were summarized in the report "2013 Worldwide Fuel Specification", issued by the International Fuel Quality Center.

2. Classification of biofuels

With regard to their state of matter, in Europe and in US, liquid biofuels are defined as liquid and gaseous fuels for internal combustion engines, obtained from biomass. According to the European Directive (2009/28/WE), biomass means "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste".

The Directive 2009/28/EC provides a definition for biofuels but it does not specify ithe respective grades or classes of the materials. That approach results from technological developments in biomass processing (BtL processes) as well as from the search for new raw materials for the production of biofuels and alternative fuels (WtL processes). Both those groups of processes are expected to ensure lower emissions arising in production processes and from the product use (LCA and WtW analysis). Thus, taking into consideration the provisions of said Directive and our own experience, gained from our research program, the following definition of biofuels is proposed: "Biofuels comprise liquid and gaseous transportation fuels, obtained from biomass or from waste substances, as well as from processes which directly or indirectly utilize waste carbon dioxide of natural and/or industrial origin".

Having in mind the historical track for the manufacture of biofuels, and meaning to promote the advancements in the second-generation and higher-generations biofuels (so-called "advanced biofuels"), it would be advisable – within the efforts intended to expand the use of biofuels – to define the raw materials and processes which would make it possible to include those biofuels into the energy carrier groups with doubled or even higher contributions to the National Index Targets, compared with other biofuels. The prospective processes have already been defined and adopted by the European Biofuel Technology Platform, Strategic Research Agenda, and they will be incorporated into the "Biofuel for Transport Roadmap" developed by the International Energy Agency.

Several supplementary definitions for biomass have co-existed so far. According to the European definition, as provided in the Directive 2009/28/EC, biomass means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Hence, coming out of biomass as a basic feed for the production of biofuels, the European definition involves two principal routes and corresponding conversion processes, i.e., BtL *("biomass to liquid")* with alternative BtG ("*biomass to gas") processes*, and WtL *("waste to liquid")* with alternative WtG ("*waste to gas*") processes.

That Directive also added the notion of *"bioliquids"* – biomass-based liquid biofuels for use as sources of energy other than in transportation, including power generation as well as production of thermal energy (heat or cold). Hence, the processes which are based on biomass and yield bioliquids fall within the categories of BtE (*"biomass to energy")* and WtE (*"waste to energy").*

The basic classification of biofuels is thus based on their state of matter. Pursuant to Annex № 1 to the Commission Communication № 34 of 2006, COM(2006)34 final, biofuels were broken up into the following groups: liquids, gases, and other fuels, and the notions of first-generation biofuels and second-generation biofuels were introduced for the first time. Moreover, the notion of "synthetic biofuels" was defined as synthetic hydrocarbons or mixtures of hydrocarbons obtained from biomass, e.g. Syngas produced in the gasification process of forest biomass, or SynDiesel.

The European classification specifies the following biofuels from the viewpoint of their state of matter:

1. Liquid biofuels:
    - bioethanol – obtained from biomass and/or biodegradable waste fraction which can be used as E10 biofuel (10 % ethanol and 90 % gasoline) and as E85 biofuel (85 % ethanol and 15 % gasoline);
    - biodiesel – which contains methyl esters (PME, RME, FAME) obtained from vegetable oils and animal oils or waste fats and oils (e.g. waste fryer oil), which meet the standard requirements for B7 diesel oil (7 % esters and 93 % petroleum diesel oil), B30 diesel oil (30 % and 70 %, respectively) and B100 diesel oil (pure esters with properties conformable with the applicable standard);
    - biomethanol – as fuel or fuel component obtained from biomass;
    - bio-ETBE, ethyl-*tert*-butyl ether – obtained from bioethanol, to be used as an antiknock agent for gasolines to improve their octane number;
    - bio-MTBE, methyl-*tert*-butyl ether – obtained from biomethanol, with the same intended use as bio-ETBE;
    - BtL – as liquid fractions and their mixtures obtained from biomass, which may be used as biofuels or fuel components;
    - pure vegetable oils – obtained by pressing, extraction or similar processes (including refining but excluding chemical modification of their compositions), which are useful as environmentally friendly biofuels for specific engine types.
2. Gaseous biofuels:
3. bio-DME – dimethyl ether, obtained from biomass, to be used directly as biofuel in spontaneous-ignition engines;
4. biogas – biofuel, obtained from biomass and/or biodegradable waste fractions, suitably purified to meet the quality of natural gas;

5. biohydrogen – biofuel, obtained from biomass or biodegradable waste fractions.
6. Other fuels derived from renewable energy sources, as biofuels which have not been listed above, obtained from the sources as defined in the Directive 2001/77/EC, which may be used to drive transport facilities.

As mentioned before, said Communication presented a basis for the classification of biofuels as the first-or second-generation materials. That division resulted from the determinant factors as discussed above and, first of all, from the assessed usefulness of fuels in present-day motor engineering, and from the availability of raw materials and their environmental impact. A formal classification of biofuels into the respective generations was published in the report "Biofuels in the European Vision, a Vision 2030 and Beyond". In the report, the materials are classified as the first-generation (or "conventional") biofuels, and second-generation (or "advanced") biofuels.

The first-generation (conventional) biofuels comprise:

- bioethanol (BioEtOH, BioEt), i.e. conventional ethanol obtained from hydrolysis and fermentation processes, from such raw materials as: cereals, sugar beets, etc.;
- pure vegetable oils (PVO) obtained from oil plant seeds in cold pressing and extraction processes;
- biodiesel which is a blend of rapeseed methyl esters (RME) or methyl esters (FAME) and ethyl esters (FAEE) of higher fatty acids from other oil plants, obtained by cold pressing, extraction, and transesterification;
- biodiesel which is a blend of methyl and ethyl esters obtained through transesterification of waste fryer oils;
- biogas obtained by treatment of humid gas from landfill facilities or from agricultural sources;
- bio-ETBE obtained by chemical processing of bioethanol.

The second-generation (advanced) biofuels include the following:

- bioethanol, biobutanol and mixtures of higher alcohols as well as their derivatives obtained from advanced lignocellulose hydrolysis and fermentation processes, where lignocellulose is obtained from biomass (excluding raw materials intended for use as foodstuffs);
- synthetic biofuels, i.e., products obtained by biomass conversion in gasification and adequate synthesis processes into liquid fuel components (BtL processes), and those produced by processing biodegradable industrial and municipal waste, inclusive of carbon dioxide (WtL processes);
- fuels for spontaneous-ignition engines, obtained by converting biomass-based lignocellulose in Fischer-Tropsch processes, inclusive of synthetic biodiesel produced by blending lignocellulose-based products;

- biomethanol obtained by lignocellulose conversion processes, inclusive of the Fischer-Tropsch synthesis, with the utilization of waste carbon dioxide;
- biodimethylether (bioDME) obtained in biomass thermochemical conversion processes, inclusive of biomethanol, biogas and synthesis gases which are obtained from biomass conversion processes;
- biodiesel, i.e., biofuel or fuel component intended for spontaneous-ignition engines, obtained from hydrofining (hydrogenation) of vegetable oils and animal fats;
- biodimethylfuran (bioDMF) obtained from sugar conversion, inclusive of cellulose, in thermo-and biochemical processes;
- biogas as synthetic natural gas – biomethane (SNG), obtained by lignocellulose gasification processes and appropriate synthesis, and by treatment of biogas collected from agricultural sources, from landfill facilities and from sewage sludge;
- biohydrogen obtained by lignocellulose gasification and further synthesis of gasification products, or from biochemical processes.

The above classification shows that first-generation biofuels after further processing may not be classified as second-generation biofuels. Hence, any downstream conversion of esters, e.g., their hydrofining, will not produce second-generation biofuels and is technically and commercially unreasonable. The idea to develop second-generation biofuels is in principle based on the assumption that they should be produced from biomass, waste vegetable oils and animal fats, and any waste organic substances which are useless for the food industry or forestry.

The European Commission Directorate-General for Energy and Transport suggested that third-generation biofuels could be defined for which the manufacturing processes may be developed and commercial implementation planned for the 2030’s or later. That group would initially comprise biohydrogen and biomethanol.

Because of the need to reduce emissions of greenhouse gases (GHG), including first of all carbon dioxide, which is the critical factor of growth in the use of biofuels, the concept of third-generation biofuels was more specifically defined and the fourth-generation biofuels group was proposed. The two groups of biofuels would be classified as advanced biofuels. So, the third-generation biofuels may be obtained from processes which are similar to those which yield second-generation fuels but the feed to those processes (biomass) would be modified at the stage of its cultivation with the use of molecular biological techniques. Such modifications should be tailored to improve the biomass conversion into biofuels (biohydrogen, biomethanol, biobutanol): trees should be grown with low lignin content, plants could be cultivated with suitably built-in enzymes, etc.

The suggestion to provide a new, fourth generation of biofuels has emerged because of the need to close the balance of carbon dioxide or to eliminate its environmental impact. Hence, the fourth-generation biofuel manufacturing processes should involve CCS (*Carbon Capture and Storage*), i.e. they should capture and store carbon at the stages of raw materials and biofuel production processes. The raw materials for that production shall involve the plants with improved (even by genetic engineering) assimilation of CO_2 during plant cultivation. The adopted technologies must capture carbon dioxide into suitable geological formations by converting it into carbonate forms or by storing it in oil and gas field pits.

Biofuels are not classified in the United States. Pursuant to NREL (National Renewable Energy Laboratory), the development and implementation of biofuel processes are planned to be implemented gradually.

According to NREL, manufacturing processes are being implemented to obtain the following biofuels:

- ethanol as a biofuel component, which is produced from cereals and cellulose obtained from agriculture and forestry;
- biodiesel, i.e., esters of higher fatty acids from vegetable oil transesterification processes, blended with petroleum diesel oil.

As regards prospective developments, the processes for further biofuels are planned:

- "Green Diesel and Jet Fuel", so-called "green diesel" and general-purpose fuel for turbine engines (chiefly as a military fuel), obtained from waste fats and oils and pure vegetable oils, which are refined in petroleum refineries to reach very low sulfur levels;
- other products of biomass fermentation processes, like: butanol, acetates (ethanates), lactates (2-hydroxypropanates), etc.;
- pyrolytic liquids from biomass pyrolysis processes, as an alternative feed for petroleum refineries or gasification processes;
- syngas obtained from biomass by the Fischer-Tropsch method, as a raw material for the production of methanol, dimethyl ether or mixed alcohols;
- "Algae-derived Fuels", fuels derived from biomass of marine algae, as sources of triglycerides for the production of biodiesel, "green diesel" and "jet" fuel, as well as raw materials for the production of hydrocarbons;
- biofuels obtained from such raw material crops as: jatropha, halophyte plants and *Camelina sativa*, to be converted into diesel oils and jet fuels;
- hydrocarbon fuels, as biofuels of a distant future, to be obtained from biological processes or biomass hydrogenation, including fuels from xtL processes.

The last of the above biofuel groups is coming more and more into prominence because of the need to significantly reduce CO_2 emissions, therefore, new methods are required for closing the CO_2 balance for that gas by finding new raw materials and new methods for their processing.

Considering the assessed potential of biomass and the need to cut down CO_2 emissions, new prospective processes are being developed in USA and in Europe, such as the following:

- biofuel production processes, including jet fuels, by growing algae in the absence of sunlight on agricultural sludge, on grass-based sludge, or on waste substances, using carbon dioxide (“SOLAZYME” process);
- plasma gasification process which involves waste biomass as well as municipal and industrial waste (BtG and WtG processes), followed by conversion of product gases into liquid biofuels (diesel oils and jet fuels) in the GtL process (“SOLENA” process, just being implemented in Great Britain and in Italy);
- processes which utilize carbon dioxide to produce energy carriers;
- complex processes for biorefineries.

Taking into consideration the previous experience and technological developments in the production of biofuels (or, more precisely, alternative fuels) from raw materials which are a waste from the viewpoint of biology and civilization (xtL processes), modern societies strive above all for reduced CO_2 emissions or for optimized balancing of CO_2 in the production and fuel combustion processes. It is assumed that, in the foreseeable future of the production and use of biofuels (alternative fuels), that such fuels should:

- be available in sufficiently high volumes;
- offer technical and energy properties which make them useful a feed to engines or heating systems;
- be cost-effective in production and sale;
- be less environmentally harmful than the fuels used to-day, through lower emissions of toxic compounds and greenhouse gases from the combustion processes;
- make the use of engines and boilers safe and cost-effective, and to enable further reductions of their operating costs;
- improve energy independence.

In view of the above, the European Biofuel Technology Platform corrected its Strategic Research Agenda for Biofuels early in 2010. That correction involved technological progress and the need to intensify efforts to reduce GHG emissions. Moreover, the following biofuel groups were defined for their specific uses:

- synthetic fuels / hydrocarbons from gasification of biomass, for application as: transportation fuels from RES (Renewable Energy Sources) for aviation engines and spontaneous-ignition engines;
- biomethane and other gaseous fuels from gasification of biomass (substitutes for natural gas and other gaseous fuels) for application as: motor fuels and in high-efficiency generation of energy;
- biofuels (bioliquids) from biomass, obtained through thermochemical processes other than pyrolysis, for application as: heating fuels, in generation of energy or, indirectly, through xTL processes, as transportation fuels;

- ethanol and higher alcohols from sugar-containing biomass, for application as transportation fuels from RES or as a component of E85 gasoline;
- hydrocarbons from biomass, obtained from saccharides, produced in biological and/or chemical processes, for application as renewable transportation fuels for aviation engines and spontaneous-ignition engines;
- biofuels obtained through the use of carbon dioxide in the production of microorganisms in biotechnological processes or from the direct synthesis of waste carbon dioxide and steam in catalyzed thermochemical processes (application in transportation fuels from RES and aviation fuels).

The above definitions include the production of biofuels which were earlier defined in SRA, such as bioDME, bioDMF and other furan derivatives, FT-diesel, HTU-diesel, as well as fuels from hydrogenation of waste vegetable oils and animal feeds which are not useful in the food industry, in HVO processes.

Regardless of the above, the International Energy Agency (IEA) has developed a Biofuel for Transport Roadmap where the need has also been included for the sustained development and reduced emissions of GHG through the utilization of carbon dioxide, among other methods. This is in conformity with the European Directive which, in its Preamble, recommends that ”The Community should take appropriate steps in the context of this Directive, including the promotion of sustainability criteria for biofuels and the development of second- and third-generation biofuels in the Community and worldwide...”.

Considering the principal purpose of using biofuels as fuels or fuel components, which results from the need to reduce carbon dioxide emissions, it is also reasonable to assess their potential as biofuels which can be obtained by utilization of spent carbon dioxide in the production of energy carriers for the needs of transport. The efforts made in this field may be illustrated by studies conducted in the USA, where syngas is produced from carbon dioxide and steam in a catalytic process with the use of solar energy.

Having in mind earlier experiences and research findings, a tendency in the foreseeable future should be to make biofuels as hydrocarbon blends which are obtained according to specific process routes. Those routes will enable the obtaining of alternative fuels for combustion engines while closing the CO_2 cycle. Hence, the fuels of the future should comprise:

- synthetic fuels as blends of hydrocarbons from biomass gasification and from pyrolysis processes;
- biomass-based biofuels obtained through other thermochemical processes, such as, pyrolysis, depolymerization processes and hydrogenation of biomass decomposition products;
- fuel compositions, blended with the use of hydrocarbons obtained from biomass which meet the quality requirements for motor fuels, inclusive of those obtained directly and indirectly from saccharides in biological and/or chemical processes;
- biofuels which are other derivatives of saccharides, inclusive of cellulose, which meet the requirements for motor fuels;

- biomethane and other gaseous fuels from biomass gasification processes and/or from purification processes of biogas from agricultural sources, landfill facilities and sewage sludge (substitutes of natural gas and other gaseous fuels);
- bioethanol and higher alcohols (biobutanol) and their derivatives obtained from biomass in biochemical and/or in catalytic thermochemical processes;
- biofuels obtained from carbon dioxide converted by microorganisms or from the direct or indirect synthesis which converts naturally occurring carbon dioxide in thermo-and biochemical processes;
- biofuels obtained from syngas by direct or indirect (through methanol) conversion of biomass and/or GHG;
- biofuels (HVO), obtained from hydrogenation processes of waste vegetable and animal fats.

The present knowledge and the research conducted in Polish and international R&D centers, and in the Seventh Framework Programme and the Polish and European Biofuel Technology Platforms, defined the areas of use for biofuels in transport and power engineering. Thus, the following can be considered as biofuels and alternative fuels for spark-ignition engines:

- ethanol;
- methanol;
- other alcohols (e.g.: *tert*-butyl – TBA, *sec*-butyl – SBA, isopropyl – IPA and neopentyl – NPA alcohols);
- ethers (ethyl-*tert*-amyl ether – TAEE, ethyl-*tert*-butyl ether – ETBE, methyl-*tert*-amyl ether – TAME, methyl-*tert*-butyl ether – MTBE and diisopropyl ether – DIPE);
- synthetic hydrocarbon fuels;
- biomethane;
- liquefied petroleum gas;
- hydrogen.

Within spontaneous-ignition engines, efforts are being made to obtain and implement the following alternative fuels, based principally on biomass:

- methyl and ethyl esters of fatty acids, FAME and FAEE, respectively, from transesterification processes of rapeseed oil, sunflower oil, soybean oil, and other oils;
- dimethyl ether (DME); the use of diethyl ether (DEE) is also considered;
- fuel-water emulsions (Aquazole);
- pure vegetable oils;
- synthetic hydrocarbon fuels.

The following fuels have also been taken into consideration for stationary applications:

- alcohols;
- esters of higher fatty acids;
- tall-based fuels (TPO-tall pitch oils) obtained by esterification of tall oils with ethyl alcohol or methyl alcohol, with tall oils being recovered from coniferous-tree resins (by-products from the production of sulfated cellulose and from low-temperature carbonization of wood);
- fuels from pyrolysis processes;
- pure vegetable oils;
- biogas.

3. Changes in the properties of vegetable oils and FAME in storage and motor operating conditions

A pre-condition for the use of other fuels in spontaneous-ignition engines, yet without modifying the design of such engines, is that the properties of those fuels must be adjusted to those of petroleum fuels. The basic parameters to be considered before using vegetable-based fuels are include: kinematic viscosity, density, calorific value and combustion properties. Table 1 compares some selected properties of diesel oil, rapeseed oil and fatty acid methyl ester (FAME) from rapeseed oil (RME).

Parameter	Unit	Diesel oil	Pure rapeseed oil	Methyl ester
Kinematic viscosity at 20°C	mm/sec^2	2.8...8.0	68...75	6...8
Calorific value	MJ/kg	42...43	36...38	39.4...40.6
Cetane number	-	45...50	40...50	50...55(60)
Composition of air-fuel mixture	kg/kg	14.4...14.6	2.2...13	13.4...13.8
Density at 20°C	kg/dm^3	0.81...0.85	0.9...0.94	0.87...0.89
Cloud point	°C	-16*	18	-9
Cold filter plugging point	°C	-20*	-	-10
Setting point	°C	-35*	-26	-15
Sulfur content	%	0.15	0.002	0.002
Coke content	%	0.01	0.17-0.5	0.05
Flash point	°C	40...50	200...300	130
Initial boiling point	°C	175	300	300

*-for winter diesel oil

Table 1. Selected properties of biocomponents and diesel oil

Viscosity affects the auto-ignition process through the size of fuel droplets, the shape of the injected fuel stream and how far it reaches. From that point of view, vegetable oils offer much inferior parameters as compared with those of diesel oil.

It should also be noted that the droplet size for rapeseed oil is about four times as high as that for hydrocarbon/petroleum diesel oil. What is essential, is the advantageous effect of transesterification of rapeseed oil since the average droplet size of rapeseed oil methyl esters is only twice that of diesel oil.

The calorific values of methyl esters and pure rapeseed oil are by about 12 % lower than those for the conventional hydrocarbon fuel. Combustion of biodiesel is more complete because oxygen atoms are present in the chemical molecules, and biocomponents, when added to regular diesel oil, increase its density.

The differences in the performance of standard rapeseed oil and its methyl esters are shown in Figure 1. Diesel oil has a rather wide pretty wide boiling range (180...380°C), while biofuels boil in a relatively narrow range (about 380°C). That narrow boiling range of FAME may be the reason for operating problems, especially for engine starting at low ambient temperatures. It should be stressed that vegetable-based fuels will solidify more easily at low temperatures.

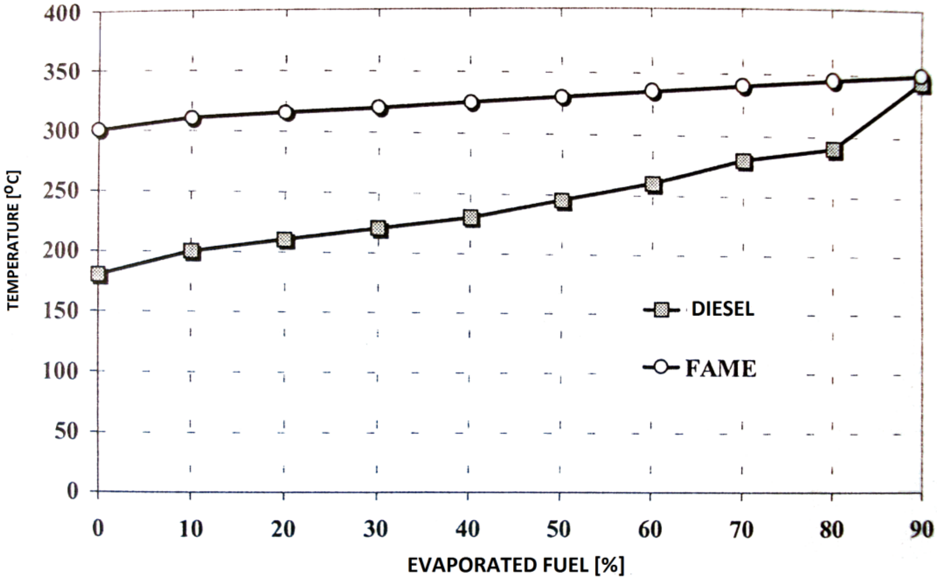
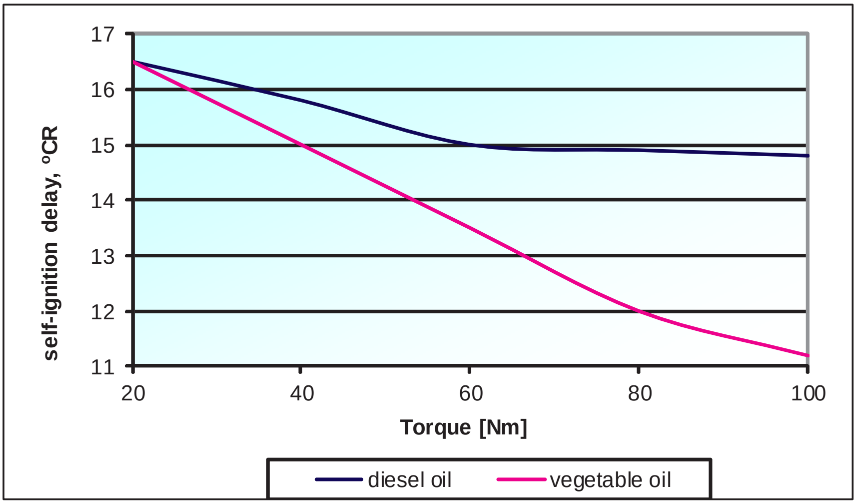


Figure 1. Boiling range for diesel oil – ON, methyl ester of rapeseed oil acids – FAME *(with consent of "Przemysł Chemiczny").*

The cetane number is a universal comparative measure but not a physical parameter of fuels. Vegetable oil molecules have completely different chemical structures than hydrocarbon molecules of diesel oil fractions because vegetable oils are predominantly composed of fatty acid glycerine esters and are usually in the form of triglycerides. Hence, different performances may be expected for both fuel types within their self-ignition delay parameters.

The cetane number (CN) for natural rapeseed oil is 37.6, while the value for rapeseed oil methyl esters falls in the range 54...58. As can be seen, the CN values are generally lower for pure rapeseed oil but are higher for rapeseed oil methyl ethers, compared with those for diesel oil. In motor tests, when those fuel types were used, no clear relation was identified between the cetane number value and the self-ignition delay. For example, the self-ignition delay time for diesel oil with a biocomponent added is shorter in a hot engine than for pure diesel oil, while it is harder to start an engine running on a vegetable-based fuel. The possibility is high that the same relationship exists between the cetane number and the self-ignition delay in engines for those fuels as for diesel oil.

In low temperature conditions inside a cylinder, at idle run, and at low engine loads, the self-ignition (spontaneous ignition, or compression-ignition) potential for vegetable oils is generally lower than that for diesel oil. At high temperatures, on the other hand, i.e., at high engine loads, the spontaneous-ignition performance of vegetable oils may be even better as compared with diesel oil, which is shown in Figure 2.



(sources J. Maćkowski, "Motor Fuels beginning of the XXI century" Publisher: Automobile Diagnostic Training Center, Katowice, 2002)

Figure 2. Effects of engine load on self-ignition delay for diesel oil and for rapeseed oil

As can be seen in Fig. 2, the self-ignition delay declines much faster for vegetable oil than for diesel oil, at increasing engine loads. When some volume of diesel oil is replaced with rapeseed oil, the self-ignition delay time will be reduced. The tests confirm that the cetane number value (as found in motor tests) gives no grounds for speculating on the self-ignition potential of vegetable-based fuels in various engine operating conditions because the effects of combustion chamber temperatures on self-ignition delays of those fuels are highly various.

Tests and measurements show that higher cetane numbers for rapeseed oil methyl esters do not provide a sound basis to expect any easier engine start when that fuel is used.

This has been confirmed by engine start tests in four farm tractors, powered with the use of methyl esters of rapeseed fatty acids. The tests failed to reveal any advantageous effect of higher cetane numbers leading to an easier engine start. A steep rise in viscosity of that fuel was also demonstrated at temperatures below-10°C, which is an additional factor affecting the engine starting properties of fuels and which in effect reduces the fuel starting charge.

A significant problem encountered in operating compression-ignition engines fuelled with FAME is that the kinematic viscosity of esters varies with temperature. The relationship is shown in Figure 3. The profile for the viscosity decrease curve indicates as well that the fuel's low-temperature properties have deteriorated. This is not expected to pose any problem in the summer or in the transition period but may lead to difficulties in engine starting or make it impossible at all in the winter. Moreover, higher viscosities are known to affect the course of fuel atomization and to cause increased injection pressures by approx. 15%, compared with diesel oil. This takes place because larger fuel drops tend to evaporate more slowly (approx. 1.5 times as slowly as diesel oil) in the combustion chamber, leading to longer initial phases of fuel self-ignition and, ultimately, to longer combustion times. An optimum solution would be to use a fuel pre-heating system (manual or automated), depending on the values shown by the temperature sensor. The solution would involve modifications in the region between the injection pump and the injectors to enable the correct engine start – as well in the fuel tank to enable the correct further operation of the unit. While the technological solution requires serious modifications, the easier way to achieve the required low-temperature properties is to simply add dedicated depressants to FAME.

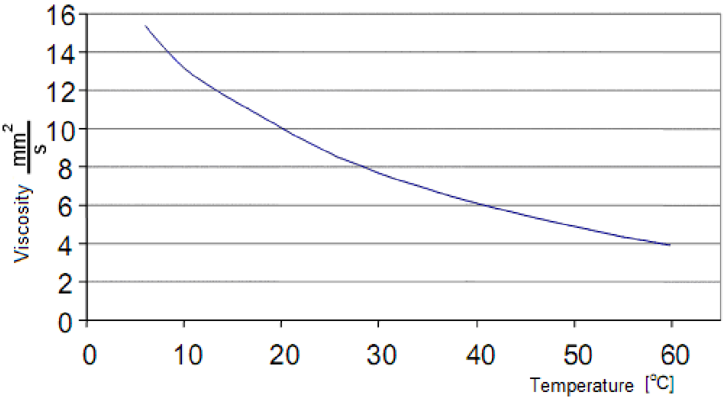


Figure 3. Effect of temperature on viscosity for FAME *(with consent of "Przemysł Chemiczny").*

Rapeseed oil is composed mainly of fatty acid glycerine esters, in the form of triglycerides. These are mixed triglycerides, formed by reacting glycerine with saturated fatty acids: palmitic acid ($C_{15}H_{31}COOH$) and stearic acid ($C_{17}H_{35}COOH$), and with unsaturated acids: oleic acid ($C_{17}H_{33}COOH$) and linoleic acid ($C_{17}H_{31}COOH$).

Oil fluidity increases for higher levels of unsaturated fatty acid esters, this involves lowering of oil viscosity and freezing point. Rapeseed oil has a freezing point of-26°C, which makes the material applicable also in winter conditions without any extra additives. However, for rapeseed oil, viscosity is 20 times as high as that for diesel oil, making difficulties in pumping and spraying the fuel; it may be necessary to heat up the fuel or air before feeding the fuel to the injection system. The rapeseed molecules contain oxygen and hence less air is required for fuel combustion than in the case of diesel oil. The calorific value per mass unit is thus lower than that for rapeseed oil. Rapeseed oil, on the other hand, has a higher density (by about 10 %), so that the "volumetric" calorific values are similar for both fuels.

The distillation curve profiles for vegetable oils are also connected with higher amounts of deposits in the combustion chambers and injectors. These may have an adverse effect on engine operation, causing extensive wear of the piston units. That situation results from relatively large and heavy molecules of triglycerides, as compared with diesel oil hydrocarbon molecules. In order to eliminate such problems, attempts have been made to eliminate glycerides from oil droplets by alcoholysis with methanol (methanolysis), followed by conversion of glycerine esters, i.e., substitution of the methyl group CH_3 instead of the glycerine group, which yields lower molecules. This method is used for manufacturing methyl esters of rapeseed oil fatty acids, which may be used directly as a fuel or as a fuel additive (5 %). The by-product from that process, glycerine, can be relatively easily separated from the ester product. The following advantages are obtained: lower fuel density and viscosity, higher volatility, and possible reduction of deposits inside the engine. The presence of esters also reduces the amount of solids and improves lubricity of diesel oils (otherwise, after elimination of sulfur from diesel oil, lubricity improvers would need to be used to prevent precision component pairs from seizing up). The use of methyl esters also has some drawbacks: high viscosity and loss of fluidity at lower temperatures, hygroscopicity and the resulting risk of extensive corrosion, potential deposits in the engine exhaust system. It is also necessary to replace gaskets and flexible tubing and to use elements made of fluorinated elastomers. The World-wide Fuel Charter which was signed by major global producers of engines and motor-cars recommends to avoid adding more than 5 % esters to conventional diesel oils. However, there are exceptions from that rule, e.g., "Skoda" and some other car manufacturers in the Czech Republic and in Germany accept the use of pure biodiesel, and "Peugeot" accepts the content of up to 30 % esters in diesel oil.

It is possible to use esters of vegetable oil fatty acids as fuels for spontaneous-ignition engines. Esters are obtained by transesterification, which involves a catalyzed chemical reaction of vegetable oil triglycerides and methyl alcohol or ethyl alcohol. Rape seeds make the most commonly used feed for the production of esters in Europe, including Poland.

Esterification processes give rapeseed oil fatty acid methyl esters (FAME), which may be used as pure esters or after blending them with diesel oils.

The FAME vegetable-based fuel is a mixture of methyl esters of rapeseed oil organic acids containing between 16 and 22 carbon atoms per molecule. The petroleum diesel oil is a mixture of hydrocarbons with boiling points from 150 to 380°C. It is produced by petroleum distillation and by secondary processing of heavy fractions (distillation residue). Diesel oils are composed predominantly of saturated aliphatic hydrocarbons and cycloalkanes with 14 to 20 carbon atoms per molecule, and of aromatic hydrocarbons. The shares of the respective hydrocarbon groups in a diesel oil product are decisive for its physico-chemical properties and affect engine performance and toxicity of exhaust gases.

Diesel oils and rapeseed oil esters are fuels obtained from different raw materials, therefore, they have different chemical compositions and different physico-chemical properties. Esters contain fewer carbon and hydrogen atoms and about 12 % more oxygen. That higher oxygen content results in lower calorific values of vegetable-based fuels. The presence of oxygen in ester molecules is favorable for the microbial growth which changes the fuel characteristics. Esters will dissolve more water than hydrocarbons, hence, biodegradability of vegetable-based fuels will be higher than that of hydrocarbons. The presence of unsaturated bonds in ester molecules leads to worse oxidation stabilities. The oxygen content in biofuels also adds some advantages: their combustibility is superior and the combustion process is more intensive and complete. This favors reduction of hydrocarbon and carbon monoxide emissions, as well as smoke level in exhaust gas, though it also increases combustion temperature and nitrogen oxide emissions. Rapeseed oil methyl esters offer higher densities and viscosities, compared with diesel oils, leading to better lubrication properties which improve the service life of fuel systems. Ester additions to low-sulfur diesel oils improves lubrication properties of the latter. The use of esters, however, may intensify deposits in the combustion chamber and fuel injectors. Esters have inferior low-temperature performance properties. They cannot be used in winter conditions unless dedicated additives are used. FAME are aggressive to rubber, to some plastics, and paint coats. Fatty acid methyl esters are miscible with diesel oils, at any proportion, which makes them useful in powering spontaneous-ignition engines.

Parameter	Value	Unit	Test method
Content of esters Methyl Esters of Linolenic Acid Methyl Esters of Poly-unsaturated Acids ("/> 4 double bonds)	96.5 min 12.0 max 1 max	% m/m % m/m % m/m	EN 14103 Other: ABNT NBR 15342 EN 14103 prEN 15779
Induction period	10 min	h	prEN 15751 or alternatively EN 14112
Iodine number	130 max	g I_2/100 g	EN 14111
Total acid number	0.50 max	mg KOH/g	ISO 6618 ASTM D664, D974 JIS K2501 Other: ABNT NBR 14448

Parameter	Value	Unit	Test method
Methanol	0.20 max	% m/m	EN 14110 JIS K2536 Other: ABNT NBR 15343
Glycerides Monoglycerides Diglycerides Triglycerides Glycerol Free glycerols Total glycerol:	 0.80 max 0.20 max 0.20 max 0.02 max 0.25 max	 % m/m % m/m % m/m % m/m % m/m	EN 14105 EN 14105 ASTM D6584 Other: ABNT NBR 15342 EN 14105 ASTM D6584 Other: ABNT NBR 15342 EN 14105 ASTM D6584 Other: ABNT NBR 15342 EN 14105/14106 ASTM D 6584 Other: ABNT NBR 15341 EN 14105 ASTM D 6584 Other: ABNT NBR 15344
Density	Report	g/ml	EN ISO 3675 ASTM D4052 JIS K2249 Other: EN ISO 12185, ABNT NBR 7148/14065
Kinematic viscosity @ 40°C	2.0-5.0	mm^2/sec	EN ISO 3104 ASTM D445 JIS K2283 Other: ABNT NBR 10441
Flash point	100 min	°C	ISO 3679 ASTM D93
Cetane number	51 min		ISO 5165 ASTM D613 JIS K2280
Water Water and deposits Impurities	500 max 0.05 max 24 max	mg/kg % v/v mg/kg	EN 12937 ASTM D2709 EN 12662 ASTM D2276, D5452, D6217
Ash content Incineration residue	0.001 max 0.005 max	% m/m % m/m	ISO 6245 ASTM D482 JIS K2272

Parameter	Value	Unit	Test method
			ISO 3987 ASTM D874 Other: ABNT NBR 984
Ramsbottom Carbon Residue, per 100 % distillation residue	0.05 max	% m/m	ASTM D4530
Corrosion: iron	some traces max.	assessment	ASTM D665 Procedure A
Sulfur	10 max	ppm	EN 20846/20884 ASTM D5453 /D2622 JIS K3541-1, -2, -6 or -7
Phosphorus	4 max	mg/kg	EN 14107 ASTM D4951, D3231
Alkali (group I) metals (Na+K)	5 max	mg/kg	EN 14108/14109, EN 14538
Alkali (group II) metals (Ca+Mg)	5 max	mg/kg	EN 14538
Trace metals	-	no willful addition	ASTM D7111

Table 2. Requirements for FAME, used as diesel additives, according to WWFC guidelines (March 2009)

The permissible duration of storage for pure esters is the subject of dedicated tests being carried out to determine the parameter. In general, it is not recommended to store pure esters for more than 12 months under typical storage conditions in closed tanks, in the absence of air or direct sunlight. It is just because of the fears for the stability of esters in long-term storage conditions that biodiesels may not be used in combat vehicles in the US army. The long-term storage of diesel-esters mixtures has not been sufficiently documented yet but it is safe to assume that their storage period is comparable to that for pure esters. As a rule, fuels should be stored in underground tanks while ground-based tanks should be provided with adequate thermal protection.

The problems faced in the manufacturing of fuel components, biofuels and final products from the middle-distillate group involve product protection issues beyond the short period of time during which the fuels are kept within the production facility. Laboratory analyses are provided to establish the acceptable fuel storage time.

4. Alcohols as fuel components

Methyl alcohol (methanol) is usually synthesized from natural gas. The first step in the production process makes use of steam reforming to convert natural gas into syngas and to adjust the CO / H_2 ratio to the required value, according to the reactions:

$$\mathrm{CH_4 + H_2O = CO + 3\ H_2}$$

$$\mathrm{CO + H_2O = CO_2 + H_2}$$

In the second step, after removal of contaminants, carbon monoxide and hydrogen are catalytically reacted to form methanol:

$$\mathrm{CO} + 2\ \mathrm{H_2} = \mathrm{CH_3OH}$$
$$\mathrm{CO_2} + 2\ \mathrm{H_2} = \mathrm{CH_3OH} + \mathrm{H_2O}$$

Methanol can be produced from biomass (cellulose, wood-based in most cases); it is technically feasible but not commercially viable at present. The raw material is to be converted into syngas which can be then processed into methanol. The raw material must be initially prepared by fragmentation, grinding and drying. Syngas is then obtained by gasification, i.e., by combustion in equilibrium with the supplied oxygen, to produce carbon monoxide and hydrogen, unlike in normal combustion which gives carbon dioxide and water. A portion of syngas is formed by oxidation of biomass and another portion – by steam reforming (pyrolysis). Crude syngas is then converted into methanol in the way which is similar to that for syngas, obtained from natural gas.

Methanol is frequently used in vehicles which are powered by fuel cells. As hydrogen is needed for fuel cells, it is produced just within such vehicles from methanol.

Methanol may also be used by reacting it with isobutylene to obtain methyl-*tert*-butyl ether (MTBE) – a high-octane component of gasoline.

The consumption of methanol as a propulsion agent for vehicles is relatively high, in particular that derived from biomass. Hydrocarbon emissions are high, especially for methanol obtained from natural gas. Carbon dioxide emissions for biomass-based methanol may be very low. As regards the rate of evaporation, it is low for methanol which leads to another very important advantage: its emission through evaporation is lower than that for petroleum. The storage conditions for methanol are shown in Table 3.

Storage		**Safety**					
		Combustion of vapor					
Weight*	Volume*	In open air	In confined space	In tank	Toxicity	Pollution of ground water	Atmospheric pollution
191	176	No risk	Risk	Very high risk	High risk	High risk	Very high risk

*) Weight and volume make the per-cent equivalent for 46 kg (~ 68 liters) of gasoline.

Table 3. Storage and safety characteristics for methanol

Alcohols may easily form explosive vapor-air mixtures within the gas space of a fuel tank at ambient temperatures. However, as regards accidents involving methanol-powered vehicles, the risk of explosion is lower than for gasoline since the rate of evaporation is lower for methanol and the fuel remains liquid. Methanol is a poison; it is toxic because of its decarboxylase taking place in the human body, which produces methanal (formaldehyde). Methanol is biodegradable.

As regards alcohol-based fuels, the principal emission connected with the production of methanol comes from the energy which is used in the synthesis processes. For natural gas-based methanol, apart from emissions of methanol itself, hydrocarbons are also released in methane effluents/leakages. CO_2 emissions arising in the production process may be equal to zero when biomass is used in the conversion process since some volumes of CO_2 are absorbed by the plants in the course of their growth. The production of wood-based methanol leaves ash as the residue.

Although the properties of ethyl alcohol (ethanol) are much similar to those of methanol, the production of ethanol is usually based on biomass (crops which are rich in sugar, starch or cellulose), and less frequently on natural gas. Yeast fermentation is required for the production of ethanol. Sugar in the form of glucose occurs in a few plant species only. Raw materials are subjected to fragmentation/grinding, and then longer molecular chains in the fermented sugar are broken down by hydrolysis. The diversity of hydrolysis techniques reveals most important differences in the production methods which are required for various raw materials. The dominant content of glucose may be extracted directly from the plants and then only mild hydrolysis conditions are required. For starch crops, the enzymatic hydrolysis technology is employed. The acid hydrolysis needs to be used for cellulose.

Ethanol for industrial use is obtained through fermentation of saccharides which become available after hydrolysis of wood or from sulfite waste liquor. Synthetic ethanol is produced in chemical processes. Although the manufacturing costs for bioethanol have dropped down recently, they still remain rather high. The bioethanol production costs are strongly affected by the cost of raw material which is as high as about (60...70) % and by the volume of production. Moreover, the cost of energy which should be added is not insignificant. What is also important for the reduction of ethanol production costs is the management and disposal of the production residual materials; the general manufacturing costs can be further cut down in this way by about (15...20) %.

A few methods have been developed for the production of bioethanol which can clearly reduce production costs: they include the use of improved bacterial strains, the use of wet milling which accelerates saccharification, or the use of reverse osmosis with synthetic membranes employed for separation in order to improve alcohol recovery from the fermentation products.

Within the use of ethanol as an energy carrier, the second-generation enzymatic processes have been developed now for the production of bioethanol from such materials as straw, waste wood, etc. Such processes are reported to have been partially implemented so far.

Emissions from the ethanol production depend on the fuel consumption involved in generation of power and steam which are indispensable for the process. CO_2 emissions relating to the production may be low when biomass is used in the conversion process since some volumes of CO_2 are absorbed by the plants in the course of their growth. Emissions from the production of cellulose-based ethanol are higher than those noted for sugar-rich or starch-rich feeds since more energy is needed for the conversion of cellulose.

Ethyl-*tert*-butyl ether (ETBE), ethanol derivative, is a 100% value component of motor spirits – there is no need to employ any additional preventive measures in the logistics or use of such gasoline. The production capacity for that ether in EU countries is unfortunately limited and cannot be expanded because of the short supplies of isobutylene. Hence, most bioethanol will be added to motor spirits directly. Moreover, it can be concluded from the above considerations relating to energy that considerable volumes of motor spirits will be required to have a bioethanol content of more than 5 % (v/v). Additional protective means will be necessary in the logistics of such fuels (elimination of moisture, completely enclosed vessels, equipment and transfer processes, etc.). Moreover, such fuels should be used in dedicated vehicles only to eliminate negative environmental impacts.

In 2009, attention was brought by the automotive industry to the fact that motor spirits will have a content of anhydrous ethyl alcohol. Without changing their viewpoints on the need to restrict the use of the component, engine and car manufacturers established the quality requirements for ethanol in their guidelines (issued in March 2009). The requirements can be found in Table 4 below.

Parameter	**Value**	**Unit**	**Test method**
Ethanol + saturated alcohols C3-C5 (dewatered)	99.2 min	% m/m	EN 15721 ASTM D5501 Other: JAAS001-6.2
Saturated alcohols C3-C5 (dewatered)	2 max	% m/m	EN 15721
Methanol	0.5 max	% m/m	EN 15721 ASTM D5501
Water content	0.3 max	% m/m	EN 15489 ASTM E203 JIS K8101
Density	Report	kg/m^3	ASTM D4052 Other: ABNT NBR 5992
Electrical conductance	500 max	µS/m	ASTM D1125 JIS K0130 Other: ABNT NBR 10547
Inorganic chlorine	10.0 max	mg/l	EN 15484 or EN 15492 ASTM D7319, D7328 Other: ABNT NBR 10894/10895
Sulfates	4 max	mg/kg	EN 15492 ASTM D7318, D7319, D7328 Other: ABNT NBR 10894/12120
Copper	0.100 max	mg/kg (ppm)	EN 15488 ASTM D1688 modified, Method A JIS K0101 Other: ABNT NBR 10893

Parameter	Value	Unit	Test method
Organic impurities	10 max (1 max)	mg/l (% m/m)	JIS JAAS001 – 6.4
Phosphorus	0.50 max	mg/l	EN 15487 ASTM D3231
Sulfur	10 max	mg/kg or ppm	EN 15486 ASTM D5453 (< 20 ppm) JIS K2541
Heavy metals	Undetectable (traces)		Other: ICP-AES
Non-volatile matter	5 max	mg/100 ml	prEN 15691 ASTM D381 JIS JAAS001 – 6.3 Other: ABNT NBR 8644
pH	6.5-9 6-8		ASTM D6423 EN 15490 JIS JASO M361-6.10 Other: ABNT NBR 10891
Acidity	0.007 max	% m/m	EN 15491 ASTM D1613 Other: ISO 1388/2; ABNT NBR 9866
Appearance	No visible impurities		Visual inspection
Color			Visual inspection

Table 4. Requirements for ethyl alcohol employed as a gasoline additive, according to WWFC guidelines (March 2009)

5. Conclusion

The growing energy crisis and restrictions in the emissions of GHG create the need (which is also boosted by regulatory provisions) to use new types of gasoline components which are not derived from petroleum feedstocks, mainly to use biocomponents, such as ethanol, FAME, etc. The course of the oxidation (ageing) process(es) of fuels which contain those components has not been established so far. Nonetheless, applicable European documents (road maps) define the process routes for the production of new components based on lignocellulose, waste, biogas, natural gas, coal, and even syngas production processes from carbon dioxide and steam (BtL, WtL, GtL and xtL processes). The course and rate of ageing (oxidation) processes should be established also for such components and for their blends with petroleum hydrocarbons.

Because of the tendency of ethyl alcohol to form mixtures (solutions) with water at any ratios (including azeotropes), because of its oxidative and corrosive impacts, and low chemical stability of FAME’s and their possible oxidation, there is a scarcity of unambiguous information indicating the permissible duration of storage and analytical methods that may be required. As mentioned before, pure esters can probably be stored for up to 12 months if placed in tightly closed tanks/containers which are insensitive to temperature fluctuations.

Adding FAME's to the pool of fuel components and biofuels affects the fuel stability, hence, such fuels cannot be stored for long periods of time. Based on the collected data, it is evaluated that the oxidative stability of FAME after one month of storage goes down below the quality requirements in some cases, thus leading to changes in the values of other parameters. The use of improver additives makes it possible to extend the storage time up to about 8 months. Research studies are in progress on the use of tailored antioxidant packages in biofuel formulations. Our own findings indicate that the antioxidant additives which are used at present will inhibit oxidation of esters but they may at the same time have an adverse effect on the oxidation of petroleum hydrocarbons.

The above discussion shows clearly that we are facing the growing trend to modify compositions of the present-day motor fuels. Those changes result principally from the obligation being imposed on fuel manufacturers to add into fuel blends components obtained from renewable sources, with unstable compositions. Since the available resources of crude oil are becoming shorter and shorter while the fuel consumption keeps growing, it is expected that more and more alternative components will be added into fuel blends. With the components derived from various waste materials, it will be harder and harder to predict the rates of fuel oxidation processes and to define the permissible durations of storage. It was found for biocomponents used in fuels that the standard requirements for petroleum fuels and for some biocomponents are maintained. However, mixtures of those components (FAMEs) fail to meet the requirements of oxidation tests. Regardless of the above, the fuel compositions of the future must satisfy the conditions as defined in LCA, inclusive of the WtW cycle for fuels.

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References

[1] K. Biernat, A. Kulczycki „Prognoza rozwoju biopaliw w Polsce", Krajowa Konferencja: "Rynek biopaliw w Polsce – szanse i zagrożenia" [*A forecast for the development of biofuels in Poland,* National Conference *The biofuels market in Poland – opportunities and risks*], Warsaw, April 2006.

[2] K. Biernat „Biopaliwa drugiej generacji", Krajowa Konferencja Biopaliw i Biokomponentów [*2nd generation biofuels,* conference proceedings*: National Conference on Biofuels and Biocomponents*], Gdańsk, October 2006.

[3] K. Biernat, J. Głąb, „Analiza wymagań technicznych, normatywnych oraz wytycznych jakościowych produkcji i stosowania biopaliw w Polsce", Krajowa Konferencja „Biopaliwa w Polsce" [*Analysis of technical and normative requirements and qualitative guidelines for the production and use of biofuels in Poland", Conference proceedings: "Biofuels in Poland" – National Conference*], Warsaw, November 2006.

[4] K. Biernat, A. Kulczycki, M. Rogulska: „Development of Alternative Fuels in Poland", conference proceedings "Expert Workshop on Biofuels Support in Baltic States, Nordic Countries and Poland". Tallin, Estonia, February 2007.

[5] K. Biernat, M.Mielczarska-Rogulska, "Implementation and Properties of Biofuels and Biocomponents", conference proceedings "European Transport in FP 7", Warsaw, March 2007.

[6] K. Maniatis "Biofuels EU policy and recent developments", conference proceedings: Materiały drugiego spotkania Mirror Group ETPB, Brussels, February 2007.

[7] W. Górski „Biopaliwa w normach: ISO, EN i PN" [*Biofuels according to ISO, EN, PN standards*],, „Przemysł Chemiczny" December 2006.

[8] B. E. Kampman, L.C. den Boer, H.J.Croezen, "Biofuels under development", Publication CE No 05.4894.11, Netherlands Petroleum Industry Association, Delft, May 2005.

[9] Ethanol Guidelines, From the Worldwide Fuel Charter Committee, March 2009.

[10] Biodiesel Guidelines, From the Worldwide Fuel Charter Committee, March 2009.

[11] A. Jeziorkowski, K. Biernat, "Możliwości dostosowania współczesnych silników spalinowych do zasilania biopaliwami" [*Opportunities for adapting contemporary combustion engines to being fuelled with biofuels*], "Przemysł Chemiczny" " No. 3/2009, pp. 234-240.

[12] K. Biernat, P. Dziołak, „Bio 2,5-dimetylofuran (BioDMF) jako nowe biopaliwo drugiej generacji" [*Bio 2,5-dimethylfuran (BioDMF) as a new* 2nd *generation biofuel*], Miesięcznik Naukowo-Techniczny „Chemik, Nauka, Technika, Rynek" No. 12, December 2008 pp.657-661.

[13] K. Biernat, A. Malinowski, M. Gnat: Chapter No 4, in Monograph, Editor:. Zhen Fang, Title: „Biofuels-Environment and Sustainability", Edition by "InTech", December 2012, ISBN 980-953-307-471-4: "The possibility of future biofuels production using waste carbon dioxide and solar energy".

Liquid Fuel Ageing Processes in Long-term Storage Conditions

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Additional information is available at the end of the chapter

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1. Introduction

As a result of the ever growing demand on liquid fuels and the ever more stringent qualitative criteria, to guarantee the high quality of the fuels during long-term storage is a priority. In consequence of various internal or external factors, processes occur in the fuels which lead to adverse physical or chemical changes and affect product's performance characteristics. The problem is particularly observable in first-generation bio-fuels: they have unstable composition, which causes problems with the development of efficient methods to protect them from ageing processes.

Discussed in this chapter are the nature and identification of changes which occur in petroleum-derived products during long-term storage. The physical and chemical properties and stability of the various hydrocarbons the petroleum products consist of are discussed, and factors which affect the rate of fuel degradation processes during storage are presented. Critical properties of petroleum products and biocomponents are selected, related to normative parameters, and measurement methods are proposed which enable the monitoring of changes in product quality.

2. The quality of engine fuels

Fuels are expected to be of high quality and to remain stable, even after prolonged storage. These aspects are governed by applicable laws, resulting from Directive 2003/17/EC of the European Parliament and of the Council of 3 March 2003 amending Directive 98/70/EC concerning the quality of gasoline and diesel fuel [1]. The EU member states have implemented fuel quality monitoring systems based on standard sampling and testing procedures. The principles of the organization and operation of a system of monitoring and control of the quality of fuels for use in vehicles for various applications have been set out. According to applicable laws, all fuels which are intended to be transported, stored or placed on the market must comply with qualitative requirements set out for the given type of fuel.

According to the quality standards that apply in Europe for gasoline (EN 228) and for diesel fuel (EN 590), the maximum permissible content of additives is 5% for bioethanol and 7% for FAME (*Fatty Acid Methyl Esters*).

3. Properties of fuels

Fuels are characterized by the following physical and chemical properties:

- evaporative power and ability to form a fuel blend, which characterize engine starting properties through the fuel’s fractional composition, vapor pressure, and volatility index,
- ignition and self-ignition temperature, which characterize ignition properties,
- octane number (RON – Research Octane Number, MON – Motor Octane Number for gasoline) and cetane number (CN for diesel fuel), which characterize an ability of combustion without knocking in normative conditions,
- resin content, which characterizes a tendency to form deposits,
- corrosive action and sulfur content, which characterize the effect of the fuel on metal parts of tanks, transport conduits and engine components,
- chemical stability (induction period, oxidation stability) which characterize the rate of oxidation and degradation of the fuel, formation of resinous compounds which affect the fuel’s quality during storage,
- tendency to form deposits – residue after coking and incineration, oxide ash and sulfate ash; they are a measure of mineral and organic contamination – metal compounds which may precipitate from the fuel when used in high-temperature conditions,
- content of water and mechanical impurities which affect quality (clarity, emulsion forming, corrosion, microbial growth, filter plugging),
- density and viscosity, which characterize flow along the tubes, filters and openings of nozzles, degree of atomization, range of evaporation stream range, and lubrication of injection system components,
- behavior at low temperatures (cloud point, cold filter plugging point, flow temperature), which characterize stability of fuels at low temperatures,
- lubrication properties, which have an effect on the wear and tear of the fuel system/fuel pump and on emission of pollutants.

Moreover, if a fuel has a content of biocomponents, it is important to know how susceptible it is to oxidation. Although no universal method exists to analyze every type of fuel, the following values are determined as a rule:

- iodine number – a measure of C=C double bonds, which are easily broken under the influence of oxygen; indirectly, it also indicates stability,
- acid value – represents the content of carboxylic groups in a chemical compound (they may induce corrosion in the presence of water),
- content of methanol, mono-, di-, tri-acylglycerol, and glycerol, indicating the purity of biocomponents.

Fuels have different compositions so the above parameters may or may not be a reliable indicator, therefore, it is necessary to continue research works on the subject.

Since it is necessary to maintain a high quality of products to be supplied to the end user, optimum storage conditions must be specified. Different raw materials and different processes of technology are used to produce biocomponents and this affects their physico-chemical properties, often to a quite large extent. In addition, since petroleum-based fuels are different in respect of structure and chemical composition, optimum storage conditions will suit the properties and requirements of every type of fuel/biofuel. The choice of qualitative criteria for fuels ought to stem from the necessity to determine those parameters only of which the values may change in the process of oxidation during long-term storage. The present authors believe that chemical stability, stability at low temperatures, and resistance to corrosion are the crucial properties. These criteria take into account factors which may change the quality of fuels, such as: structure, use at low temperatures, and storage conditions. The importance of such criteria may change, depending on the critical factor.

3.1. Chemical stability

Chemical stability of a fuel is understood as resistance to oxidation processes and to all chemical reactions that may be initiated by external factors (especially by atmospheric oxygen). Adverse changes which may occur lead to autocatalytic oxidation, polymerization and condensation of compounds which contain unsaturated bonds (olefins) and compounds of sulfur, oxygen, and nitrogen. As a result of oxidation, high-molecular resins are formed along with gums, insoluble deposits, and acidic compounds which may attack metals. Thermal stability of a fuel is defined as resistance to complex degradation processes that occur at elevated temperatures.

A number of theories describe the mechanisms of oxidation of petroleum products. The first known theories concerned, first of all, the mechanism of action of oxygen. Lavoisier and Schönbein [2] claimed that only the active form of oxygen (identified with ozone) is able to cause oxidation of fuel. A similar theory was proposed by Claussius [2], who maintained that there exist oxygen atoms with negative and positive polarity, which combine with neutral molecules of oxygen, forming anti-ozone and ozone. Other researchers were of the opinion that oxygen contains a certain balanced quantity of negative and positive ions of oxygen which oxidize substances to various extents (Vant Hoff [2]). That theory was challenged by still others, who believed that there is no difference between oxygen atoms and that substances are oxidized when breaking the oxygen molecule (Hoppe, Seiler [2]). At present, those theories have purely historical value.

Generally, it is assumed that the process of self-oxidation of a fuel occurs as the result of a number of radical-chain reactions, which can be divided into initiation, propagation, and termination reactions. The initiation reaction, also called initiation of the oxidation reaction chain, begins as a molecule of oxygen from the air attacks the C-H bond of hydrocarbons, of which the mechanism is described in the reactions below (1, 2):

$$RH + O_2 \rightarrow HO_2\bullet + R\bullet \tag{1}$$

$$2RH + O_2 \rightarrow= 2R\bullet + H_2O_2 \tag{2}$$

The initiation reaction produces alkyl radicals, which further react with oxygen to form hydroxyperoxides; they are aggressive oxidants.

The next step of the reactions, during which the chain growth and branching occur, includes propagation reactions which run according to the mechanism described below, in (3...7)

$$R\bullet + O_2 \rightarrow RO_2\bullet \tag{3}$$

$$RO_2\bullet + RH \rightarrow ROOH + R\bullet \tag{4}$$

$$ROOH \rightarrow RO\bullet + \bullet HO \tag{5}$$

$$RO\bullet + HR \rightarrow ROH + R\bullet \tag{6}$$

$$HO\bullet + HR \rightarrow H_2O + R\bullet \tag{7}$$

Decomposition of peroxides gives active alkoxyl and hydroxyl radicals which, in the next steps of the reaction, detach more hydrogen atoms from the hydrocarbons. These changes lead to the formation of aldehydes, ketones, acids or alcohols, having an adverse effect on the performance properties of petroleum-derived fuel [3].

The last step of self-oxidation of hydrocarbons is the reaction termination, or closing phase. Owing to recombination, free hydrocarbon radicals and peroxide radicals that have been formed are deactivated according to the reactions (8...10):

$$2R\bullet \rightarrow R-R \tag{8}$$

$$R\bullet + RCOO \rightarrow ROOR \tag{9}$$

$$2RCOO\bullet \rightarrow ROOR + O_2 \tag{10}$$

In addition to peroxide theories, descriptions of hydroxylation theories are found in available literature as well.

According to Bach and Engler [2], oxygen only reacts in its excitation state. One bond between oxygen atoms becomes weaker, according to (11):

$$O{=}O \rightarrow \text{-O-O-} \tag{11}$$

Readily oxidized substances A are oxidized by this form of oxygen, forming peroxides, an initial product of self-oxidation of hydrocarbons (the peroxide theory). A molecule of atmospheric oxygen, when contacted with the fuel, will behave like an unsaturated compound and may react without being broken into atoms beforehand, according to the reaction (12,13).

$$A + O_2 = AO_2 \tag{12}$$

$$AO_2 + B = AO + BO \tag{13}$$

where:

A – readily oxidized substance,

B – not-readily oxidized substance,

AO_2 – peroxide.

The resulting peroxides may give away part of their oxygen to other, less readily oxidized substances, which results in oxidation of the latter. The theory was confirmed by Czernożukow and Iwanow [4, 5]. Iwanow adapted the peroxide theory to the chain mechanism of oxidation of hydrocarbons. He maintained that the oxidation reaction is initiated by active hydrocarbon particles (oxygen attacks the C-H bond rather than the C-C bond which is weaker) and runs in accordance with the mechanism shown in Fig.1 below for the respective hydrocarbon groups.

A different theory, proposed by Siemionow [6], explains that oxygen attacks the C-H rather than the C-C bond, in the first place. Although C-C is weaker, it takes extra energy to break the C-C bond, because of the shielding effect of hydrogen atoms.

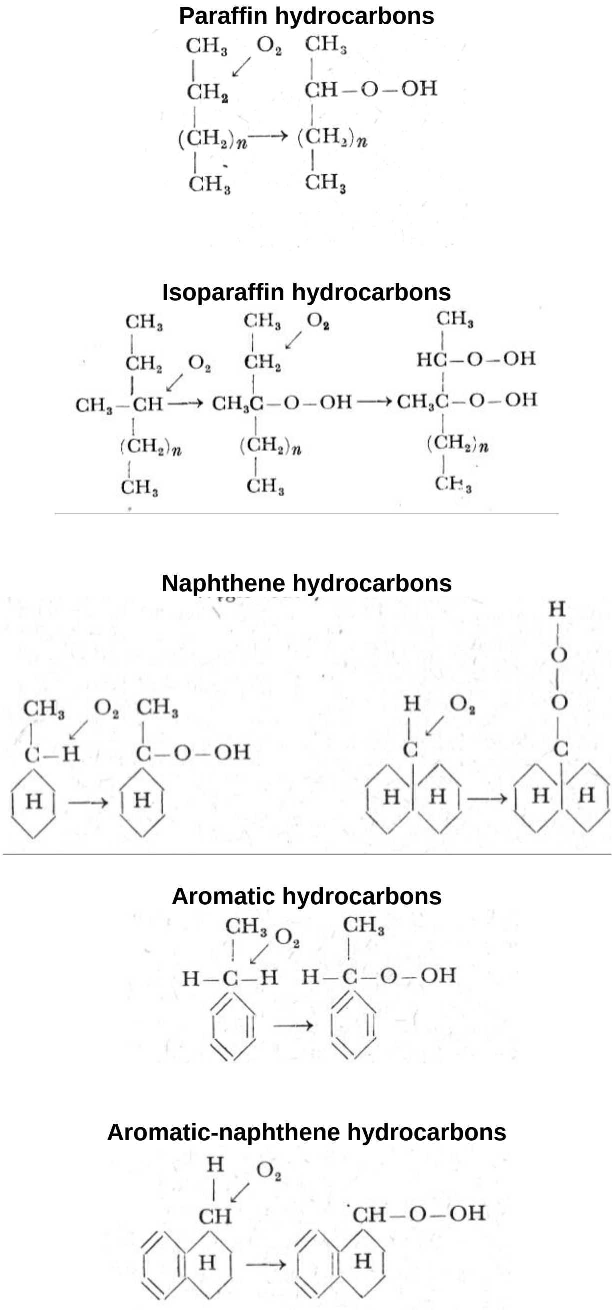

Figure 1. Step I of oxidation of hydrocarbons according to the peroxide theory [2].

The theory was based on a chain-like pathway of the oxidation process. In addition to final products, the reactions produce active or unstable bonds which initiate further changes; as a result, the reaction is repeated without participation of external factors, as shown below:

a. Backbone chain

$$CH_4O + O_2 \rightarrow CH_4O_2 + O \tag{14}$$

$$CH_4O_2 \rightarrow CH_2O + H_2O \tag{15}$$

$$CH_4 + O \rightarrow CH_4O \text{ etc.} \tag{16}$$

b. Chain scission

$$CH_2O + O_2 \rightarrow CH_2O_2 + O \tag{17}$$

$$CH_2O_2 \rightarrow H_2O + CO \tag{18}$$

c. Chain breaking

$$CH_2O + O_2 \rightarrow H_2O + CO_2 \tag{19}$$

$$2CH_2O + O_2 \rightarrow H_2O + 2CO \tag{20}$$

$$O + \text{wall} \rightarrow 1/2O_2 \tag{21}$$

Other authors maintain that free radicals (R*) are formed in the first step of oxidation of hydrocarbons according to the following reaction (22):

$$R\text{–}H \xrightarrow{\text{energy}} R^* \tag{22}$$

The resulting free alkyl radical reacts with atmospheric oxygen, forming a peroxide radical (ROO*), as in the previous theories. The peroxide radical reacts with another hydrocarbon molecule. The reaction products at this step are acid and one more alkyl radical, as shown in the reaction below (23, 24). These are chain-like reactions.

$$R^* + O2 \rightarrow ROO^* \qquad (23)$$

$$ROO^* + R–H \rightarrow ROOH + R^* \qquad (24)$$

In addition to reactions which accelerate the oxidation of hydrocarbons, there occur also ones that slow down the process. Alkyl radicals are able to combine, forming hydrocarbon molecules with different properties, compared with hydrocarbons in a fresh fuel.

$$R1^* + R2^* \rightarrow R1–R2 \qquad (25)$$

Some of the products of oxidation have acidic properties or readily become acidic compounds (the fuel's acid number is higher). Moreover, hydrolysis of esters (the biocomponent of the fuel) may occur, leading to higher acid content, as may be indicated by the ester value.

In addition to the peroxide theories, also proposed in the available literature is Bone's [7] hydroxylation theory. It says that alcohols are formed in the first step of oxidation, the process runs via a number of hydroxylation steps and peroxides are products of secondary reactions of aldehydes. However, the theory was criticized by others, who propose that the reaction starting from alcohols is not much probable because aldehydes are formed by dehydrogenation more readily than by hydroxylation. In addition, if alcohols actually were the first products of oxidation, then oxygen would dissociate into atoms. Objectors also maintained that alcohols may be formed by decomposition of peroxides. Speaking of energy, it is more probable that breaking the C-C and C-H bonds leads to peroxides rather than alcohols, since the latter require dissociation of oxygen.

Wiegand proposed a different theory, saying that the process of oxidation is activated by molecular hydrogen rather than by oxygen and that the process is reverse to hydrogenation [2].

Generally, the mechanisms governing fuel degradation and deposit formation include the following [8]:

- self-oxidation: a spontaneously catalyzed reaction of oxidation (typical process accompanying long-term storage of fuels in storage tanks),
- thermal oxidation (at temperatures higher than 200°C): a typical process for fuels which are in contact with hot surfaces in aircraft fuel systems,
- pyrolysis: decomposition of the structure of fuels and the formation of deposits due to thermal oxidation on very hot surfaces (deposits are formed in nozzles and sprayers).

The following are typical forms of degradation for different fuel types [8]:

a. for gasolines:
  - self-oxidation during storage,
  - rapid self-oxidation and thermal oxidation in the vehicle's fuel system.

b. for diesel fuel:

- self-oxidation during storage, condensation, esterification, and reactions involving acids and bases, forming insoluble microparticles and deposits in the fuel,
- thermal oxidation, during which deposits are formed in fuel injectors,
- pyrolysis, during which deposits are formed and accumulated over the injector surfaces and on moist surfaces of the combustion chamber.

c. for turbine oil:

- self-oxidation, during which resins and peroxides are formed,
- thermal oxidation, which leads to the formation of deposits over fuel-wetted, hot surfaces of heat exchangers, in valves and nozzles.

Shawn P., Heneghan and Long P. Chin proposed in [9] the radical-based mechanism of oxidation of hydrocarbons present in aircraft fuel:

a. initiation:

$$R-R\xrightarrow{k_1}R\cdot+R\cdot \tag{26}$$

b. propagation:

$$R\cdot+O_2\xrightarrow{k_2}RO_2\cdot \tag{27}$$

$$RO_2\cdot+RH\xrightarrow{k_3}RO_2H+R \tag{28}$$

c. termination:

$$RO_2\cdot+RO_2\cdot\xrightarrow{k_4}produkty \tag{29}$$

d. chain transfer

$$RO_2\cdot+AH\xrightarrow{k_5}RO_2H+A\cdot \tag{30}$$

e. autocatalysis

$$RO_2H+RO_2H\xrightarrow{k_6}ROH+RO_2\cdot+H_2O \tag{31}$$

$$RO_2H \xrightarrow{k_7} RO\cdot + OH\cdot \tag{32}$$

where:

RH – hydrocarbons contained in the fuel,

R , RO_2 – radicals,

AH – compounds with antioxidant properties, present in the fuel,

A – radical with low reactivity.

Considering the mechanism, Jones's research team proposed two possible pathways of the autocatalysis step, presented in reactions (31, 32). In the first case, the general reaction rate for oxidation of organic compounds which are present in fuels is expressed in Equation (33) [10]:

$$\frac{-d[O_2]}{dt} = k_3\left(\frac{R_i}{2k_4}\right)^{0,5} \cdot [RH] \tag{33}$$

where:

R_i – reaction rate of initiation step;

k_3, k_4 – reaction rate constants for (3) and (4);

[RH]-concentration of hydrocarbons.

Jones's research team demonstrated that, in the case of fuels, the rate of the initiation process (R_i) increases with time and is proportional to the squared, decreasing concentration of oxygen, as shown in Equation (34):

$$R_i = k_6\left([O_2]_0 - [O_2]_t\right)^2 + k_1 \tag{34}$$

where:

k_1-reaction rate constant for formation of radicals in the initiation step,

k_6-reaction rate constant for formation of radicals RO_2 from oxidation products.

According to Jones, radicals RO_2, which are responsible for catalyzing the oxidation process, are formed in a reaction which involves two hydroperoxide molecules – reaction (31), as suggested earlier by Halling [11].

Heneghan and Zabarnick [12] demonstrated that, where the course of reaction (4) is limited by the presence of antioxidants, the oxidation reaction rate may be described by Equation (35):

$$\frac{-d[O_2]}{dt}=\frac{k_3[RH]R_i}{k_5[AH]} \tag{35}$$

In this case, the reaction rate of initiation is described by Equation (36):

$$R_i = k_7\left([O_2]_0-[O_2]_t\right)+k_1, \tag{36}$$

where:

k_7-reaction rate constant.

Jones presumes that, owing to the limited availability of oxygen in the storage tanks, the concentration of the peroxides being formed in the fuel is not high, which strongly favors the occurrence of single-molecule decomposition, as in Equation (32). The reaction produces highly reactive radicals *RO* and *OH* from products of oxidation.

In addition, as found by other researchers, the rate of fuel oxidation (especially at high temperatures) is affected by the presence of metal ions [13]. According to Clark, Cu^{2+} cations catalyze the self-oxidation process, thus accelerating the initiation step, that is, the formation of free radicals [13, 14]:

$$RH(fuel)+O_2\xrightarrow{Catalyst(\mathrm{Cu}^{2+})}RO_2\cdot, R\cdot \text{ etc.} \tag{37}$$

According to Walling [11], copper cations dissolved in the fuel tend to react directly with hydroperoxides which have resulted from oxidation of the fuel components and which form highly reactive radicals *ROO* , *RO*, responsible for the fuel's further degradation:

$$Cu^{2+}+ROOH\rightarrow Cu^{+}+ROO\cdot+H^{+} \tag{38}$$

$$Cu^{+}+ROOH\rightarrow Cu^{2+}+RO\cdot+OH^{-} \tag{39}$$

On the other hand, one cannot say without hesitation that the amount of deposit depends solely on the concentration of hydroperoxides [13]. Harde's research team has studied [15] fuels which, in spite of a high content of *ROOH*, demonstrated higher thermal stabilities in comparison with the fuels in which a lower amount of hydroperoxides was formed. The different reactivity of hydroperoxides depends probably on the fuel's composition. Nonetheless, high-temperature deposits in the fuel are formed as the result of the reaction between ageing precursors, which are generated as the result of self-oxidation of the fuel, and polar compounds of sulfur and nitrogen which are present in the fuel [3]:

$$RH + O_2 \rightarrow \text{reactive } ROOH \rightarrow \text{precursors} \xrightarrow{\text{polar compounds}} \text{thermal deposits} \tag{40}$$

Another, less popular potential mechanism of oxidation of fuel components is the Electron Transfer Initiated Oxygenation (ETIO) [3] where, in the step of initiation, electrons are transferred from electron-rich molecules of the fuel to oxygen molecules. ETIO is to be considered as a whole group of oxidation mechanisms which have the common feature of the rate-determining step of electron transfer. A majority of antioxidants, presently used in petroleum products, are designed to control oxidation of fuels, which follow according to the radical mechanism discussed earlier. The ETIO mechanism is an alternative model of oxidation and may be a rational explanation of oxidative degradation of fuels which takes place in spite of the presence of antioxidants.

The simplified model shown below illustrates the principle of ETIO. The oxidation mechanism is explained using dibenzopyrrole (THC), Fig. 2:

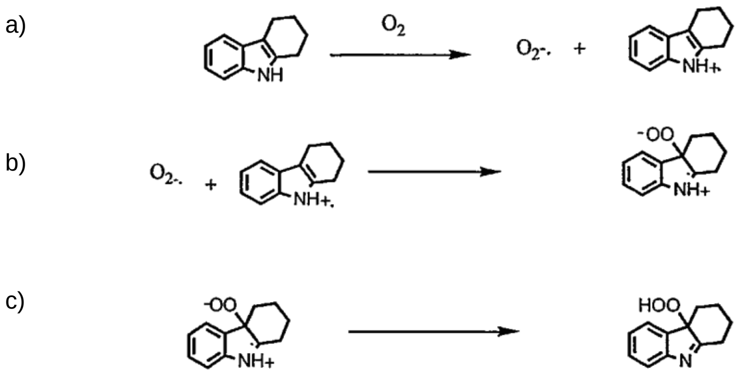

Figure 2. ETIO – simplified mechanism [3]

In that mechanism, reaction a) (electron transfer mechanism) is the slowest reaction, thus limiting the rate of the entire process. The total rate of the process may be expressed by means of rate equation for a second-order reaction (41) [3]:

$$\frac{-d[THC]}{dt} = k[THC][O_2] \tag{41}$$

where:

[THC] – concentration of dibenzopyrrole,

$[O_2]$ – concentration of oxygen,

k – reaction rate constant.

Generally, the mechanisms governing fuel degradation include the following [8]:

- self-oxidation: a spontaneously catalyzed reaction of oxidation (typical process accompanying long-term storage of fuels in storage tanks),
- thermal oxidation (at temperatures higher than 200°C): a typical process for fuels which are in contact with hot surfaces in aircraft fuel systems,
- pyrolysis: decomposition of the structure of fuels and the formation of deposits due to thermal oxidation on very hot surfaces (deposits are formed in nozzles and sprayers).

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  - thermal oxidation, during which deposits are formed in fuel injectors,
  - pyrolysis, during which deposits are formed and accumulated over the injector surfaces and on moist surfaces of the combustion chamber.

c. for turbine oil:

  - self-oxidation, during which resins and peroxides are formed,
  - thermal oxidation, which leads to the formation of deposits over fuel-wetted, hot surfaces of heat exchangers, in valves and nozzles.

It is extremely difficult to establish a single, universal model of oxidation of fuels based on available literature data. This is caused by the chemical structure of the fuel, which is a mixture of many compounds, their different susceptibilities to degradation processes, and their different rates of oxidation. The formation of various deposits and resins in the fuel may follow a variety of mechanisms and take place at different times – during storage and use.

Numerous reports, concerning identification of the mechanisms of degradation of petroleum products indicate that the rate of oxidation depends, first of all, on the following factors:

- physico-chemical properties of the fuel itself, i.e., chemical composition, percentages of respective compounds, and the way they react to oxygen,
- atmospheric conditions (temperature, humidity, pressure),
- presence of compounds which either inhibit or activate oxidation, type of construction material of the storage tank.

The effect of such factors on the quality of the fuel depends on its storage conditions. To minimize their potential adverse influence, efforts are made to reduce the impact of external conditions as much as possible, for instance, by using hermetic tanks, addition of antioxidants and corrosion inhibitors.

3.1.1. Composition of fuel

Every group of hydrocarbons which are the components of a fuel have a different susceptibility to oxidation due to their different structure. Based on the works of N.I. Czernożukow and S.E. Krejn [4, 16] resistance of hydrocarbons to self-oxidation was arranged in the following order, starting from those least susceptible to oxidation:

aromatic hydrocarbons > naphthenes > paraffins

Aromatic hydrocarbons are characterized by the highest oxidation stability due to the absence or small number of side chains. During the oxidation of aromatic hydrocarbons a molecule of atmospheric oxygen locates itself between the carbon and hydrogen atoms, which is accompanied by the formation of low-molecular volatile acids, phenols, quinones and high-molecular products of polymerization, tars, and asphaltenes. C-H bonds in the side chains are attacked first, therefore, susceptibility to oxidation increases in proportion to the number of side chains and to the number of carbon atoms per molecule. Moreover, the larger the number and the length of the side chains, the more acids are formed by decomposition, while the products of condensation are formed in a lesser amount. After decomposition of the side chains into peroxides, aldehydes and acids, oxygen attacks the ring the aromatic hydrocarbon is made of.

Oxidation of naphthene hydrocarbons is much faster and simpler. As in the case of aromatic hydrocarbons, susceptibility to self-oxidation is higher for larger molecules, higher number of side chains, and more complex structures as well as higher temperature. The oxygen molecule will attack, first of all, tertiary carbon atoms leading to the breaking of the hydrocarbon chain with generation of carboxylic acids, hydroxy acids which precipitate in the form deposits, esters, tar and asphaltenes.

Paraffin hydrocarbons were found to be quite resistant at moderate temperatures, although their susceptibility to oxidation is higher at higher temperatures. The process produces carboxylic acids, hydroxy acids and asphaltene-type of products.

Fuels are blends, made of hydrocarbons. Therefore, the compounds interact during the process, thus affecting susceptibility of the fuel to oxidation, providing final products which are a combination of those described above. A mixture of aromatic hydrocarbons without any side chains and naphthene hydrocarbons has a higher oxidation stability, compared with naphthenes alone. It was found that the concentration of aromatic hydrocarbons of around (20...30)% has an anti-oxidative effect when mixed with paraffins and naphthenes, in which case less tars and less deposits are formed as products of oxidation. Concentrations of aromatic hydrocarbons below and above that range tend to inhibit oxidation only to a certain extent, producing more asphaltenes and more high-molecular compounds, which do not dissolve in the fuel. The optimum effect is observed for polycyclic aromatic hydrocarbons with short side chains.

A slightly different mechanism of oxidation was found for biocomponents added to fuels (FAME is added to diesel fuel and bioethanol is added to gasoline). FAME oxidation mechanism is a sequence of reactions involving free alkyls. In the first phase of oxidation, oxygen breaks double bonds of polyunsaturated fatty acids which have low stability, leading to peroxides. In the next step of the process, the peroxides undergo scission (into alcohols, aldehydes and free acids), dehydration (into ketones) and the formation of free radicals which initiate further reactions forming oxidized monomers, dimers and polymers. Oxidation of FAME is a self-oxidative reaction of which the rate is higher as the reaction continues (the products of oxidation tend to catalyze the processes that follow). By oxidation of FAME, acids with strong anti-corrosive properties and insoluble high-molecular compounds (polymers, resins) are formed, leading to deposits on components of the injection system and engine combustion chambers. FAME ageing processes run much faster, compared with changes in diesel fuels [17]. They do not only depend on the quality of the raw material but also on the choice of production technology and method of purification of vegetable oil [18]. The chemical stability of FAME during storage is also affected by temperature and the construction material for the storage tank. Addition of FAME as a component to a fuel results in its lower stability, which may drop dramatically below standard requirements just within a month, affecting other parameters as well. The parameters are not exactly established. Different criteria apply in different countries, resulting in a lack of universal methods for evaluation of this type of fuel. As a general rule, it is possible to extend the safe storage time of FAME by using improvers. Moreover, it is not recommended to store them for more than 12 months in typical fuel storage conditions (closed tanks, absence of oxygen, dark). Stability of FAME is indicated by such parameters as: acid value (represents the amount of free fatty acids), iodine number (measure of the amount of unsaturated compounds C=C), and oxidation stability at 110°C.

In gasolines with a content of bioethanol, fuel ageing processes may run faster as well. Ethanol accelerates the formation of reactive compounds such as free peroxides, which leads to polymerization. In effect, the fuel will change color and resinous compounds will be formed. After addition of the biocomponent to the fuel, its safe storage time is shorter while quality is unaffected. In the case of ethyl alcohol, this results from its susceptibility to form mixtures with water at any chosen ratio, including azeotropic mixtures, as well as susceptibility to oxidation and corrosive effect, while for FAME it is caused by its low chemical stability and susceptibility to oxidation.

3.1.2. Atmospheric conditions

The rate and course of oxidation of petroleum products depend on a number of factors which have nothing in common with the chemical structure of fuels. The essential external factors, in addition to the presence of atmospheric oxygen, include temperature, pressure, and humidity.

The susceptibility of fuels to oxidation is higher for higher temperatures, since more products of oxidation are formed, with different conversions.

A change in the fuel storage temperature from –30 to 50°C leads to the following:

- physical effects: crystallization of certain components of fuels, formation of ice crystals, change in solubility of oxygen and water, leading to the formation of new phases,
- chemical effects: change in the rate of oxidation, polymerization or corrosion, formation of dispersed phases (such as emulsions, micelles), solids, deposits, etc.

The rate and frequency of temperature fluctuations favors accumulation of higher amounts of oxygen and water in storage tanks. A significant drop or temporary fluctuations in the fuel's temperature cause changes which are not always reversible (any generated deposits or highly dispersed phases do not always disappear after the temperature has risen).

The relationship between changes in the rate of chemical and biochemical reactions and temperature is exponential, therefore, the most active components of fuels, contained in refinery products may react at a temperature of 40°C even several times as fast, compared with their reaction rates at –30°C. For that reason, the surface of fuel storage tanks must be protected from the direct impact of thermal and solar radiation.

Łosikow and Łukaszewicz reported [6] that the optimum storage temperature for petroleum products is in the range (20...30)°C, in which the rate of self-oxidation of hydrocarbons is rather low. Thermal decomposition of hydrocarbons may take place as parallel processes at very high temperatures, producing, *inter alia,* carbon dioxide and water.

A similar relationship which accelerates oxidation was observed for increased pressures. Pressure buildup is accompanied by an increase in the rate of oxidation reactions. The external factors discussed in herein lead to breaking the unsaturated bonds, as shown in (42), which generates long-chain compounds, leading to the formation of carbon deposits and settling of resinous compounds.

$$\underset{\text{monomer}}{nCH_2{=}CH_2} \xrightarrow{p,\,T} \underset{\text{polymer}}{[\text{-}CH_2\text{-}CH_2\text{-}]_n} \tag{42}$$

Moisture is another weather condition which affects oxidation of fuels. Water takes part in certain reactions which involve radicals. The following forms of co-existence of fuel and water are of the highest importance both in the fuel storage and distribution:

- water dissolved in fuel,
- water emulsified in fuel,
- water as a separate phase at the bottom or on the walls of the tank or pipeline,
- ice crystals dispersed in fuel,
- ice as a separate phase at the bottom or on the walls of the tank or pipeline.

These forms may convert between one another depending on ambient temperature and pressure conditions.

Solubility of water in the fuel is higher for higher temperatures and lower for higher molecular weights of hydrocarbons. When fuels are stored at low temperatures, their water content will crystallize forming ice crystals which may plug filters or tubing in the fuel system.

Information describing the mechanism of interaction between fuels and water is scarce in the available literature. There is a theory which says that the respective components of the fuel on storage undergo hydrolysis (this includes amines, polyesters, organometallic compounds, salts, esters of phosphoric acid, and sulfonic acids).

The presence of water in the fuel storage tanks also contributes to the growth of microorganisms, which are part of the cause of its oxidation. Along with the increasing count of microorganisms, the concentration of surface active agents also increases. The water phase, both dispersed (emulsion) and its separated layer at the bottom of the storage tank, has its pH reduced by the activity of microorganisms, which is a potential cause of corrosion.

The effect of weather conditions may be moderated by using hermetic designs of storage tanks and by the use of optimum technological solutions (for instance, by the use of improvers). In addition, a fuel is expected to satisfy the requirements of quality as set in applicable standards and its long-term storage time should not go beyond safe limits.

3.1.3. Oxidation catalysts

The rate of oxidation of petroleum products is higher in the presence of oxidation catalysts, which include metals (copper, lead, iron) and organic acid salts. Fig. 3 shows active compounds which are most frequently found in fuels and have a significant effect on the rate and course of degradation processes during long-term storage.

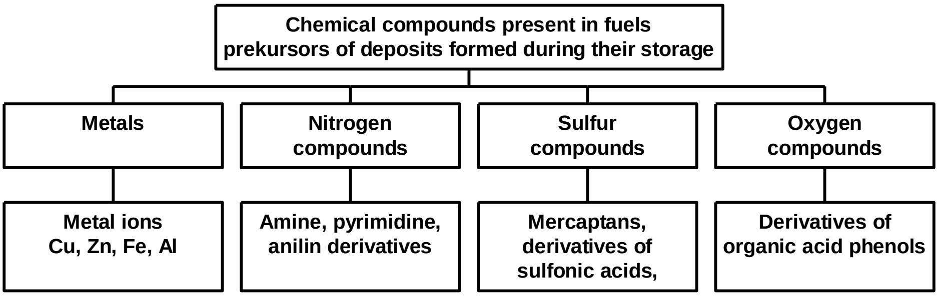

Figure 3. The chemical compounds which most frequently affect degradation processes during long-term storage

Particularly active metals include copper, cobalt, iron, lead, manganese, zinc. Oxidation of hydrocarbons is based on decomposition of hydroperoxides which is accompanied by the formation of active peroxide and hydroxyl hydrocarbon free radicals, as shown in the following reactions (43...46):

$$Cu^{2+} + RH \rightarrow Cu^{+} + H^{+} + R\bullet \tag{43}$$

$$Cu^{+} + O_2 \rightarrow Cu^{2+} \tag{44}$$

$$Cu^{2+} + ROOH \rightarrow Cu^{+} + H^{+} + ROO\bullet \tag{45}$$

$$Cu^{+} + ROOH \rightarrow Cu^{2+} + OH^{-} + RO\bullet \tag{46}$$

The presence of catalysts expedites branching of the chain of oxidative changes, and the resulting products accelerates corrosion of metal parts (engine, tank, tubing etc.). The catalysts have different activities, depending on external conditions.

The effect of total sulfur content on the tendency of resinous deposits to be formed in fuels is not a linear relationship. Sulfur compounds are effective over a specific range of concentrations; as soon as that range is exceeded, their activity will cease (the phenomenon is also observed for alkaline nitrogen compounds). Sulfur compounds which are typically present in fuels and show such activity include derivatives of thiophenols, such as thiopenol, tetrahydrothiophenol, alkyl-substituted thiophenols, and condensed dibenzothiophenols. Studies reported by Mushrush [19] confirmed the generally known view that fuels which have a high sulfur content and are intended for storage are regarded as having poor stability and their long-term storage should rather be avoided. Moreover, a kind of synergistic effect of sulfur and nitrogen compounds was observed, resulting in that stability of fuels was reduced by excessive reactivity and by formation of resinous agglomerates.

Addition of compounds which tend to inhibit oxidation will block the activity of oxidation catalysts in fuels. Such compounds are derivatives of aromatic amines, phenols, thioethers, dithiocarbamates, sulfur compounds, which have an ability to bind metals forming complex bonds. What inhibitors do is they break oxidation process chains or decompose hydroperoxides, peroxide radicals etc., to form non-active compounds. The presence of oxidation inhibitors in effect extends the possible time of storage and use of petroleum products.

3.1.4. Products of oxidation

As the process of oxidation continues, sparingly soluble deposits are formed in the fuels. In gasolines, agglomeration of deposits results from the formation of resins. The resins are organic compounds with a complex chemical structure, composed mainly of long-chained compounds, originating from polymerization. They are highly viscous, dark-brown or black compounds.

With regard to method of determination, resins in gasolines are classified as:

- actual resins (dissolved in fuel) – defined as the dry residue of fuel, they do not dissolve in n-heptane,

- unwashed gum (dry residue of fuel; not washed with a solvent; the parameter represents the amount of non-volatile compounds),
- potential resins (formed by accelerated oxidation; in real conditions, their formation may be induced by oxygen, temperature, light).

Owing to the very strong impact of resins on the performance properties of fuels, it is considered that resin content is an essential measure of the quality of fuel and of its usefulness during long-term storage. After exceeding a certain concentration, actual resins tend to separate, forming deposits which then tend to accumulate on various components of the fuel system. In high-temperature conditions, the resins may convert to substances with a very high-density (lakes, carbon deposits etc.).

The potential resin content enables determination of the content of present resins, which may be formed in the fuel on storage. The potential resin content has no significant effect on the performance properties of fuels.

The following factors have an effect on the formation of carbon and other deposits, in the case of spontaneous ignition engines:

- excess of unsaturated hydrocarbons (expressed as iodine number),
- incomplete combustion of fuel,
- presence of asphalt-resinous substances, unsaturated hydrocarbons and sulfur compounds,
- content of contaminants which form ash during combustion.

The following parameters characterize the tendency of diesel fuels to form deposits:

- coking residue (what remains after the fuel is burnt at a high temperature in the absence of air),
- incineration residue (what remains after the fuel is burnt at a high temperature in the presence of air),
- actual resin content (as in gasolines).

Care should also be taken to control the content of impurities, which lead to excessive wear and tear of the fuel supply system components.

3.1.5. Accelerated ageing and stability tests

Fuel stability tests are typically based on the method of determination of the induction period for gasolines. This applies to testing the oxidation stability of gasolines and aircraft fuels. The **ASTM D 873** test enables evaluation of the tendency of resinous deposits to be formed in fuels under accelerated ageing conditions. The test is carried out in a pressurized steel bomb. After the test is completed, the generated amounts of potential, adsorbed, washed, and unwashed resins are determined in accordance with the **EN-5** method, and the amount of deposits in the filtration apparatus is found in accordance with **ASTM D 6217**.

The accelerated ageing test according to **ASTM D 873** is useful in measuring the stability of gasolines (determination of potential resins) in the oxidation reaction conditions. The behavior of the gasoline sample in the test conditions is analyzed by determining the amount of generated deposits which do not dissolve in the hydrocarbon solvent, and the amount of soluble resins which were formed during the test. Although used for testing aircraft fuels, the test has been adapted to unleaded gasolines and is used worldwide. The induction period may also be used by the method according to **ISO 7536**.

Accelerated ageing of averaged distillates is typically determined by the method described in **ASTM D 4625**. The fuel is subjected to oxidation in mild conditions in the air at a temperature of 43.3°C. Samples are analyzed for an increased content of resinous compounds, structural changes in the resins (IR spectrum), and change in the color of the test sample. The test takes a long time and is costly, therefore, alternative faster methods are searched for to evaluate stability.

In the case of aircraft fuel stability tests, additionally, the thermo-oxidation stability test is performed to control any changes taking place. The test enables the assessment of the fuel's tendency to decompose and the susceptibility of deposits to be formed in the fuel system.

The **ASTM D 2274** or **ISO 12205** takes 40 hours. Based on a study which took several years to complete, a good correlation was shown between the oxidation stability test and the results obtained in field conditions. The method is intended for testing the oxidation stability of average petroleum distillates. The total quantity of filterable and adherent deposits which are formed in the process of oxidation is the final result of determination.

ASTM 5304 describes another test, designed for the accelerated ageing of diesel fuels in the presence of pure oxygen under pressure. The method comprises the assessment of potential stability during the storage of average distillates. This applies to fresh distillates and those after storage, with or without stabilizers. The result is a gravimetric assessment of the total content of resins formed as the result of ageing.

The RANCIMAT test according to **EN 14112** is the method of assessment of oxidation stability both for diesel fuel and for biodiesel. Oxidation proceeds according to the radical mechanism. Oxidation products are transferred in a stream of air to the measuring cell filled with deionized water of which the conductivity is measured in a continuous manner. The conductivity vs. time diagram is the oxidation curve. Its inflexion point indicates the what is called the "induction period". The RANCIMAT test is also used for assessing the efficiency of oxidation inhibitors.

In the fuel stability tests according to **ASTM D 525** "Oxidation Stability of Gasoline (Induction Period Method)", oxidation stability is tested by observation of oxygen pressure drop in the test chamber, filled with the test fuel. The test is deemed completed after the oxygen pressure is 10% lower than the maximum value recorded in the test. The test results are similar to those obtained in the RANCIMAT test. The oxidation stability assessment criterion using the modified method described in ASTM D 525 and ASTM D 5304 is similar, although the test conditions, such as sample quantity, oxygen pressure and temperature are different.

The induction period tests may also be carried out according to the modified method described in **ASTM D 525** (the PetroOxy test). The induction period in the PetroOxy test is the duration of the test from the moment the test chamber was filled with oxygen to the time of recording a 10% pressure drop, compared with the highest value recorded in the system during the test.

The choice of the most suitable accelerated ageing test method ought to take into consideration the fact that the more similar are the testing conditions to natural storage conditions (that is, relatively low sample exposure temperature and long duration of test), the more reliable test results are obtained (e.g., ASTM D 4625). To obtain more details on the process of oxidation of the respective fuel components, it is necessary to carry out ageing tests using a model sample.

3.2. Low-temperature stability of fuels

Low-temperature parameters of fuels are: cloud point, cold filter plugging filter, and flow temperature. These properties affect the possibility to start the engine at low ambient temperatures and the fuel's behavior during its transmission, pumping and refuelling. While cloud point and cold filter plugging point are important for vehicle users, flow temperature makes a difference while the fuel is transported or pumped from storage tanks (especially at ambient temperatures below 0˚C).

The low-temperature characteristics of a fuel largely depend on which hydrocarbon fractions it contains. In diesel fuel, hydrocarbons chains are likely to precipitate at low temperatures. Therefore, a petroleum-based fuel may contain up to 20% paraffin hydrocarbons, which precipitate from the system as crystals because of their poor solubility in the process of cooling the fuel.

Cloud point (CP), according to ISO 3015, is a temperature at which paraffin crystals first start to precipitate as the fuel is cooled. On further cooling the fuel sample, the crystals will agglomerate and the fuel's density will increase throughout its volume until freezing point.

The highest temperature at which, after being cooled at normal conditions, a specific volume will not flow through a standard filter system within specified time limits is called the Cold Filter Plugging Point (CFPP) according to EN 116.

According to ISO 3016, the flow temperature is the lowest temperature at which a petroleum fuel sample is still able to flow as the temperature is lowered, in specified conditions.

A fuel which contains long hydrocarbon chains has a tendency to stratify and settle at the tank bottom, therefore, it is necessary to make sure the blend remains homogeneous, especially during long-term storage, and especially at low temperatures. Paraffin crystals at the cloud point or below the cloud point will travel to the bottom of the tank, gradually forming there a gelous layer, which is likely to cause an irreversible fluctuation of paraffins, eventually plugging the tubes and fuel pumps. To achieve the low-temperature parameter values which are specified in EN 590 (for transitional period, CFPP from -10˚C, for winter conditions-below -20˚C), it is indispensable to use appropriate additives for low-temperatures. Their function is to postpone the precipitation of paraffins from the fuel and/or prevent their agglomeration to sizes which cause filter plugging. The values of such parameters are largely affected by the fuel's contamination, its water content, and time of storage in the storage tanks. Mechanical impurities settle on filters and accelerate their plugging In addition, microparticles of dust and dirt tend to attract particles of paraffin hydrocarbons and enhance crystallization. Water content considerably affects low-temperature properties of diesel fuels. Resinous compounds (products of ageing) which may be formed in diesel fuels after prolonged storage interfere with their flow through the filter, accelerating crystallization.

3.3. Corrosion resistance of fuels

As the oxidation process continues, a variety of compounds are formed in the fuel, generally such as the following:

- acidic compounds (organic acid, keto-and oxo acids, phenols) – they are aggressive to metals (corrosion),
- neutral compounds – those with no effect on the physico-chemical properties of fuels (alcohols, esters) or those which form deposits of all sorts due to condensation processes (aldehydes, ketones, resins, asphaltenes).

If present in excess in the fuel, the acidic compounds may cause corrosion of metal parts both during storage and in a working fuel system. Organic acids may accelerate ageing processes, form insoluble deposits and soaps with selected metals and contribute to the formation of permanent emulsions with water. Therefore, it is necessary to control the fuel's quality, monitoring such parameters as acid value, water content, and emulsification properties.

The copper corrosion test indicates potential problems in the case of prolonged contact of the fuel (which contains sulfur) with the structural components of fuel systems which are made of copper or bronze. For a majority of ready-to-use fuels, the parameter satisfies normative requirements.

Another test, based on ASTM D 665 ("Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water"), is performed in more stringent conditions. The test is used mainly for evaluation of the rust-preventing properties of turbine and hydraulic mineral oils. The method is based on visual assessment of corrosion damage on the surface of a steel roll after it was immersed in a mixture of the product with distilled water or a solution of inorganic salts at an elevated temperature, in conditions specified in the standard. After examination, the steel roll is washed with acetone and the corroded surface is evaluated with reference to the scale. Acidic products of oxidation may degrade structural materials, leading eventually to the presence of cracks, corrosion pits, damaged spots in metal surfaces, the construction material may swell or be dissolved. Such phenomena lead to changes in the material's microstructure which were present on its surface and throughout its volume, thus reducing its mechanical strength, that is, performance properties of the material. Changes which are caused by the fuel on the surface of metal parts may occur according to various mechanisms, for instance, due to galvanic processes. The driving force of galvanic corrosion is the difference in the electrochemical potentials of different metals in the presence of the conducting fluid. The fuel's conductivity is increased by its ability to absorb water and by the presence of soluble ions of contaminants. Higher concentrations of inorganic components, salts, acids may promote corrosion by attacking the oxide film and/or increase conductivity, which more favors galvanization.

Corrosion may also be caused by biochemical processes connected with microbial growth in the fuel, especially in the presence of water. Microbial growth in fuels is manifested by the presence of their metabolites, i.e., all sorts of sludge, slimy residue, emulsions or biofilms. On the one hand, such foul material will change the fuel's appearance and physico-chemical properties (decomposition) and, on the other, it will lead to changes in the structure of the shells the fuel tanks are made of (surface corrosion). The presence of water is the essential condition of the presence of microorganisms in fuel tanks. Water may migrate into the tank as moisture from the air, as precipitation water or ground water, or as the result of condensation on the tank walls. Biological activity of microorganisms in fuels also depends on the concentration of dissolved oxygen, optimum temperature, pH of the water environment, and the presence of hydrocarbons (especially saturated ones) and improvers (especially those which contain nitrogen). Apart from water, which is the source of building material for microbial cells, the fuel is the source of nutrients for the microbial growth. The most intense microbial growth is observed at the water-fuel interface. Energy, which is indispensable for the essential biological functions of microorganisms, is supplied as the result of biological oxidation of fuel components by the enzymes being produced, which work in the environment as long as there is an amount of matter left to be decomposed into such substances as are bio-available to the microbial cells. Decomposition of fuel into bio-available nutrients is continued regardless of microbial demand until the nutrients are entirely depleted or the volume of their metabolites is too large.

The kinetics of the biodegradation process is the fastest for n-alkanes, second fastest for branched alkanes, low-molecular aromatic compounds, and the slowest for polycyclic aromatic compounds [20]. Biodegradation of hydrocarbons may occur both in aerobic conditions (aerobic conversions), where oxygen is the electron acceptor, and in anaerobic conditions (anaerobic conversions, caused by anaerobic microorganisms), where a different electron acceptor is used, for instance, CO_2, NO_2, SO_4 etc.

Changes which occur in fuels under the influence of microorganisms at stable conditions typically depend on the fractional composition of a given motor blend. LPG, kerosene or gasoline have rather low susceptibility to biodegradation. Biological instability is usually observed for diesel fuel with addition of a biocomponent in the form of FAME. Heavier petroleum products, obtained in high-temperature processes, are sterile and free of any content of microorganisms, even in their dormant forms. Contamination may occur only after temperature drop, i.e., in storage tanks, in the presence of water, air, non-petroleum based contaminants.

The pathway of decomposition of fuels induced by microorganisms is governed by the same laws of thermodynamics, kinetics, and catalysis as chemical reactions. Hydrocarbons decompose into fatty acids and alcohols, which are then used by microorganisms in metabolic processes, whereby water and carbon dioxide are obtained as final products. Microbial growth deteriorates the quality of fuels, as shown by the following parameters [21]:

- water separation index,
- surface tension,
- resin content,
- condition of the water-fuel interface,
- chemical stability and thermal stability of fuel,
- content of mechanical impurities.

Such changes will not usually disqualify any fuel, except for the phase separation index, of which the value may be so affected due to the microorganisms as to exclude the fuel from any further use. Changes in the fuel's composition are not the same for the entire tank volume. Any decomposition process taking place is local by nature, usually having the form of corrosion on the tank walls, and causes filter plugging in the fuel system.

Standard IP 385/94, developed by the Institute of Petroleum in London, provides a method to determine the count of microorganisms per unit volume of fuel at the fuel/water interface and in water.

In available literature reports there is not information on the permissible limits of contamination of fuels with microorganisms. Although the contemporary petroleum products as used in aviation, navigation, and in road traffic do have a minor content of microorganisms (usually less than 50 cfu/dm^3), the quality of such fuel is not affected by such contamination [22]. Since it is not possible to entirely prevent petroleum products from becoming contaminated with water, care should be taken to establish more stringent requirements and regularly monitor the permissible limits of the count of microorganisms in those fuels which are intended for long-term storage (protection by the use of biocidal products).

4. Long-term storage

A number of research projects have been carried out by the Automotive Industry Institute (PIMOT), Poland, to determine the effect of long-term storage of fuels on the their quality. The fuels tested included lead-free gasoline, aircraft fuel, diesel fuel, and fuel oil, before and after subjecting them to long-term storage.

The composition of the fuels tested was as follows:

- gasoline – containing various amounts of cracked gasoline (14...34) and various amounts of MTBE (methyl-*tert*-butyl ether) (1,4...4,2),
- diesel fuel.

The fuels were stored in steel drums, in variable weather conditions. The fuel was sampled at certain time intervals during storage to test their physico-chemical properties and chemical stability. The duration of such tests was 4 years and 2 years for gasoline and for diesel fuel, respectively.

4.1. Gasolines

From tests and analyses carried out after 4 years of storage it was found that the physico-chemical properties of gasoline were not affected as regards the following parameters:

- sulfur content,
- microbial content,
- copper corrosion,
- pH of a water extract.

However, the following parameters did change after storage for 4 years:

- Research Octane Number (RON) and Motor Octane Number (MON),
- resin content (including actual, total, acetone, and potential resins),
- induction period,
- hydrocarbon content, as measured by FIA and GCMS,
- fuel coloration, as indicated in a selected scale.

Only slight changes after storing the fuel for 4 years were observed in: density, fractional composition, vapor pressure, content of water, and of MTBE.

With the lapse of storage time, all the gasoline samples showed reduced values of RON and MON. It was found that such changes may have been caused by chemical reactions taking place in the fuel ageing process, leading to the generation of resins with a low octane number in the fuel. After 4 years of storage, only the gasoline with the lowest cracked gasoline fraction was found to satisfy applicable requirements for MON. On the other hand, all samples of engine gasoline were compliant with such requirements in respect of RON.

The analysis confirmed that the present and total resin content tests of the gasoline samples were reliable in determining resistance of the fuel to external factors during long-term storage. Analysis of the generated amounts of actual/total resins confirmed the conclusions made after an analysis of changes in the octane number values. The studies indicate that a drop in the total resin content at the end of the first year of storage was connected with the fresh fuel stabilization in new conditions. Such stabilization processes were followed by the proper reactions of fuel oxidation during long-term storage.

For low percentages of the cracked gasoline fraction, only a slight increase was detected for actual resins, although as the cracked fraction was gradually increased (in the same period of time) the amount of generated resins was growing exponentially, going beyond the permissible values for the parameter, as specified in applicable standards. Analyses were performed to determine the fractional and chemical compositions of the gasoline samples by FIA and GCMS, which indicate that the extent of fuel degradation depended on the presence of unstable (reactive) hydrocarbon compounds, oxygen compounds, and improvers. The gasoline samples were found to contain a higher content of paraffin-naphthene compounds while less aromatic and olefin compounds were present. This indicates that the oxidation, polymerization and sedimentation processes were going on, leading to degradation of the fuel. IR spectroscopy studies indicate that the fuels' condition could be monitored provided that the compounds of interests (i.e., the resins) have been separated.

After the separation of acetone resins from the gasoline using column chromatography followed by an IR analysis, it was found that band intensities for the selected functional groups were becoming higher with the lapse of time, while variations in the spectrum course depended on the unstable, cracked fraction content. A quantitative analysis of the separated acetone resins was performed for reference, using the gravimetric method and it was found that the resin content had decreased after the first year of storage and increased in the years which followed. The amount of acetone resins in the test fuel changed at a faster rate, accompanying an increase in the concentration of the cracked fraction.

Determination of oxidation stability by the induction-period method enabled identification of products with respect to their content of cracked-gasoline. Such determination appeared to be of little use in examining changes in the stability of gasolines on storage. The studies indicate that it possible to determine a forecast storage time for gasoline, using the accelerated ageing test (ASTM D 873) both for the fresh fuels and for those after long-term storage. An attempt was made to estimate the actual storage time of the gasolines. From the accelerated ageing tests for gasoline and from the Stavinoha equation [8], it was estimated that gasolines containing a package of improvers could safely be stored for 6 to 9 years, depending on how much of the cracked fraction gasoline they contain: specifically, the lower their cracked fraction content, the longer the storage time (for the percentages tested).

In the case of gasolines without improvers, storage time was up to 6 years while the dependence of time on the cracked fraction percentage was similar.

4.2. Diesel fuel

After storing diesel fuels and fuel oils for 2 years, the physico-chemical parameters which had changed were:

- acid value,
- oxidation stability at a temperature of 95°C,
- acetone resins content.

The studies indicate that the acid value depends on the content of improvers added to the fuels in their production process.

As in the case of gasolines, the content of acetone resins tended to decrease initially during storage, which was associated with the fuel's adaptation to the storage conditions. After the lapse of 18 months, as more acetone resins were formed in the fuel, their formation was not slowed down even by oxidation inhibitors. An IR analysis of the spectra obtained for the oil samples in the respective series of tests showed the presence of similar bands of characteristic vibrations of which the intensities depended on how much resins had been formed in the oil sample during storage. After storing the diesel oil for 2 years the samples were found to comply with EN 590 requirements for the parameters tested.

5. Conclusion

The analyses indicate that external factors involved in the storage of fuels lead to their degradation (oxidation), deteriorating their quality. Oxidation leads to the formation of high-molecular resins, gums, insoluble deposits and acidic compounds which are aggressive in contact with metals. The rate of oxidation depends on the fuel's physico-chemical properties, weather conditions and on the presence of compounds which either inhibit or activate oxidation.

Fuel stability, understood as its resistance to changes in quality, should be specified at the stages of transport, storage and use, however, there exist no legal documents establishing appropriate storage conditions for fuels and methods to monitor heir quality during long-term storage.

To better protect a fuel from factors which lead to its ageing, appropriate construction materials ought to be selected for the fuel-wetted parts, storage systems should be hermetic, and a selected package of improvers should be added to the fuel, to protect it from the dominant oxidative factor.

The fuel storage facility is a complex system and it is not possible to create a single algorithm describing all model processes of their ageing during storage. Therefore, it is necessary to continue research works on the subject, to search for and identify precursors of fuel oxidation processes and develop efficient methods to eliminate fuel oxidation and prevent its ageing.

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References

[1] Directive 2003/17/EC of the European Parliament and of the Council of 3 March 2003 amending Directive 98/70/EC concerning the quality of gasoline and diesel fuel.

[2] Wachal A., Materiały pędne i oleje silnikowe do współczesnych silników tłokowych, odrzutowych i rakietowych [Propellants and motor oils for contemporary piston-, jet-and rocket engines], Wydawnictwo Ministerstwa Obrony Narodowej, 1959..

[3] Beaver B.D.; Demunshi R., Sharief V., Tian D., and Teng Y., Development of oxygen scavenger additives for jet fuels, 5th International Conference on Stability and Handling of Liquid Fuels Rotterdam, the Netherlands October 3-7, 1994.

[4] Černožukov N. I., Krejn S. E., okisl'ayemost' mineral'nych masel, Gostoptechizdat [Oxidation of mineral oils], Gostoptechizdat, Moscow 1955

[5] Iwanow K. I., Promieżutocznyje produkty i promieżutocznyje reakcji awtookislienija uglewodorodow [Intermediate products and reactions in autoxidation of hydrocarbons], Moscow 1949.

[6] Łosikow B.W., Łukaszewicz P., Towaroznawstwo naftowe [Petroleum Products], Państwowe Wydawnictwo Techniczne, Warsaw 1953

[7] Bone W., Haffner A., Proc. Roy. Soc., A 143, 16, 1933.

[8] Stavinoha L.L.; Westbrook S.R.; and McInnis L.A. Mechanism of deposit formation on fuel-wetted metal surfaces, 5th International Conference on Stability and Handling of Liquid Fuels Rotterdam, the Netherlands October 3-7, 1994.

[9] Heneghan, S. P.; Zabarnick, S. Fuel 1994, 73,35.

[10] Jones, E. G.; Balster, W. J.; Post, M. E. International Gas Turbine and Aeroengine Congress and Exposition: Cincinnati, OH, May 1993; Paper No. 92-GT-334. (Accepted for publication in Trans ASME, Jour. Eng. Gas Turb. Power.)

[11] Walling, C. Free Radicals in Solution, John Wiley and Sons, NY, 1957, p 427.

[12] Heneghan, S. P.; Williams, T. F.; Martel, C. R.; Ballal, D. R. Trans. ASME, Jour. Eng. Gas Turb. Power 1993, 2i J, 480.

[13] Pande S. G.; D.R. Hardy; The effect of copper, MDA and accelerated aging jet fuel thermal stability as measured by the gravimetric JFTOT, 5th International Conference on Stability and Handling of Liquid Fuels Rotterdam, the Netherlands October 3-7, 1994.

[14] Clark, R.H. In Proceedings of the 3rd International Conference on Stability and Handling of Liquid Fuels, London, UK, 13-16 Sept. 1988, p. 283.

[15] Hardy, D.R.; Beal, E.J.; Burnett, J.C. In Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels, Orlando, Florida, 19-22 November, 1991; published 1992, p. 260.

[16] Černožukov N. I., Rafinacja produktów naftowych [Refining of petroleum products], Wydawnictwo Naukowo – Techniczne, Warsaw 1968.

[17] Jakóbiec J; Ambrozik A. Badania FAME w zakresie oceny właściwości fizykochemicznych i użytkowych; III Konferencja Naukowa EKOENERGIA 2007 [Examination

of FAME in respect of physical, chemical and performance properties; 3rd Scientific Conferemce ECOENERGY 2007], University of Agriculture in Lublin, Institute of Agrophysics, PAN – Lublin – Krasnobród.

[18] Jakóbiec J; Baranik M; Duda A. Wysoka jakość estrów metylowych kwasów tłuszczowych oleju rzepakowego to promocja transportu samochodowego [High quality of rapeseed oil fatty acid methyl esters promotes vehicle transport]; Archiwum Motoryzacji No. 1/2008..

[19] Mushrush G. W., Speight J. G., Petroleum Products: Instability and Incompatibility, November 1995 Taylor & Francis, Washington, DC. Reviewed JACS 4/96. March 1999, pages 383-427.

[20] Kołoczek H., Kaszycki P., Biologiczne mechanizmy oczyszczania skażeń organicznych w glebie. [Biological mechanisms of treatment of organic contamination in soils] http://fundacja.ogr.ar.krakow.pl/pdf/Koloczek%20Kaszycki%20str%2028-40.pdf

[21] Górska K, Górski W., Materiały pędne i smary, [Propellants and lubricants]Wydawnictwa Komunikacji i Łączności, Warszawa 1986.

[22] Zyska B., Żakowska Z., Mikrobiologia materiałów, [Microbiology of materials], Wydawnictwo Politechniki Łódzkiej, Łódź 2005.

Chapter 5

Corrosiveness of Fuels During Storage Processes

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Additional information is available at the end of the chapter

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1. Introduction

Corrosion, or destruction of materials in consequence of chemical or electrochemical interactions between the material and its environment, has been a major problem in industry for years. The petrochemical industry being no exception, corrosiveness has been blamed, as the major perpetrator, for costly failures of equipment. Knowing well and understanding the process of corrosion enables its effective control and prevention of the problems caused by corrosion. Bear in mind that corrosion attacks a variety of materials, not just metals alone: the destructive effect of the environment on ceramics, plastics, as well as composites is also observed.

In a more complex environment, it is more difficult to investigate and find a solution to the corrosive effect. Paradoxically, corrosion is a common problem wherever petroleum products are in contact with metal parts and alloys, whether during production, distribution, operation, or storage – even though non-polar hydrocarbons contained in the fuel do not cause corrosion. Corrosion changes are caused by certain constituents of the fuel: sulfur compounds, organic acids, and water-soluble inorganic acids and bases. Among the aforementioned compounds, the most aggressive ones, having the highest corrosive effect are active sulfur compounds (e.g., free sulfur, hydrogen sulfide), especially in the presence of water. The content of water in the refinery fuels is usually very low (30-80 ppm) and its effect on corrosion rate is insignificant. If increased (for instance, due to the penetration of steam into storage tanks), it does have an effect on corrosion processes. In gasoline with a water content of 80 ppm or less, the rate of corrosion on carbon steel is 0.001 mm/year; in those with a water content of 200 ppm – corrosion rate is as high as 0.4 mm/year [1]. Part of the steel or metal surface is wetted with water, which forms thin (from 3-10 μm), interrupted water films between the metal and the organic phase. Since oxygen has different solubilities (higher for the organic and lower for the aqueous phase), anode or cathode regions are formed on the steel or metal surface. This creates favorable conditions for electrochemical corrosion in a given environment. Also microbial growth in fuels causes corrosion damage during the storage and transport of fuels. Above a certain limit, which usually is low, the presence of each of the aforementioned factors of corrosion is unacceptable. Bear in mind that fuel ageing and corrosion are coexistent processes. According to certain reports, the presence in fuels of metal ions originating from corrosion processes accelerates the formation of deposits and gums [2] which, in turn, lead to problems in the fuel distribution system, such as filter plugging or damage to engine parts. Therefore, it is very important to determine the corrosive effect of fuels on the construction materials, widely used in automobile engines or storage tanks.

2. Corrosion in storage tanks

Corrosion is also a problem during fuel storage in storage tanks. Corrosion leads to the formation of products which are likely to cause changes in the quality of fuels (affecting their physical and chemical properties), may accelerate oxidation of hydrocarbon ingredients of the fuel – this leads to higher acid values and to the development of gum and sludge in the fuel. Carbon-steel storage tanks, intended for long-term (5 years a minimum) storage of fuels, may affect the chemical stability of fuels (increased content of oxidation products) [1].

Any sludge developed in the fuel will promote microbiological corrosion. Steam and atmospheric oxygen may dissolve in the fuel during storage. Water and atmospheric oxygen may penetrate into the storage tanks during their evacuation and during what is called “tank breathing”. As temperature fluctuates between day and night, water with its contaminants may be separated from a fuel being stored in aboveground tanks, forming a thin aqueous electrolyte film. Typically, the film is formed on the tank walls and travels downwards, to reach the bottom. This creates conditions in which electrochemical corrosion processes are likely to occur. In storage tanks, there are several corrosion zones with different susceptibilities to corrosion:

- Zone 1 – Top of the tank (inner surfaces of the roof and side walls), which contacts the fuel vapors.
- Zone 2 – Splashing zone: a border between the gas phase and liquid phase. The size of it is variable and depends on how much fuel is in the tank and how the tank is filled/evacuated.
- Zone 3 – Liquid zone: that part of the storage tank which is permanently in contact with the liquid fuel; same as above, its size depends on how much fuel is in the tank.
- Zone 4 – Bottom of the tank and, optionally, its immediately adjacent region. That part of the aboveground tanks is most exposed to contact with water, any salts that may be dissolved in it and its organic and inorganic deposits. The organic deposits are composed of hydrocarbons and bio-films, whereas the inorganic deposits may comprise corrosion products, salts, and sand [1].

The mechanisms of corrosion taking place on the inner parts of the tank are more complex, compared with those describing the corrosion processes that may occur on its outer surface. The rate and type of corrosion taking place in aboveground tanks depends on what petroleum

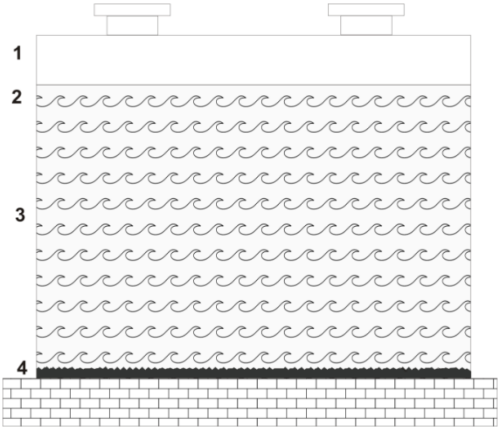

Figure 1. Corrosion zones in storage tanks

product is stored, on solubility of water and oxygen in that kind of fuel, tank capacity, filling/evacuation frequency, and on temperature. Also important are the design features of the tank itself, such as roof type (floating or fixed), the presence of pontoons, tank breathing solutions, as well as its location. Typical tanks for storing gasoline or petroleum are provided with floating roofs and pontoons which limit fuel evaporation and losses through safety valves [1].

Depending on the type of fuel, corrosion processes may take place in different tank zones. In aboveground storage tanks for gasoline, corrosion is observed usually on the south-facing part of the tank. This is probably due to the fact that the day and night temperature fluctuations are higher on the south-facing surface. The south part of the storage tank is more exposed to sunlight, this causes a local temperature increase in daytime and improves the solubility of water in the fuel. In the night, the temperature goes down, again, causing separation of water and its adsorption on the steel surface of the tank walls. Such circumstances, combined with the presence of oxygen, lead to electrochemical corrosion. During the storage of gasoline, the bottom surfaces of storage tanks are less exposed to corrosion.

2.1. The mechanism of corrosion taking place in fuels

With the exception of noble metals, all metals are thermodynamically unstable under normal conditions and it is natural for the system (comprising metals and their alloys) to achieve a form with a better thermodynamic stability (oxidized form). Although a number of types and mechanisms of corrosion are known, it is believed that in the case of fuels there occur electrochemical corrosion (in the presence of electrolytes) and chemical corrosion (in the absence of electrolytes). Compounds which are formed as the result of corrosion, also called corrosion products, may accelerate or inhibit corrosion, or may have no effect on the further course of the metal destruction process. In the case of certain metals, weakly soluble metal compounds (usually oxides) are formed, creating a protective film on its surface, it reduces the rate of corrosion to negligible values – the metal then remains passive. The presence of such naturally formed surface films has an effect on the corrosion resistance of such construction materials as alloy steels, titanium alloys, or aluminum. The oxide layer significantly inhibits corrosion of the metal on which it is formed. This enables designing of components and storage tank fittings without any extra safety devices against corrosions. For instance, in alloy steels, the formation of a thin passive film is connected with a suitable content of chromium in the steel. Under certain conditions, a chromium-rich oxide film on the surface will practically prevent general corrosion. A problem appears as soon as the passive film is destroyed locally and its continuity is interrupted, leading to the formation of active-passive galvanic cells and to the development of corrosion pits. In such galvanic cells the area which is devoid of the passive film becomes the anode where the metal is oxidized while the passivated metal area functions as the cathode. This is very dangerous because the anode/cathode surface area ratio is often unfavorable, very much accelerating metal digestion. For certain conditions, this may have serious consequences, for instance, perforation of the tank walls. The Figure below illustrates the idea of how the galvanic cell works, on the example of iron.

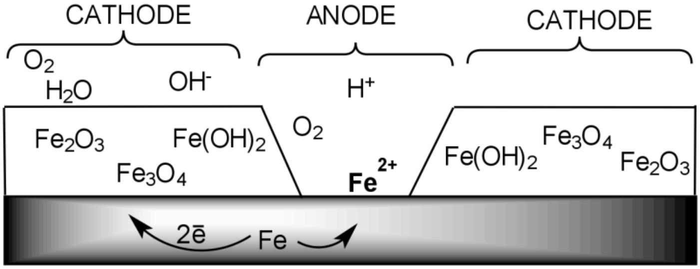

Figure 2. Galvanic cell – the principle of operation

The rate of electrochemical corrosion depends on the nature of the protective film being formed on the metal or alloy surface, the presence of polar solvents (especially water) in the environment of the metal (fuel), the presence of electrolytes (salts, acids, bases), as well as temperature. For a given material, corrosion resistance depends on its structure, composition and the various forces acting upon it. In the case of metal, its electrochemical potential is important as well. Metals having a positive electrochemical potential in relation to hydrogen will undergo oxidation more readily and the process is the more intensive the higher the potential.

To explain the mechanisms of corrosion is a great challenge because fuels are very complex mixtures and corrosion processes are complicated. Corrosion interactions remain to be the subject of studies globally. Studies are carried out to investigate the details of the mechanism of corrosion – both in order to fill some gaps in our knowledge of the problem, and to find better ways to prevent corrosion and minimize corrosion damage. Understanding corrosion processes is important both for economic and safety reasons. One must not forget that losses caused by corrosion involve not only damaged or destroyed tanks, pumps, engines, but also loss of energy, utilities, or the human effort involved in the manufacturing of materials or products. In the case of fuel storage, on the one hand, the ongoing corrosion processes may destroy tanks or fittings, generating high costs of maintenance or even creating a necessity to replace the damaged parts, posing realistic environmental hazard (leakage of fuel); on the other hand, the products of corrosion may affect the quality of fuel during storage, intensifying the process of fuel ageing as well as vehicle engine problems.

Corrosion of metals while in contact with the fuels occurs under the influence of products which are formed by oxidation of gasoline, diesel fuel or biofuels. Such factors cause morphological changes taking place on metal parts, which is manifested by changes in coloration of the fuel, among other things. In the case of biofuels and alternative fuels, the problem of their corrosive effect is not very well known yet; this is because of the variability of raw materials and progress in the production technology of such fuels.

2.2. Corrosive effect of biodiesel on copper, aluminum, carbon steel and stainless steel

Biodiesel is perceived as a novelty fuel, based on renewable sources, having a potential to replace the conventional diesel fuel. From the point of view of chemistry, biodiesel is a combination of fatty acid methyl or ethyl esters. In spite of its numerous advantages, it does have certain drawbacks. Test reports indicate that biodiesel causes more corrosion, compared with the petroleum-based diesel fuel, especially in the presence of water [3].Corrosive effect on metals is one of the major parameters of biofuels, determining their usefulness as engine fuels.

Studies on the corrosive effect of Jatropha biodiesel were carried out before, using such materials as copper, zinc, lead, tin, bronze. It was found that the rate of oil degradation was increased by oxidation which, in turn, was catalyzed by the presence of the metal (the most pronounced catalytic effect was recorded for copper) [4, 5].

Reported in [6] are findings of studies concerning the effect of biodiesel and bioethanol on corrosion for selected materials. Immersion tests were carried out at room temperatures which demonstrated that copper and aluminum are susceptible to corrosion both in biodiesel and in bioethanol. Corrosion pits were also observed on carbon-steel and cast-iron surfaces. A research team of Fazal reported, in [7], their findings on the effect of palm-oil biodiesel on the structural materials of engine components, and compared their findings with similar tests on the conventional diesel fuel. Their findings indicate that the extent of corrosion was higher for biodiesel, compared with diesel fuel. Copper and aluminum appeared to be quite readily corroded in biodiesel and stainless steel was found to resist corrosion.

The corrosive effect of biodiesel and bioethanol on copper, aluminum, carbon steel and stainless steel was also investigated in [8]. Immersion corrosion tests were carried out in accordance with ASTM G32-72 at 43ºC for two months. For comparison, similar tests were carried out for a petroleum-based diesel fuel. The results indicate that corrosion rate of copper in biodiesel was roughly 6 times as high as that in diesel fuel. A similar phenomenon occurred when carbon steel plates were immersed in biodiesel: corrosion rate was 12 times as high as that in diesel fuel. On the other hand, corrosion rate of stainless steel and aluminum in biodiesel was only slight, in the same range as that found for diesel fuel. In the case of aluminum, its surface was covered with a thin, strongly sticking layer of oxides (passive film). The passive film forms a barrier between the metal surface and the fuel, preventing also any access of oxygen of which the presence is essential in corrosion processes; this results in lower corrosion rates. Materials such as copper or carbon steel are readily oxidized. When exposed to biodiesel, metal oxides are formed, including: CuO, Cu_2O, Fe_2O_3 etc., which adhere less strongly to metal surfaces, compared with aluminum [8]. Later in the tests, surface analyses were carried out using SEM, EDS, XPS, and the concentrations of the respective ions in biodiesel before and after the corrosion tests were measured using AAS. Based on their findings, the authors proposed a possible mechanism of the reaction for copper and iron, which could have been working during the corrosion processes taking place. Initially, at room temperatures, copper slowly reacts with oxygen, forming the red copper(I) oxide according to the following reaction:

$$4\,Cu + O_2 \rightarrow 2\,Cu_2O \tag{1}$$

At elevated temperatures, the black copper(II) oxide may be formed directly (reaction 2).

$$2\,Cu + O_2 \rightarrow 2\,CuO \tag{2}$$

If water is present in the biodiesel, processes may take place which result in its degradation. The presence of water leads to hydrolysis of esters and, eventually, to the formation of free fatty acids and glycerol. Each of the oxides formed in reactions 1 and 2 may react with fatty acids, forming organic salts (reactions 3 and 4) and water, which accelerates corrosion.

$$2CuO + 4R'COOH \rightarrow 2Cu\left(R'COO\right)_2 + 2H_2O \tag{3}$$

$$Cu_2O + 2R'COOH \rightarrow 2Cu\left(R'COO\right) + H_2O \tag{4}$$

Similar reactions take place for iron, exposed to biodiesel. Initially, metallic iron is oxidized to form iron oxide (reaction 5).

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \tag{5}$$

In the next step, the iron oxide may react with the fatty acids being formed in the biodiesel (reaction 6).

$$Fe_2O_{3\,+}6R'COOH \rightarrow 2Fe\left(R'COO\right)_3 + 3H_2O \tag{6}$$

Another possibility is that iron reacts directly with fatty acids, forming organic salts which are adsorbed on the metal surface, in addition to hydrogen (reaction 7).

$$2\mathrm{Fe} + 6\mathrm{R'COOH} \rightarrow 2\mathrm{Fe}\left(\mathrm{R'COO}\right)_3 + 3\mathrm{H}_2\uparrow \tag{7}$$

The corrosion processes taking place were also indicated by changes in the fuel's coloration after exposure of the test metal samples. Its color depended on what kind of ions were released from the test samples. Specifically, a greenish shade of biodiesel after exposure of copper plates was attributed to the presence of Cu^{+2} ions in the fuel. A brownish shade after testing the carbon steel plates may indicate the presence in the fuel of Fe^{+2} or Fe^{+3} ions. Discoloration of biodiesel after immersion tests with aluminum samples is attributed to Al^{+3} ions, whereas a slightly yellowish shade after exposure of the stainless steel samples – to Fe^{+3} or Cr^{+3} ions. In addition to discoloration, sufficient evidence confirming the passage of the metal ions into the solution was that the weight of the test samples was reduced after the corrosion tests.

With the exception of stainless steel, metal surfaces tend to change coloration when reacting with biodiesel, for instance, the copper plate was coated with some black material. Examination indicates [8] that the black deposit may be composed of oxides or organic salts. On the other hand, the presence of organic salts and no iron oxide was observed on the carbon steel plate. Organic salts may also be present on aluminum surfaces. Compared with copper surfaces, aluminum showed only slight discoloration though the entire surface grew a little darker. Certain products of oxidation of the surface of metal or metal alloys, such as ions or deposits, may penetrate into the biodiesel fuel, causing changes in its physico-chemical properties, other products may react with free fatty acids leading, eventually, to the formation of fatty acid organic salts on metal surfaces. This is potentially the main cause of diversification in the appearance of biodiesel and metal surfaces. Examinations were carried out using atomic absorption spectroscopy (AAS), which confirmed that the content of copper and iron ions in biodiesel was high after corrosion.

The carbon steel surface in biodiesel was found to have a higher content of carbon and oxide after the corrosion test. This was caused by the reaction between metal oxides and fatty acids to form salts, which strongly stick to the metal surfaces.

Also traces of carbon, oxygen, nitrogen and sulfur were detected on non-corroded metal surfaces. This was caused by exposure of the metal to the influence of air, and its reaction with atmospheric oxygen whereby metal oxides are generated and certain organic contaminants are absorbed on the surface. Literature reports indicate that, after corrosion, the content of carbon was higher on copper, carbon steel and aluminum and lower on stainless steel. This indicates the formation of organic deposits, such as fatty acid salts, and oxides. The deposits strongly adhere to metal surfaces and are hard to remove with a solvent such as acetone. No significant changes were noticed on stainless steel, indicating the absence of organic deposits on the metal surfaces. Spectral analysis of stainless steel suggested the presence of carbon complexes, including organic deposits and amorphous carbon. The formation of carbon complexes reduces the carbon content on steel, compared with other metal surfaces, where such complexes are not formed.

Certain organic deposits tend to develop on metal surfaces only after exposure to atmospheric air; this was observed for such metals as copper, carbon steel, or aluminum. In such tests, the metal surfaces had a higher carbon content and the level of –COOH carboxylic groups also was higher after corrosion in biodiesel. The increased content of carboxylic groups indicates oxidation of the biodiesel and the formation of carboxylic acids. Reactions between carboxylic acids and metal oxides produce organic salts which deposit upon the metal surfaces [8].

Such conclusions are confirmed by IR spectral analysis. After the corrosion tests, the intensity of the peaks corresponding to iron oxides (Fe_3O_4 and Fe_2O_3) was higher, indicating the presence of such oxides; at the same time the iron peak intensity was lower. This explains why organic salts are present on the steel surface, while the content of iron is lower. The same phenomenon was observed for the aluminum surface. A higher intensity of the Al_2O_3 peak and lower intensity of the aluminum peak indicates the formation of organic salts. Aluminum reacts quite readily with atmospheric oxygen, generating Al_2O_3, and tends to adsorb organic compounds. It is safe to say that the formation of an aluminum oxide film inhibits corrosion reactions with the metal surface. Oxygen, dissolved in biodiesel induces further formation of the aluminum oxide film, preventing access to the surface.

From among copper, aluminum, carbon steel and stainless steel, the rate of corrosion in biodiesel was the highest for copper (0.02334 mm/year), second highest for carbon steel (0.01819 mm/year), 0.00324 mm/year for aluminum and 0.00087 mm/year for stainless steel. The corrosion products included mainly fatty acid salts, and metal oxides. It was also demonstrated that decomposition of biodiesel is catalyzed by elements such as copper and iron, creating an environment for corrosion of engine components [8].

2.3. Corrosive effect of biodiesel on copper and brass

Copper and copper alloys undergo corrosion in fuels probably according to the same mechanism as iron and iron alloys. However, the corrosion processes taking place on copper are less destructive and slower – corrosion pits, if present all, are limited to extreme conditions; corrosion is usually manifested by discoloration of the metal or alloy surface. It was demonstrated that even the lowest concentrations of sulfur present in the fuel will take part in corrosion reactions taking place on copper, forming sulfides on its surface. Destructive oxidation reactions are catalyzed by Cu^{2+} ions which pass into the fuel due to corrosion processes. According to literature, the effect is observed when the concentration of copper ions in the fuel is between 100 and 3000 ppm [2].

Oxidation of biodiesel leads to the formation of various products such as peroxides and hydroperoxides. During degradation, these products transform into shorter-chain compounds such as low-molecular weight acids, aldehydes, ketones, and alcohols [9]. Moreover, oxidative polymerization may lead to the formation of macromolecular chemical compounds [10]. Thus, oxidation of biodiesel intensifies its corrosive effect, affecting the physico-chemical properties of the fuel [7]. The corrosiveness of biodiesel is also connected with the presence in it of contaminants, such as: water, alcohol, free fatty acids.

Studies on the effect of light, temperatures, and selected metals on corrosiveness and degradation of biodiesel are reported in [11]. The corrosiveness studies were carried out for copper and brass using the immersion method according to the standards ASTM G31 and ASTM G1.

The experiment was continued for 5 days at room temperatures (ASTM G1) in the presence or absence of light. The studies were also carried out at 55ºC for comparison with the findings of tests according to ASTM G31 (with air bubbling). In the tests referred to in ASTM G31, the test samples were placed at 3 different levels (totally immersed in fuel, partly immersed in fuel, exposed to fuel vapors only). The copper and brass plates had more corrosion-induced changes after being immersed in biodiesel, compared with the test plates exposed to fuel vapors only. The corrosion processes were accelerated by bubbling with air, leading to larger weight losses in the copper and brass plates. After 5 days of exposure, a slightly higher corrosion rate was recorded for the plates exposed to light at room temperatures, compared with those tested in the absence of light. Interestingly enough, in the tests carried out in the dark, corrosion rate was much slower for copper and for brass after increasing the temperature to 55ºC; presumably, this was caused by the fact that oxygen is less soluble at higher temperatures. Moreover, biodiesel samples were found to have higher viscosities and higher water contents after the corrosion tests according to ASTM G31.

2.4. Corrosive effect of bioethanol on aluminum

The presence of alcohols in the fuel has a significant effect on its corrosion behavior. The alcohol itself is a corrosive medium, additionally, it is able to dissolve in and be mixed with water at any ratio. Studies on the effect of bioethanol on corrosion for an aluminum alloy (A348) were described in [12]. Corrosive properties were tested by its immersion in fuel blend samples, made of unleaded gasoline with various concentrations of bioethanol (10, 15 and 20% (v/v)). The tests were carried out at temperatures 60, 80 and 100ºC, by immersing the test metal samples in the prepared blends for 24 hours. The test results indicate the presence of local corrosion pits on the surface of the aluminum alloy plates after continuing the tests for 24 hours at a temperature of 100ºC. The extent of corrosion was higher for higher concentrations of ethanol in the blends, as indicated by the higher number of corrosion pits on the surface of the test alloy samples. No corrosion damage was observed at lower temperatures (60 and 80ºC).

Presumably, a protective film of hydrated aluminum oxide was formed on the aluminum alloy surface during the tests at temperatures below and including 80ºC. Only after increasing the temperature to 100ºC was the reaction triggered between aluminum and bioethanol (reaction 8).

$$6C_2H_5OH + 2Al \rightarrow 3H_2 + 2Al\left(C_2H_5O\right)_3 \tag{8}$$

The reaction involves substitution of the aluminum atom originating from the metal or from the oxide film with a hydrogen atom originating from bioethanol; hydrogen and aluminum acetate are formed.

Reported in [13] are results of studies, intended to determine the effect of oxygen present in the fuel on the corrosive properties of aluminum alloy. The test fuel blend was composed of 80% unleaded gasoline and 20% of 99.9% pure ethanol. The fuel blends were heated up to 100ºC after being subjected to bubbling with nitrogen or gaseous oxygen for 2 hours. This provided fuels with different concentrations of oxygen. The effect of oxygen, dissolved in the fuel, on a high-temperature corrosion of aluminum alloy was investigated in electrochemical tests, using impedance spectroscopy and by evaluating the condition of the surface of the aluminum alloy samples before and after the tests. It was shown that corrosion resistance was increased with the increasing concentration of oxygen dissolved in the fuel, indicating the passive film formation on the test sample surface. On the other hand, it was demonstrated that bioethanol may be oxidized by the oxygen dissolved in the fuel, generating acetic acid and water. Each of the products is able to have an effect on corrosion of aluminum alloys. In further tests, the authors attempted to determine the effect of those factors on aluminum alloy destruction processes: to achieve this, specified amounts of acetic acid and/or water (0, 0.1, 0.5, 1.0 % v/v) were added to a fuel blend comprising 80% unleaded gasoline and 20% bioethanol after passing nitrogen through the blend. The test alloy plates were immersed for 6 hours in the prepared fuel blends after heating the blends to 100°C. It was demonstrated that water had a beneficial effect on the corrosion resistance of the aluminum alloy, having formed a hydrated aluminum oxide film on the metal surface, which acted as a protective film. Changes on the surface of the alloy sample were not observed for blends with a water content of more than 0.5 % v/v. Addition of acetic acid worked quite differently: it had a harmful effect, destroying the protective film and causing corrosion pits even at as low concentrations as 0.1 % v/v, and the process was intensified by addition of more acetic acid.

3. Corrosion processes in fuels during storage

Storage of fuels is accompanied by various processes, including oxidation, condensation, and polymerization. Contaminants which were detected during long-term storage of fuels included products of corrosion, organic particulate matter, and deposits. Part of such impurities tended to settle at the tank bottom and side walls, although most of them remained in the fuel and were present in the engine chamber during its operation. Such impurities were not flammable, they tended to escalate soot formation during combustion, affecting the engine's performance. Certain components and impurities (iron oxides, sulfides) also had an effect on the fuels tribology, causing increased wear and tear of the surfaces of the engine's major components. That is why investigating the influence of the storage process on the durability of the selected materials and on the quality of the fuel itself seemed so important. That fuels have a corrosive effect on materials they contact in at every step of their life cycle, is an established fact. What remains to be provided is the findings of studies describing the influence of the degree of fuel ageing on its corrosiveness – both to the materials applied in design solutions for storage tanks, and to the materials applied in vehicle engines. It is the objective of this paper to find out whether and how, if at all, the corrosive effect of various fuels varies in time during storage.

3.1. Corrosiveness tests of gasoline and diesel fuels

The gasoline and diesel fuels which are the national strategic reserve have a zero content of bio-components. The content of bio-components in fuels is known to affect the kinetics of corrosion processes. In order to determine the actual effect of bio-components on the rate of corrosion, and on fuel ageing processes, tests were carried out using fuels with and without a content of bio-components.

The following fuels were used in the tests:

- 95 octane gasoline containing a maximum of 5% (V/V) of bioethanol (E5);
- 98 octane gasoline containing a maximum of 15% ETBE and no bioethanol (E0);
- diesel fuel containing a maximum of 7% (V/V) of FAME (B7);
- diesel fuel containing no FAME (B0).

The above-mentioned fuels were stored in underground storage tanks to cause their ageing in field conditions. Samples were collected from the storage tanks at certain intervals in order to find out how the physico-chemical properties of the stored fuels were changing and to test the fuels for their corrosive effect. The fuel samples were collected after 6 and 12 months of storage. Tests of the corrosive effect of fuels during storage were carried out using test samples of the following metals or alloys:

- aluminum with an aluminum content of max. of 99.5%;
- copper with a copper content of max. of 99.9%;
- lead with a lead content of a max. of 99.9%;
- brass (copper and zinc alloy, with a copper content of 60%, and a zinc content of 40%);
- C45 steel with a carbon content from 0.42 to 0.5%;
- S235JR steel with a carbon content of max. of 0.2%.

The above-mentioned materials are commonly used as structural materials for vehicle engines. For instance, aluminum alloys are used for making engine blocks, cylinder heads, oil sumps, drive shafts, and rocker arms. Owing to its good conductive properties, copper is used for making windings for alternators, starters, or ignition coils. Brass is used for tubes in fuel distribution systems, tubing for coolers, electrical connections. Steel is used for making major components, including connecting rods, timing gear, and piston pins. Moreover, each of the selected metals and alloys has a different corrosion resistance (different electrochemical potential), which adds to the comprehensiveness of evaluation of the corrosive behavior of fuels. If a fuel contains factors of corrosiveness, such as sulfur compounds, organic acids, and water soluble inorganic acids and bases, in the presence of water and oxygen, each of the above-mentioned metal/alloy plates will be affected by electrochemical corrosion, although the process will be running at different rates. A copper plate with an electrochemical potential of 0.337 V in relation to the hydrogen electrode is classified as a semi-noble metal. In theory, its electrochemical corrosion resistance is high although, if water soluble acids are present (pH below 6.5), it may be corroded in oxygen depolarization conditions. The corrosion resistance of steel depends on its chemical composition. Higher carbon concentrations have an adverse effect on corrosion resistance (C45 grade steel is expected to be corroded sooner than S235JR grade).

Test samples of the selected materials in the form of 15 x 50 x 2 mm plates were sanded with abrasive paper with different grain-sizes, so as to obtain smooth and scratch-free test surfaces. The resulting plates were then defatted with acetone and dried.

3.2. Corrosiveness tests of fuels by the immersion method

The tests were carried out by immersion, using a dedicated, custom-made glass connected vessel which is illustrated in Figure 3. One part of the glass vessel was filled with 100 ml of the test fuel and the other remained empty. The vessel was heated for about 2 minutes to remove any air therefrom, so that the volume just above the fuel was filled with fuel vapors. Both parts of the vessel were then plugged with stoppers having plates of a same kind attached to them. The plates were weighed previously to an accuracy of 0.0001 g, using an analytical balance. The length of the threads was selected so as to enable one plate to be fully immersed in the fuel in one part of the vessel. The other plate, attached in the other part of the vessel, was suspended at the same height. The resulting measuring vessel was placed in a Binder KBF/KBF-ICH chamber in an oxygen free environment.

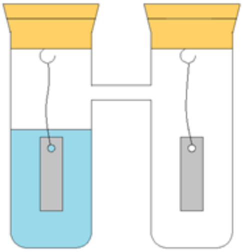

Figure 3. Measuring vessel diagram

The tests were carried out in mixed cycles of ambient temperature and elevated temperature, as follows, respectively:

- 40°C for diesel fuel containing up to 7% (V/V) FAME (B7) and with no FAME (B0),
- 25°C for 95 octane gasoline containing a maximum of 5% (V/V) bioethanol (E5) and for 98 octane gasoline containing a maximum of 15% ETBE and no bioethanol (E0).

The duration of a single cycle was 24 hours, including 8 hours at an elevated temperature and the other 16 hours at an ambient temperature. The tests were completed after 16.5 cycles. The vessel remained at elevated temperatures for a total of 100 hours. The conditions simulated temperature fluctuations between day and night, prevailing in storage tanks.

After the tests were completed, the plates were taken out from the vessels, cleaned with acetone, dried, and weighed to the same accuracy as before the measurements.

Corrosion was measured in terms of the sample weight changes before and after exposure in fuels with different degrees of ageing. In addition, the condition of the plate surfaces was visually examined and evaluated with regard to the size, distribution, and type of changes on the plate surfaces.

4. Corrosive effect on metals

The corrosive effect of petroleum products was tested by two groups of methods: visual evaluation of samples of materials after exposure in fuels – this only enabled finding out whether corrosion did or not take place. If corrosion changes have taken place, the method provides no information on the rate of the process, therefore, it is important to add to the information a specific quantitative description of the changes taking place.

Changes in the weight of the test material before and after exposure in the given fuel were adopted as the criterion of the evaluation of the corrosive effect of the test fuels. To enable a comparison of the changes taking place in the test metals and steels, it was necessary to use a parameter, taking into account the different densities of the test materials. This purpose is served by linear corrosion rate, defined as the cross-sectional loss per year [mm/year]. The linear corrosion rate was found from the following formula:

$$K_L = \frac{(\mathrm{m}_1 - m_2) \times 24 \times 365}{\rho TS \times 1000} = 8.76 \times \frac{\Delta m}{\rho TS}$$

wherein:

m_1 – sample weight before corrosion [g],

m_2 – sample weight after corrosion [g],

Δm – change in sample weight [g],

ϱ – density of material [g/cm^3],

T – time of exposure at elevated temperatures [hr],

S – surface area of sample [m^2].

Findings for each of the test fuels after 6 and 12 months of storage are given below.

4.1. Corrosive effect of 95 octane gasoline containing ethanol

In the corrosive-effect tests for commercial 95 octane gasoline (containing a maximum of 5 % V/V of ethanol) after 6 months of storage, weight changes were observed for all of the exposed metal and steel plates. Such weight changes were recorded after exposure to liquid gasoline and to gasoline vapors. The linear rate of the process of corrosion was found from weight changes and density of the metal (steel), taking into account the duration of exposure of the test samples at elevated temperature (Figure 4).

Based on the test results, it was found that such corrosion rates are rather insignificant, and fall in the range from 0.001 to 0.004 mm/year. The highest corrosion rate was recorded in the case of lead samples, both for the plate immersed in the liquid gasoline, and for the one exposed to its vapors.The lowest corrosion rates in the test gasoline were recorded for the plates made of S235JR (constructional steel), which indicates its optimum corrosion resistance. For the other materials, such as copper, brass, aluminum and C45 carbon steel, corrosion rates were similar. None of the materials was affected by corrosion to a significant degree, which was assessed as corrosion resistance grade 2 – materials with high corrosion resistance – Table 1.

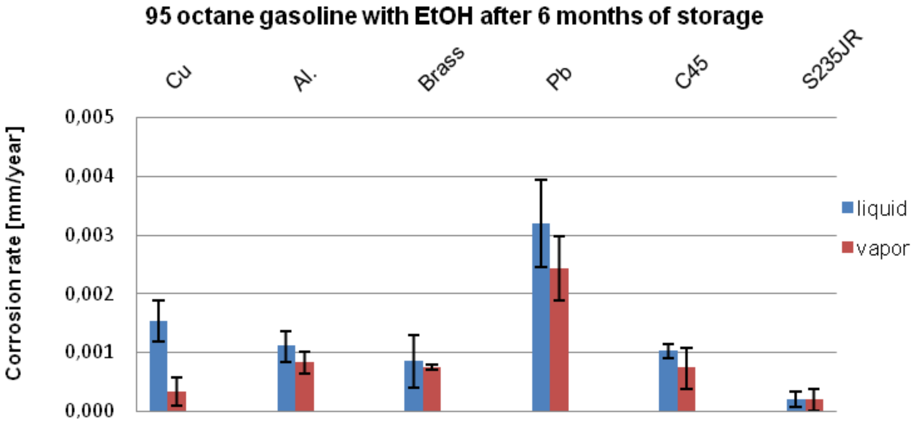

Figure 4. Linear corrosion rate for the test metals and steel, obtained for 95 octane gasoline after 6 months of storage

Corrosion resistance group	Symbol	Corrosion resistance grade	V_p [mm/year]
Entirely resistant	I	1	> 0.0001
Highly resistant	II	2	0.001- 0.005
		3	0.005 - 0.01
Resistant	III	4	0.01 - 0.05
		5	0.05 - 0.1
With reduced resistance	IV	6	0.1 - 0.5
		7	0.5 -1.0
With low resistance	V	8	1.0 - 5.0
		9	5.0 - 10.0
Non-resistant	VI	10	> 10.0

Table 1. Corrosion resistance groups

Figure 5 shows the appearance of the plates after the tests. Only the copper plate was slightly discolored after being immersed in gasoline. Its discoloration was uniform and present all over the surface.

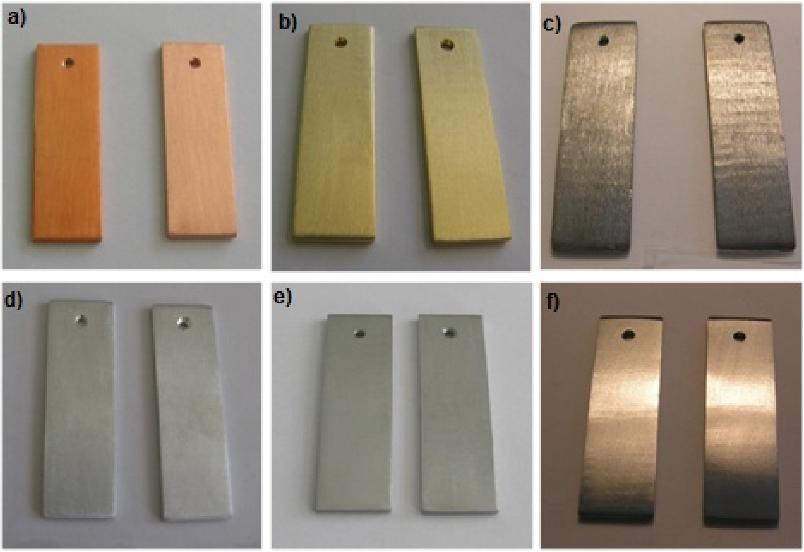

Figure 5. Appearance of samples after corrosion tests for 95 octane gasoline after 6 months of storage a) copper, b) brass c) lead, d) aluminum, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

A similar phenomenon was observed for the same gasoline after 12 months of storage: exposure did not cause any significant changes in the test materials. Here again, the highest corrosion rate was observed for lead, although it was slightly lower, compared with that for gasoline after 6 months of storage (Figure 6).

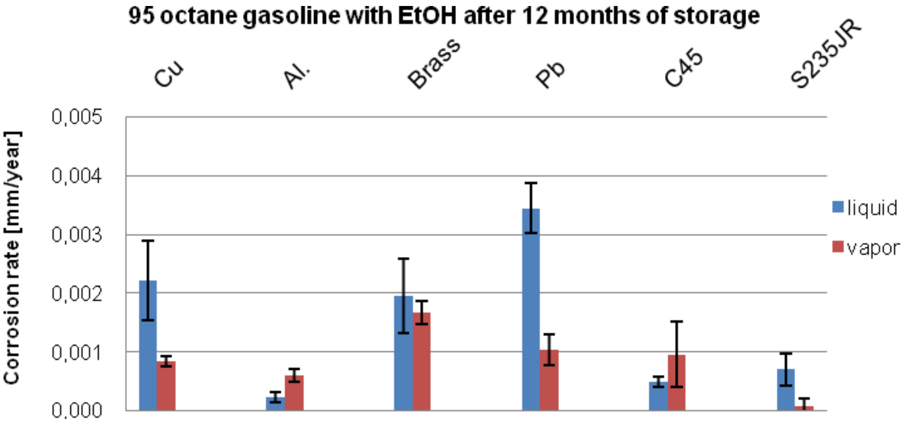

Figure 6. Linear corrosion rate for the test metals and steel, obtained for 95 octane gasoline after 12 months of storage

Interestingly enough, the calculated corrosion rate in the case of aluminum appeared to be much lower than that for gasoline after 6 months of storage. This is probably due to the formation, on the surface of aluminum, of a passive film (the metal is capable of self-passivation). This is connected with the presence of a thin film of oxygen or other compounds on the metal surface. The film is a specific barrier to the environment. Hence, passivation is accompanied by a decrease in the rate of degradation of the substrate. In the case of copper, brass, and the S235JR steel, corrosion rates after 12 months were roughly twice as high, compared with the tests for gasoline after 6 months of storage. On the other hand, one must bear in mind that the results are burdened with a rather serious error, which may be connected both with the fact that the plates were not uniform, and with the complexity of the processes leading to corrosiveness.

The above results were confirmed also by observation of the plates after exposure in the test fuel and its vapors. No changes were visible to the naked eye either on the plates exposed to the liquid gasoline or to its vapors. All of the test materials after exposure in a gasoline containing bioethanol after 12 months of storage were rated as materials with corrosion resistance grade 2.

4.2. Corrosive effect of 98 octane gasoline containing ETBE

For 98 octane gasoline containing ETBE after 6 months of storage, the highest corrosion rate was recorded for lead (Figure 7). Interestingly enough, in this case, a higher corrosion rate was noted for the plate exposed to the gasoline vapors. The lowest corrosion rate after exposure in gasoline was recorded for brass. For the other metals and steels, the rates were comparable. One should bear in mind that the ranges of linear corrosion rate for all of the test materials were rather not large, indicating their good corrosion resistance in a given environment (corrosion resistance grades 1-2).

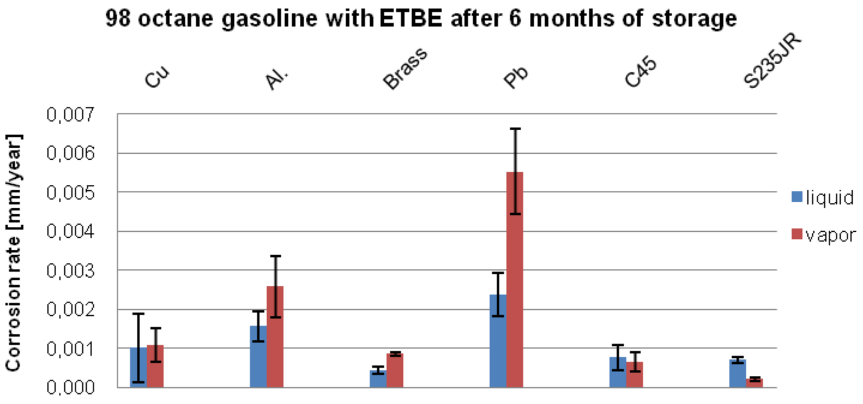

Figure 7. Linear corrosion rate for the test metals and steel, obtained for 98 octane gasoline after 6 months of storage

No significant changes were noted by observation of the plate surfaces, their condition after the test was similar to that before the test. The appearance of the plates after the tests for gasoline after 6 months of storage is shown in Figure 8.

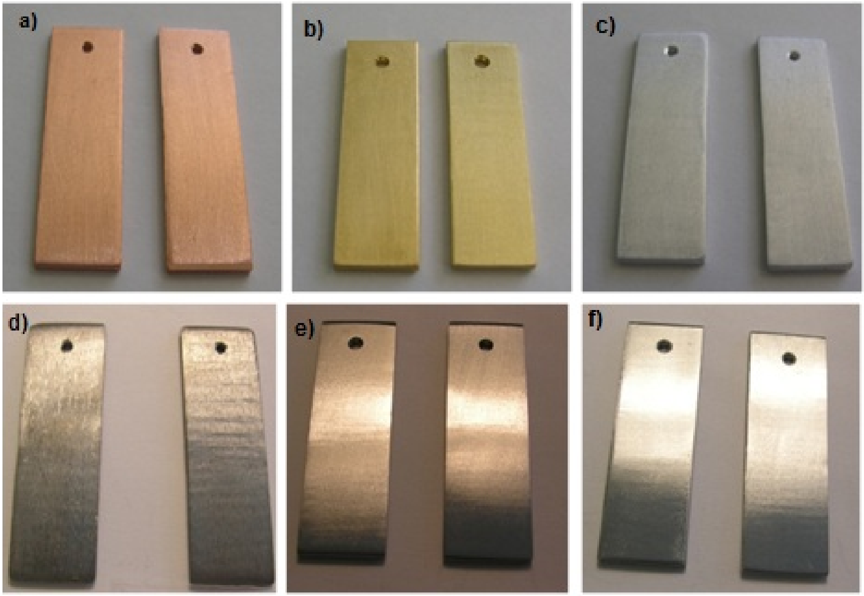

Figure 8. Appearance of samples after corrosion tests for 98 octane gasoline after 6 months of storage a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

Tests for 98 gasoline containing ETBE indicate that, after 12 months of storage, corrosion rates were lower (for aluminum, lead, C45 steel and S235JR steel) or remained at a similar level (copper, C45 steel and S235JR steel), which is a desirable phenomenon (Figure 9).

In the case of brass plates immersed in gasoline, corrosion rates after 12 months and after 6 months of storage were similar. In the case of brass, a difference was noted for exposure to vapors – corrosion rate was 3 times as high after 12 months of storage. The calculated corrosion rates for all the metals and alloys were very low, indicating that the test materials demonstrate good resistance. A decrease in corrosion rates after 12 months may be connected with changes in the fuel taking place during storage, which promote passivation of metal surfaces (formation of thin film of metal oxides or organic salts).

No changes were observed on the test plate surfaces for gasoline after 12 months of storage (Figure 10).

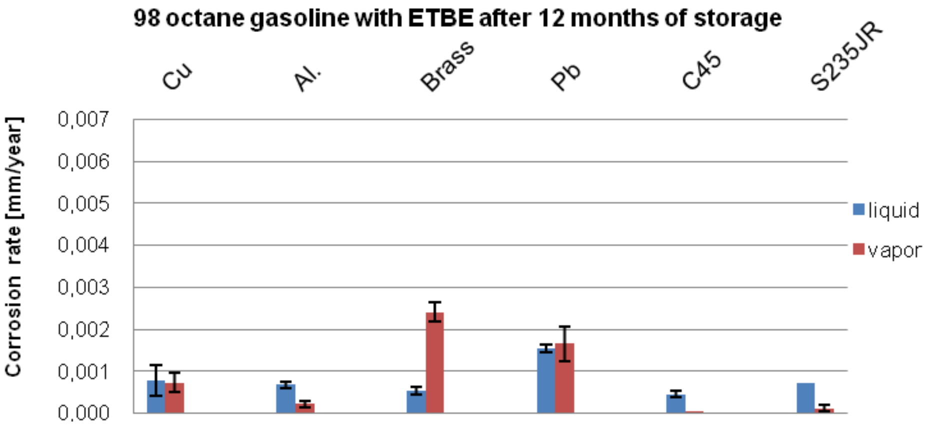

Figure 9. Linear corrosion rate for the test metals and steel, obtained for 98 octane gasoline after 12 months of storage

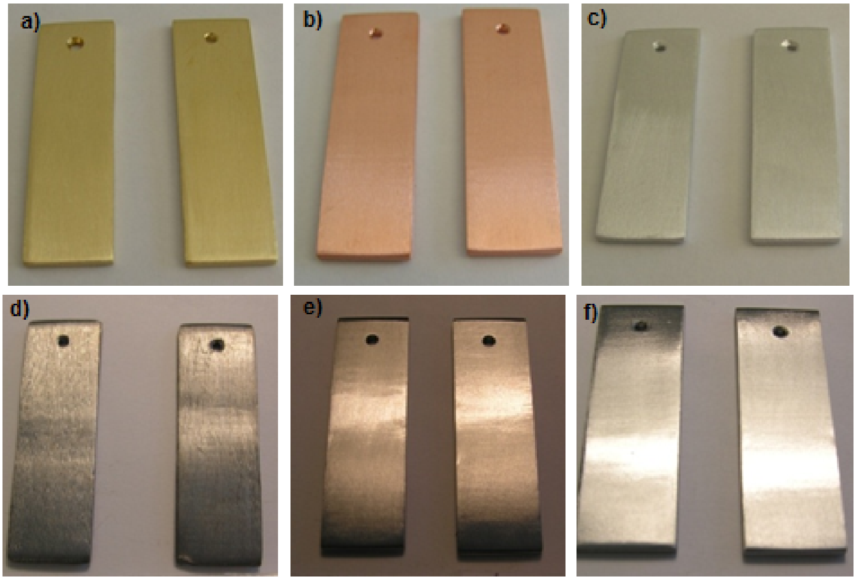

Figure 10. Appearance of samples after corrosion tests for 98 octane gasoline after 12 months of storage a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

4.3. Corrosive effect of diesel fuel containing up to 7% FAME

For lead samples after exposure in the diesel fuel containing up to 7% FAME, corrosion rate was very high after just 6 months of storage (Figure 11).

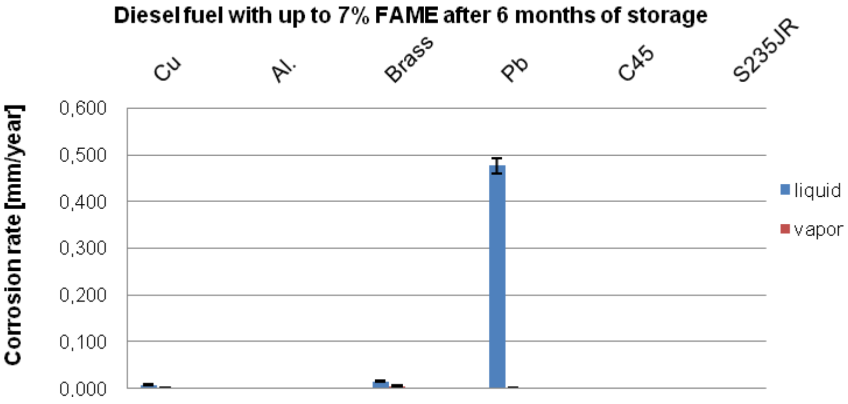

Figure 11. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

Corrosion rate for lead was more than 33 times as high as that for brass. According to the data shown in Table 1, lead may be classified as a material with corrosion resistance grade 7 (out of 10 grades). The other test metals and steels showed better corrosion resistance: copper and brass were classified as materials with corrosion resistance grade 4, aluminum, C45 steel and S235JR steel – as materials with corrosion resistance grade 2.

For a better illustration of their corrosion rates, Figure 12 shows the test results obtained for the test materials with the exception of lead.

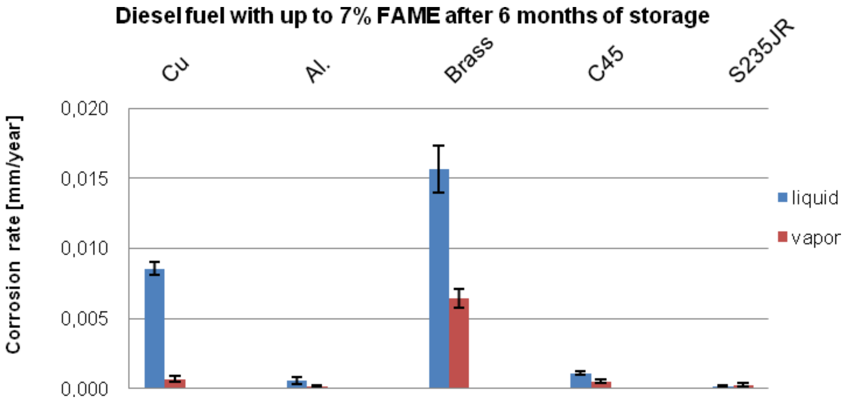

Figure 12. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

Among these test materials, the highest corrosion rate was observed for brass, the lowest was observed for the S235JR steel.

The appearance of the samples after subjecting them to the corrosive effect tests is shown in Figure 13. Significant changes were observed in the case of lead, following its direct exposure to diesel fuel (Figure 13 d)), as confirmed by the calculated corrosion rates. The lead plate is coated with corrosion products. No changes were detected in the lead plate after exposure to the fuel vapors. The copper and brass plates showed discoloration after exposure in the test fuel.

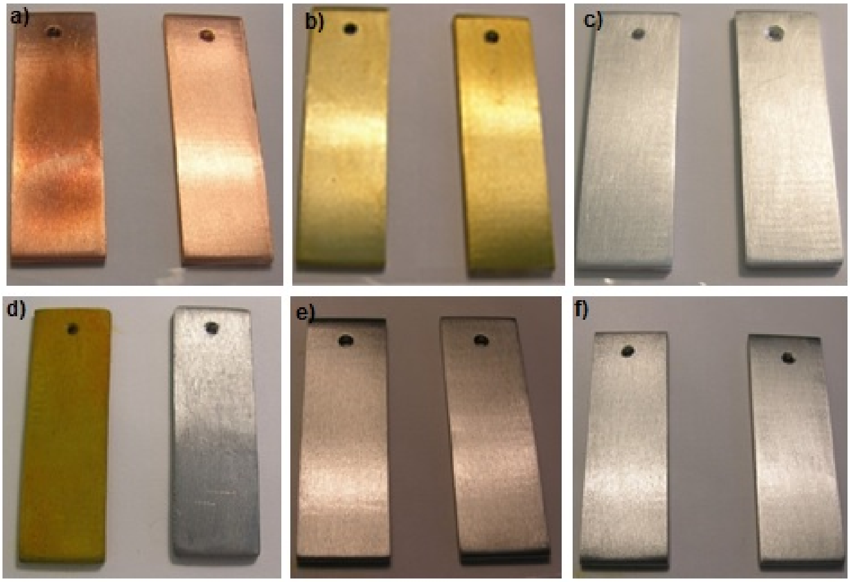

Figure 13. Appearance of samples after corrosion tests for diesel fuel containing up to 7% FAME after 6 months of storage: a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: – after exposure in vapors)

In corrosive effect tests after storing diesel fuel for 12 months, lead appeared to be the material with the highest susceptibility to corrosion. The calculated linear corrosion rate for lead was approx. 0.450 mm/year, which is slightly lower than that obtained after exposure in diesel fuel after 6 months of storage. In the case of copper and brass, corrosion rate was much reduced (Figure 14).

Corrosion rates for aluminum, C45 steel and S235JR steel were comparable and very low, indicating their good resistance to the effect of diesel fuel as early as in the initial period of its storage.

Figure 15 shows the appearance of copper, brass, and aluminum plates after exposure in commercial diesel fuel after 12 months of storage. Macroscopic examination of the plates indicates no corrosion changes on their surface.

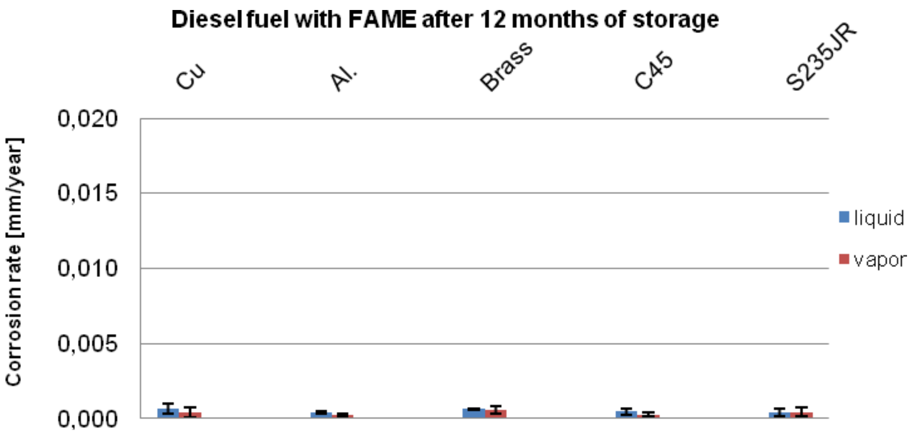

Figure 14. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

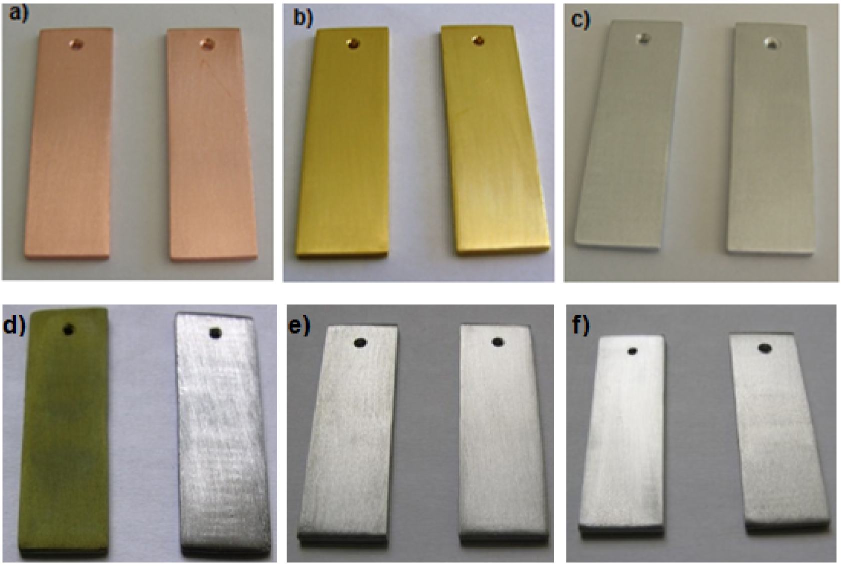

Figure 15. Appearance of samples after corrosion tests for diesel fuel containing up to 7% FAME after 6 months of storage: a) copper, b) brass c) aluminum d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

4.4. Corrosive effect of diesel fuel containing no FAME

The same kind of tests were carried out for a diesel fuel containing no FAME. Also in this case, the highest susceptibility to corrosion in a fuel stored for 6 months was found for lead (linear corrosion rate of about 0.170 mm/year) (Figure 16). Such rate was much higher, compared with the other test metals and steels. The second highest corrosion rate was recorded for brass; moreover, corrosion rate was higher for the brass samples immersed in the liquid fuel, compared with those obtained for the plates exposed to vapors.

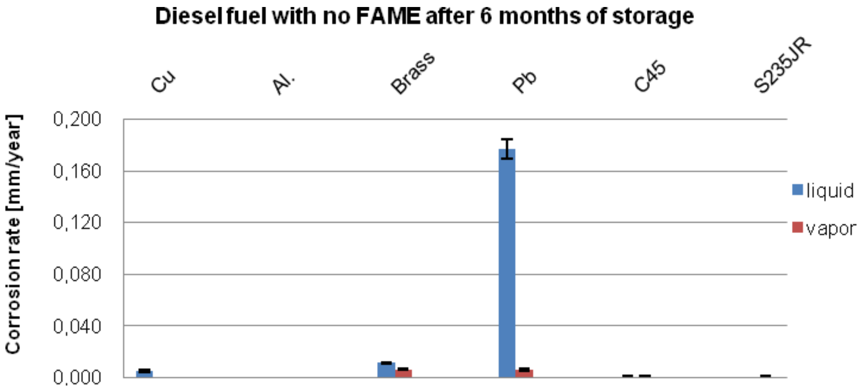

Figure 16. Linear corrosion rate for the test metals and steels, obtained for diesel fuel containing ETBE after 6 months of storage

Same as in the case of the previous diesel fuel, high corrosion resistance was observed for the aluminum and the steel samples (Figure 17).

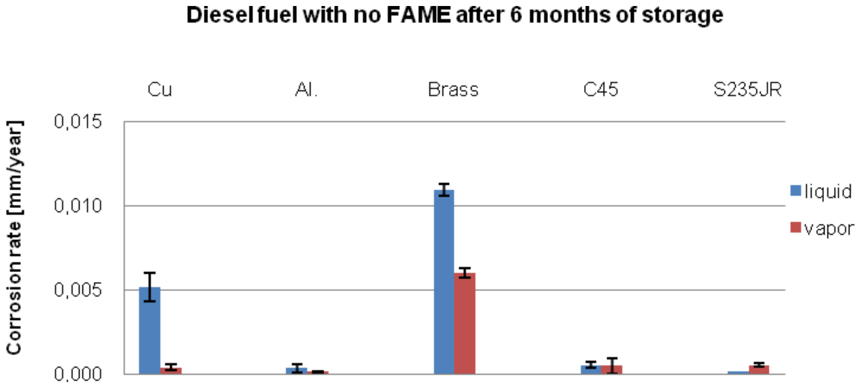

Figure 17. Linear corrosion rate for copper, aluminum and brass after exposure in diesel fuel with no FAME after 6 months of storage

Figure 18 shows the appearance of the plates after immersion tests for diesel fuel, after 6 months of storage.

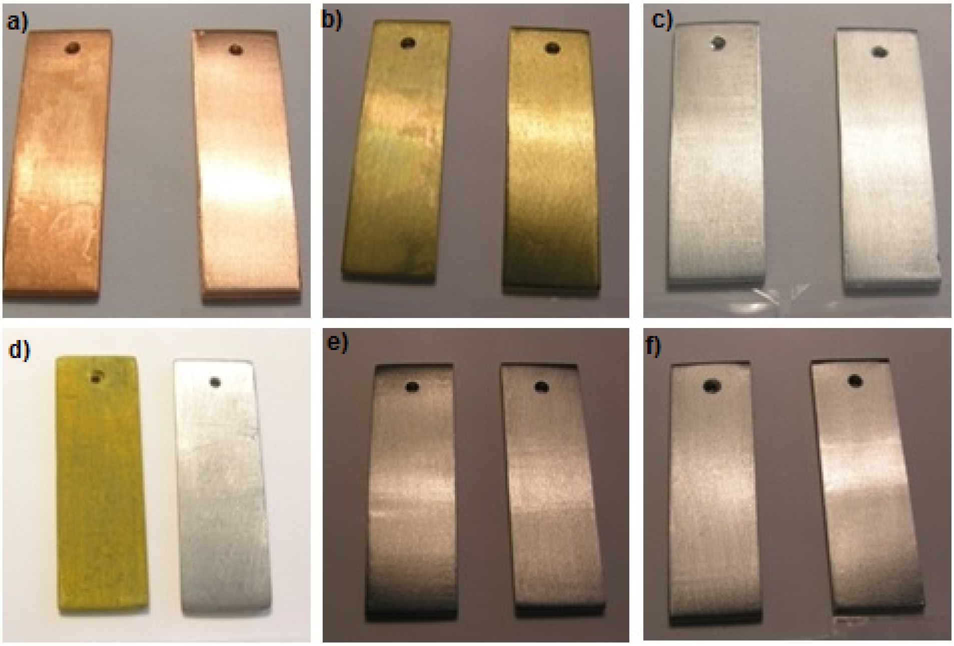

Figure 18. Appearance of samples after corrosion tests for a diesel fuel containing no FAME after 6 months of storage: a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

Changes were detected in the appearance of the plate surfaces for copper, brass, and lead which were exposed to the test fuel. Such changes were not observed in the case of plates after their exposure to the effect of vapors.

After storing the diesel fuel with no FAME for 12 months, the highest corrosion rate was recorded for lead (0.165 mm/year). The other test metals and steels showed high corrosion resistance (grade 2) (Table 1), and linear corrosion rate did not exceed 0.001 mm/year (Figure 19).

The appearance of the test samples after corrosion tests for a diesel fuel collected after 12 months of storage is illustrated in Figure 20. The surface of the copper plate after direct exposure to the fuel had not changed, which was the case for diesel fuel after 6 months of storage. This is confirmed by the value of linear corrosion rate, which is 4 times as low for the tests in the fuel after 1 year of storage.

Changes in the appearance of the plate surfaces were detected only for lead, which was exposed to the diesel fuel.

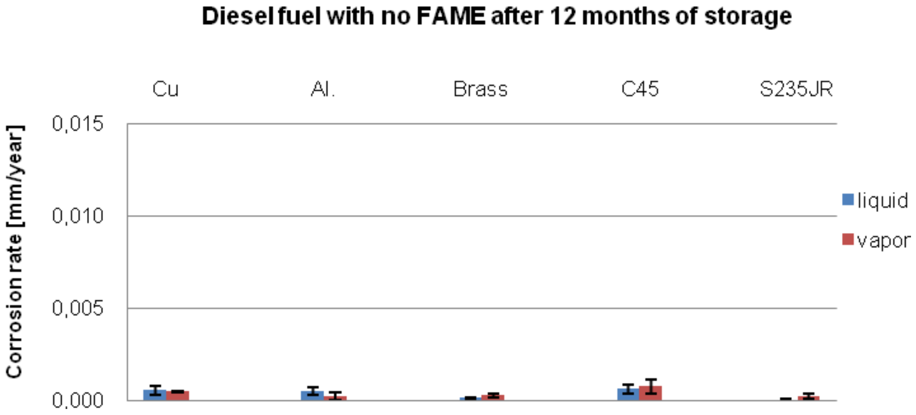

Figure 19. Linear corrosion rate for copper, aluminum, brass, C45 and S235JR steel after exposure in diesel fuel with no FAME after 12 months of storage

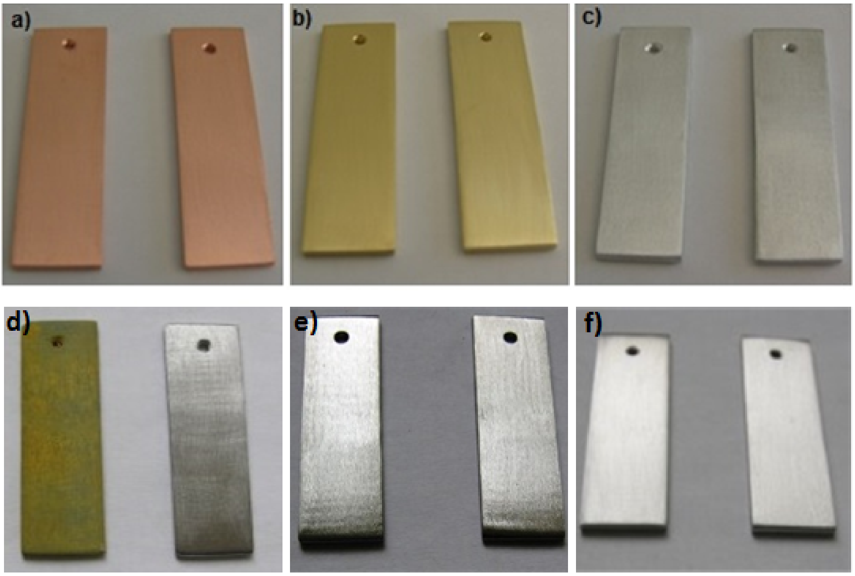

Figure 20. Appearance of samples after corrosion tests for a diesel fuel containing no FAME after 12 months of storage: a) copper, b) brass c) aluminum d) lead e) C45 steel f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

5. Conclusion

The present studies indicate that the test samples of gasolines showed a lower corrosive effect on the materials, selected for the corrosion tests, compared with diesel fuels. Regardless of the type of fuel, the highest rate of corrosion among the test samples of steel and other materials was observed for lead, both after 6 and after 12 months of storage. In the case of diesel fuels after 6 months of storage, a more pronounced effect on degradation of the test lead sample was observed for diesel fuel with FAME. Corrosion rate for lead in the diesel fuel with FAME was 3.5 times as high as that for the diesel fuel without FAME. For the other metals and alloys, tested in diesel fuel with FAME, corrosion rate was also higher, compared with the oil without the bio-component; this confirms literature reports relating to the adverse effect of the bio-component on the durability of structural materials. A macroscopic examination of the condition of the plate surfaces, tested in diesel fuels, indicated changes in the surface of copper, brass, and lead samples. For gasolines, the highest weight losses were recorded, again, for lead; in the case of gasoline with ETBE, higher losses were observed for the plates exposed to the gasoline vapors, compared with those directly immersed in the fuel. This may be attributed to the different composition and higher vapor pressure of the gasoline with ETBE. Compatibility with the test fuel samples was the highest in the case of steel and aluminum. Considering the duration of fuel storage time, corrosion rate was reduced for both test samples of diesel fuel after 12 months of storage, which is a beneficial phenomenon. On the other hand, the plates were exposed to the fuel for a rather short duration (approx. 17 days). In the aspect of the fuel blends' complexity and their storage for a relatively short period of time, the aforementioned tests ought to have been be carried out in fuels, exposed to storage for even longer durations. It seems that it would be beneficial to test the corrosiveness of the test fuel samples also with the use of other methods, such as impedance spectroscopy, techniques enabling a microscopic examination of the surface condition and composition, as well as measuring the rate of the corrosion, initiated in the early phase of storage.

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References

[1] Groysman A. Corrosion for Everybody.Springer; 2010.

[2] Teixeira L. S.G. et al.The influence of Cu, Fe, Ni, Pb and Zn on gum formation in the Brazilian automotive gasoline.Fuel Processing Technology 88; 2007. p.73–76

[3] Demirbas A. Progress and recent trends in biodiesel fuels.Energy Convers.Manag.; 2009:50:p.14-34

[4] Sarin A., Arona R., Singh NP, Dharma M., Malhotra RK.Influence of metal contaminants on oxidation stability of Jatropha biodiesel, Energy 2009; 34: p.1271-3

[5] Konthe G, Dunn RO. Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. I Am Oil Chem. Soc; 2003:80:p. 1021-6

[6] Chen L, Chen K, Deng B, Li Z.The metal corrosion of bio-fuel – Corros. Protect.; 2009:30(3):p.168-71

[7] Fazal MA, Haseeb ASMA, Masjuki HH. Comparative corrosive characteristics of petroleum diesel and palm biodiesel for automotive materials. Fuel Process Technol.; 2010:91(10):p.1308-15

[8] Hu E., Hu Y., Pan L., Jiang S. Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol Renewable Energy 37; 2012. p.371-378

[9] Karavalalus G, Stournas S, Karonis D. Evaluation of the oxidation stability of diesel/ biodiesel blends. Fuel; 2010; 89: p. 2483-9

[10] Karavalalus G, Hilary D, Givolou L, Karonis D, Stournas S. – Store stability and ageing effects of biodiesel blends treated with different antioxidants – Energy 2011; 36: p.369-74

[11] AquinoI.P., HernandezR.P.B., ChicomaD.L., PintoH.P.F.,.AokiI.V.Influence of light, temperature and metallic ions on biodiesel degradation and corrosiveness to copper and brass. Fuel 102; 2012. p.795-807

[12] YooY.H., ParkI.J., KimJ.G.,. KwakD.H, Ji W.S. Corrosion characteristics of aluminum alloy in bioethanol blended gasoline fuel: Part 1. The corrosion properties of aluminum alloy in high temperature fuels.Fuel 90; 2011. p. 1208-1214

[13] ParkI.J, Yoo Y.H., KimJ.G., KwakD.H., Ji W.S. Corrosion characteristics of aluminum alloy in bioethanol blended gasoline fuel: Part 2. The effects of dissolved oxygen in the fuel Fuel 90; 2011. p. 633-639

Chapter 6

Autoxidation of Fuels During Storage

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Małgorzata Odziemkowska

Additional information is available at the end of the chapter

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1. Introduction

Petroleum fuels are expected not to show any chemical changes during storage under certain conditions. Yet, a slow process of uncontrollable oxidation, also called autoxidation or self-oxidation, of which the mechanism is not thoroughly investigated, may occur even in a stable storage environment. The problem of autoxidation of fuels has gained particular importance after the introduction of product streams originating from the deep-processing of petroleum, e.g., cracking, as components of fuels.

The chemical changes, involved in the degradation of fuels, are not very well known yet, therefore, it is hard to predict the duration of storage for such fuel or to control the rate of its ageing. Stability of fuels during storage depends on their chemical composition, especially, the presence in them of compounds containing heteroatoms of oxygen, sulfur, nitrogen, traces of metal ions which catalyze oxidation processes, as well as on their storage conditions, such as temperature, access of light, possibility to absorb oxygen.

Hydrocarbons, the essential component of petroleum-based fuels, are likely during storage to react with atmospheric oxygen and with one another. Products which originate from oxygenation will undergo further changes, resulting in change of coloration, the presence of non-volatile, macromolecular substances (gum), as well as development of particulate matter followed by sediment/deposit [1]. There are many theories on the autoxidation of liquid hydrocarbons. One of them is based on the chain mechanism of radical reactions, formulated by Backstrom [2].

The theory is based on chain radical reactions with participation of peroxy and hydrocarbon free radicals, leading to the precipitation of substances which contaminate storage tanks, promote corrosion of transfer pipelines, cause filter plugging and similar problems in the fuel distribution system.

Descriptions of the specific steps of radical reactions are available from numerous reports. The changes, at all times, involve the presence of peroxides, as shown in the diagrams below [3]:

a. Initiation:

$$\text{R-H} + \text{Initiator (e.g., } \textit{light}, \ \textit{temperature}, \ \textit{catalyst}) \rightarrow \text{R}\bullet + (\text{H}\bullet)$$

b. Propagation:

$$\begin{gathered} \text{R}\bullet + \text{O}_2 \rightarrow \text{R-O-O}\bullet \\ \text{R-O-O}\bullet + \text{R-H} \rightarrow \text{R}\bullet + \text{R-O-O-H} \end{gathered}$$

c. Termination:

$$\begin{aligned} &\text{R}\bullet + \text{R}\bullet \rightarrow \text{R-R} \\ &\text{RO}_2\bullet + \text{RO}_2\bullet \rightarrow \text{ROOR} + \text{O}_2\text{, inactive products (alcohols, ketones)} \\ &\text{R}\bullet + \text{R-O-O}\bullet \rightarrow \text{ROOR} \\ &\text{RO}^\bullet\left(\text{or RO}^\bullet{}_2\right) + \text{ROOH} \rightarrow \text{different products} \\ &\text{ROOH} \rightarrow \text{non-radical products} \end{aligned}$$

d. Chain branching:

$$\begin{aligned} &\text{R-O-O-H} \rightarrow \text{RO}^\bullet + {}^\bullet\text{OH} \\ &\text{RH} + \text{RO}^\bullet \rightarrow \text{R}\bullet + \text{ROH} \\ &\text{RH} + {}^\bullet\text{OH} \rightarrow \text{R}\bullet + \text{H}_2\text{O} \end{aligned}$$

wherein: R–H – denotes hydrocarbon,

R• – hydrocarbon radical,
R-O-O• – peroxide radical,
R-O-O-H – hydroperoxide.

In the initiation step, the reactions generating hydrocarbon free radicals $\text{R}^\bullet$ run at a very slow rate, especially at ambient temperatures. The process rate may be increased by temperature and the presence of transition metals. The position where the hydrogen atom is detached from the hydrocarbon molecule is determined by the force of the C-H bond and the resonanse energy of the radicals being formed; the higher the resonance energy, the weaker the C-H bond force [4].

The chain growth or propagation step consists of two reactions. In the first reaction, which is irreversible, the hydrocarbon radical being formed in the initiation step reacts instantaneously with molecular oxygen, whereby a peroxide radical is formed. In the second reaction, which determines the rate of chain propagation, the peroxide radical will attach a hydrogen atom after detaching it from another hydrocarbon molecule. This produces a hydroperoxide and a hydrocarbon radical which is able to react with another oxygen molecule in accordance with the first reaction of the propagation step. The rate of C-H bond cleavage (initiation – the first reaction of the propagation step), depends on the type of substitutes: those hydrocarbons which contain a tertiary hydrogen or a hydrogen in the alpha position relative to the double bond or to an aromatic ring, are the most susceptible to oxidation.

The chain termination step includes recombination between the radicals and decomposition of hydroperoxides to non-radical products, such as alcohols, ketones, acids; they may react further, leading to macromolecular substances.

Branching of the reaction chain accelerates the formation of free radicals in the system – every single radical gives three more, which may participate in the process of propagation. That step is initiated by homolytic decomposition, at a slow rate, of the hydroperoxide R-O-O-H to the radicals RO• and •OH, which then very fast recombine with hydrocarbons, detaching the hydrogen atom therefrom. Cleavage of the O-O bond is characterized by a very high activation energy and it matters when temperature in the system is higher than 150°C [5]. The process is also accelerated by transition metal ions. The chain branching reactions are very important in the aspect of product stability. At high temperature conditions, aldehydes and ketones are able to react, producing acids and macromolecular substances.

The necessary conditions for autoxidation to take place in a system are: the suitable pressure of oxygen (50 Tr) [6], temperature in the range 30-120°C, the presence of a certain amount of hydroxides which initiate the aforementioned processes, or other factors which favor the formation of free radicals, for instance, active metal ions, water, microorganisms, light. Organic peroxides are merely intermediate products which may decompose to free, reactive radicals which initiate chain branching. In the initial stage of autoxidation, when the amount of free radicals in the system is small, the changes occur slowly. After the induction period, oxidation is rapidly accelerated due to the autocatalytic effect of intermediate products which accumulate in the fuel, and due to the reaction chain branching. The rate of oxidation reaches its maximum value after which it slowly decreases [7].

How the autoxidation chain is formed in the absence of oxidation promoters such as sunlight, sources of free radicals and metals, remains to be unknown. For gasolines which contain cracked components, it is safe to assume that active radicals as well as traces of metal ions originating from catalysts are present in the system. Moreover, as shown by Nagpal J.M. et al. [8], a tendency to develop gum depends on the amount and type of unsaturated hydrocarbons, present in the fuel. Studies reported by Pereira et al. confirmed [9] that not all of the olefins which are present in fuels will be transformed into resins to the same extent. Among those studied, the olefins forming secondary allyl radicals (cyclohexene and 2,4-hexadiene) had the highest contribution to the formation of macromolecular substances. The stability of allyl and alkyl radicals and the autoxidation reaction mechanism, confirming the occurrence of chain radical reactions, were also discussed.

2. Tests of RON 95 and RON 98 gasolines

Gasolines and compounds generated in degradation process have a complex chemical structure, therefore, it is hard to develop a reliable test to determine oxidation stability of fuels during storage. Although there do exist standard laboratory procedures for evaluation of oxidation stability of gasolines at certain intervals during storage, such procedures do not enable prediction of the potential duration of their further storage. Such methods are based on accelerated ageing processes which require elevated temperatures, high concentration of oxygen in the test sample and the presence of free metal ions which catalyze the reaction. The chemistry of the reactions taking place in accelerated ageing conditions may be far from changes associated with autoxidation of fuels during ambient storage. Therefore, chemical stability tests for fuels (such as induction period, potential resin content) are characterized by different correlations to changes occurring in real conditions in the storage tank. As mentioned before, some of the compounds taking part in oxidative chain reactions in gasolines are organic peroxides. The process is also affected by the content of unsaturated compounds, especially the precursors of secondary allyl radicals (e.g., cyclohexene, 2,4-hexadiene). In reactions involving peroxide radicals, which may occur at low (ambient) temperatures, the peroxide radicals are attached to the double bond.

As part of their experimental work on autoxidation of gasolines, including the effect of organic peroxides and cyclic olefins on the process, the present authors have studied the correlation between changes in the chemical composition of fuel and its chemical stability after the lapse of a certain time of storage. Two types of winter-time gasoline with the research octane numbers (RON) of 95 and 98, respectively, compliant with the quality requirements of EN 228 were tested [10]. Oxygen compounds were present in both types, with the total oxygen being lower than 2.7%(m/m). The RON 95 gasoline contained ethanol and ethyl *tert*-butyl ether (EETB), while the RON 98 gasoline contained only ethyl *tert*-butyl ether. Moreover, gasoline samples doped with 5.3 M solution of *tert*-butyl-hydroperoxide (TBHP) in decane were prepared. TBHP, a stable organic substance and a convenient source of radicals, is used for simulating oxidized liquid conditions [11]. The concentration of TBHP in the fuel was 50 millimols per liter.

Moreover, gasolines were included in the test which were doped with cyclohexene, a representative of cyclic olefins contributing to the intensification of autoxidation processes. Owing to environmental requirements, the total content of olefins in the fuels had to be a maximum of 18% (v/v), therefore, the maximum concentration of cyclohexene was 3% (v/v).

The gasoline samples were stored for 6 months in laboratory conditions at 15°C. Rapid ageing tests were carried out at certain intervals and chemical stability was monitored using selected methods.

The laboratory samples and methods of testing are shown in Table 1.

Gasoline samples	Symbol	Method of test
RON 95 gasoline	RON_95	FTIR spectroscopy ISO 7536 EN 16091 modified ISO 6246 ASTM D 873
RON 95 gasoline with TBHP	RON_95+PEROX	
RON 95 gasoline with cyclohexene	RON_95+OLEF	
RON 98 gasoline	RON_98	
RON 98 gasoline with TBHP	RON_98+PEROX	
RON 98 gasoline with cyclohexene	RON_95+OLEF	

Table 1. Gasoline test samples and methods of test

2.1. Usefulness of infra-red spectroscopy for studies on autoxidation of gasolines

Infra-red spectroscopy enables examination of the structure of molecules. It helps determine what functional groups the analyzed compound has in it. Functional groups are a group of several atoms connected with one another by means of chemical bonds (for instance, carbonyl group –C=O, hydroxyl group –OH). When present in the molecule of a given chemical compound, functional groups have characteristic vibration bands which are visible in the spectrum. A given functional group which is present in various compounds has similar vibration frequencies.

Autoxidation of hydrocarbons in gasolines leads, in the first place, to alcohols. They, in turn, are further oxidized to form aldehydes and ketones, leading to organic acids. The compounds have the following characteristic groups: hydroxyl group (for alcohols and acids) and carbonyl group (for acids, aldehydes and ketones). Although gasoline has a very rich IR spectrum, the characteristic bands for the aforementioned fuel oxidation products are manifested in easily identified ranges. For the hydroxyl group, it is a wide range with its maximum around 3300 cm^{-1}, while the carbonyl group gives a signal in the spectrum in the range from 1750 to 1650 cm^{-1}, depending on the type of compound (acids, aldehydes, esters, ketones). The location of the respective bands may be shifted, depending on the structure of a given compound (vicinity of other groups). IR spectroscopy is a fast and rather simple method, therefore, it was selected by the authors for establishing the correlation between changes in the chemical composition of fuels and their current chemical stability.

Oxidation stability of the gasolines during storage was tested at regular intervals. The results were compared with the IR spectra of the collected samples. The spectra were recorded using the Magna 750 apparatus from Nicolet in the wave number range from 4000 to 400 cm^{-1}, in a 0.065 mm thick KBr cell.

Comparison of the IR spectra for the RON 95 gasoline, recorded after various times of storage, enabled detection of changes in the area which is typical of the O-H and C=O groups (Figure 1).

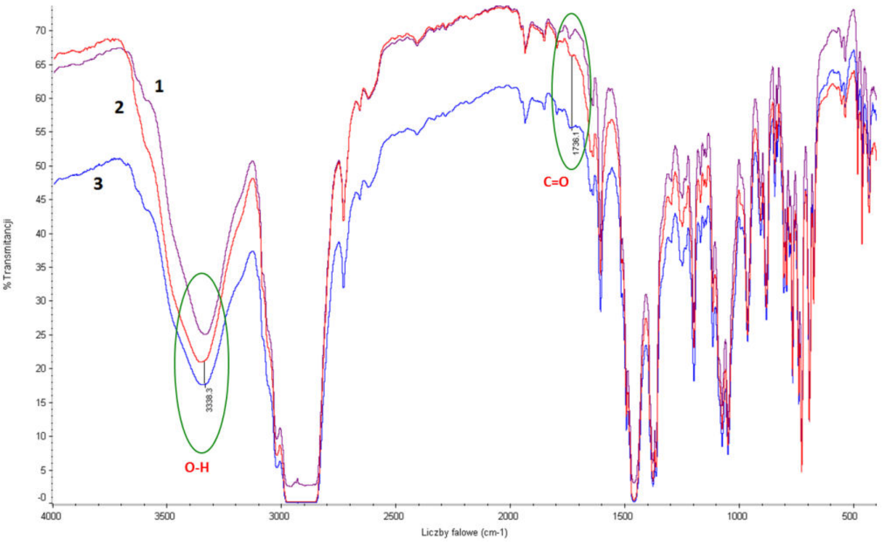

Figure 1. IR spectra, recorded for RON 95 gasoline samples: 1) fresh, 2) after 3 months of storage, and 3) after 6 months of storage.

The RON 95 gasoline had a content of alcohol (ethanol added during its production), therefore, the fresh fuel sample had a spectrum with the wide, strong band with its maximum at ab. 3330 cm^{-1}, typical of the O-H groups. The intensity of that band was increasing during the initial months of storage and decreasing in the later months. The changes are clearly seen after comparing the surface areas below that particular peak in the respective spectra – Table 2. Lowering of the spectrum for gasoline after 6 months of storage, clearly seen in Figure 1, is probably due to the fact that the sample was darker, compared with its initial color. Changes in the coloration of fuel during its ageing process are due to the formation of chromophore groups in it.

Sample number	3330 cm^{-1} band
RON_95 (1)	8426
RON_95 (2)	9120
RON_95 (3)	9746
RON_95 (4)	11021
RON_95 (5)	9198
RON_95 (6)	8677
RON_95 (K)	7009

Table 2. Surface area below the peak, typical of the OH group for RON_95 gasoline samples

The largest number of hydroxyl groups were detected in the RON_95 (4) gasoline sample, as shown by the largest surface area below the peak in question (Table 2). The surface area was growing larger during the initial months of storage, which is attributed to the formation of oxidation products (alcohols and/or acids). During the next months, the surface area was getting smaller which may have been caused by two phenomena: firstly, oxidation of alcohols to ketones and aldehydes, and the resulting disappearance of the O-H group; secondly, development in gasoline of some compounds in the form of gum. The emergence of carbonyl compounds is indicated by changes observed near the band at ab. 1743 cm^{-1} – Figure 2. Moreover, it should also be borne in mind that alcohol, an oxygen compound added to the gasoline, may be the precursor of the ageing processes.

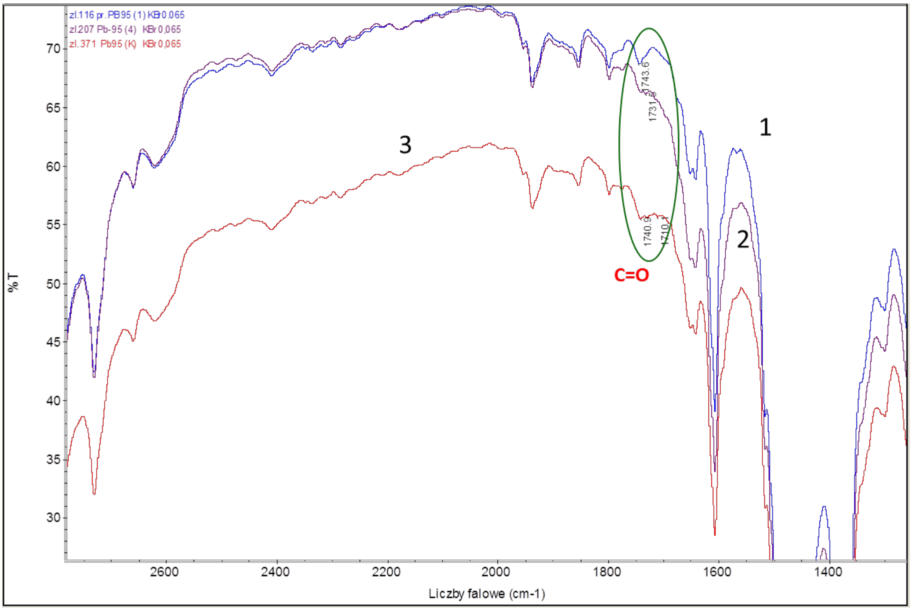

Figure 2. IR spectra in the range 2700-1300 cm^{-1}, recorded for RON 95 gasoline samples: 1) fresh, 2) after 3 months of storage, and 3) after 6 months of storage

There was a small, narrow peak in the spectrum of the fresh gasoline sample, with its maximum at ab. 1743 cm^{-1} (Figure 2). Minor changes were detected around that band in the spectra of gasoline samples after various periods of storage two more peaks were detected for lower wave numbers (ab. 1730 and 1710 cm^{-1}), tending to combine and form a wider, single band. The peaks may be attributed to various compounds containing a carbonyl group, which are formed in the fuel as the result of chemical changes during its storage.

In their own research, the present authors have demonstrated that changes observed in the RON 98 gasoline spectra after various periods of storage were different, compared with those observed for RON 95. The only similarity was that the gasoline spectrum was lowered after long-term storage. Figure 3 shows IR spectra, recorded for the RON 98 gasoline samples: fresh and those being stored for 3 and 6 months. Changes in the typical areas for the hydroxyl and carbonyl groups were less intense than those for RON 95. Surface areas below those bands were observed to change irregularly with time, although they were larger in every case than those in the fresh sample. The phenomenon made it impossible to predict the tendency of such changes – Table 3. Nonetheless, it was found that changes (increase or decrease) in the surface area below the characteristic band for the hydroxyl group involved a similar change below the peak for the carbonyl group. Such behavior was attributed by the authors to transformation processes taking place in oxidation products as well as to the precipitation of certain compounds in the fuel in the form of gum.

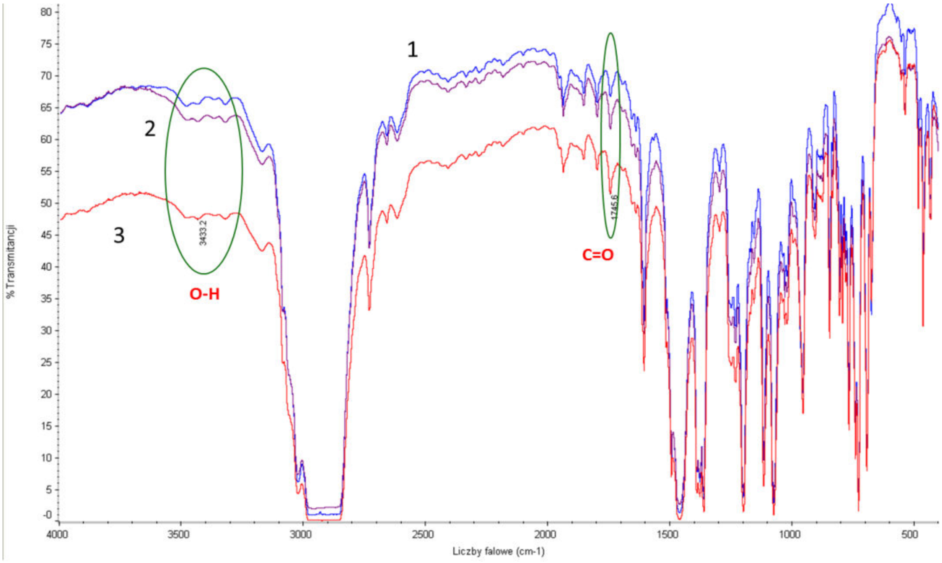

Figure 3. IR spectra, recorded for RON 98 gasoline samples: 1) fresh, 2) after 3 months of storage, and 3) after 6 months of storage

Sample	Band 3635-3281 cm^{-1}	Band 1746 cm^{-1}
RON_98 (1)	306	77
RON_98 (3)	542	182
RON_98 (4)	466	97
RON_98 (5)	-	132
RON_98 (6)	569	119
RON_98 (K)	388	110

Table 3. Surface area below the characteristic peak for the OH group in RON_98 gasoline

The authors' own research indicates that introduction to the fresh RON 95 gasoline of peroxides (precursors of oxidation) has no effect, during the short observation period, on changes in the chemical composition of the fuel due to autoxidation. The spectra of the fuels with TBHP, recorded during storage, were not different from those of the fuels without TBHP. Changes within the characteristic band for the carbonyl group, occurring in the gasoline during storage, were similar to those observed in the fuel without peroxides – the emergence of low intensity peaks below 1743 cm^{-1}, combined of low intensity peaks, combined to form a wider band. Similar changes as for the fuel without the compound were obsrved also in the surface area below the characteristic peak for hydroxyl groups: an initial increase in surface area during the first two months of storage was followed by its reduction. Comparison of the spectra for the RON 95 gasoline samples (fresh, stored for 6 months, and the one doped with peroxides and stored for 6 months) indicates that the presence of peroxides has caused a minor increase in the characteristic peaks for the carbonyl and hydroxyl groups, compared with the fuel which was stored without addition of TBHP.

Similar studies, carried out on the RON 98 gasoline, indicate that the presence of TBHP has not affected the nature of the fuel's autoxidation. The increase or reduction of the surface area below the characteristic vibration bands for the O-H and C=O groups, has not had any specific tendency. Comparison of the spectra for the RON 98 gasoline samples (fresh, stored with and stored without peroxides) has shown that addition of TBHP in this case has not had an observable effect on its oxidation rate.

The findings clearly indicate that autoxidation rate is affected by the type of gasoline while the oxidation precursor in the form of hydroperoxide, added to the gasoline, tends to enhance the differences.

Introduction to the gasolines to be stored of a substance which is susceptible to oxidation is expected to enhance their autoxidation. The hypothesis was validated by the findings reported by the present authors only for the RON 95 gasoline. The presence of cyclohexene in the fuel during storage has had a minor effect on the increase in the surface area below the characteristic peaks for the O-H and C=O groups. After the olefin was added to the RON 98 fuel, no significant changes in the nature of changes were observed in the bands under consideration for the hydroxyl and carbonyl groups. The results confirm the earlier conclusion made by the authors, concerning the effect of the gasoline type on the rate of processes which occur during its storage.

The tests, carried out by the authors, indicate that infra-red spectroscopy is useful for monitoring the processes taking place in gasolines, even during short-time storage. The processes are chiefly oxidative, as confirmed by changes, for instance, in intensity, shape, or the emergence of new peaks in the IR spectrum in the wave number ranges which are typical of the carbonyl and hydroxyl groups. They depend, for instance, on the type of gasoline stored (for instance, RON 98 is more stable) and on the presence of precursors of oxidation. When testing the stored gasolines periodically, the authors did not find any changes in their physico-chemical properties. The IR method enables the recording of even minor chemical changes resulting in deterioration of the fuel, which do not involved changes in physico-chemical properties, as determined by standardized methods.

2.2. Application of rapid ageing tests for evaluation of gasolines

Along with examination of their physico-chemical properties, the authors tested the gasolines periodically for their oxidation stability during storage and recorded the spectra of fuels after subjecting them to accelarated ageing.

Oxidation stability is commonly evaluated by determination of induction period according to ISO 7536 [12].

Induction period indicates the tendency of gasoline to develop gum during storage. The parameter is measured by the time that has lapsed from the beginning of the test to the occurrence of what is called "break point". According to the standard, the break point is defined as the point on the curve showing the pressure vs. time relationship before which the pressure drops by exactly 14 kPa within 15 minutes and after which the pressure increases by not less than 14 kPa within 15 minutes. It is assumed that a chemically stable gasoline will not, under conditions of test, be oxidized within less than 240-480 minutes [13].

In the stability tests according to the aforementioned standard, none of the gasoline samples actually had a break point after storage. Analyses of the pressure vs. time relationship during a 24-hour test indicate an incessant pressure drop, although the values were lower, compared with those required for the break point. The authors are of the opinion that pressure drop in the test cell indicated chemical reactions taking place in the system. IR spectra of fuel samples, prepared before and after the oxidation test clearly indicate the presence of oxidation products in the fuel.

Figure 4 shows a typical IR spectrum of RON 95 gasoline after 6 months of storage, subjected to the induction period test. Weak signals in the range that is characteristic for carbonyl groups, visible in the spectrum recorded after 6 months of storage (Figure 2 and Figure 3), are combined to form a strong, single band with its maximum at ab. 1710 cm^{-1}.

The spectrum of the fuel subjected to the induction period tests showed a strong, sharp signal with its maximum at the wave number 2332 cm^{-1}. The IR spectra recorded for samples collected after various times of storage and subjected to accelerated ageing indicate that the peak intensity at 2332 cm^{-1} increases slightly with longer storage times. The peak is characteristic, for instance, for the triple bond in nitriles C≡N. In that range, the signal may also originate from the C≡C group, although the characteristic peak for that group in pure compounds is in the lower wave number range 2100-2270 cm^{-1}. On the other hand, it should be noted that in the case in question, the sample was a complex mixture of organic compounds which may have led to band shifts in the spectrum. In the case of alkynes, where the triple bond is at the terminal carbon atom, the spectrum also has signals generated by the ≡C-H group: a strong and sharp band of stretching vibrations at ab. 3300 cm^{-1} and deformation bands in the ranges 1220-1370 cm^{-1} and 610-700 cm^{-1}. In the analyzed spectrum of RON 95 gasoline (sample after induction period), the presence of the aforementioned bands cannot be confirmed expressly because, if present at all, such bands were masked by other strong signals. Only a weak peak was visible at ab. 620 cm^{-1}, which might indicate that alkynes are one of the products of autoxidation of the fuel. Although such compounds might be just a temporary product, it would take detailed tests to confirm the hypothesis.

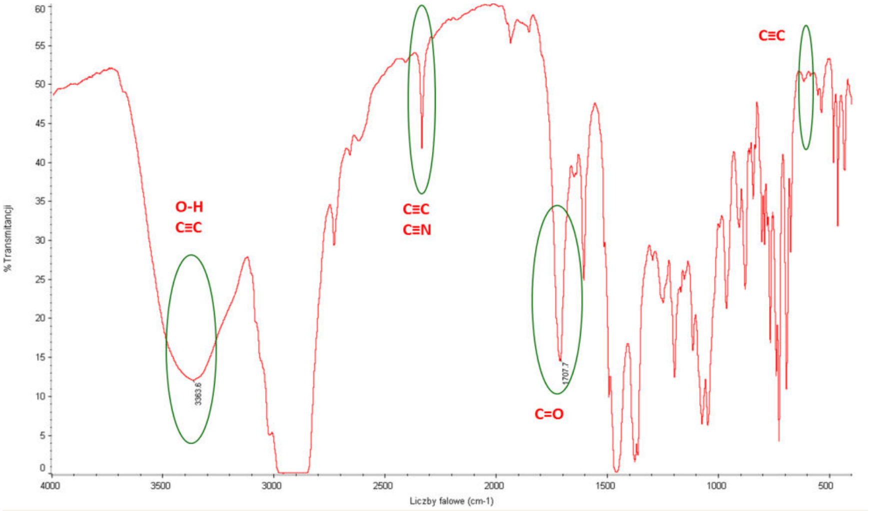

Figure 4. IR spectrum of RON 95 gasoline after 6 months of storage, after induction period tests

The authors observed that the oxidation tendency of RON 95 gasoline was getting higher after every month of storage, as indicated by the intensity of the signal, generated by the C≡C group. Even though a slight decrease in the surface areas below the characteristic peaks for the O-H and C=O groups was observed, this may have been caused by the ever more intense precipitation from the fuel of some compounds in the form of gum or by other, unidentified changes.

Subjecting the RON 98 gasoline samples to accelerated oxidation clearly improved the intensity of the signals attributed to the carbonyl group at 1730 cm^{-1} and to the hydroxyl group at the wave number 3322 cm^{-1} – Figure 6. Interestingly enough, compared with the spectrum for the RON 95 gasoline, the carbonyl band has its maximum shifted towards higher wave numbers. This may have been caused by the formation of other compounds containing a carbonyl group.

As in the case of the RON 95 gasoline, a peak having its maximum at the wave number 2332 cm^{-1} and a weak signal at ab. 620 cm^{-1} were observed in the spectrum for the RON 98 gasoline which was recorded in the sample after the induction period. The bands were attributed by the authors to unsaturated compounds having a triple bond (Figure 5). The signal at 2332 cm^{-1} in the spectrum for the RON 98 gasoline had a lower intensity, compared with that for RON 95, which might be due to the lower quantity of groups having a multiple bond in the structures of compounds formed in the fuel during its oxidation. However, the surface area below the peaks at the wave numbers 3300 cm^{-1} and 1730 cm^{-1} for RON 98 was getting smaller with the lapse of every month of storage; the same phenomenon was observed in the lower-octane number gasoline.

Addition of peroxides to the gasolines and subjecting the latter to the accelerated oxidation thereafter, has confirmed the nature of changes taking place in their composition, which were observed by the authors in the samples without peroxides. In the spectra of fuels, there is an

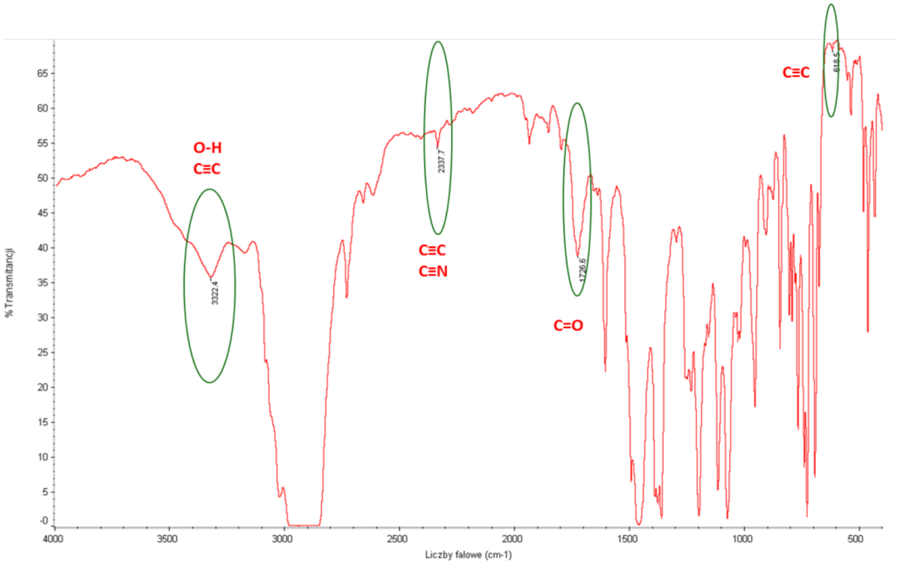

Figure 5. IR spectrum for RON 98 gasoline after 6 months of storage, after induction period test

intense band at the wave number of ab. 1720-1710 cm^{-1}, indicating the presence of compounds containing a carbonyl group. Moreover, the surface area below the peak (3300 cm^{-1}) corresponding to the –OH group vibrations tended to increase. A band appeared which had its maximum at 2332 cm^{-1}; its intensity varied with the fuel type and duration of storage. In the gasoline samples with peroxides added to them, part of the compounds containing –OH and C=O groups tended to precipitate or were further transformed during the subsequent months of storage. This was indicated by the slightly reduced surface area in the peaks of interest in the spectra of those fuels, subjected to accelerated oxidation. Similar changes were also observed in the fuel samples with cyclohexene added to them.

2.3. Application of the induction period in the evaluation of gasolines

The authors' own findings indicate that it is not possible to differentiate between the chemical stabilities of gasolines during short-term storage using the induction period method according to ISO 7536. Therefore, chemical stability was evaluated using the oxidation stability test based on rapid small-scale oxidation according to EN 16091 [14]. The test also uses the pressure drop criterion vs. duration of test. However, for the purpose of this test, the induction period is defined as the time that has lapsed from the commencement of test to the critical point, understood as a pressure drop by 10% relative to the maximum pressure, recorded during oxidation. The oxidation stability findings obtained by this method are referred to later in this paper as the "induction period by micro method".

The method is mainly used for determining oxidation stability of diesel oils, methyl esters and mixtures thereof, although it is also useful for determining the chemical stability of gasolines, in suitably selected conditions of test. The gasoline samples described above were tested by the authors in the following conditions: temperature 140°C, initial pressure of oxygen - 500 kPa, sample volume - 5 cm^3. Findings for RON 95 are shown in Figure 6, those for RON 98 are shown in Figure 7.

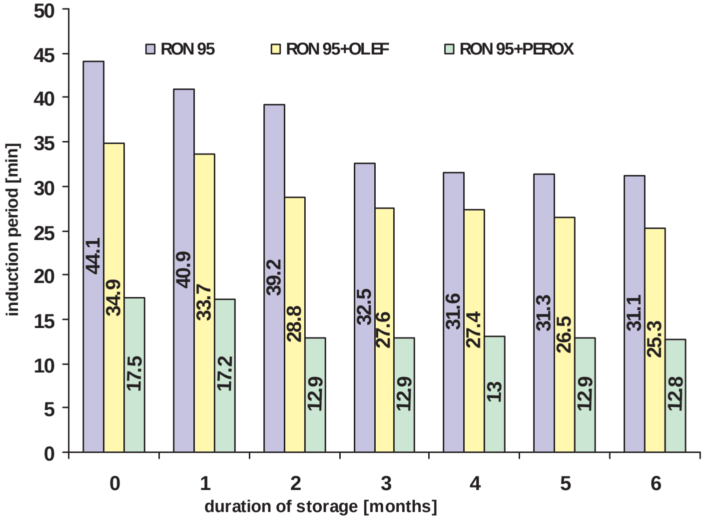

Figure 6. Induction period by micro method for RON 95 gasoline samples vs. duration of storage

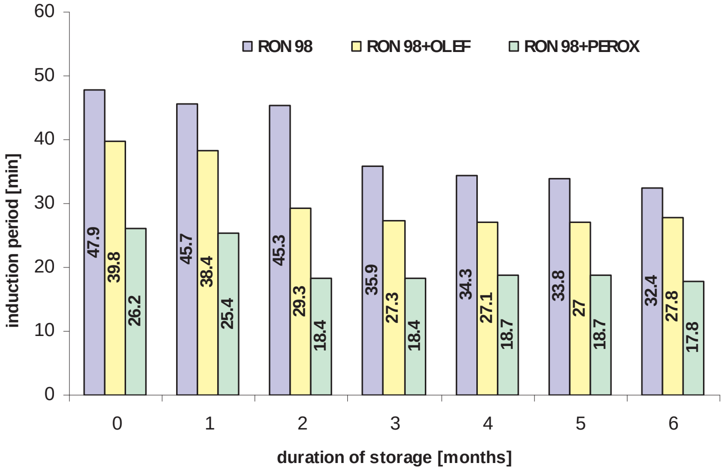

Figure 7. Induction period by micro method for RON 98 gasoline samples vs. duration of storage

During a 6-month period of storage under established conditions, induction period by micro method according to EN 16091 was shorter for every test sample. As expected, the gasolines without addition of olefin or peroxide were characterized by longer induction periods, compared with the doped gasoline samples, while the RON 95 gasoline showed lower stability, compared with RON 98. In both gasoline types, addition of TBHP reduced the induction period more than did addition of cyclohexene. The most markedly reduced induction period in the samples with the peroxide and olefin was observed during the initial two months of storage, and changes were only slight in the months which followed; for pure gasoline samples the tendency was observed after three months of storage.

The authors are of the opinion that the findings have confirmed the hypothesis that addition of an organic peroxide or cycloolefin to the fuel has had a deteriorating effect on the chemical stability of the fuels. Degradation of gasoline was accelerated by the substances. This proves the assumption that the substances take part in autoxidation processes. Regardless of the chemical composition of the initial fuel, the degrading effect of TBHP was more prominent than that of cyclohexene. Moreover, the findings indicate that the standard method to measure the induction period for gasoline during storage is not reliable in detecting minor changes in the chemical composition of hydrocarbons which occur due to autoxidation. On the other hand, measuring the induction period using the micro method may be useful in evaluating the chemical stability of fuels. Moreover, it is a rapid test, which is an advantage.

2.4. The contents of gum, inherent and potential resins vs. chemical stability of fuels

When studying the chemical stability of fuels during storage, the contents of inherent resins and gum was determined according to ISO 6246 [15]. The term "gum" is understood as the residue on evaporation of the test fuel, not subjected to further chemical treatment. It comprises an n-heptane-insoluble portion, non-volatile compounds such as contaminants, and additives. What remains after washing the resins with n-heptane and the solvent evaporation is a residue, referred to as "inherent resins"; its maximum level in the finished fuel is limited at 5 mg per 100 ml fuel.

The resistance of fuel to chemical changes is determined by its potential resin content, though only with reference to its current condition. The parameters may indicate oxidation processes taking place in the fuel, though it should be remembered that the value of the parameter will be increased by the improvers, added to the fuels. Even though the potential resins do not tend to cause any specific disturbances with the operation of fuels they may, in unfavorable conditions, settle in transfer lines and fuel filters, plugging them.

The content of gum vs. time of storage is shown in Figures 8 and 9; that of inherent resins is shown in Table 4.

In the case of RON 95, the lowest values of gum content were found in the gasoline samples with no admixtures. The parameter showed a growing tendency for samples with addition of cyclohexene, although no distinct tendency was found for the gasoline with a peroxide content.

For RON 98 – whether pure or with addition of cyclohexene – no tendency to change the gum content was detected. To the contrary, in the gasoline samples with a peroxide content, the

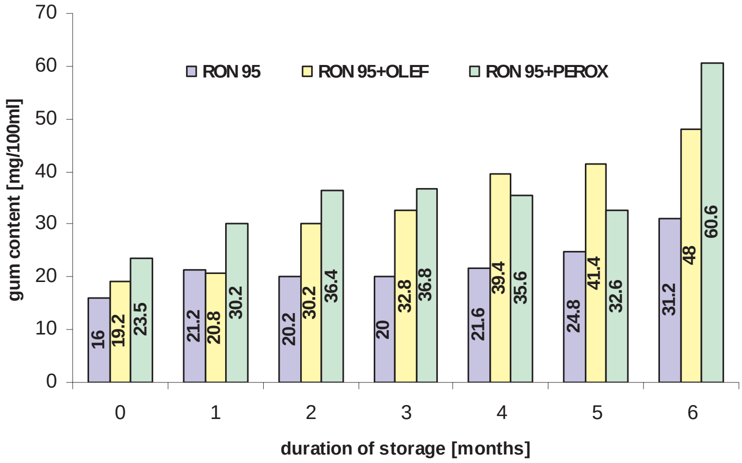

Figure 8. Gum content in the RON 95 gasoline vs. time of storage

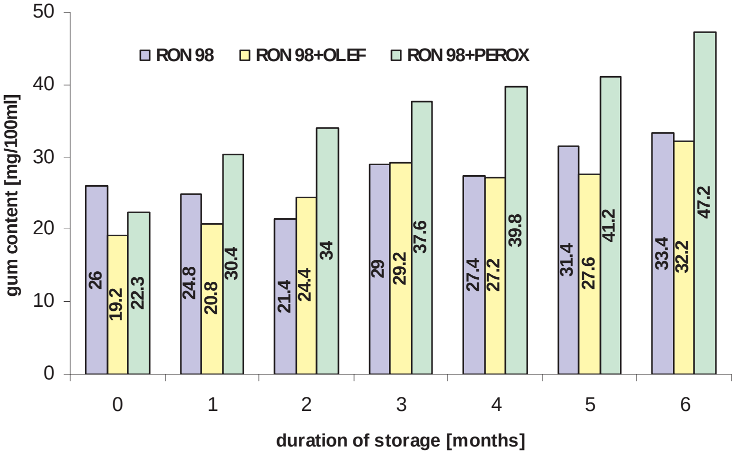

Figure 9. Gum content in the RON 98 gasoline vs. time of storage

value of the parameter was found to increase with storage time. When comparing the gum content in pure RON 95 and RON 98 samples vs. time of storage, lower values of the parameter were detected for alcohol-ether gasoline.

Table 4 shows the inherent resin content.

Storage time	Inherent resins mg/100 ml					
	RON 95	RON 95 +OLEF	RON 95 +PEROX	RON 98	RON 98 +OLEF	RON 98 +PEROX
Initial condition	0.0	0.4	0.5	0.0	0.4	0.5
1 month	0.0	0.0	0.0	0.2	0.0	0.0
2 months	0.0	0.0	0.6	0.0	0.6	0.0
3 months	0.0	0.4	0.0	0.0	0.0	0.4
4 months	0.4	0.0	0.8	0.0	0.3	0.0
5 months	0.3	0.0	0.0	0.0	0.2	0.6
6 months	0.0	0.0	1.4	0.0	0.0	0.0

Table 4. Inherent resin content in gasoline after storage

Based on the analysis of the findings shown above, it was not possible to find any explicit relationship between the inherent resin content in the gasoline samples and their time of storage. After 6 months storage, the inherent resin content was determined only in one sample out of a total of six samples tested.

The induction period data according to ISO 7536 for the stored samples did not make it possible to expressly evaluate the ageing tendency of fuels during long-term storage and they did not correlate with the resin content according to ISO 6246; therefore, stability tests were carried out according to ASTM D 873 [16]. Ageing was carried out for 4 hours under oxygen flow conditions: pressure 690-705 kPa, temperature 100°C. The result of determination was the potential resin content, being the sum of solubles and insolubles. In the present test, insolubles are defined as a deposit which adheres to the glass wall of a test cell from which an aged fuel was removed along with precipitates and solubles; such insolubles are determined from an increase in the weight of the test cell after the test, as compared with the clean test cell, weighed before the test. Soluble resins are regarded as oxidation products which are dissolved in the aged fuel plus deposits which adhere to the cell walls, soluble in a toluene-acetone mixture. A non-volatile residue on evaporation of the aged fuel and the solvent which was used for washing the test cell after the test is the soluble resin content.

Determination of the potential resin content enables the evaluation of the fuel’s ability to develop gum and deposits and is an additional indicator of chemical stability for gasolines.

Results for the solubles content of the gasoline samples vs. time of storage are shown in the graphs below. The insolubles content is shown in Table 5.

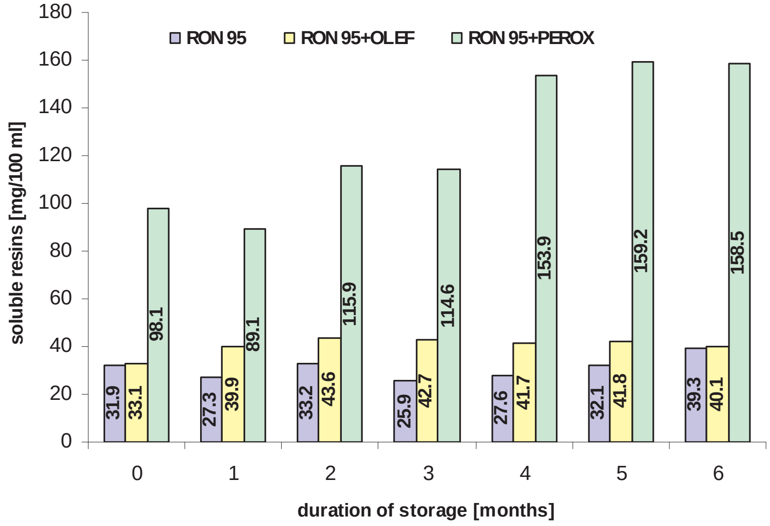

Figure 10. The soluble resins content according to ASTM D 873 in RON 95

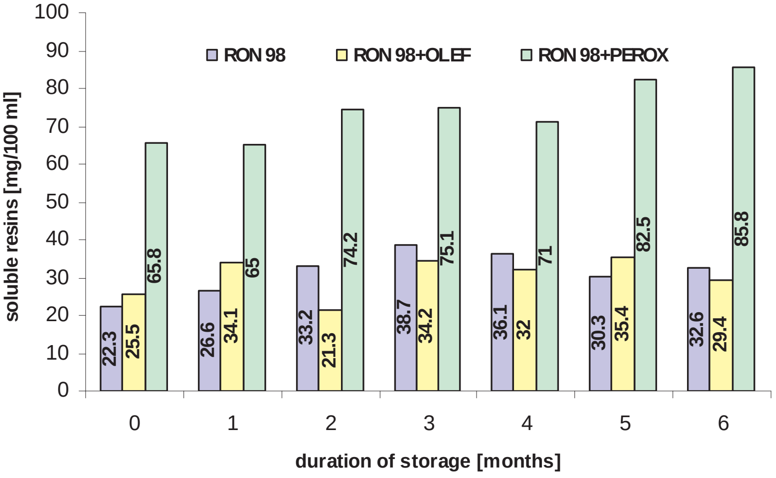

Figure 11. The soluble resin content according to ASTM D 873 in RON 98

Storage time	Insolubles mg/100 ml					
	RON 95	RON 95 +OLEF	RON 95 +PEROX	RON 98	RON 98 +OLEF	RON 98 +PEROX
Initial condition	0.2	1.1	1.0	0.3	1.2	1.1
1 month	0.2	1.1	0.5	0.3	1.4	1.5
2 months	0.4	0.9	1.2	0.5	1.3	0.7
3 months	0.9	0.6	0.8	1.1	0.7	0.7
4 months	0.5	0.5	0.6	1.0	0.7	1.2
5 months	0.7	0.6	0.9	1.0	0.4	0.7
6 months	0.8	0.9	0.9	1.0	0.8	1.1

Table 5. The insolubles content according to ASTM D 873 in gasoline during storage

The gasoline samples with a peroxide content have a very high soluble resins content, except that, for RON 95, the value is nearly twice as high as that for RON 98 (for samples stored for more than 3 months).

For alcohol-ether gasoline without admixtures and for that with an admixture of cyclohexene, the value of that parameter grows moderately with storage time while there is an observable tendency toward change in similar ether-based gasoline samples.

Every oxidized sample was tested to determine its content of insolubles, although no different storage times. No precipitated or suspended deposit was detected in the fuel in either sample after ageing.

3. Tests on diesel oil

The chemical instability of diesel oil is caused by the presence in the fuel of compounds which act as precursors of the formation macromolecular structures with limited solubility. Generally, such compounds include components containing nitrogen and sulfur, reactive olefins, as well as organic acids.

A quite well known mechanism, generating insolubles in diesel oil, is the transformation of phenalenones and indoles to indolephenalene salt complexes. The reaction is favored by acid conditions. Phenalenones are formed by oxidation of active olefins whereas indoles are a natural component of fuels. Organic acids, the indispensable catalyst for the reaction, are usually present in components of fuels or are generated by oxidation of mercaptanes to form sulfonic acids. The mechanism of deposit formation may be interrupted by neutralization of acidic conditions or elimination of the precursors with the use of hydrogen or suitable additives having a stabilizing or antioxidative properties.

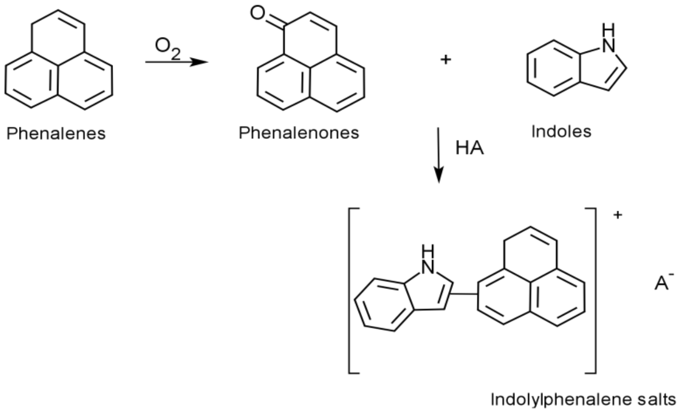

Figure 12. The mechanism of formation of deposits in diesel oil.

S.J. Marshaman and P. David [17] proposed a reaction mechanism comprising several steps and leading to the development of deposits by oxidation of phenalenes to phenalenones, followed by addition to the phenalenones of indoles, which later form indolephenalene salt complexes in an acidic environment. The reaction mechanism is shown in Figure 12.

S.J. Marshaman and P. David developed methods to monitor the level of phenalenes and phenalenones, compounds leading to the development of deposits in fuels. It was a two-way study: the fuels were subjected to long-term ambient storage while, at the same time, rapid ageing tests were carried out at elevated temperatures and/or oxygen at a positive pressure. The concentration of phenalenes and phenalenones was measured by chromatographic methods (HPLC). After being subjected to a standard ageing test according to ASTM D 2274, the fuel samples did not show any tendency to develop large amounts of insolubles. On the other hand, when subjected to the test method simulating long-term storage conditions in accordance with ASTM D 4625, the fuel samples showed a regular increase in the amount of gum/resin or deposits, corresponding to an increase in the time of storage. After 16 weeks of testing, the amount of filterable deposits was 4.0 mg/100 cm^3, and that of resins was 6.9 mg/100 cm^3, with the initial value being less than 0.1mg/100 cm^3. For the initial 2 months of storage, the fuel was not undergoing any intensive ageing and a significant increment in the amount of total deposits was recorded only after ab. 12 weeks.

In the case of the fuels which were stored in steel tanks in ambient conditions, the amount of insolubles was observed to grow around the 30th week of storage, and the total deposit was 16.8 mg/100 cm^3 after 50 weeks.

The levels of phenalenes (and their alkyl homologs) and phenalenones were measured during the entire process of ambient storage of the fuel samples. The tests indicate that, for longer storage times, the content of phenalenes decreased from 860 mg/l to 135 mg/l in the 46th week of storage, while that of phenalenones increased from 15 mg/l to 188 mg/l. This confirms the proposed mechanism for oxidation of phenalenes to phenalenones. The present authors monitored the fuel for coloration and acidity while carrying on this study. They found that changes in the color of fuel was connected with increased concentrations of phenalenones: the longer the storage time, the darker the fuel. Its darkening was deemed to indicate the formation of precursors of deposits. Furthermore, the present authors have demonstrated that the presence in the fuel of strong acids, such as aromatic sulfonic acids, accelerates the formation of deposits.

Indole, along with its alkyl derivatives, is another important compound, participating in the development of deposits. L.A. Beranek *et al.* [18] have carried out studies on fuel blends comprising straight run distillate (SRD) and light cycle oil (LCO) fractions. The latter are classified as chemically unstable compounds. Compounds such as 2-methylindole, 3-methylindole and 1-phenalenone were introduced, additionally, to the model fuel samples. The samples were subjected to rapid ageing in pressurized bombs for a period of 64 hours at elevated oxygen pressure conditions, at a temperature of 95°C.

For the fuel blends which were composed of straight run distillate only, the amount of insolubles was not observed to increase, regardless of whether indoles and phenalenone were added thereto. In the case of fuel blends comprising, additionally, a fraction rich in cyclic compounds, the level of deposit after the test was definitely higher for the samples with a content of indoles and phenalenone. The findings also indicate a decrease in the concentration of indoles in the samples which were subjected to rapid ageing; on the contrary, the content of phenalenone was not reduced. More deposit is formed for the samples containing 2-methylindole, compared with those containing 3-methylindole.

One more mechanism explaining the course of the fuel ageing process is postulated, especially for low-sulfur fuels which contain biocomponents, where the formation of deposits and gum is a multi-step radical reaction, involving the participation of hydroperoxides. Dan Li *et al.* [19] have described studies on the thermooxidative stability of aviation fuel. They have observed that degradation of aviaton fuels may be caused by the short-term effect of high temperatures. To validate the hypothesis, they tested several samples of aviation fuel by subjecting them to oxidation at various temperatures (120–180°C) for a maximum of 20 hours. Small amounts of the fuel were sampled at intervals in the process of testing in order to determine the level of hydroperoxides and for spectral analyses.

The content of hydroperoxides in the test fuel samples varied, depending on time and oxidation temperature. The general relationship observed during the test, regardless of process temperature, was that the level of hydroperoxides will increase up to a certain maximum, followed by a decrease to a certain level. The higher the process temperature, the faster the increase in the hydroperoxide concentration. The hydroperoxide was formed at a higher rate than decomposition, which resulted in an increase in the resultant amount of the hydroperoxide. The authors emphasize that such behavior is in agreement with the free radicals mechanism, as described by Zabarnick [20]; hydroperoxides may be regarded as intermediate compounds in the consecutive reactions of autoxidation of hydrocarbons. During the tests, it was also observed that the fuel with a higher content of polar components would be oxidized sooner. Generally, the presence of polar components is the principal factor of instability. An analysis of the FTIR spectra of fuel samples, collected at various intervals during the process of oxidation, indicated the development in the fuels of structures which are typical of oxidation products: carbonyl and hydroxyl groups were identified. The peak intensity of such groups was the higher, the longer the time of oxidation.

S. Gernigon *et al.* [21] investigated the probability of inhibiting the hydrocarbons radical oxidation reaction by using suitable anti-oxidants. They selected BHT (butylated hydroxytoluene), 2,4-DTBP (2,4-di–tert-butylphenol), TBMP (2-tert-butyl-4-methylphenol). Their studies were carried out on four selected, pure hydrocarbons, representing aviation fuel components. Degradation of the test hydrocarbons was carried out by oxidation at a temperature of 185^{o}C for 72 hours. For identification of the compounds being formed by oxidation, as well as to study the kinetics of decomposiiton of hydrocarbons and the additives used, the hydrocarbon samples were analyzed by GC/MS, GC and FTIR. The authors found that the hydrocarbons were decomposed in the process of oxidation forming new compounds, usually ketones, alcohols and carboxylic acids. The longer the time of degradation, the higher the amount of such compounds. Moreover, it was found that the amount of antioxidants was reduced in the course of oxidation and their efficiency depended on the concentration of a given additive, oxidation time, and composition of the fuel. BHT degradation products were identified as ketones, alcohols, carboxylic acids and BHT dimers. The antioxidants tested were found to be more effective toward alkanes, compared with cyclic compounds. Deposits were not formed in the degraded hydrocarbons, even though oxidation was taking place, as confirmed by the presence of ketones, carboxylic acids, and alcohols.

The process of degradation of stability of fuels relates also to products which contain biocomponents; in diesel oil, the biocomponent is fatty acid methyl esters (FAME). Esters are a non-toxic, sulfur-free, biodegradable biocomponent with low oxidation stability. In esters, stability largely depends on the profile of the fatty acids they are made from. Polyunsaturated fatty acids are more reactive, compared with saturated compounds. G. Karavalakis *et al.* [22] report that esters react with oxygen via an autoxidation mechanism involving a radical reaction through the steps of initiation, propagation, chain branching and termination. The essential products of oxidation include allyl hydroperoxides, unstable products which form secondary products of oxidation such as aldehydes and ketones, cyclic acids, polymeric compounds. The presence of macromolecular, polymerized compounds, may lead to the development of gum.

G. Karavalakis, S. Stournas and D. Karonis [23] have studied the oxidation stability of biodiesel (100% FAME) and blends of diesel oil with FAME, according to the methodology described in EN 14214 and EN 15751. The authors have demonstrated that the larger the ester content in diesel oil, the shorter its induction period, therefore, the product is more susceptible to oxidation. Susceptibility of such blends to oxidation depended also on the type of raw material the ester was made from, and on the composition of diesel oil.

The present authors have attempted to validate the hypothesis, proposed by S.J. Marshaman and P. David, concerning the mechanism of deposit formation due to the oxidation of phenalenes in relation to the contemporarily used low-sulfur diesel oils with a content of fatty acid methyl esters. Methyl esters are known to be readily decomposed to acids; therefore, it was assumed in the present work that the acid being formed by fuel oxidation may favor the transformation of phenalenones and indoles to indolephenalene salt complexes, finally generating deposits and gum. An indole derivative (2-methylindole) was added to the test samples in order to intensify the process of oxidation of diesel oil. The tests were continued for 6 months while monitoring the fuel degradation rate with the use of normative and supplementary tests enabling the measurement of deposits and gum and of the induction period.

3.1. Methods of tests

Several accelerated ageing tests, which are most commonly used for determining the degree of fuel degradation, were selected for the study. All of the selected tests are dedicated to testing straight run distillates. The research problem assumed by the authors requires determination of the amount of deposits which may potentially be developed from degradation of a fuel doped with 2-methylindole; for that reason the ASTM D 5304 and EN ISO 12205 tests were used. Both these tests determine the amount of filterable and adherent insolubles (gum). All the same, in order to verify the theory of fuel degradation without deposit formation, two tests were selected EN 16091 (PetroOxy) and EN 15751 (Rancimat), of which the result is presented as the induction period. Elevated temperatures were used in each of the four proposed methods for determining oxidation stability of fuels, oxygen environment was used in three of them. In the method according to ASTM D 5304 and EN 16091, oxygen is used at a pressure in the range 700-800 kPa.

Definitions of terms:

1. Filterable insolubles – deposit/sediment formed during the test, which may be removed from the fuel by filtration using a filter pore size of 0.8 μm. This type of deposits includes both the particulate matter and deposits washed out using a unary solvent (isooctane).
2. Adherent insolubles (gum) – deposit formed during the test, sticking to the glass parts of the fuel filtration system. Deposits from the walls are washed using a ternary solvent before evaporating it.
3. Total insolubles – a sum of filterable and adherent deposits.
4. Induction period in the Rancimat test – the time that lapses from the commencement of measurement to the time when the formation of oxidation products is severely intensified, as recorded by changes in electrolytic conductivity.
5. Induction period in the PetroOxy test – the time that lapses from the commencement of measurement to the time when oxygen pressure in the test chamber is 10% below its initial value.

The Rancimat test is carried out mainly for straight run distillates with a content of more than 2% (V/V) FAME as well as for FAME as a pure biofuel. The other tests may be used for testing a petroleum-based hydrocarbons fuel or one with biocomponents. The test conditions are described in the Table below.

Test	Conditions of test	Form of results
EN ISO 12205	temperature 95°C, oxygen flow, duration 16 hours	Deposits and gum
EN 15751 Rancimat	temperature 110°C, air flow	Induction period
ASTM D 5304	temperature 90°C, oxygen pressure 800 kPa, duration 16 hours	Deposits and gum
EN 16091 PetroOxy	temperature 140°C, oxygen pressure 700 kPa	Induction period

Table 6. Conditions of rapid oxidation tests

A spectrophotometric analysis of the fuel samples was performed using the FT-IR spectrophotometer Magna 750 from Nicolet. The fuel samples were subjected to oxidation at a temperature of 140°C, under oxygen-flow conditions at a pressure of 700 kPa. After ageing, the fuel samples were subjected to a spectral analysis. The spectra were measured in a 0.065 mm thick KBr cell in the wave number range from 4000 to 400 cm^{-1}. The same technique was used for measuring the samples not subjected to rapid ageing.

3.2. The use of rapid ageing tests in the assessment of rate of change in fuels during storage

The test material consisted of two samples of diesel oil with different contents of fatty acid methyl esters. Each sample was doped with 130 mg/kg of 2-methylindole. The value was assessed based on literature reports. The samples were stored at a room temperature for 6 months in a dark place and were collected for testing at 30-day intervals. Their compositions are shown in the Table below.

Composition of samples	Sample symbol	Methods of tests
Diesel oil with 1.3% (V/V) FAME	A	EN ISO 12205 ASTM D 5304 EN 16091 FTIR spectra
Diesel oil with 1.3% (V/V) FAME + 130 mg/kg 2-methylindole	AM	
Diesel oil with 7.2% (V/V) FAME	B	ISO 12205 EN 15751 ASTM D 5304 EN 16091 FTIR spectra
Diesel oil with 7.2% (V/V) FAME + 130 mg/kg 2-methylindole	BM	

Table 7. Compositions of samples and methods of tests

When testing the diesel oil samples with a low content of FAME, no effect of an increased level of indole compounds on the rate of fuel degradation, expressed as the induction period, was observed. The induction period value was lower after 6 months of storage, compared with the beginning of tests. For sample A (without indole), the induction period was reduced from the initial 41.9 minutes to 32.8 minutes, for the sample AM (with indole) it was reduced from 38.7 minutes to 30.9 minutes. The rates of fuel oxidation were similar, both for the samples with and without methylindole. The induction period values were comparable in the first, second or third month of storage and identical in the fourth month of storage; a definitely shorter induction period was recorded only after 6 months of storage.

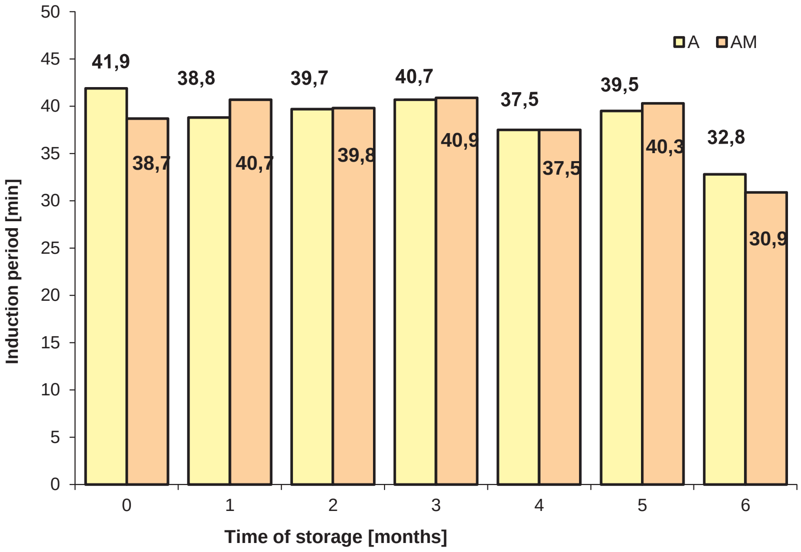

Figure 13. Induction period, as found according to EN 16091, for diesel oil samples containing 1.3%(V/V) FAME and methylindole.

The thermooxidation stability test according to ASTM D 5304 has demonstrated that, for a same duration of storage, more insolubles are formed in diesel oil samples with methylindole, compared with those without methylindole. After running the test for 3 and 4 months, sample AM was found to contain 2-3 more deposit, compared with sample A which had no content of indole. After 5 and 6 months, the amount of deposit was reduced although still higher than in sample A. No obvious relationship between the duration of storage and the content of filterable or adherent deposits was noted.

Determination of oxidation stability according to EN ISO 12205 was performed twice: at the beginning of tests and after 6 months of storage. Sample A was initially found to contain: 4 g/m^3 of filterable deposits, 3 g/m^3 of adherent deposits, a total of 7 g/m^3. After being stored for 6 months, the same sample contained 25 g/m^3 of filterable deposits and 2 g/m^3 of gum, a total of 27 g/m^3. Very similar values were obtained for sample AM with a content of methylindole: initially, the content of filterable deposits was 3 g/m^3, that of gum 2 g/m^3; after 6 months, the sample contained 26 g/m^3 of deposits and 3 g/m^3 of gum. It was found that the amount of adherent deposits was not changed in the samples during storage,

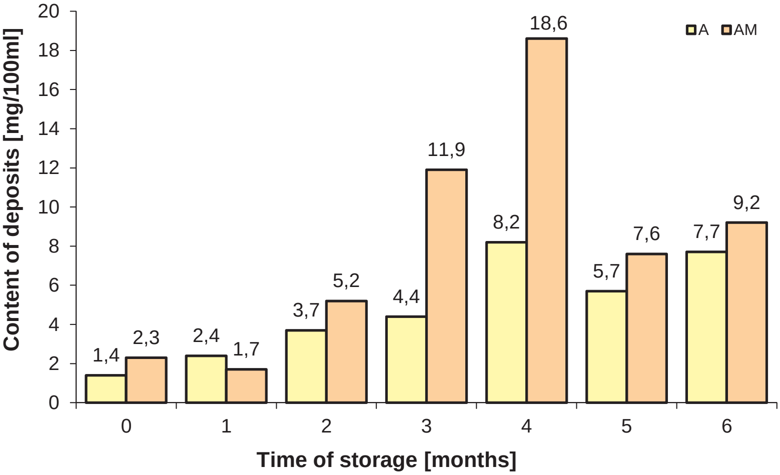

Figure 14. Total insolubles, as found according to ASTM D 5304 for diesel oil samples with 1.3%(V/V) FAME and methylindole.

although that of filterable deposits was definitely increased, regardless of whether the sample contained any methylindole.

Tests of diesel oil samples with a content of 7.2% (V/V) FAME showed a certain relationship between the induction period and time of storage. The longer the time of storage, the shorter the induction period. The fuel oxidation process was running faster for the samples with a content of methylindole.

The thermooxidation stability test according to ASTM D 5304 was carried out for samples with a higher content of FAME. The test showed, just like for the samples with 1.3%(V/V) FAME, that a higher amount of total insolubles was formed in the samples with methylindole, compared with those without methylindole. After storing the samples for 3 months, the maximum amounts of deposit were recorded in sample BM - 18.2 mg/100 cm^3 and in the indole-free sample B - 11.5 mg/100 cm^3. This means a 6-7-fold increase, compared with the initial amount of deposits. The amount of total deposit depended on filterable deposit because the content of adherent deposits was not high-just between 0.1 and 1.9 mg/100 cm^3.

Measurement of the induction period by the Rancimat method did not yield the expected results. Fuel oxidation rates were comparable, regardless of storage times and sample compositions.

Determination of oxidation stability according to EN ISO 12205, carried out for diesel oil containing 7.2% (V/V) FAME yielded the following results: for sample B, initially, the amount of filterable deposits was 7 g/m^3, adherent deposits was 1 g/m^3, giving a total of 8 g/m^3; after being stored for 6 months, the same sample had 56.2 g/m^3 of filterable deposits and 2 g/m^3 of gum, a total of 58.2 g/m^3. Different values were obtained for sample BM with methylindole:

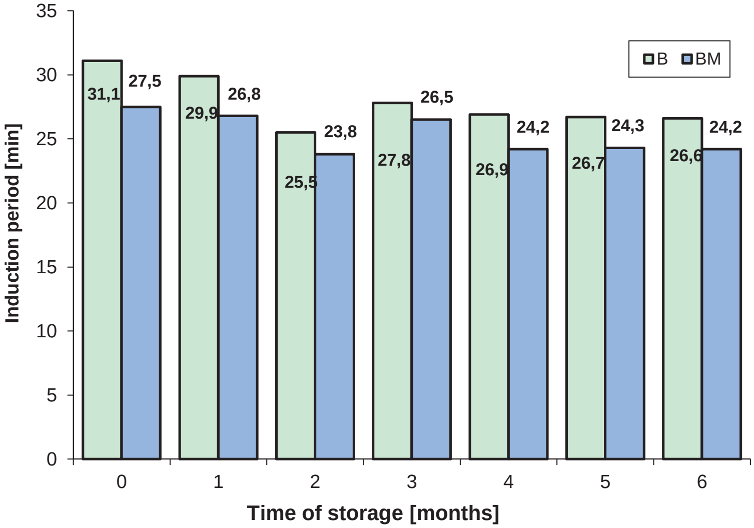

Figure 15. Induction period according to EN 16091 for diesel oil samples with a content of 7.2% (V/V) FAME and methylindole.

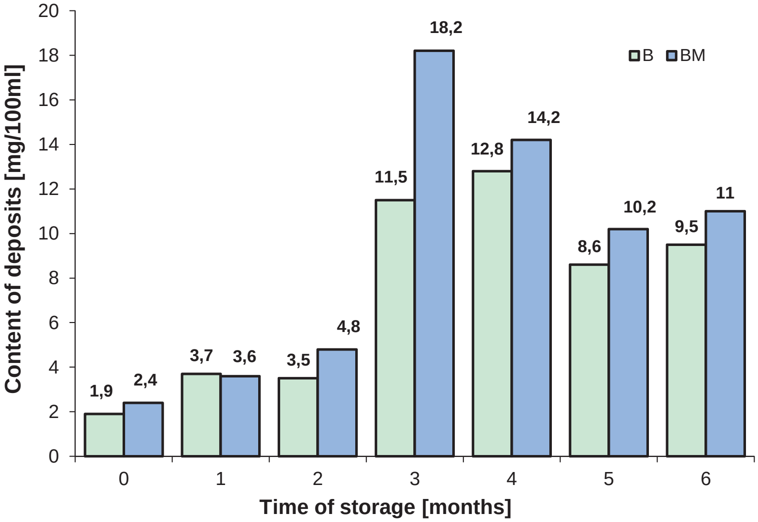

Figure 16. Total insolubles, as found according to ASTM D 5304 for diesel oil samples with a content of 7.2%(V/V) FAME and methylindole.

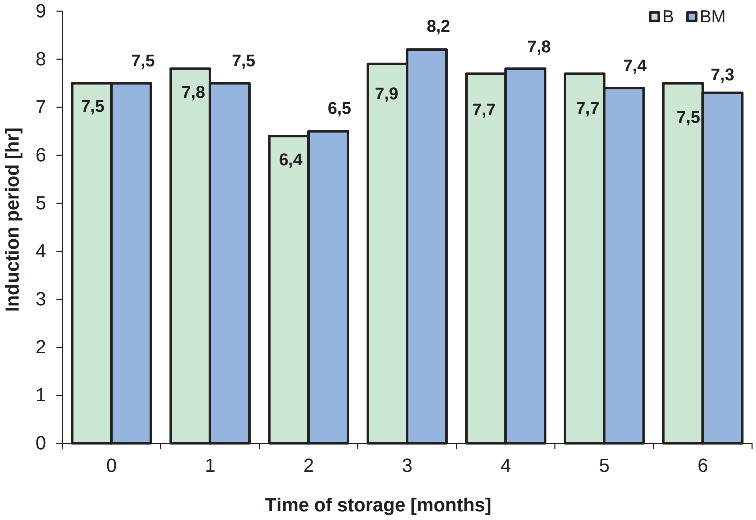

Figure 17. Induction period, as found by the Rancimat method for diesel oil samples with a content of 7.2% (V/V) FAME and methylindole.

initially, 4 g/m^3 of filterable deposits and 2 g/m^3 of gum; after 6 months of storage - 336 g/m^3 of filterable deposits and 13 g/m^3 of gum. The value for total deposits in sample BM also was higher, compared with sample B without indole. Samples B and BM had a positively higher contents of total deposits, compared with samples A and AM, which contained only 1.3% (V/V) of FAME.

The findings indicate that addition of methylindole helps intensify the deposit formation process, especially filterable deposits and especially in the samples with a significant content of fatty acid methyl esters. The tests, performed in accodance with EN 16901 and EN 15751, did not confirm the effect of 2-methylindole on the induction period value for fuels during the period of time covered in the tests.

3.3. IR spectral analysis

Identification of the products resulting from fuel oxidation was performed based on the analysis of FT-IR spectra. The spectra obtained for samples A, AM, B and BM before and after the oxidation process were subjected to a qualitative analysis.

When stored in laboratory conditions at a room temperature for 6 months, the fuel samples were not degraded enough to show any visible changes in their spectral analysis. On the contrary, the spectra of stored fuel samples after subjecting them to rapid ageing did show visible changes.

The fuel samples after oxidation showed changes in the spectral ranges 3600-3200 cm^{-1} and 1800-1600 cm^{-1}. For samples A and AM, which had negligible ester contents, changes were less intense than for sample B and BM with a content of FAME of 7.2 % (V/V). In the spectral range 3600-3200 cm^{-1}, there appears a wide absorption band, connected with valence vibrations for O-H groups. In the range 1800-1600 cm^{-1}, there is a visible narrow carbonyl band, connected with the presence of fatty acid methyl esters (1745 cm^{-1}) in the fuel. In samples A and AM, the peak is smaller than in samples B and BM. In the oxidized samples, in the carbonyl band 1745 cm^{-1} range, there appears a second band, at 1720 cm^{-1}. The band is better discernible for samples with longer storage time and is well visible in the spectres for samples A and AM because of their low content of FAME.

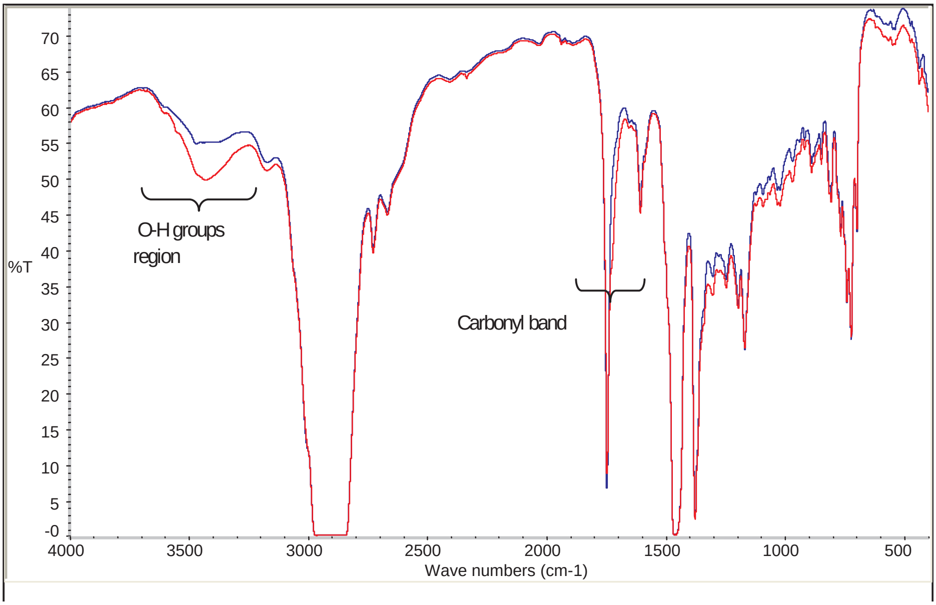

Figure 18. Spectra for sample B with regions of change marked: blue – sample before oxidation, red – sample after oxidation.

It is hard to say without a doubt what products have been formed in the fuel samples as the result of oxidation. The carbonyl band region is connected with the presence of acids, esters, aldehydes or ketones. The band region which is characteristic for O-H groups is connected with the presence of alcohols, phenols, carboxylic acids, or water which may be formed in the oxidized fuel as the result of decomposition of methyl esters. A different measurement technique should be used to identify the resulting products of oxidation more reliably.

A rough quantitative analysis of the analytical band at 3440 cm^{-1}, consisting in measuring the surface area below the peak, indicates that the surface area tended to grow with storage time, reaching its maximum after 3-4 months of storage, then was getting smaller. This is attributed to the radical mechanism of fuel degradation, where initiation of the reaction is followed by propagation, then by termination of oxidation.

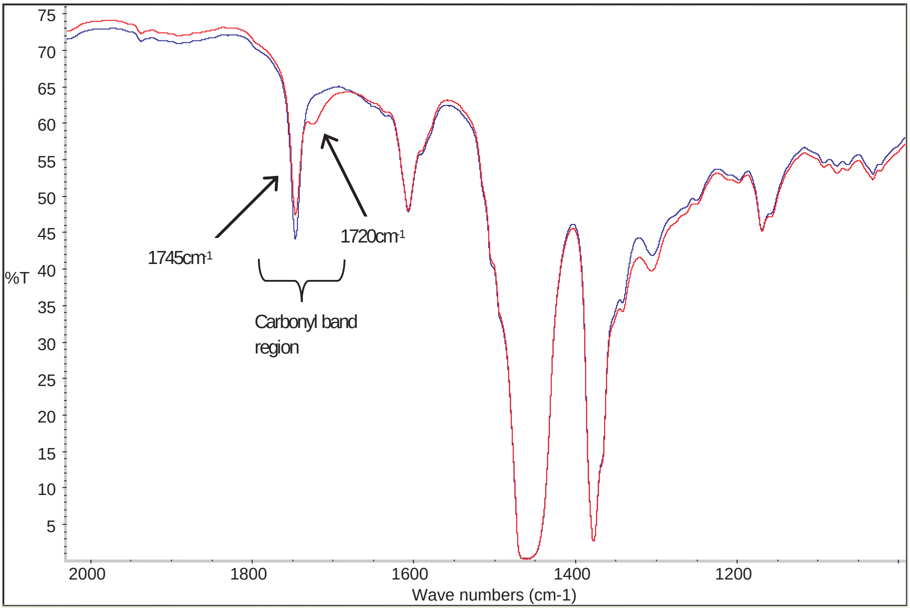

Figure 19. Spectra for sample A in the carbonyl band region: blue – before oxidation, red – after oxidation.

Surface area below the carbonyl peak at 1745 cm^{-1} is seen to decrease with an increasing sample storage time; this may be indicative of decomposition of esters due to the presence of high temperatures and oxygen and is particularly well visible for samples B and BM (they have a higher ester content, compared with samples A and AM). Although in the vicinity of the 1745 cm^{-1} peak, another one is formed at 1720 cm^{-1}, indicating the formation of products of fuel ageing, the total area below the carbonyl peak is only slightly reduced with the increasing storage time of the fuel samples.

Based on the comparative qualitative analysis of the spectra, no visible changes are seen in the spectra of fuel samples with or without methylindole.

4. Conclusion

IR spectra indicate that only slight changes occur in the chemical composition of the RON 95 and RON 98 gasolines during storage for 6 months, due to their autoxidation. Predominantly compounds which contain carbonyl and hydroxyl groups are formed, which is typical of hydrocarbon oxidation products. Addition of precursors of oxidation, such as peroxides or cyclohexene, to the stored fuels slightly intensified the changes. Subjecting the fuel to rapid ageing by exposing it to elevated temperatures and oxygen pressure, shows that oxidation of hydrocarbons is accompanied by other changes, leading to the formation of compounds with a triple bond.

Determination of induction period by the micro method, of the content of inherent and potential resins, indicate changes in the chemical stability of the gasoline samples, although the tendency of such changes cannot explicitly be identified nor can it be related to chemical changes, as shown by IR spectra.

From a detailed analysis of the results of stability tests, combined with an analysis of changes in the IR spectra, it follows expressly that the RON 95 gasoline with ethanol is more susceptible to autoxidation, compared with RON 98, which has no ethanol content.

In the case of diesel oil, the tests indicate that the formation of deposits is favored by acidic products of decomposition of fatty acid methyl esters; moreover, addition to the diesel oil of 2-methylindole, which is one of the compounds taking part in the autoxidation reaction chain, has led to the formation of a higher amount of deposits, chiefly filterable insolubles. In the 3rd and 4th months of testing, deposits developed in the fuels with the highest intensity. IR spectrophotometric analysis has shown that fuel oxidation products are formed in the fuel during its degradation; they include carboxylic acids, aldehydes, ketones or phenols. This confirms the adopted assumption that, as the result of oxidation of fuel, organic acids and other acidic compounds tend to catalyze the formation of indolephenalene salt complexes leading, eventually, to the development of deposits.

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References

[1] Batts B.D., Zuhdan Fathoni A. A literature review on fuel stability studies with particular emphasis on diesel oil. Energy Fuels 1991;5(1) 2-21.

[2] Pedersen C.J. Mechanism of Antioxidant Action in Gasoline. Industrial & Engineering Chemistry 1956;48(10) 1881-1884.

[3] Totten G.E., editor. Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing. West Conshohocken: ASTM International; 2003.

[4] Pedersen C.J. Inhibition of Deterioration of Cracked Gasoline during Storage. Industrial & Engineering Chemistry 1949;41(5) 924-928.

[5] Rudnick L.R., editor. Lubricant Additives: Chemistry and Applications. Boca Raton: CRC Press; 2010.

[6] Mortier R.M., Fox M.F., Orszulik S.T., editors. Chemistry and technology of lubricants. Springer; 2010.

[7] Ingold K.U. Inhibition of the Autoxidation of Organic Substances in the Liquid Phase. Chemical Reviews 1961;61(6) 563-589.

[8] Nagpal J.M., Joshi G.C., Rastogi S.N. Stability of cracked naphthas from thermal and catalytic processes and their additive response. Part I. Evaluation of stability and additive response. Fuel 1995;74(5) 714-719.

[9] Pereira R.C.C., Pasa V.M.D. Effect of mono-olefins and diolefins on the stability of automotive gasoline. Fuel 2006;85(12-13) 1860–1865.

[10] Standard EN 228. Automotive fuels – Unleaded petrol – Requirements and test methods.

[11] Harrigan Sr. M.J., Banda A., Bonazza B., Graham P. Slimp B. A rational approach to qualifying materials for use in fuel systems. SAE Technical Paper series 2000–01–2013; 2000.

[12] Standard ISO 7536. Petroleum products – determination of oxidation stability of gasoline – Induction period method.Standard EN 228. Automotive fuels – Unleaded petrol – Requirements and test methods.

[13] Pałuchowska M., Danek B. Zmiany stabilności chemicznej benzyny silnikowej zawierającej do 10% (V/V) bioetanolu, podczas jej przechowywania w warunkach laboratoryjnych. [Changes in the chemical stability of motor spirits with a max. of 10% (V/V) of bioethanol during storage in laboratory conditions]. Nafta-Gaz 2010;4 297-301.

[14] Standard EN 16091. Liquid petroleum products-Middle distillates and fatty acid methyl ester (FAME) fuels and blends-Determination of oxidation stability by rapid small scale oxidation method.

[15] Standard ISO 6246. Petroleum products – gum content of light and middle distillate fuel – Jet evaporation method.

[16] Standard ASTM D 873. Oxidation Stability of Aviation Fuels (Potential Residue Method).

[17] Marshman S.J, David P. Storage Stability of Distillate Diesel Fuels: Changes in Phenalene and Phenalenone Concentrations During Long Term Ambient Storage. Preprint of Papers-American Chemical Society, Division of Fuel Chemistry 1990;35(4) 1108-1116.

[18] Beranek L. A., McVea G.G., O'Connell M.G., Solly R. K. Rates of Indole – Phenalenone Reactions in Middle Distillate Fuel. Preprint of Papers-American Chemical Society, Division of Fuel Chemistry 1990;35(4) 1117-1124.

[19] Li D., Fang W., Xing Y., Guo Y., Lin R. Spectroscopic studies on thermal-oxidation stability of hydrocarbon fuels. Fuel 87;2008(15-16) 3286-3291.

[20] Zabarnick S., Chemical kinetic modeling of jet fuel autoxidation and antioxidant chemistry. Industrial and Engineering Chemistry Research 1993;32 1012-1017.

[21] Gernigon S., Sicard M., Ser F., Bozon-Verduraz F. Hydrocarbon liquid fuels thermal stability, antioxidants influence and behaviour. Proceedings of 11th International Conference on Stability, Handling and Use of Liquid Fuel, October 18-22 2009, Prague, Czech Republic.

[22] Karavalakis G., Hilari D., Givalou l., Karonis D., Stournas S. Storage stability and ageing effect of biodiesel blends treated with different antioxidants. Energy 2011;36 369-374.

[23] Karavalakis G., Stournas S., Karonis D. Evaluation of the oxidation stability of diesel/biodiesel blends. Fuel 2010;89 pp.2483-2489.

A Review of Selected Methods of Measurement Used for the On-Line Analysis of Liquid Fuels

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Additional information is available at the end of the chapter

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1. Introduction

Liquid fuels are complex, multicomponent mixtures of paraffins, isoparaffins, olefins, naphthenes, and aromatic hydrocarbons having a wide range of molecular weight, as well as heteroorganic components and improvers. The group composition of liquid fuels depends on the initial parameters of raw materials used for making their components and on the characteristics of the respective refinery streams, used in the blending process. Standardization systems exists which are intended to provide fuels with specific, fixed, comparable properties, even for products made in different periods of time and supplied by different manufacturers. Qualitative evaluation involves a number of physico-chemical factors which characterize the properties of fuels during their manufacturing, storage, distribution, and use. Analyses of liquid fuels are intended to confirm their uniform quality, resulting from a number of variables which have an effect on their properties during the product's entire lifecycle.

Liquid fuels are governed by various requirements, depending on their use. Motor fuels are expected to enable the correct operation of the fuel distribution system as well as efficient, cost-effective combustion. It is essential to ensure a maximum power, fluidity, and reliable motor operation in different conditions of use. The fuel's composition should be so selected as to reduce toxic emissions into the environment. The quality of liquid fuels available on the wholesale and retail markets is of essential importance to virtually every user of motor vehicles.

Stability of liquid fuels is the essential criterion of their quality during transport and storage. The presence in fuels of diverse individual chemicals may affect their mutual interactions. The presence of unsaturated compounds and biocomponents in fuels does not seem to improve their resistance to ageing processes. Sufficient stability can be provided by addition of a wide range of improvers which slow down the dynamics of the various processes taking place, while modifying compositions and physico-chemical parameters. Improvers tend to reduce the blend's reactivity: a fuel with improvers will not tend to undergo quick physico-chemical changes when inside storage tanks or tankers, and its components will be less susceptible to oxidation processes.

It is not feasible to obtain a fuel which has all those properties at a time: they exclude one another. A maximum engine power is typically achieved in return for increased emissions and higher consumption of fuel. Reduction of the environmental impact of fuels is connected with optimization of the combustion process. Improvement of fuels in respect of their physico-chemical parameters has a positive impact on their functionality in operating conditions although, on the other hand, it may have an adverse effect on their stability during storage.

Blending of liquid fuels requires the implementation of assorted technological procedures in order to attain the final compromise: compliance with normative requirements and provision of desirable properties to fuels. This requires the knowledge of the characteristics and dynamics of changes in the physico-chemical properties of commercial fuels and their individual components. Applicable analyses, which confirm compliance of the properties of gasolines and oils with normative requirements, are carried out by accredited organizations to guarantee quality to the users of the liquid fuels available in the market.

Faster and less expensive, alternative methods to analyze fuels are required. The market is calling for rapid developments in fast and inexpensive fuel analyzers. This type of devices have the essential advantage of requiring a small sample volume only, short duration of analysis and no extra chemical reactants. The various methods are described and selected types of commercially available equipment are presented in the chapters which follow. Moreover, the possibility of adaptation of classical nephelometry method to measuring the selected parameters of fuels using optoelectronic sensors, developed at the Regional Office of Measures (OUM) in cooperation with scientists at PIMOT (Automotive Industry Institute, formerly Institute for Fuels and Renewable Energy), Warsaw.

2. Normative fuel testing methods

According to European standards, liquid fuels are required to comply with certain qualitative requirements in every step of their lifecycle, including their manufacturing and use. Such standards are a set of requirements concerning the quality of fuels. They establish testing methods which enable verification of their properties.

Qualitative requirements concerning the physico-chemical properties of liquid fuels are amended in accordance with applicable legislation and are affected by changes in engine designs over the years. Such factors involve the necessity to eliminate any sulfur compounds from gasolines and oils, therefore, the presence of sulfur is constantly monitored. Any other heteroorganic particles that may be present in the improved fuel in addition to sulfur are eliminated by commonly used sulfur removal technologies. In the long run, there has been a tendency to lower the permissible limits for aromatic compounds in fuels and for olefin hydrocarbons in gasoline. Elimination from engine fuels of compounds which contain unsaturated bonds and heteroelements has a direct effect on deterioration of parameters which are responsible for the lubricating properties of fuels. The quality of fuels is improved by addition of suitable improvers. Both the content of aromatic hydrocarbons in fuels and their lubricating properties are issues to which normative studies, carried out by accredited laboratories, are dedicated.

Motor fuels are expected to comply with many requirements which affect the safety and comfort of vehicle users. The performance properties of liquid fuels and their stability during storage and transport are determined by the percentage of the respective groups of chemicals in them.

The qualitative properties of liquid fuels are related to engine type: type of ignition and manner of combustion of the fuel blend. Gasoline is expected to be characterized by suitable volatility to provide an optimum fuel blend and to guarantee its knock-less combustion in the engine. Requirements being posed to diesel fuels are mainly connected with providing the correct functioning of the entire supply system, efficient combustion in various engine operating conditions, suitable lubrication, and the correct low-temperature parameters. Moreover, motor fuels are expected to display physical and chemical stability during their entire lifecycle, not to pose environmental hazard, and to generate only minimized harmful emissions in the process of combustion. Occasionally, those parameters which determine fuels' high operating quality, are not desirable in the aspect of storage, transport or safety in its wide sense, and conversely – those properties which are desirable during storage and transport may not be desirable in the aspect of use.

The physical and chemical characteristics of fuels as well as their performance properties are determined by the structure of hydrocarbons. For instance, the degree of fuel atomization in the combustion chamber depends on its density, viscosity, and surface tension, and is the higher, the lower the values of those parameters. The parameters are monitored in order to provide liquid fuels with a suitable quality. In aromatic compounds, the values of the above mentioned parameters are higher, compared with isoparaffins and paraffins – typical components of gasolines and diesel fuels, respectively. Therefore, their variable concentration in fuels, as shown by the characteristics of the refinery streams used for fuel blending, affects the performance properties of fuels.

Volatility of liquid fuels is an important parameter for the gas phase formation process just after a fuel is injected into the combustion chamber, and it also helps avoid excessive losses during storage, transport and distribution. The optimum level of evaporation is made up of the fuel's heat of evaporation and vapor pressure. Volatility index, an important quality indicator for gasolines, is evaluated based on the normative assessment of fractional composition, that is, determination by normal distillation of the fuel volumes which boil at the stated temperature ranges, and of vapor pressures – a supplementary indicator of volatility. In the case of gasoline as well as diesel fuel, the respective fraction percentages per unit of volume determine not only their behavior during the engine starting, formation of air-fuel mixture, and combustion process, but also their tendency to form carbon deposits in operating conditions, deposits in stationary conditions, and harmful emissions into the atmosphere during storage and operation.

Liquid fuels have different chemical compositions, depending on the type of engine they are designed for. Although the combustion process is different for gasoline compared with diesel fuel, the important thing is that the air-fuel mixture should be a uniform and complete process regardless of the engine design and ignition. Resistance of gasoline to detonation combustion, as expressed by the octane number, is a normative parameter indicating the quality of gasoline. The tendency of a fuel to undergo spontaneous ignition in certain conditions is used in commonly used diesel engines; it is shown as the fuel's cetane number. According to applicable standards, the research octane number (RON) and motor octane number (MON) for gasoline and cetane number for diesel fuel are established in standard, single-cylinder engines with variable compression ratio.

The stability of liquid fuels during storage is directly related to their chemical composition. The reason why fuel ageing occurs is that processes take place gradually in them, leading to changes in their physico-chemical properties. Typical ageing processes in liquid fuels occur due to oxidation. The chemical compounds that are present in fuel blends change their properties, color and smell. Ageing processes taking place in fuels lead to higher levels of organic acids, as indicated by the acid value which says how much potassium hydroxide is required for neutralizing acid substances present per unit of fuel. Typically, the test is used for assessing degradation of oils. The aggregation of oxidation products along with unsaturated and aromatic compounds present in fuels leads to the formation of high-molecular, viscous substances. High molecular weight, often resulting from polymerization and polycondensation, causes the formation of deposits. Such deposits tend to plug filters, suction tubes, and lead to the formation of carbon deposits, disturbing engine operation. Indirectly, the loss of valuable components from the fuel blend leads to reduced octane or cetane values, which is undesirable: the fuel's commercial value is affected, its further use becomes dangerous and may damage engine components. To establish the amount of deposit, tests are carried out to determine inherent gums, especially in gasoline. Not only the presence in fuels but also the tendency of fuels to form gums is an important issue. The resin content is an indicator, used for determining oxidation stability of gasoline under operating conditions. During distribution, oxidation stability is indicated by what is called induction period: the time during which a fuel, subjected to the effect of oxygen, will not react in conditions referred to in the applicable standard. The tendency of diesel fuels to form carbon and other deposits is assessed by the normative method to determine coking residue and ash residue after incineration.

The permissible limits of contaminants, sulfur, water or heavy metals in fuels are governed by applicable standards. The parameters evaluated include the effect of fuels on the corrosion of metal parts, connected with the presence of organic acids, sulfur compounds, and water in the fuel. The corrosive effect is evaluated using a copper plate in the water bath in standardized conditions (EN ISO 2160).

Gasolines and diesel fuels have also some individual features which provide fuels with a functional value. Those intended for use in engines with a different design or method of operation have the appropriate, different chemical composition. Therefore, quality control involves a number of parameters which affect both the performance of liquid fuels and their properties in the aspect of logistics.

The use of normative control conditions and methods is meant to provide fuels originating from different sources with the desirable quality. However, such analyses are time- and labor-consuming and quite costly: they require rather large samples, which are to be collected as prescribed in the applicable standard, and a series of analyses using specialist equipment are to be carried out by qualified personnel. The long duration and high cost of such analyses in accredited laboratories may, at times, be a stimulus for seeking less expensive and faster analyses of the quality of liquid fuels.

In addition to the high costs, such analyses have the disadvantage of long duration and difficulties in the comprehensive interpretation of results, leading to the unambiguous classification of the performance of the specific fuel sample. A fuel analysis according to the standards EN 590 for diesel fuel and EN 228 for gasoline takes not less than several days.

3. The test methods, used for the on-line analysis of liquid fuels

Recent years have seen the development of alternative methods to the costly and complicated laboratory analyses: such methods are applied in universal fast fuel analyzers. Fast analysis is very important in the qualitative evaluation of fuels, used for refueling vehicles with advanced drive units. Using a poor quality fuel may, at best, result in having to clean the fuel system; in the worst case, it may cause permanent damage to the engine and the injection system [1, 2]. Commercially available fuel analyzers are based on a wide array of analytical methods, representing different levels of technological advancement.

3.1. Spectral analysis

Infrared (IR) spectroscopy is a commonly used advanced method for optical analysis of liquids. It is based on the interactions between the particles of matter and the electromagnetic field. The specificity of electromagnetic waves enables interactions with those particles in which polar bonds are present. When passing through a sample, part of radiation is reflected. The absorbed quantity of such radiation depends on the level of energy and the type of matter it interacts with. If molecular bonds are devoid of a dipole moment, the result is that there is no active interaction between matter and infrared radiation, and the IR spectrum is not generated. Information about the structure of particles is obtained by determining the quants of energy absorbed [3].

In the structural examination of organic compounds, the range of radiation, typical of the specific infrared ($4000 - 400\ cm^{-1}$) is the most significant. Absorption of radiation in that range leads to changes in the rotation and oscillation energies of molecules. The use of absorption of radiation in the mid-infrared range provides information about the structure of a wide array of chemical compounds with a variety of properties. Infrared spectroscopy belongs in the nondestructive category of physico-chemical methods, therefore, a number of data may be obtained using a small quantity of test material.

Contemporary spectroscopic methods are based on advanced information technology in the area of recording interference images followed by its transformation into a spectrum using the Fourier transform. FT-IR spectroscopes are characterized by high sensitivity, resolution, and easy data processing. Compared with classical methods based on the diffraction network and dispersion, the advanced Fourier-transform methods offer a much higher precision. Contemporary devices use the Michelson interferometer to generate spectra; its design enables the passage of a larger quantity of radiation, compared with classical equipment. The solution has the advantage of the continuous detection of a wider radiation band. The FT-IR method generates a top quality spectrum from a small sample, and in a short time.

In IR spectroscopy, the structure of the components of petroleum fractions is established based on the specific absorption bands in the infrared radiation range for the respective functional groups. The structure and size of substitutes in the molecules may cause a minor shift of the band locations within the spectrum. Changes in the position of the absorption bands and changes in their shape, which reflect the molecular environment of a compound’s functional group, may indicate important structural details, whereby they may have a significant effect on substance identification.

A qualitative analysis of the composition of mixtures can be performed using reference spectra, which are available for the users’ convenience in the form of computerized databases or libraries. Oscillation spectra are typical of a given molecule and enable its explicit identification. A quantitative compositional analysis is based on the Lambert-Beer law which says that band intensity in the spectrum is proportional to component’s concentration in the mixture.

IR spectroscopy is widely used for substance determination and identification in laboratories and for quality control in industry. Furthermore, it is useful in forensics.

A combination of IR spectroscopy and multi-dimensional calibration is used for predicting the physico-chemical properties of fuels and validation of their authenticity [4, 5]. The use of near-infrared spectroscopy (NIR) for determination of the content of soy biodiesel in conventional diesel fuel was described by Knothe [4].

In [5], the authors proposed the use of absorption spectroscopy for detecting adulteration of gasoline (in the case of Jordanian gasoline types – by addition of the cheaper RMG to the more expensive, unleaded UMG gasoline). In the comparative analysis of the spectra, recorded for the prepared blends with different unleaded-to-leaded gasoline ratios, 13 characteristic bands were selected of which the intensity varied with changes in the content of RMG. Using multi-dimensional calibration, it was found that contamination of a given sample of unleaded gasoline with leaded gasoline can be proved and its quantitative determination is possible.

The applicability of FT-IR spectroscopy in determination of the physico-chemical properties of fuels is the subject of numerous reports. The obtained spectra and methods of mathematical analysis were used for finding the values of RON and MON [6, 7, 8] or the content of oxygen compounds [9].

Interesting studies are reported in [10]. The objective was to establish 10 parameters of gasoline from the spectra obtained using near infrared absorption spectroscopy and chemometrical methods. The target parameters included RON, MON, vapor pressure, API index, content of aromatics, olefins, and benzene, and other ones.

Examples of devices used for the on-line analysis of fuels include IROX 2000 [11] – a medium IR range spectrometer, used for an automated measurements of essential parameters of gasoline. The device has a mathematical model implemented in it which enables determination of such parameters as octane number, fractional composition, vapor pressure, etc. IROX Diesel is a variety of the device, dedicated to measuring the respective parameters of diesel fuel, such as: cetane number, cetane index, FAME content.

Eraspec [12] from Eralytics (Fig. 1) is another example of the solution: a universal multi-functional apparatus, designed for the spectral analysis and assessment of the parameters of diesel fuels and gasoline.

Figure 1. Eraspec – fuel analyzer from Eralytics [12]

Eraspec is dedicated to the measurement of such parameters of liquid fuels as: octane number, cetane number, content of FAME, distillation fractions, and other ones.

3.2. Raman spectroscopy

Raman spectroscopy is another method, applicable in the on-line analysis of fuels. Same as IR spectroscopy, it is designed to provide information about molecular structure, that is, about the interactions between the atoms in molecules. Raman spectroscopy is based on the Raman effect: the phenomenon of non-elastic diffusion of radiation by the sample [13, 14]. Even though it was discovered nearly 90 years ago, the method was developed only after the use of lasers and computers with higher computational capabilities. The mechanism which causes the

Raman effect is quite different from the mechanisms based on infrared analysis, functioning in other techniques; therefore, water molecules in the sample do not interfere with the spectra recording. The method has one great advantage: it is not necessary to collect a sample, the analysis may take place in-situ, using probes which are immersed directly in the fuel [15]. Owing to the use of light pipes, the probe may be located as far as hundreds of meters away from the fuel analyzer. This eliminates the necessity to introduce live parts in fuel storage tanks, which otherwise would pose a realistic threat in explosion hazard zones [15].

Raman spectroscopy was used, for instance, in studies carried out by Shoute's research team, analyzing a range of petroleum products (such as commercial gasoline). The authors reported results which show that the so-called "finger-print region" of the spectra is very characteristic and may be useful for the qualitative identification of mono-, bi-, tri-, and polycyclic aromatic hydrocarbons. Preliminary tests of commercial gasoline samples indicate that Raman spectroscopy may be used by refineries or fuel suppliers for identification of gasolines of unknown origin [16].

Gorelik's research team examined a series of motor gasoline with the octane numbers 80, 92 and 95. Correlations between spectra were analyzed for gasolines and saturated hydrocarbons. It was found that Raman spectra for various types of gasoline showed certain discrepancies, resulting from compositional differences between gasolines with respect to hydrocarbons, including aliphatic and cyclic hydrocarbons. The authors showed that even small band frequency shifts could be observed, depending on the number of carbon atoms in the hydrocarbon chain. Owing to the resemblance of Raman spectra for saturated hydrocarbons and gasolines, they demonstrated the usefulness of Raman spectroscopy in the compositional analysis of gasoline and other petroleum products [17].

Raman spectroscopy may be used for the identification and classification of fuels in qualitative analysis [18]. Scheng's research team have examined 128 gasoline samples, originating from three refineries and having different octane numbers (90, 93 and 97). The authors demonstrated that it was possible to identify the brand of the gasoline samples and to find their correct octane numbers using the spectra obtained and the mathematical analysis methods available (Least-Squares Support-Vector Method).

In [19], Raman spectroscopy was used for the rapid quantitative detection of ethanol in gasoline. Spectra were obtained for blends with various ethanol-to-gasoline ratios as well as for pure substances. From the results obtained, two bands were selected (the 1030 cm^{-1} band for gasoline and the 912 cm^{-1} band for ethanol), of which the intensities could be linked quantitatively with the content of ethanol in the ethanol-gasoline blends.

Raman spectroscopy solutions dedicated to the on-line analysis of fuels are known and available. Process Instruments offers a number of Raman analyzers for laboratory and industrial applications. Using chemometrical methods, a number of parameters, including octane number, cetane number, fractional composition, or content of oxygen compounds, are measured based on the recorded spectra. Based on the location and surface area of typical peaks, especially in the so-called "finger print region", the content of benzene, toluene, MTBE, aromatic compounds or olefins are found in the fuel sample (Figure 2). The manufacturer also offers a PI-200 Raman Analyzer applicable to the laboratory analyses of fuels. E-Z-RAMAN is intended for industrial applications [15].

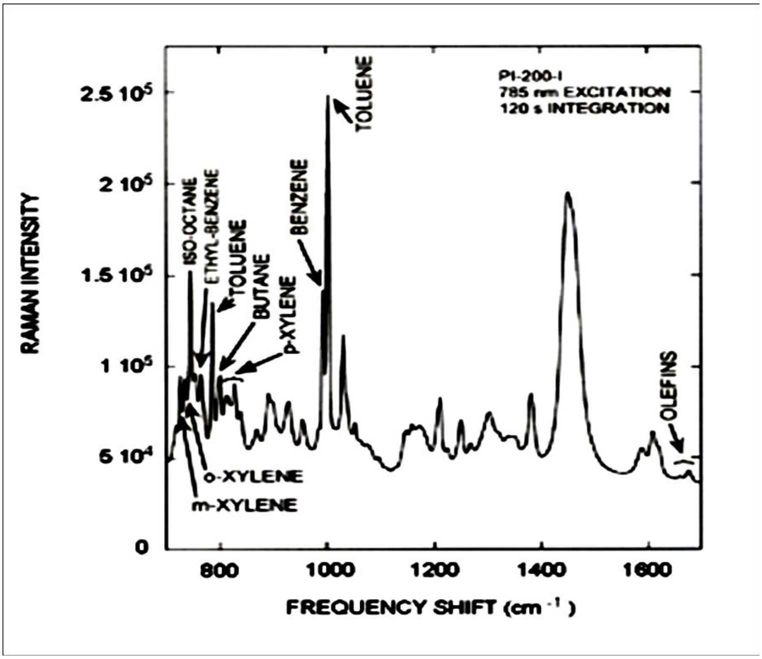

Figure 2. A Raman spectrum fragment with typical peaks [15]

An interesting solution is offered by Real Time Analyzer: the company developed, for the US Army, a compact, portable, case-size fuel analyzer based on Raman spectroscopy [20]. It has an incorporated spectra library which enables fuel identification based on the recorded spectrum (gasoline, diesel fuel, aircraft fuel) as well as its qualitative verification with respect to the applicable normative requirements (compliant/non-compliant).

3.3. Permittivity measurement method

Another interesting fuel analysis solution was proposed by Delphi and has obtained patent coverage. The method is based on the permittivity phenomenon. The device uses the radio frequency oscillator technology, measuring complex permittivity with a tranducer placed in the fuel sample. The solution is quite new and details of the technology are not commonly available yet. The method was used in the YDT553 analyzer [21], of which a picture is shown in Figure 3.

The YDT553 fuel analyzer enables the immediate determination of any unacceptable level of esters or contaminants in the fuel sample. This type of analysis was previously restricted to analytical laboratories only. The fuel analyzer is useful to the personnel of service stations

Figure 3. YDT553 fuel analyzer from Delphi

where fuel injection systems are repaired, who are able to use the device for the quick verification of the quality of the fuel in the vehicle tank.

3.4. Nephelometry

Liquid fuels may also be examined using the nephelometric method. The method consists in the turbidity analysis of solutions based on the measurements of transmission and scattering of light after passing through a given test sample. In addition, the range of parameters to be determined by the classical nephelometric method is significantly extended by the use of optical capillaries, that is, thin glass pipes as measurement cells. They have the specific ability of fluid elevation and light conducting inside the capillary and in the walls, which makes them an excellent choice for an analysis of the parameters of liquids. The filled optical capillary forms a liquid light pipe where the light propagation conditions in the pipe as well as in the pipe walls depend on the filling substance, especially on the difference between the refractive index values for the capillary filling and for the capillary material [22]. This enables identification of the refractive index as well as determination of other parameters of the liquid, such as turbidity and concentration of solutions after diluting them with a known solvent. In the case of transparent liquids, the test may be limited to turbidimetry, rather than using the nephelometric method. In this way, the liquid analysis is reduced to an analysis of the classical liquid light pipe, which is constituted by the liquid filling the entire capillary volume.

Optical capillaries may be equipped with zone heating of the liquid in the capillary: this extends the test method by evaluation and classification of the liquid’s parameters. The idea of the liquid zone heating is shown in Figure 4.

The passage of current through a resistive heater causes evaporation in the capillary region, which is accompanied by the formation of a liquid vapor bubble. The stability of the bubble depends on the ratio between the vapor pressure and the pressure being generated by the surface tension forces. The specific vapor pressure for a given liquid is determined by the pressure at which the gas is in equilibrium with the liquid. The pressure depends on the type

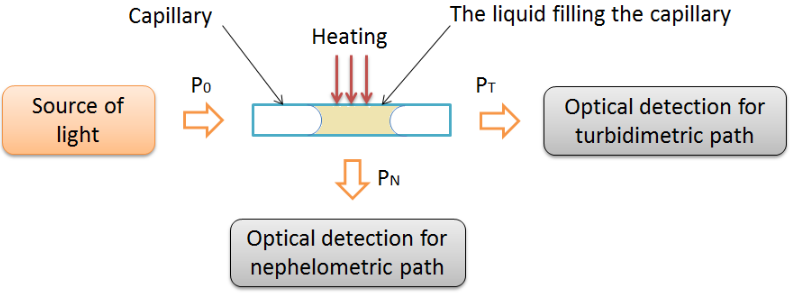

Figure 4. Modified classical nephelometric system, with the zone heating technique.

of liquid and on temperature: the higher the temperature, the higher the pressure of saturated vapor. In the course of heating in the capillary, the vapor pressure is counteracted by the pressure resulting from surface tension forces. Heating of a portion of the capillary causes rapid evaporation, leading to the formation of regions, filled with the liquid vapor. The resulting vapor bubbles form a liquid-vapor interface and the resulting lens effect, having a specific (for a given liquid) impact on signal propagation in the turbidimetric and nephelometric paths.

The measurement of light transmission changes, performed in a repeatable manner for a given liquid in the cycles before heating / in the course of heating / after switching off the heater, of which the results are compared with the appropriate standard characteristics enable identification of the liquid type or analysis of changes in its parameters.

4. The use of optoelectronic sensors for analysis of gasoline

Optoelectronic sensors for the analysis of selected properties of fuels were developed by OUM in cooperation with researchers from PIMOT. Gasoline types for spark ignition engines, being commonly available from fuelling stations, were selected for the analysis of fuels using such optoelectronic sensors. Figure 5 shows the results of analysis of three different samples of gasoline, originating from different manufacturers (samples A and B with the octane number of 95 and sample C with the octane number of 100). The phase curves for the 95 octane gasoline samples A and B are similar: same transmitted optical powers, phase separation induction times, and similar power transmission changes during and after heating may indicate similar compositions and octane numbers, which is 95 for the two gasoline samples. The curve for the gasoline sample C with the octane number 100 is slightly different. The higher octane number for sample C causes a longer phase separation time, which is typical of fuels with higher octane numbers.

Higher octane numbers tend to reduce the risk of the undesirable phenomenon of knocking combustion of fuels [23].

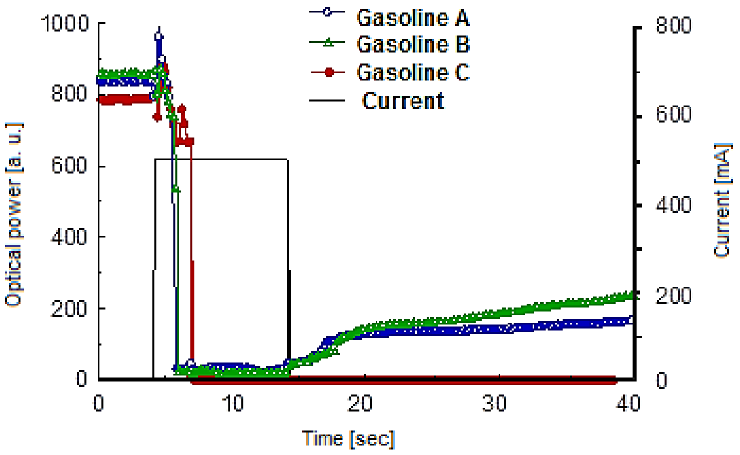

Figure 5. Results of transmission measurements for gasolines A, B and C vs. time and heater current

5. Results of tests for biodiesel

The test method was also used for the analysis of pure biodiesel and of a mixture of conventional diesel fuel with FAME. The test samples included biodiesel B20 (20% FAME and B100), and the test results are shown in Figure 6.

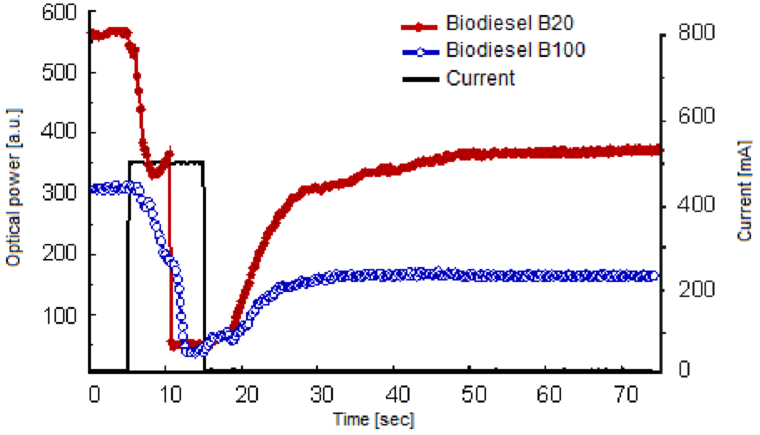

Figure 6. Results of transmission measurements for Biodiesel B20 and B100 vs. time and heater current

A comparison of the transmission results for the diesel fuel samples indicates that addition of biocomponents leads to a loss of power in the transmission path, causes changes in the time and shape of the phase separation curve. Comparison of biodiesel B20 and B100 indicates that after addition of biocomponents to the diesel fuel samples, the power transmission in the turbidimetric path was approx. 50% lower. The above characteristics show that analysis of power transmitted before/during/after the heater operation provides, in a short time, explicit information about the quantity of biocomponents added to the fuel.

5.1. Measuring the repeatability of results of the measurement method

Table 1 shows the results of a repeatability analysis for 12 measurements of average optical power in the turbidimetric path and standard deviation for samples of liquid fuels before, during and after the resistive heating. The analysis was carried out for diesel fuel, diesel fuel with 20% FAME, biodiesel, and for a diesel fuel blend with biodiesel.

	Before heating [a.u.]		**While heating [a.u.]**		**After heating [a.u.]**	
Fuel	**Average value**	**Standard deviation**	**Average value**	**Standard deviation**	**Average value**	**Standard deviation**
Diesel fuel	702.60	0.86	72.94	4.72	379.37	8.01
Biodiesel B20	568.45	0.85	54.76	1.45	368.31	17.19
Biodiesel B100	309.22	0.76	38.57	2.65	189.92	1.32
50% diesel fuel plus Biodiesel B100	455.33	0.70	46.29	3.53	264.12	1.72

Table 1. Repeatability of results of measurement of average optical power in the turbidimetric path for fuel samples before, during, and after resistive heating

The measurement results are illustrated in Figure 7.

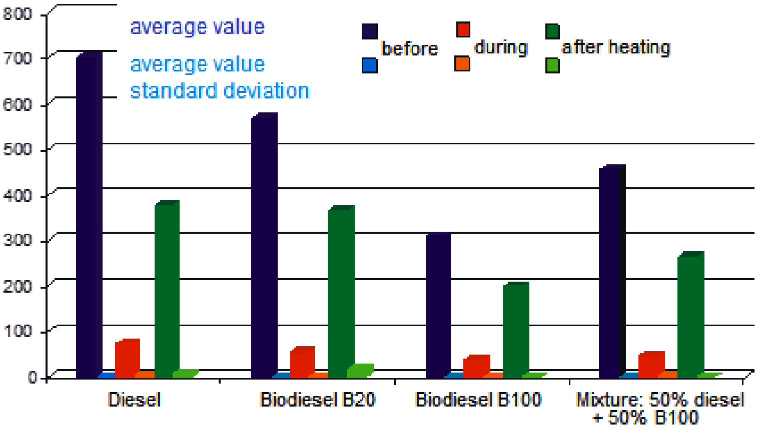

Figure 7. Graphical representation of results of repeatability analysis for a series of 12 measurements of average values of optical power and standard deviation for fuel samples before, during, and after resistive heating

The analysis indicates that the measurement method is characterized by a very high repeatability, as shown by low average value standard deviations, especially before the heating process.

6. Conclusion

The development of an electronic device enabling the measurement and/or scanning of the parameters of fuels seem to be very important for the fuel economy and for the end user. In view of price rises in the fuel market, the consumers are expecting simple and inexpensive fuel analyzers or fuel quality indicators, enabling them to control fuel quality or to measure its biocomponent concentration when refueling. It is to be remembered that new biocomponents or advanced, second generation fuels based on renewable resources may be invented. Fast assessment of fuel quality is important in the aspect of fuelling advanced engines, in which poor fuel quality may reduce the engine's lifetime or – in the extreme cases – lead to damage.

The innovative fuel analyzer based on optoelectronic sensors may be a desirable alternative in uses where normative analyses are not required. At the present stage of research, the existing results seem promising on the way to the target end result which is a cost-effective, universal fuel quality analyzer.

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References

[1] Mekisz J., Pielecha I., Alternatywne napędy pojazdów, Wydawnictwo Politechniki Poznańskiej, Poznań, 2006.

[2] Postrzednik S., Żmudka Z., Termodynamiczne oraz ekologiczne uwarunkowania eksploatacji tłokowych silników spalinowych, Wydawnictwo Politechniki Śląskiej, Gliwice, 2007.

[3] Collective work, Ed. W. Zieliński, Metody spektroskopowe i ich zastosowanie do identyfikacji związków organicznych, Wydawnictwo Naukowo-Techniczne 2000

[4] Knothe G., Determining the blend level of mixtures of biodiesel with conventional diesel fuel by fiber-optic near-infrared spectroscopy and 1H nuclear magnetic resonance spectroscopy. J Am Oil Chem Soc 2001;78:1025–8.

[5] M.A. Al-Ghouti, Y.S. Al-Degs, M. Amer, Determination of motor gasoline adulteration using FTIR spectroscopy and multivariate calibration, Talanta 76 (2008) 1105–1112

[6] P. E. Flecher, W. T. Welch, S. Albin, J. B. Cooper, Determination of octane numbers and Reid vapor pressure in commercial gasoline using dispersive fiber-optic Raman spectroscopy, SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy Volume: 53, Issue: 2, February, 1997, pp. 199-206

[7] J Kelly, CH Barlow, TM Jinguji, JB Callis, Prediction of gasoline octane numbers from near-infrared spectral features in the range, 660–1215 nm. Anal Chem 1989;61, pp. 313–20.

[8] G. E. Fodor, K. B. Kohl, R. L. Mason, Analysis of gasolines by FT-IR spectroscopy. Anal Chem 1996;68, pp. 23–30.

[9] A. Iob, R. Buenafe and N. M. Abbas, Determination of oxygenates in gasoline by FTIR, Fuel Vol. 77, No. 15, pp. 1861–1864, 1998

[10] I. Litani-Barzilai, I. Sela, V. Bulatov, I. Zilberman, I. Schechter, On-line remote prediction of gasoline properties by combined optical methods, AnalyticaChimicaActa Volume: 339, Issue: 1-2, February 28, 1997, pp. 193-199

[11] Grabner Instruments, IROX 2000 Fuel Analyzer, User Manuals, Grabner Instruments MesstechnikNfg. GmbH & Co KG, 1220 Vienna, Austria, 2010.

[12] Eralytics GmbH, Lohnergasse 3, A-1210 Vienna, Austria, 2010.

[13] Collective work, Ed. W. Zieliński, Metody spektroskopowe i ich zastosowanie do identyfikacji związków organicznych, Wydawnictwo Naukowo-Techniczne 2000

[14] Smith E., Dent G.: Modern Raman Spectroscopy – A Practical Approach. John Wiley & Sons Ltd, 2005

[15] Information from Process Instruments INC, www.process-instruments-inc.com

[16] L.T.C. Shoute, K. J. Schmidt, R. H. Hall, M.A. Webb, S. Rifai, P. Abel, P. H. Arboleda, A. Savage, J. T. Bulmer, G. R. Loppnow, UV Raman Spectroscopy of Oilsands-Derived Bitumen and Commercial Petroleum Products, Applied Spectroscopy, vol. 56, issue 10, pp. 1308-1313

[17] V. S. Gorelik, A. V. Chervyakov, L. V. Kol'tsova, S. S. Veryaskin, Raman spectra of saturated hydrocarbons and gasolines, Journal of Russian Laser Research, July–August, 2000, Volume 21, Issue 4, pp. 323-334

[18] L. Sheng, D. Lian-kui, Classification of gasoline brand and origin by Raman spectroscopy and a novel R-weighted LSSVM algorithm, Fuel, Volume 96, June 2012, pp. 146–152

[19] Qing Ye, QinfengXu, Yongai Yu, Ronghui Qu, Zujie Fang, Rapid and quantitative detection of ethanol proportion in ethanol–gasoline mixtures by Raman spectroscopy, Optics Communications 282 (2009) pp. 3785–3788

[20] Information from Real Time Analyzer

[21] Delphi Customer Technology Center, L-4940 Bascharage, G.D. Luxembourg, Press Releases, Release Date: September 14, 2010.

[22] Dragavon J., Burgess L., Detection technologies in micro-fluidic systems for the single cell metabolomics and other applications, Center for Process Analytical Chemistry University of Washington, 2005

[23] Hoogers G., Fuel Cell Technology Handbook, CRC Press, Boca Ration, New York, 2003.

Analysis of Changes in the Properties of Selected Chemical Compounds and Motor Fuels Taking Place During Oxidation Processes

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Additional information is available at the end of the chapter

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1. Introduction

Given the existing energy crisis and restrictions on GHG emissions, it has become a necessity to introduce to motor fuels newer and newer types of non-petroleum components – especially biocomponents such as ethanol or FAME.

The path of the oxidation (ageing) process for fuels which contain biocomponents as additives has not been determined so far.

Under the circumstances, the ever more increasing demand on liquid fuels obtained by petroleum processing, combined with the ever more stringent quality requirements, it has become an important aspect to maintain a high quality of fuels during long-term storage. The different physical and chemical characteristics observed in petroleum products after storing them for a long time depend mainly on the chemical composition of petroleum, 90% of which is a mixture of hydrocarbons having different structures.

Petroleum contains the following types of hydrocarbons [1]:

- paraffins (n-paraffins, isoparaffins),
- olefins,
- cycloparaffins (naphthenes),
- aromatic hydrocarbons.

Paraffin hydrocarbons (paraffins) are present in large amounts in petroleum and they predominate in large amounts in gasoline fractions. They include straight chained n-paraffins and branched isoparaffins. n-Paraffins are low-reactivity compounds, therefore, they are applicable in the refinery and other industries. Isoparaffins are also found in petroleum but the number of potential compounds is immense. Isoparaffins have lower boiling points, compared with n-paraffins.

Naphthene hydrocarbons (naphthenes) are the largest fraction in petroleum. A naphthene ring contains typically 5 or 6 carbon atoms. Dicyclonaphthenes C8 and C9 and (more condensed) cycloparaffins, are present in addition to monocyclonaphthenes. Cycloalkanes are less volatile compounds, compared with alkanes.

Aromatic hydrocarbons (aromatics) have a ring-like structure. The benzene ring comprises alternate double and single bonds with adjacent carbons atoms. Monocyclic aromatics are valuable components in fuels, especially gasolines, because they improve their octane number. Aromatic hydrocarbons are highly stable at high temperatures, thereby leading to the desirable effect of knock-less combustion in gasoline-fueled engines. They are not desirable in fuels intended for use in spontaneous-ignition engines because they cause rough engine operation and decrease the fuel’s cetane number, thus delaying spontaneous ignition.

In addition to the aforementioned groups of hydrocarbons, petroleum also comprises non-hydrocarbon ingredients of which the molecules contain atoms of sulfur, nitrogen, and oxygen, organometallic bonds and inorganic salts.

The following types of motor fuels are available in the market:

- motor fuels for use in vehicles equipped with spark-ignition engines,
- diesel fuel for use in vehicles equipped with spontaneous-ignition engines.

Motor gasolines are a mixture of organic compounds which boil in the temperature range from 30 to 200°C [1, 3]. The mixture contains components from the paraffins, naphthenes, olefins, and aromatic hydrocarbon groups with C4 to C10 carbon atoms per molecule. As used currently, motor gasolines also have a content of non-hydrocarbon components, such as ethers, and alcohols, as well as additives which improve the motion performance of fuels. The content of the various hydrocarbon fractions in gasoline may vary widely for different types of raw material, refining technology, process conditions, and qualitative requirements.

Most frequently, the streams used for blending motor gasolines are derived from such processes as:

- distillation of petroleum,
- alkylation, isomerization, and solvent extraction,
- thermal cracking,
- catalytic cracking,
- catalytic reforming,

- hydrocarbon processes (hydrorefining, hydrocracking),
- other processes.

A gasoline from vacuum-oil catalytic cracking comprises a large fraction of isoparaffins, olefins, and aromatics (aromatic hydrocarbons). A product of reforming (reformate) has a high content of aromatics. A product of isomerization (isomerizate) contains essentially 2, 2-dimethylbutane and isopentane as well as certain amounts of 2-methylpentane and 2, 3-dimethylbutane. Polymerization gasoline obtained from C3 and C4 olefins is an olefin product, while an alkylate is a component with a zero content of aromatics, olefins or benzene. In addition to the hydrocarbon fractions, gasolines may have a content of oxygen components such as alcohols (including methyl, ethyl, isopropyl, and isobutyl alcohols), butyl ether as well as methyl *tert*-butyl ether, ethyl *tert*-butyl ether, methyl *tert*-amyl ether. Other alcohols may also be present although their presence is limited by their boiling point (max. 215^{o}C).

In the storage, transport, and handling processes during the distribution train, motor gasolines are affected by physical and chemical factors, whereby their physical and chemical processes are changed. As the result, the motor gasoline in one’s vehicle’s fuel tank may have different properties, compared with those of a fresh made product from the refinery: its quality may be deteriorated. Its properties may be affected by the following phenomena:

- evaporation of light ends during the handling (filling) and storage of gasoline,
- the effect of atmospheric oxygen, leading to the occurrence of oxidation and polymerization of certain components of the fuel,
- penetration of impurities (particles) into gasoline,
- penetration of atmospheric moisture into gasoline.

Oxidation and polymerization of motor gasoline take place usually during long-term storage in storage tanks and in vehicle fuel tanks. The intensity of such processes is higher in fuels with a higher percentage of reactive components, increased contact with oxygen (less fuel in the tank), and at higher temperatures of the fuel itself. Such processes lead to the formation of asphalts and gums which are suspended in the engine gasoline along with corrosion products and mineral particles, and may also precipitate in the form of deposits.

Diesel fuels are a mixture of hydrocarbons with C11-C25 carbon atoms per molecule and a boiling range from 150 to 400^{o}C [1, 2]. The properties of the fuels intended for use in spontaneous-ignition engines are much different from those of motor gasoline. Diesel fuels consist of the following hydrocarbon groups:

- n-paraffins : 9-13% (V/V)
- isoparaffins: 30-55% (V/V)
- naphthenes: 25-35% (V/V)
- aromatics: : 15-30% (V/V)
- olefins: : 0-5% (V/V)

Paraffin hydrocarbons have between 10 and 20 carbon atoms per molecule. They improve the fuel's cetane number while deteriorating its low-temperature properties.

Cycloparaffins (also called naphthenes) in diesel fuels are mainly alkylcyclohexanes, decahydronaphthalenes and perhydronaphthalenes. The percentage of that group of compounds depends on what type of petroleum is processed and on how much of the diesel fuel fraction originates from catalytic cracking.

Aromatic hydrocarbons include alkylbenzenes, indanes, naphthalenes, biphenyls, acenaphthenes, phenanthrenes, chrysenes and pyrenes. Among those compounds, the highest percentage is that of naphthalenes.

Crude components of diesel fuel originate from the following processes:

- atmospheric distillation of petroleum,
- catalytic cracking of various petroleum fractions,
- thermal cracking of various petroleum fractions,
- hydrocracking of distillates or distillation bottoms,
- vacuum distillation,
- and other ones.

The principal contaminants of diesel fuel include:

- asphaltenes and gums (they are formed by oxidation and polymerization of reactive components of diesel fuel (unsaturated hydrocarbons, sulfur, nitrogen, and oxygen compounds),
- sulfur and sulfur compounds which were not removed in the production process,
- dust particles,
- corrosion products from tanks and pipelines,
- water,
- microorganisms and their metabolites.

As in the case of gasoline, oxidation and polymerization of diesel fuel take place during its long-term storage, when the fuel is in contact with oxygen or contains reactive components, or when the storage temperature is too high. Such processes produce asphalts and gums which form sludge-type deposits. The formation of such deposits is induced by diesel fuel oxidation products, corrosion and dust particles.

This chapter is intended to provide an answer to some of the important issues connected with the effect of the chemical structure of organic components of fuels on the oxidation stability of motor gasolines and diesel fuels which are used in motor transport.

2. Research methodology

2.1. The selected motor-fuel ageing method

The principal hydrocarbon components of fuels and their derivatives which occur or potentially occur in fuels were selected for the examination of fuel ageing processes, and their stability was determined. The compounds were oxidized in accordance with EN 16091 in order to find the time of stability of the respective fuel components. The resulting products were then analyzed using infrared spectrometry and gas chromatography with mass detector.

The selected accelerated fuel ageing test enables evaluation of the oxidation stability of test products in a short time. Only a small fuel volume is required for the test (approximately 10 ml was used in this case). The test is safe and is controlled using a microprocessor. The automatic control process covers heating, cooling, as well as rinsing, and filling with oxygen. Pressure drop is measured and recorded using a suitable microprocessor with a highly sensitive pressure sensor; the data are transmitted to a computer using an interface for further processing and the final result is a diagram which shows the pressure vs. time relationship. The sample preparation process is highly automated and the sensors function very precisely. Therefore, information about the oxidation process pathway shows that the test method is highly repeatable, compared with currently used test methods.

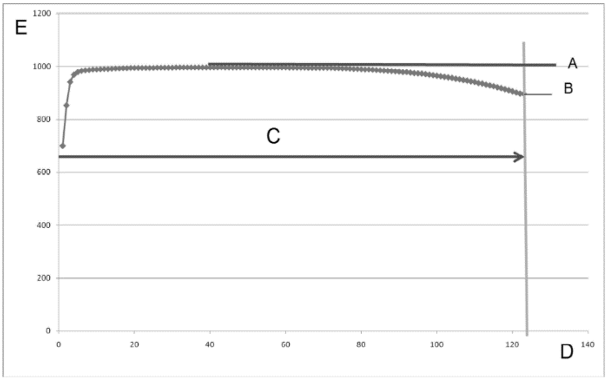

Figure 1. The rapid-oxidation test course diagram, **A** – the maximum pressure recorded, P_{max}, **B** – breakpoint, **C** – induction period (min), **D** – duration of test (min), **E** – pressure value recorded, kPa

The test method is based on the measurement of pressure changes in a tightly-sealed test vessel. The test vessel (made of metal and coated with a thin coat of gold) is filled with 10 ml of the test sample. After being tightly covered with a lid, the test vessel is rinsed with oxygen to remove any air present in the space above the test sample. The test vessel is then filled with oxygen to obtain a pressure of 500 kPa (at ambient temperatures). The pressurized vessel, filled with the test sample and oxygen, is heated to 140°C; the temperature increase causes pressure buildup. The test conditions (temperature and pressure) are stabilized within about 2 minutes.

The period of time of pressure stabilization is strictly related to the sample's oxidation stability. Fuel samples with low oxidation stabilities will soon become oxidized throughout their volumes, leading to a considerable pressure drop in the closed vessel. The time of pressure stabilization for samples with high oxidation stabilities will be much longer. Temperature and pressure in the vessel are recorded at 1 sec intervals until the end point is reached, that is, the pressure drops by 10% of its highest value. The test measure is the time which has lapsed between the test commencement (that is, the time when the sample reached 140°C) and the time when pressure inside the test vessel dropped by 10%. Figure 1 shows the characteristics of the course of the oxidation stability test for a motor fuel.

2.2. Selected analytical methods

2.2.1. Chromatography with Mass Spectrometry (GC MS)

Among all chromatographic techniques known in the art, gas chromatography provides unsurpassed resolutions. Therefore, the technique is most frequently combined with the spectroscopic technique for a fast identification of the separated compounds. Mass spectroscopy is most typically used for the purpose.

In the chromatographic technique, the mixture separation takes place on the chromatographic column. Three types of chromatographic columns are known: column with solid adsorbent, columns with solid-liquid adsorbent, and capillary columns. The capillary columns are typically used in gas chromatography.

Detector is a major component in every gas chromatograph. It is the part all the substances flow into after being separated on the chromatographic column. The ideal detector is sensitive only to the concentration of a compound, regardless of its chemical structure. However, detectors have different sensitivities to various chemical compounds, therefore, its is necessary to calibrate detectors and establish what is called "response factor" separately for every chemical compound to be able to determine with good precision the percentages of the various chemical compounds contained in the analyzed sample.

The Electron Ionization Detector (EID), also called the Mass Selective Detector (MSD), provides information about the analyzed compound in the form of its electron ionization mass spectrum. The spectrum is characteristic of every chemical compound, except certain isomers – they may have same spectra [4].

The interface is an important part, connecting the gas chromatograph with the mass spectrometer. While the pressure at the outlet of the chromatographic column is atmospheric, the next component of the system (ionization chamber of the mass spectrometer) typically operates at pressures in the range 10^{-4}-10^{-3} Pa. It is the primary task of the interface to form a connection which provides optimum operating conditions for the two parts.

Ions from the ionization chamber are introduced into the mass analyzer, where they are separated according to their mass-to-load ratios and, since the load is usually equal to 1, then separation takes place by the mass value. Out of a number of types of analyzers, the following ones are most suitable for the connected GC-MS system: quadrupole analyzer (so called “ion trap”), magnetic analyzer, and time-of-flight analyzer.

The operation of a detector is based on substance introduction – from the chromatographic column – into the vacuum chamber, where the substance is ionized. The ions being formed are focused and accelerated in the mass filter. The mass filter selectivity enables the passage of all ions having a certain mass into the electron multiplier. All of the ions having that certain mass are detected. The mass filter then enables the passage of another mass which is different from the mass of other ions. The preset mass range is scanned by the mass filter gradually, several times a second. The total number of ions is counted every time. The ion intensity or number after each scan is plotted vs. time in the chromatogram (for TIC – total ionic current). A mass spectrum is obtained for each scan; it indicates various ion masses vs. their intensity or number.

The analyses were performed using a GC-MS apparatus from Agilent. The apparatus is equipped with a non-polar HP-5MS column having the following parameters: length: 30 m, diameter: 0.25 mm, film thickness: 0.25 mm, and packing: (5%-phenyl)-methylpolysiloxane. The operating parameters of the apparatus were as follows:

- injector temperature: 250°C (optionally for heavier components 300°C, injection volume: 0.2 ml, stream split: 1:50,
- oven temperature program: 40°C (70°C optionally for heavier components) – 4 min, 10°C/min to a temperature of 180°C (305°C),
- flow of carrier gas (He) – 1 ml/min,
- ion source temperature: 230°C.

2.2.2. Infrared spectrometry

Matter is able to interact with radiation through absorption or emission. The two processes are based on photon absorption or emission through a particle of matter; the photon energy corresponds to the energy difference between the initial and final states of the molecule: in the case of absorption, the final state is the one having a higher energy, compared with the initial state; in the case of emission, the energy of the final state is lower than that of the initial state: the difference indicates the energy of the absorbed or emitted photon, respectively. Infrared spectroscopy measures the absorption of infrared radiation by the molecules of chemical compounds [5].

Infrared is the range of radiation with a wavelength from 780 nm (a conventional end point of the visible range) to 1 mm (a conventional start point of the microwave range). In practice, the medium infrared range from 2.5 μm to 25 μm (or from 4000 cm^{-1} to 400 cm^{-1}) is typically applied.

The absorption of infrared radiation for a majority of known particles causes their excitations (passages) onto higher oscillation levels. However, not all passages are active or have measurable intensities. The active passages, also referred to in spectroscopy as permissible passages, must satisfy certain criteria, referred to as the rules of choice. In the infrared, the only active passages are those of polar molecules having non-zero dipole moments. Speaking in more precise terms, only those vibrations may be excited in the molecule which change the dipole moment of that molecule. Moreover, the most active passages exist between the adjacent levels of oscillation for a given vibration.

The total number of vibrations is 3N-6 for a non-linear molecule and 3N-5 for a linear molecule, where N is the number of atoms per molecule. If the molecule has an element or elements of symmetry, then not all vibrations will be shown in the spectrum. Infrared spectroscopy provides information about the test material in the form of a spectrum – a diagram showing absorption vs. energy of radiation, which is usually expressed as the wave number ($\tilde{\nu}$ [cm^{-1}]).

Every molecule has its unique set of energy levels, therefore, infrared spectra are typical of specific chemical compounds. Comparing the spectrum of a given substance with a previously created spectral library is one of the available methods to identify compounds by means of infrared spectroscopy.

Another method is based on the assigning of bands to the vibrations of the specific functional groups present in the molecule of a given chemical compound, using vibration correlation tables. A given functional group (several atoms, connected by means of chemical bonds eg., carbonyl group –C=O, hydroxyl group –OH) occurring in different compounds has similar values of vibration frequency (energy). The observed frequency ranges which are typical of a given group along with its vibrations, have been collected in correlation tables. Table 1 shows the wave numbers for the characteristic absorption of several frequently occurring functional groups.

Measurement techniques may, essentially, be divided into transmission and reflection techniques. In the transmission techniques, the oscillation spectrum is measured by measuring the radiation intensity after passing through the sample. A drop in intensity for the incident beam indicates absorption of radiation by the sample. Owing to the low transparency of materials in the medium infrared range, the use of the method requires an amount of effort and resourcefulness in preparing the samples. Measurements of the transmission spectra for gases and liquids are carried out using cells with window cells made of materials (such as KBr, NaCl) which are transparent to the infrared range. The spectra of solids can be measured in pellets made of alkali metal halides (KBr), in the form of suspension in Nujol (liquid paraffin), on silicon plates. If the test object is thin enough for radiation to be able to pass through, transmission spectra may be measured directly. In transmission techniques, the measure of absorption of a radiation with a specific wave number ($\tilde{\nu}$) through the sample may either be transmittance ($T(\tilde{\nu})$) or absorbance $A(\tilde{\nu})$, both of which are defined by means of Equations (1) and (2). Absorbance is a practical value: it is useful for the quantitative description of absorption and its value is directly proportional to the number of the absorbing molecules according to the Bouguer-Lambert-Beer rule.

$$T\left(\tilde{\nu}\right)=\frac{I}{I_0} \tag{1}$$

Bond	Type of vibration	Location [cm^{-1}]
O-H (water)	stretching	3760
O-H (alcohols and phenols)	stretching	3650-3200
O-H (carboxylic acids)	stretching	3650-2500
N-H	stretching	3500-3300
C-H (alkynes)	stretching	3350-3250
C-H (vinyl and aryl)	stretching	3100-3010
C-H (aliphatic)	stretching	2970-2850
C≡N	stretching	2280-2210
C≡C	stretching	2260-2100
C=O	stretching	1760-1690
C=N	stretching	1750-1500
C=C (alkenes)	stretching	1680-1610
N-H	deformation	1650-1550
C=C (aryl)	stretching	1600-1500
C-C (aliphatic)	stretching	1500-600
C-H (aliphatic)	deformation	1370-1340
C-N	stretching	1360-1180
C-O	stretching	1300-1050
C-H (vinyl)	deformation	995-675
C-H (aryl)	deformation	900-690

Table 1. Characteristic wave numbers of bands originating from typically existing bonds in organic compounds.

$$A(\tilde{\nu}) = \log \frac{I_0}{I} = -\log T \tag{2}$$

wherein: I_0 – incident beam intensity when falling onto the sample, I – beam intensity after passing through the sample.

Reflection techniques enable the infrared spectra to be obtained by measuring radiation after it is reflected from the sample. The reflected radiation is measured by means of various optical systems used in attachments for spectrometers. The most typical systems are based on total reflection (mirror reflection), attenuated total reflection (ATR) or diffuse reflectance infrared Fourier transformed spectroscopy, DRIFT).

The ATR method is based on the total internal reflection of light. In that phenomenon, the light beam is introduced into a material which is transparent to the infrared and has a high refractive index (eg. for diamond) and falls onto its inner surface. The test sample is pressed to the outer side of that surface at the reflection point. Such radiation is subject to the total internal reflection and will not get outside the medium in which it was moving, although its energy may be absorbed by the sample located on the other side. The beam light is then taken out of the medium where the total inner reflection occurred, thus making it possible to measure its intensity and the infrared spectrum.

The diffuse reflection is the type of reflection where the angle of reflection is different from the angle of incidence. It occurs when the surface roughness is rather significant, compared with the wavelength. The incident radiation may penetrate deep into the sample where it is reflected off the consecutive layers of atom a number of times and is somewhat attenuated, only to leave the sample at a different angle, compared with the angle if incidence. The intensity of radiation which is reflected in a diffuse manner is measured with a system of mirrors or a spherical mirror whereby the radiation, after being reflected in all directions, is directed into the detector. In addition, beam stops are used in order to eliminate part of the radiation which is reflected in the mirror-like manner. The method of diffuse reflectance infrared Fourier transformed spectroscopy (DRIFT) is used for examination of samples in the form of powder or matt surfaces.

In reflection techniques, the absorption measures used are reflectance ($R(\tilde{\nu})$) and the negative logarithm of reflectance ($-\log R(\tilde{\nu})$). The values are analogs of transmittance and absorption, used in the case of transmission techniques and are described by the formulas (3) and (4).

$$R(\tilde{\nu}) = \frac{I}{I_0} \tag{3}$$

$$-\log R(\tilde{\nu}) = \log \frac{I_0}{I} \tag{4}$$

wherein: I_0 – incident beam intensity when falling onto the sample, I – beam intensity after being reflected from the sample

The spectrometric analysis was carried out using the Magna System 750 spectrometer, equipped with: white light source, a DTGS KBr detector, and KBr cell.

Its operating parameters were as follows:

- number of scans: 32,
- length of measurement: 38.73 s,
- resolution: 4 000.

3. Oxidation stability of pure compounds

Compounds which are typically present both in gasoline and diesel fuel were selected for oxidation stability tests. The following hydrocarbons and their derivatives were selected: n-hexane, 1-hexene, 1-hexyne, n-heptane, n-octane, isooctane, cetane (n-hexadecane), benzene, toluene, cyclohexane, o-xylene, ethanol, methyl t-butyl ether (MTBE), pentanoic (valeric) acid methyl ester.

In addition, a mixture of fatty acid methyl esters (FAME) was subjected to ageing. Findings of the oxidation stability tests for the selected compounds are shown in Figure 2.

The results shown in Figure 2 indicate that oxidation stability is the lowest for the hydrocarbons having multiple bonds and for FAME with a large number of double bonds. High oxidation stability is shown by short-chained hydrocarbons, branched hydrocarbons, aromatics, and ethers.

3.1. Aliphatic chain length vs. oxidation stability

Saturated hydrocarbons with different chain lengths were selected for the oxidation stability tests. Their oxidation stability was tested (Figure 3) and their oxidation products were analyzed (Figure 4).

The findings shown in Figure 3 indicate that oxidation stability of hydrocarbons decreases with the carbon chain length. Short-chained saturated hydrocarbons can be stored for longer periods of time because of their lower reactivity.

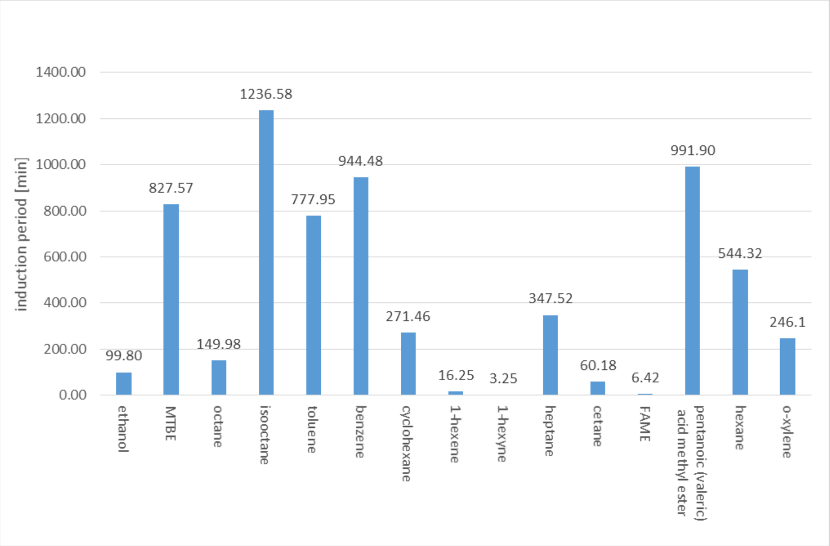

Figure 2. Results of oxidation stability tests of selected chemical compounds

An analysis of the IR spectra of oxidized hydrocarbons indicates that the most significant changes in the n-heptane sample occurred in the wave numbers, corresponding to stretching vibrations of the OH group (approx. 3550 cm^{-1}) and C=O (approx. 1900 cm^{-1}).

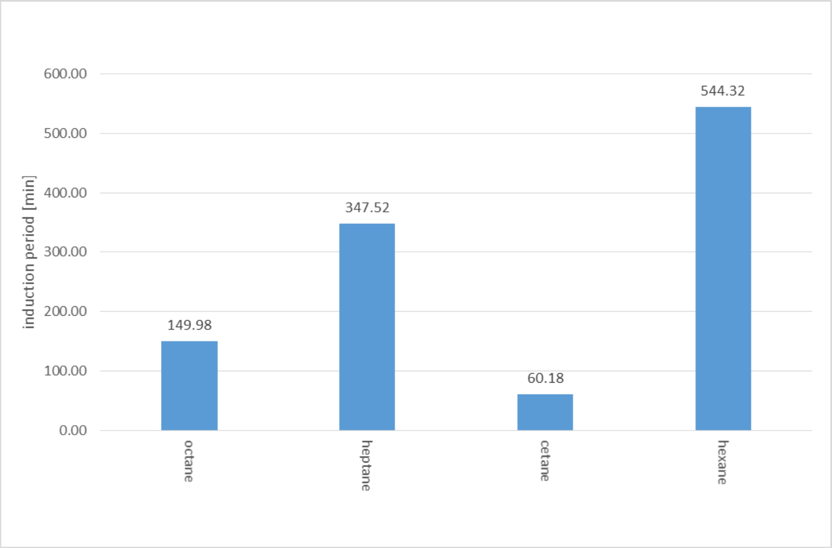

Figure 3. Carbon chain length vs. oxidation stability of hydrocarbons

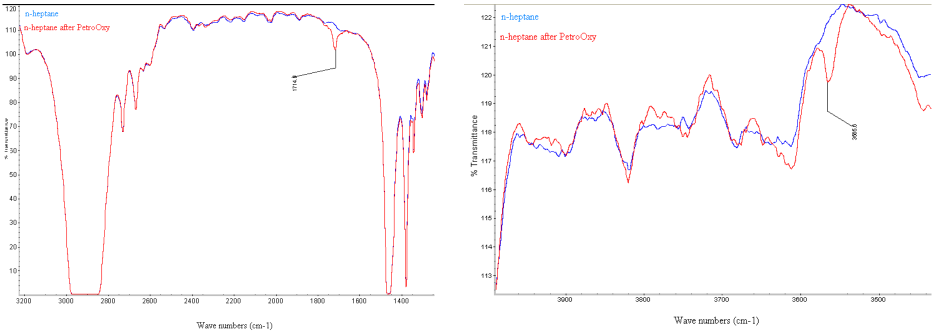

Figure 4. IR spectra for n-heptane before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

From a chromatographic analysis (GC-MS), it follows that the principal products of ageing of heptane are: ketones (i.e., 2-heptanone, 3-heptanone, 4-heptanone) and secondary alcohols: 2-heptanol, 3-heptanol.

Similar changes caused by oxidation were observed in the case of oxidation of n-hexane and n-octane, although the number of carbon atoms per molecule for ketones and alcohols was six and eight, respectively. A different phenomenon was observed for cetane, where the oxidation processes had led to the formation of oxygen compounds (alcohols and ketones) with lower numbers of carbon atoms per molecule, i.e., 2-heptanol, 3-heptanol, 2-heptanone, 3-heptanone, 4-heptanone, 6-dodecanone.

3.2. Type of bonds vs. oxidation stability

The type of bonds, especially the unsaturation ratio for a chemical compound or mixture is essential to the oxidation stability of a final product. The more saturated compounds (with single bonds) are present, the better the stability of the mixture. On the contrary, if a double or triple bond is present in a molecule, then oxidation stability decreases dramatically (Figure 5).

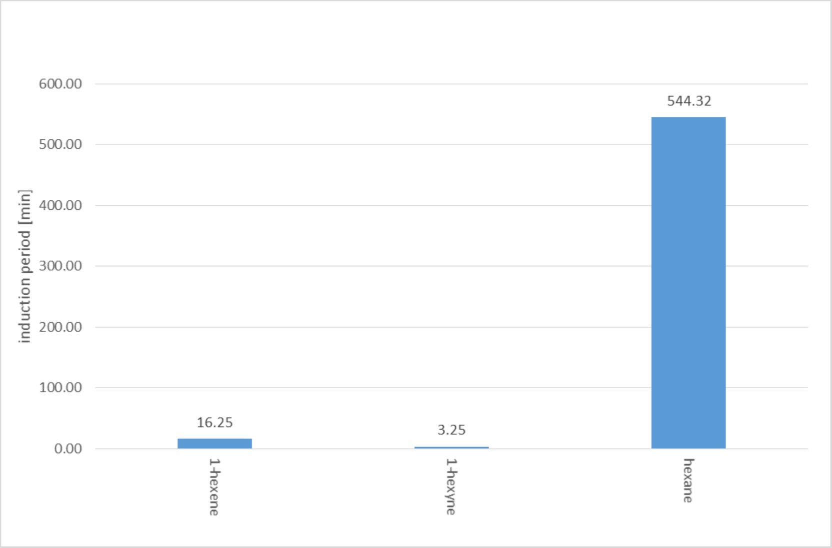

Figure 5. Type of bonds vs. oxidation stability of compounds.

Induction period for hexane is nearly 200 times as high as that for 1-hexyne and more than 30 times as high as that for its double-bond equivalent. Analyses by GC MS and IR indicate that products of oxidation do have a content of aldehydes, carboxylic acids, ketones, and alcohols and aldehydes with a double bond.

3.3. Structure vs. oxidation stability

Hydrocarbons containing 6 carbon atoms per molecule and having different structures were selected for the structural examination of hydrocarbons on their oxidation stability: hexane, cyclohexane, and benzene.

The oxidation stability tests results are shown in Figure 6.

The findings indicate that the highest oxidation stability in the above hydrocarbon group was shown by aromatic hydrocarbons with very high chemical stability, followed by hexane, while that of cyclohexane was the lowest. No changes in the IR spectrum of benzene were observed and no new chemical compounds were found after oxidation, as confirmed by the GC MS

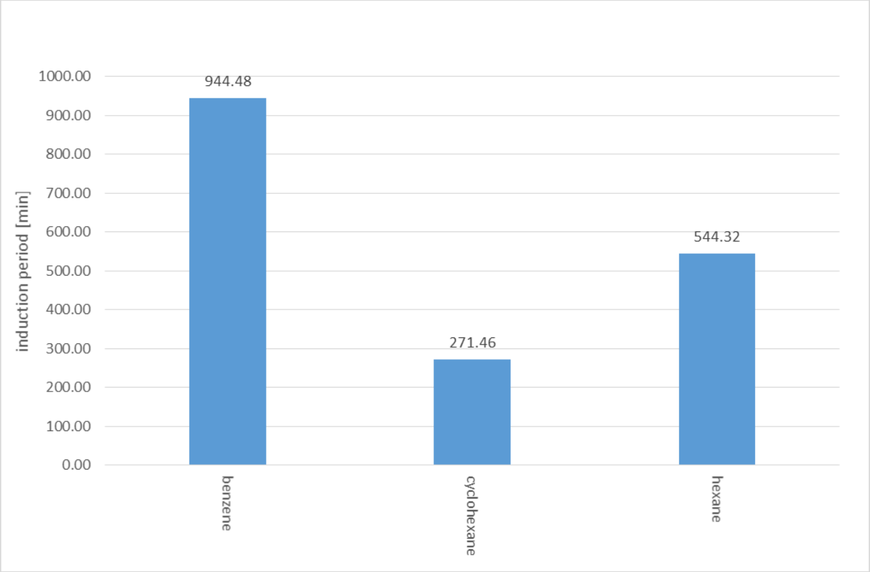

Figure 6. Structure vs. oxidation stability

analysis. Oxidation products included benzaldehyde in the case of toluene, while cyclohexanone and cyclohexanol were found in cyclohexane after oxidation.

3.4. The effect of isomerization on oxidation stability

Chemical compounds with different spatial structures and branching ratios were selected for fuel tests, intended to establish the effect of their isomerization on oxidation stability. The findings shown in Figure 7 indicate that linear compounds are characterized by lower stabilities, compared with their isomers. Induction period for isooctane was nearly 10 times as high as that for octane. This leads us to the conclusion that the oxygen molecule will have a more difficult access to the spatial molecule of isooctane and that the compound will show higher stabilities. In the case of a linear octane molecule, induction period was about 150 minutes. Oxidation of isooctane led to the formation of branched ketones and branched secondary and tertiary alcohols. Oxidation of octane led to the formation of straight-chained ketones and alcohols, such as 2-octanone, 3-octanone, 4-octanone, 2-octanol, 3-octanol, 4-octanol.

3.5. Oxidation stability of oxygen compounds

Ethanol and methyl *tert*-butyl ether (MTBE) – components of commercially available motor gasoline – were selected for the tests. The compounds were oxidized by rapid oxidation of which the findings are shown in Figure 8.

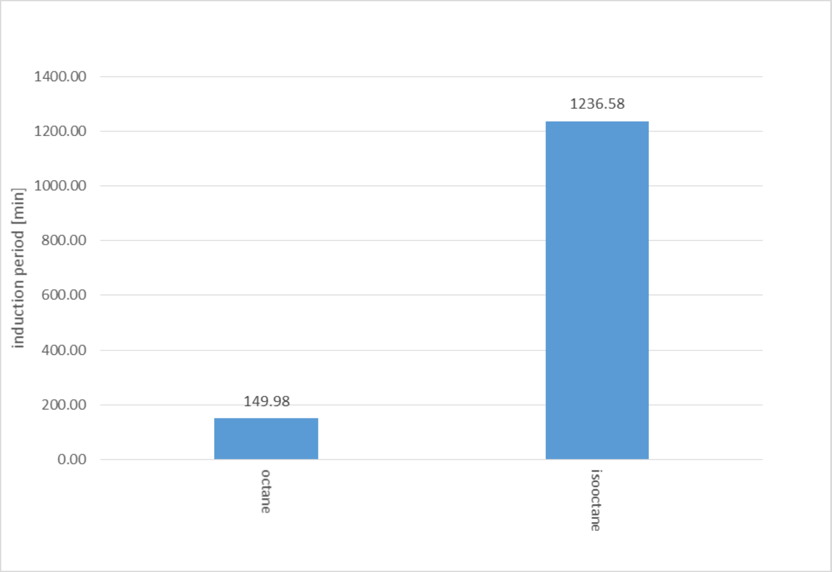

Figure 7. Isomerization vs. oxidation stability of hydrocarbons

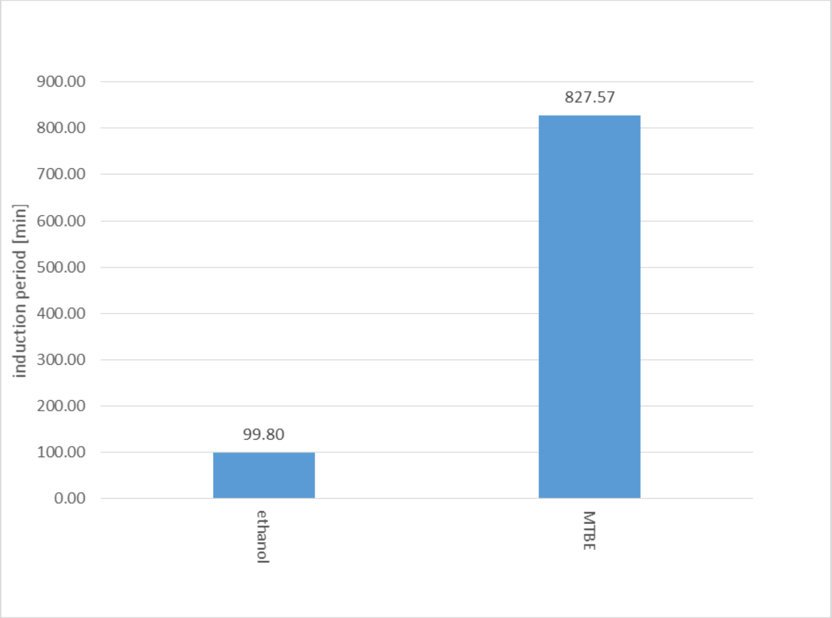

Figure 8. Results of oxidation stability tests for selected oxygen compounds

The results shown in Figure 8 indicate that ethanol has an induction period nearly 10 times as low as that of methyl *tert*-butyl ether (MTBE). According to the standard EN 228, the maximum permissible content of alcohol in gasoline is 5% (V/V), and the content of ethers is such that the total concentration of oxygen is a maximum of 2.7% (m/m).

4. Ageing of model fuel blends

4.1. Stability of mixture vs. stability of compounds

Compounds having extreme oxidation stabilities were mixed together. The experiment was intended to investigate the possibility of addition of oxidation stabilities for the respective compounds and to show the effect of the compound stabilities on that of their mixture.

In the first experiment, two compounds with different oxidation stabilities were mixed together. The resulting mixture was characterized by an oxidation stability which was nearly an arithmetic mean of the two component oxidation stabilities.

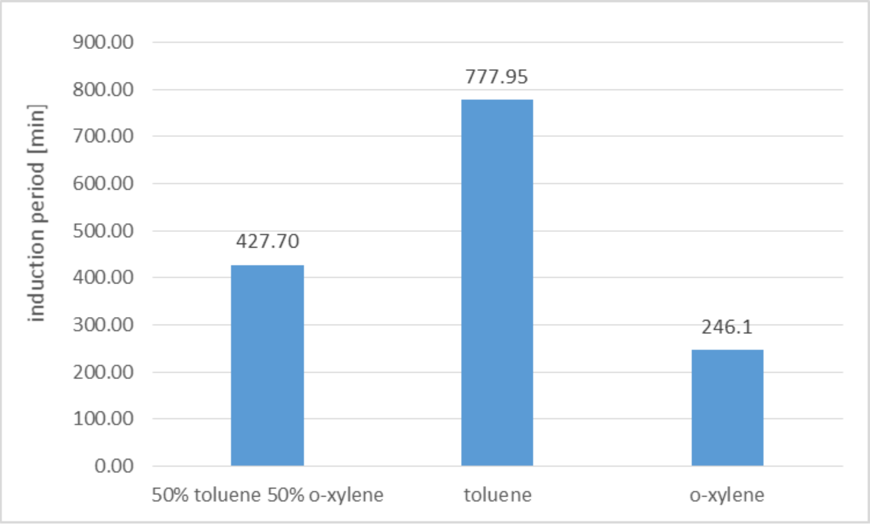

Figure 9. Oxidation stabilities for toluene and o-xylene and their 50/50 mixture

The other experiments indicate that oxidation stability for the 50/50 mixture is between the two values for the pure individual compounds, though not an arithmetic mean, in a majority of cases.

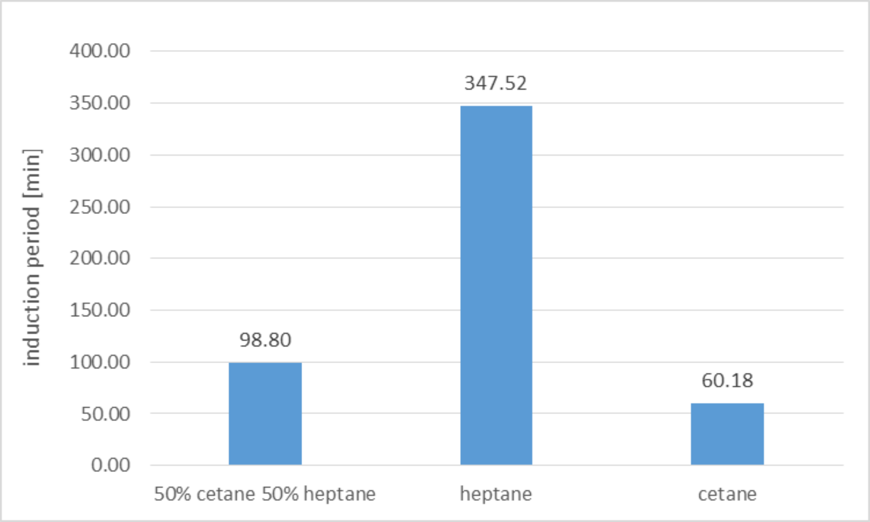

Figure 10. Oxidation stabilities for heptane and cetane and their 50/50 mixture

Figure 11 indicates that oxidation stability for a mixture of two compounds having extreme values of the parameter is not a mean value of the parameter; rather, the value for the mixture is determined by that of the compound for which the oxidation stability is lower.

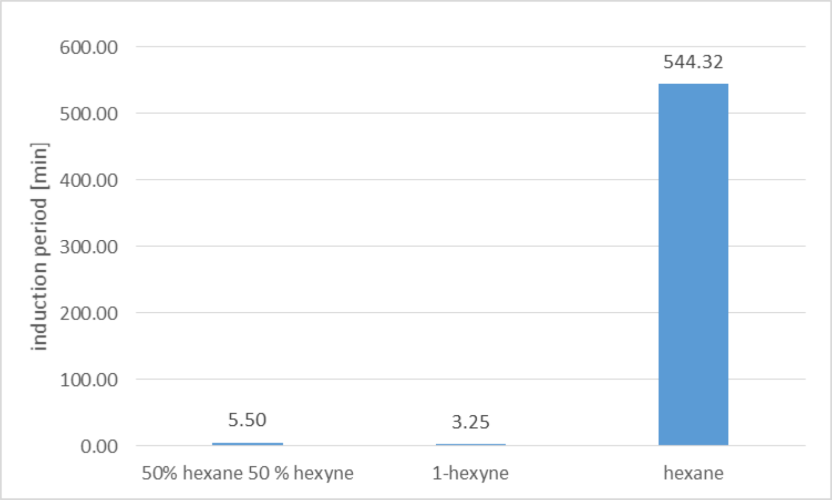

Figure 11. Oxidation stabilities for hexane and 1-hexyne and their 50/50 mixture

After obtaining a 50/50 mixture of MTBE and isooctane, the value of oxidation stability for the mixture is lower than that for each of the respective chemical compounds.

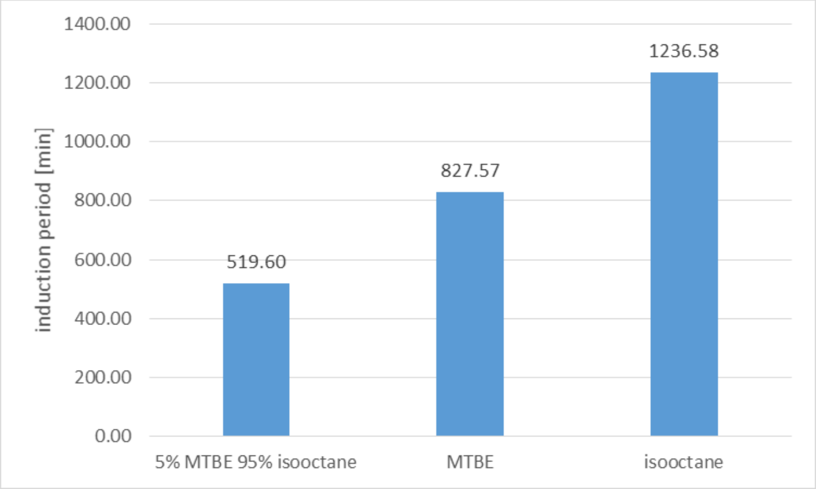

Figure 12. Oxidation stabilities for isooctane and MTBE and their 50/50 mixture

4.2. Oxidation stability tests for fuel blends

In this experiment, model fuels were prepared and were subjected to ageing by the rapid oxidation method. An analysis was then carried out for samples collected before and after ageing, using the infrared spectrometry technique. Blending was intended to reproduce the actual fuels (gasoline and diesel fuel) as best as possible. In the case of gasoline, blends applicable in octane number determination were used; the octane numbers were approximately the same as that for the gasoline stored for the purposes of this project. In the case of diesel fuel, the mixture was blended by adding to cetane (n-hexadecane) about 20% toluene, just as for actual diesel fuels, in which the content of monocyclic aromatic hydrocarbons is about 20%.

The oxidation stability test results for the model fuel blends are shown in Table 2 and in Figures 13, 14, 15 and 16.

Mixture	Induction period [min]
95% (94 % isooctane + 6 % n-heptane) + 5 % MTBE	670
95% (94 % isooctane + 6 % n-heptane) + 5 % ethanol	519
50% (95 % isooctane + 5 % n-heptane) + 5 % ethanol + 5 % MTBE + 15% 1-heptyne + 25% toluene	183
80 % cetane + 20 % toluene	138.2

Table 2. Induction period results for the test mixtures

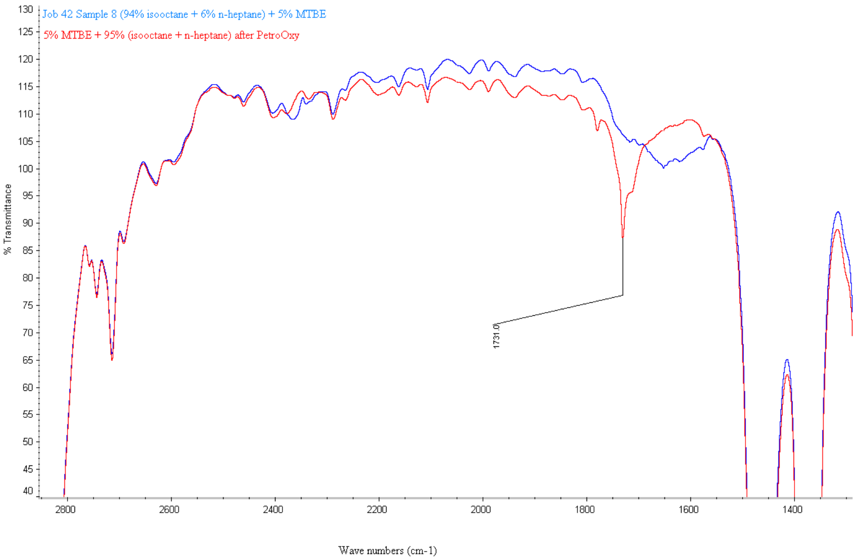

Figure 13. Superimposed IR spectra for 95% (94% isooctane + 6% n-heptane) + 5% MTBE before and after ageing (blue-spectrum before ageing, red-spectrum after ageing)

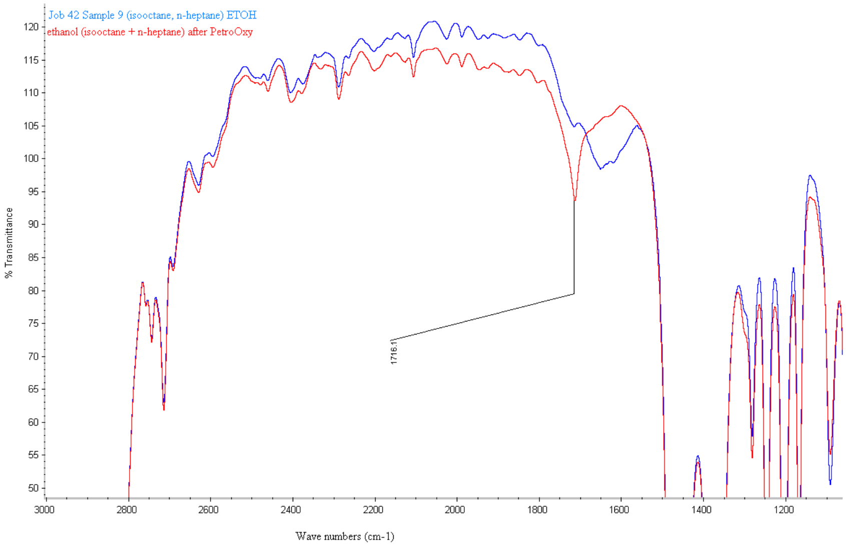

Figure 14. Superimposed IR spectra for 95% (94% isooctane + 6% n-heptane) + 5% ethanol before and after ageing (blue-spectrum before ageing, red-spectrum after ageing)

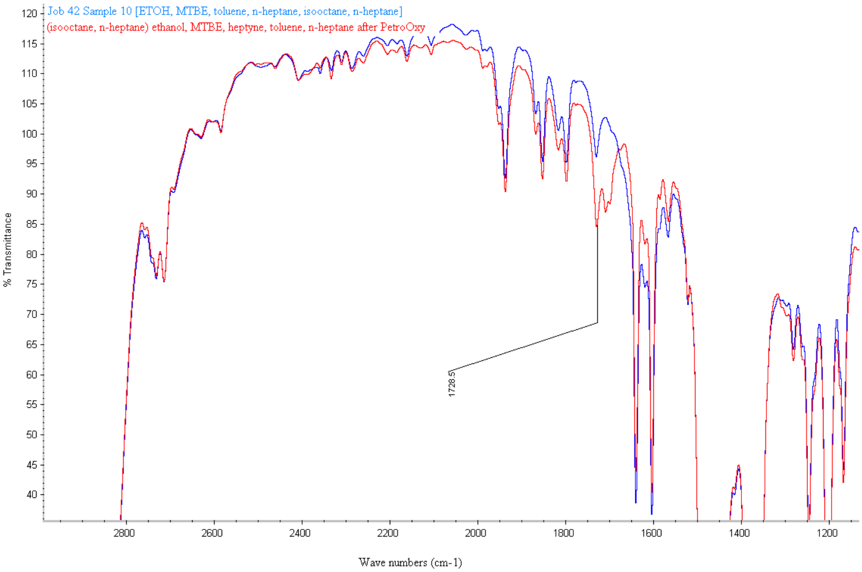

Figure 15. Superimposed IR spectra for 50% (95% isooctane + 5% n-heptane) + 5% ethanol + 5% MTBE + 15% 1-heptyne + 25% toluene before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

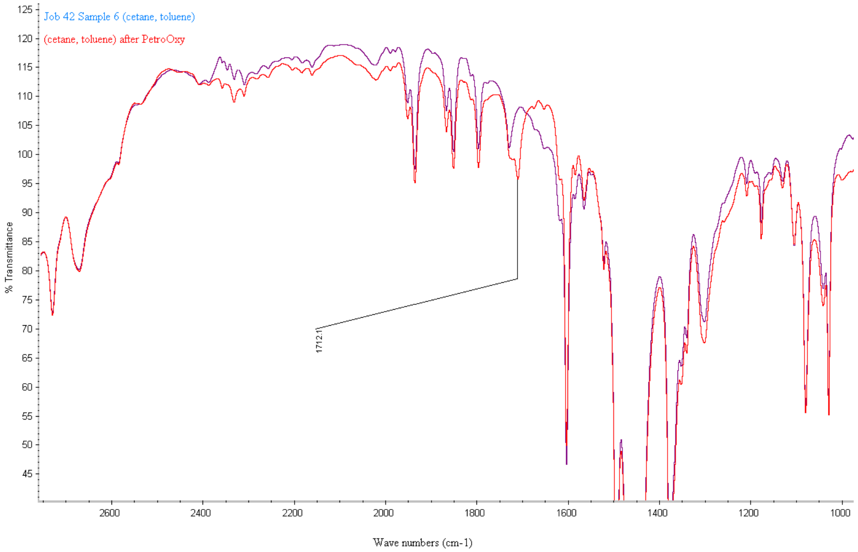

Figure 16. Superimposed IR spectra for 80% cetane + 20% toluene before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

After oxidation of various types of model mixtures showing fuel compositions after spectral analysis before and after ageing by the rapid-ageing method, all the spectra after oxidation show a characteristic band for the wave numbers in the range 1760-1690 cm^{-1}, corresponding to stretching vibrations from the carbonyl group (C=O). The appearance of the carbonyl group indicates that the sample has been oxidized which means that its initial properties have been changed.

5. Changes in oxidation stability which occur in classic motor fuels during long-term storage

Examination of the various processes taking place in the course of motor fuel ageing during storage was performed using the following fuels:

- 95 octane unleaded gasoline (Pb95),
- 98 octane unleaded gasoline (Pb98),
- diesel fuel with up to 7% (V/V) of biocomponent (ONH),
- diesel fuel with less than 2% (V/V) of biocomponent (ON).

The Pb95 gasoline had a content of not more than 5% (V/V) of a biocomponent in the form of ethyl alcohol. The Pb98 gasoline was an ether-based gasoline, with an ethyl *tert*-butyl ether (ETBE) of not more than 15% (V/V).

The diesel fuels had a content of generation I biocomponent in the form of fatty acid methyl esters (FAME) obtained from rape-seed oil. The ONH diesel fuel had a content of up to 7% (V/V) of the biocomponent. The ON diesel fuel had a content of less than 2% (V/V) of the biocomponent.

The selected fuels were stored for 12 months in 5-m^3 stationary tanks.

The fuels complied with the requirements of applicable standards in respect of the properties of motor gasolines and diesel fuels (EN 228 and EN 590) as at the day of purchase.

5.1. The fuel storage station

The purchased motor fuels were stored in 5-m^3 underground storage tanks. The storage tanks were equipped with a dedicated piping system to enable fuel sampling at various heights from the tank. The sampling pumps did not cause mixing of the stored fuel when sampling. Samples of the motor fuels were collected every 2 weeks, as follows: every 4 weeks from level 2 for a full analysis, and every 4 weeks from all levels for a short analysis.

The fuels were sampled at 20 cm, 90 cm and 160 cm above the tank bottom. A fourth pipe was used for collecting fuel vapor samples from above the liquid.

A diagram of the storage tank is shown in Figure 17, the fuel sampling station is shown in Figure 17.

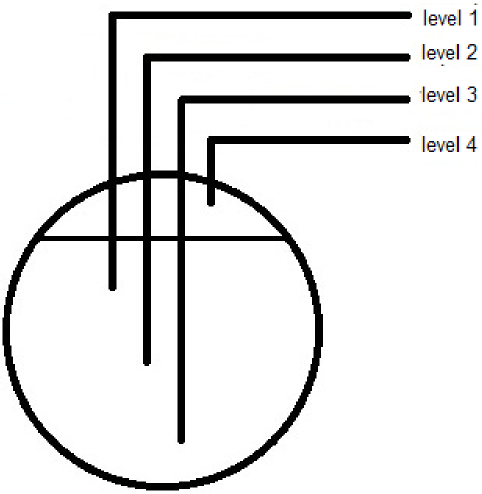

Figure 17. A diagram of the liquid fuel storage tank and the fuel sampling levels in the tank.

Figure 18. Liquid fuel sampling station.

The scope of analysis was established at the beginning of the fuel storage period.

6. Methods of ageing of motor gasolines

The following test methods were selected for testing the oxidation stability of motor gasolines:

- oxidation stability test, also referred to as the induction period method according to the standard EN 7536;
- oxidation stability test for small amounts of motor fuels, as described in the standard EN 16091, modified for oxygen pressure (500 kPa).

6.1. Induction period test

The test method consists in the oxidation with oxygen of the test motor gasoline in a pressurized bomb. A 50 ml volume of the test motor gasoline was placed in a special pressurized bomb (Figure 19) which enables a continuous recording of gas pressure variations, and oxygen was introduced at a pressure in the range 690-705 kPa. The pressurized bomb with the sample in it was then thermostated at 100^{o}C. The test result, referred to as the induction period, is expressed as the time that has lapsed until the maximum pressure has changed by 14 kPa within 15 minutes. The pressure vs. time relationship is plotted in the diagram.

The induction-period method is recommended in the standard EN 228 as the parameter which indicates the quality of the test motor gasoline. A fuel which complies with the standard is expected to have an induction period of more than 360 minutes.

For the induction-period test, samples of the stored motor gasolines were collected from level 2 of the storage tanks (Figure 13) every 4 weeks.

The intention was to continue every test until the gasoline breakpoint. However, the test was discontinued after 60 hrs and it was established that the result was higher than 3600 minutes.

Findings for the test motor gasolines were shown in Figure 20.

The induction-period test results are more than 10 times as high as the minimum value referred to in the standard EN 228, showing very good oxidation stabilities of the stored gasolines.

The selected induction-period method to test motor gasolines in the pressurized bomb did not enable it to be established which of the stored motor gasolines had a better oxidation stability.

Figure 21 shows an oxidation curve for the Pb95 and Pb98 motor gasolines after storing them for 50 weeks, as found in accordance with the standard EN 7536.

Figure 21 indicates that ageing runs faster for the Pb95 gasoline, compared with the Pb98 gasoline. The faster drop of oxidation stability for Pb95 is caused by the addition of ethanol, of which the reactivity with oxygen is higher than that of ether.

Figure 19. Pressurized bomb for oxidation stability tests of motor gasolines

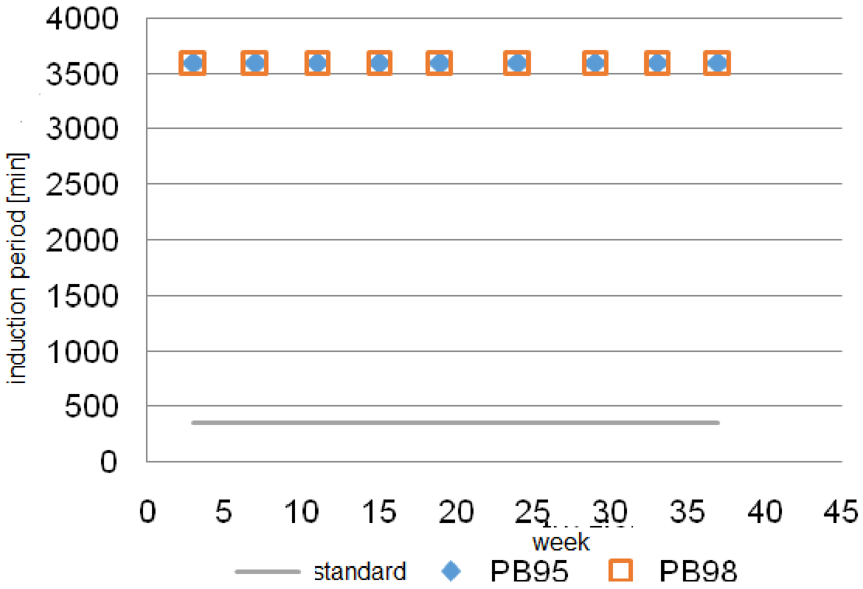

Figure 20. Graphical representation of findings for the test motor gasolines.

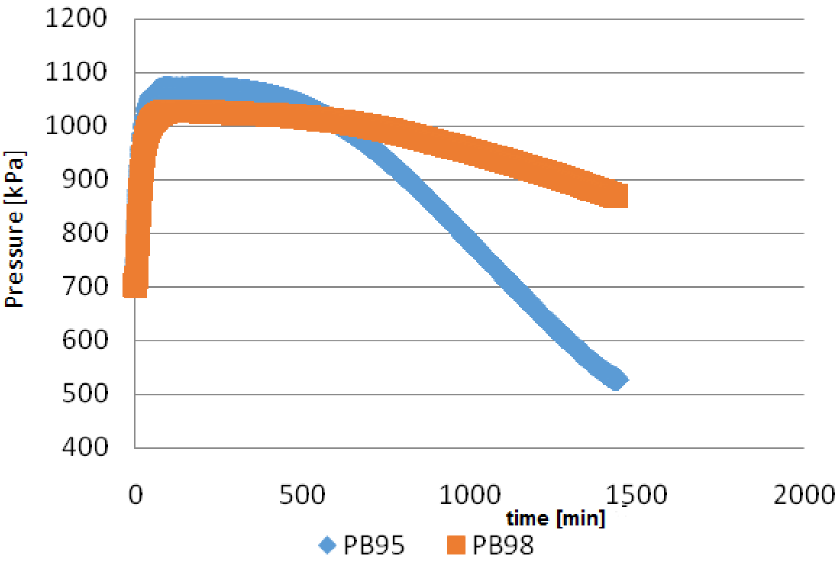

Figure 21. The course of oxidation of motor gasolines after 50 weeks of storage, as found by the induction-test method.

6.2. The rapid-oxidation test of motor gasolines

The rapid-oxidation test, intended to measure oxidation stability of motor gasolines, was carried out in the apparatus shown in Figure 22. The test method is described in the standard EN 16091. The method has the advantage of requiring only a small volume of the test sample. The oxidation stability test of motor gasolines was carried out at the following conditions: temperature: 140°C, pressure of oxidizing factor 500 kPa, test sample volume: 5 ml. Oxygen was used as the oxidizing factor.

The oxidation stability test of motor gasolines was carried out for stored motor gasolines every 2 weeks, using the rapid-ageing method. Figure 23 shows the test results for the Pb95 and Pb98 gasolines after storage.

Only a small sample volume is required for the test, therefore, the method was used also for testing gasoline samples collected from various tank levels to find out whether fractionation occurred during stationary storage. Findings for the 95-octane and 98-octane gasolines are shown in Figure 24 and Figure 25, respectively.

Figure 26 shows the course of a representative test – the diagram illustrates a change in the pressure generated in the test vessel vs. time for the test fuel sample.

The method confirms earlier observations that the gasoline with a biocomponent content (bioethanol) has a lower oxidation stability, compared with that which contains ethyl *tert*-butyl ether.

Figure 22. Oxidation stability test apparatus.

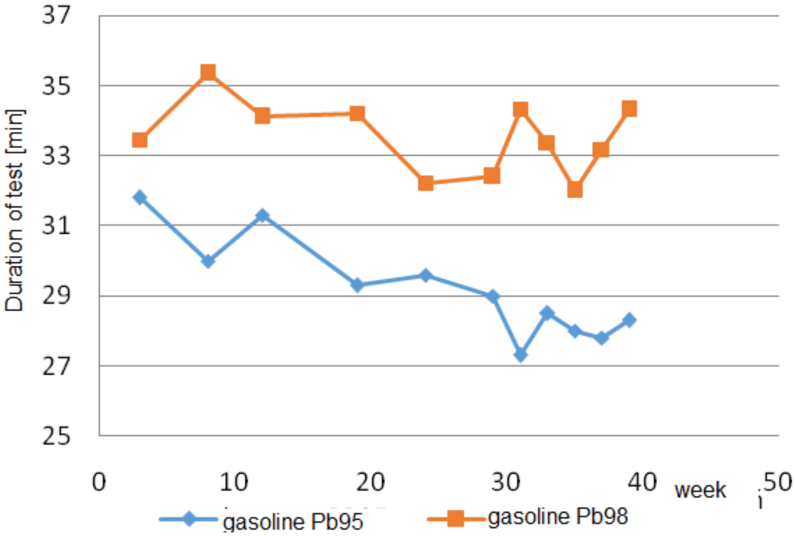

Figure 23. Results of the rapid-oxidation test for PB95 and PB98 gasolines.

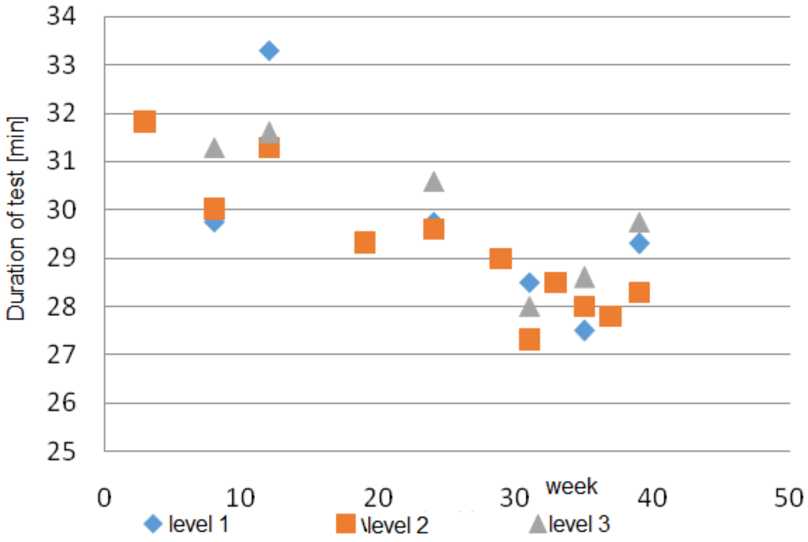

Figure 24. Results of the oxidation stability test for the PB95 gasoline, collected from various tank levels.

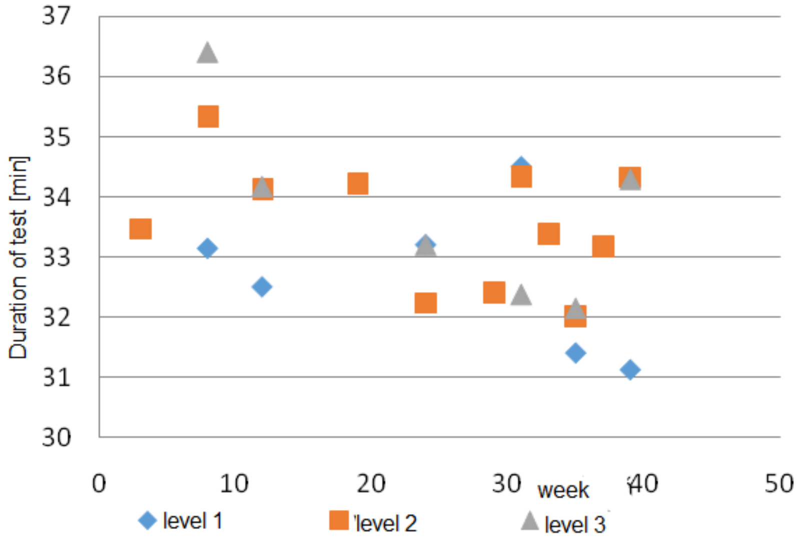

Figure 25. Results of the oxidation stability test for the Pb98 gasoline, collected from various tank levels

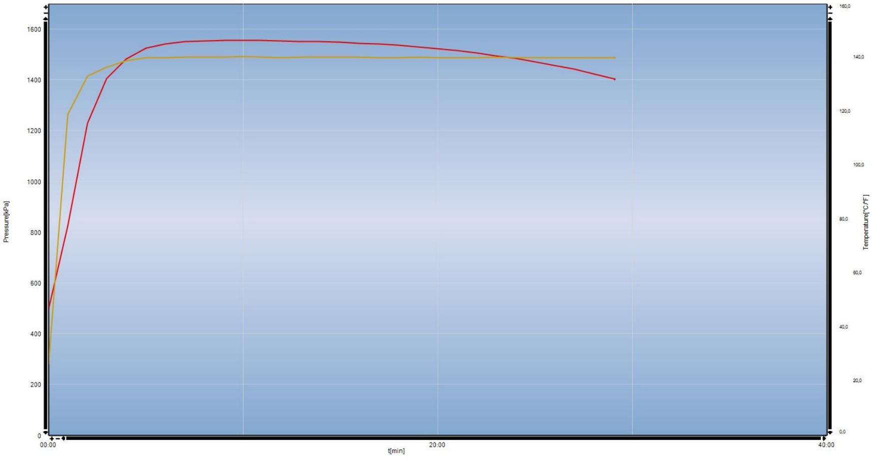

Figure 26. Graphical representation of oxidation of the test motor gasoline.

7. Diesel fuel ageing methods

Oxidation stability tests were carried out on diesel fuels after storage, using the following methods:

- determination of the amount of deposit formed in diesel fuels during oxidation;
- determination of oxidation stability of diesel fuels having a content of biocomponents;
- rapid-oxidation test for diesel fuels.

7.1. Determination of oxidation stability from the amount of deposit formed

The method consists in oxygen-based oxidation of diesel fuel test samples at a flow rate of 3 l/hr and a temperature of 95°C. The test is continued for 16 hours, during which time reactions take place in the diesel fuel sample, leading to the formation of macromolecular organic compounds. The quality of diesel fuel is evaluated from the amount of deposit formed as the result of oxidation of the fuel. According to the standard EN 590, a fuel meets the requirement if the amount of deposit is less than 25 g/m^3. The method is dedicated to all types of diesel fuel and is carried out in accordance with the methodology, described in the standard EN 12205. Figure 27 shows the components of the test assembly for diesel fuel ageing (thermostating bath for the test sample, test tube with a suitable condenser and a filtering assembly).

Oxidation stability was tested using the method for two types of diesel fuel after storage: one of them (ON) had a content of biocomponents of less than 2% (V/V), the other was a diesel fuel with 7% (V/V) of a biocomponent (ONH). In this method, oxidation stability is evaluated from the sum of adherent solubles and filterable insolubles, present in the diesel fuel after oxidation.

Figure 27. A test assembly for oxidation-stability tests of diesel fuels according to the standard EN 12205.

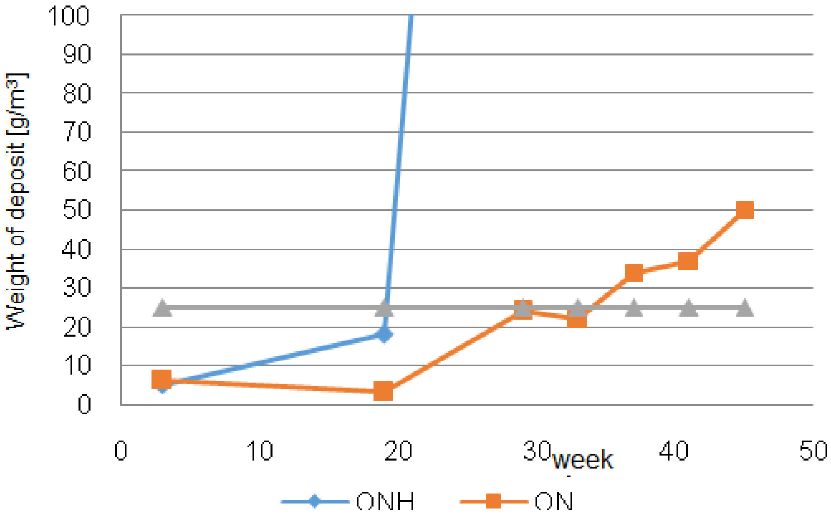

Figure 28. Results of oxidation stability tests.

Figure 28 is a graphical representation of the oxidation-stability test results, obtained by the test method described in the standard EN 12205. The blue color in the diagram shows results for the diesel fuel with 7% (V/V) of a biocomponent, orange color shows the results for the diesel fuel with less than 2% (V/V) of a biocomponent. The grey line shows the permissible value of oxidation stability for diesel fuels (25 g/m^3) according to the standard EN 590.

The results in Figure 28 indicate that the content of deposit in the diesel fuel with 7% (V/V) of a FAME after being stored for 20 weeks is so high that the diesel fuel becomes virtually unsuitable for use as a fuel for combustion engines. In Week 45 of storage, the diesel fuel had a content of solubles (gums) of more than 3000 g/m^3. The solubles and insolubles formed are shown in Figures 29 and 30.

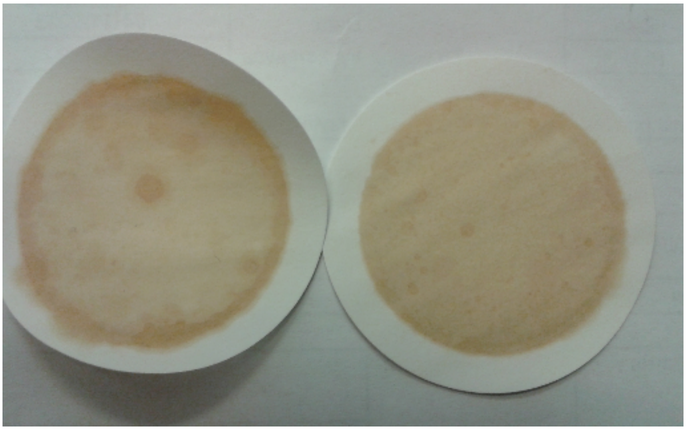

Figure 29. Insolubles, formed by oxidation during storage of diesel fuel with 7% (V/V) of a biocomponent.

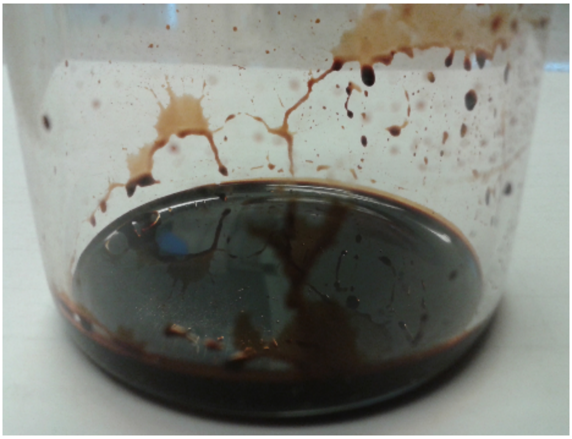

Figure 30. Solubles (gums), formed by oxidation during storage of diesel fuel with 7% (V/V) of a biocomponent.

For the diesel fuel with less than 2% (V/V) of a FAME, ageing is a much slower process. In Week 33 of storage, the deposit content in the diesel fuel is near the maximum value of 25 g/m^3, as stated in the standard EN 590.

The results of oxidation stability tests, carried out by the method referred to in the standard EN 12205, indicate that the diesel fuel with 7% (V/V) of a FAME is affected by ageing at a faster rate, compared with that containing less than 2% (V/V) of a biocomponent.

7.2. Oxidation stability tests of diesel fuel with more than 2% (V/V) of biocomponents (Rancimat method)

Oxidation stability tests of diesel fuels are carried out in accordance with EN 15751 and dedicated, according to the standard EN 590, only to fuels with more than 2% (V/V) biocomponents in the form of fatty acid methyl esters (FAME).

The test method is based on oxidation under the effect of air (10 l/hr) and temperature (110°C), causing the ester to decompose, whereby acid compounds are released which affect the electrical conductivity of water, as controlled during the test.

The test is carried out at a temperature of 110°C and air flow rate of 10 l/hr. The required sample volume is 7.5 g of product. Diesel fuels comply with the requirements of the standard EN 590, if the time that lapses until the break point in the electrical conductivity curve exceeds 20 hrs.

The test was carried out using the device shown in Figure 31.

Figure 31. A test assembly for oxidation stability tests according to EN 15751 (Rancimat method).

The test result, expressed in hours, is found from the curve which illustrates changes in the electrical conductivity of water vs. time (Figure 32).

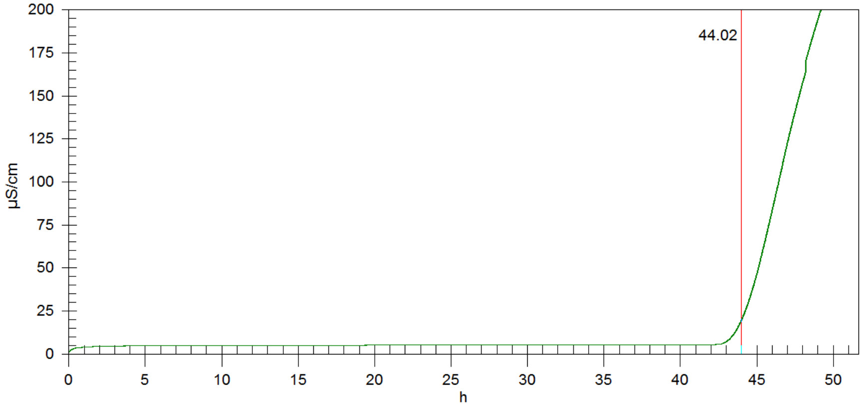

Figure 32. The course of oxidation of diesel fuel according to EN 15751 (Rancimat method).

The tests results were shown in Figure 33. The blue line shows the ageing processes taking place in the diesel fuel with 7% (V/V) of a FAME, the red line refers to the oil with less than 2% (V/V) of a biocomponent. The oil with less than 2% (V/V) of a biocomponent was tested for comparison of its results with those obtained for the oil with 7% (V/V) of FAME.

The results seem to confirm the observation that ageing processes run at a faster rate in the diesel fuel with 7% (V/V) of a FAME, compared with the oil containing less than 2% (V/V) of a biocomponent.

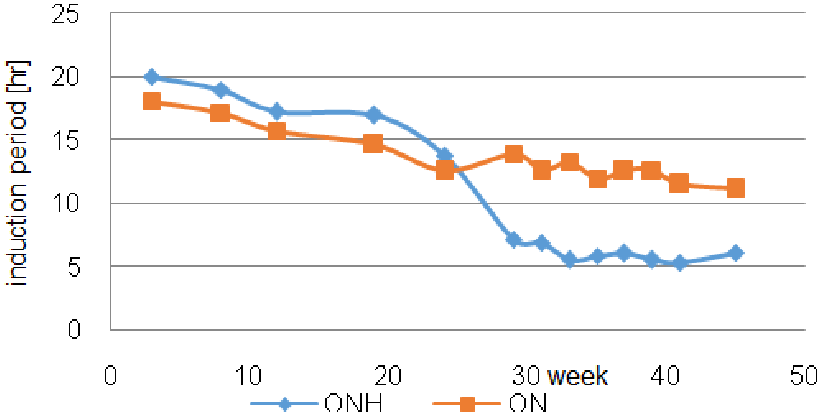

Figure 33. Results of ageing for diesel fuels during storage.

7.3. Rapid-oxidation method for diesel fuels

The third method to test the diesel fuels for oxidation stability is the most recent method, recommended for the purpose. The test procedure was described in the standard EN 16091. The criterion of evaluation of the quality of diesel fuels is the time that has lapsed until pressure in the reaction vessel has dropped by 10%, compared with its initial value, and is expressed in minutes. The test method has the advantage of short duration, requiring only a small sample volume and providing results with high repeatability.

The procedure and conditions of the oxidation stability test were the same as for motor gasolines (Item 6.2.), except that the initial pressure of oxygen was 700 kPa for diesel fuel.

The fuel samples were collected at level 2 of the fuel tank every 2 weeks.

The oxidation stability test results for the diesel fuels during storage are shown in Figure 34. The blue line refers to the diesel fuel with 7% (V/V) of a biocomponent (ONH), the red line indicates the fuel with less than 2% (V/V) of a FAME biocomponent (ON).

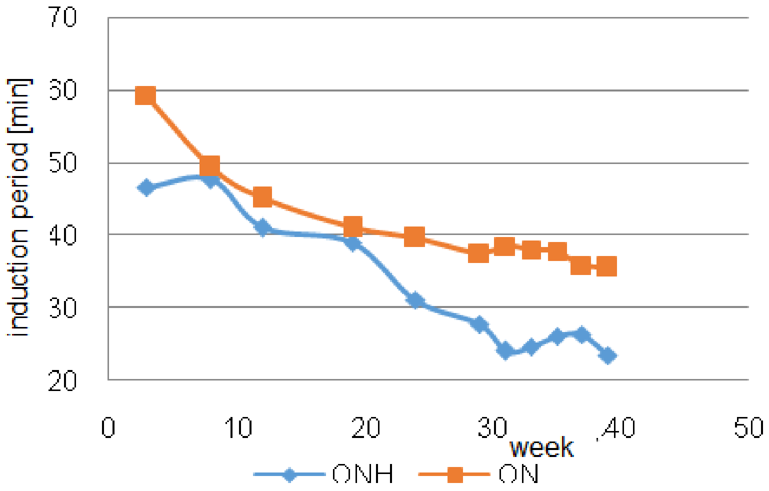

Figure 34. Results of oxidation stability tests for diesel fuels during storage.

The results of oxidation stability tests, as shown in the diagram, indicate that the diesel fuel with 7% (V/V) of FAME is much inferior in respect of oxidation stability, compared with the diesel fuel with less than 2% (V/V) of FAME.

While the ONH diesel fuel sample, after being stored for 40 weeks in an underground storage tank, had an induction period of 23 minutes, the ON diesel fuel sample had an induction period more than 50% higher, indicating a superior oxidation stability of the diesel fuel with the lower content of FAME biocomponent.

8. Conclusion

Based on oxidation stability tests, an increase in the chain length of hydrocarbons was found to cause a decrease in oxidation stability. The longer the hydrocarbon chain of a compound, the lower its stability. The presence of multiple bonds leads to lower oxidation stabilities. Unsaturated compounds display higher reactivities, compared with saturated ones: they tend to be oxidized and polymerized more readily. Cyclic compounds are less stable than aromatic or aliphatic compounds because of the presence of stresses in their ring. Aromatic compounds are more stable because of the presence of a system of three coupled double bonds in their molecules.

Toluene has a lower oxidation stability compared with benzene because aromatic compounds with a hydrocarbon chain are more susceptible to oxidation compared with rings without substitutes. The aromatic ring is highly stable and double bonds will resist cleavage. If, therefore, a single bond exists between a carbon atom in the ring and a carbon atom in the substitute, then location at the substitute's carbon atom is preferential for the incorporation of oxygen atoms (oxidation of toluene produces benzaldehyde).

Branched isomers are more stable than linear hydrocarbons because interactions between carbons atoms in the branched isomers are more difficult.

Ethyl alcohol is oxidized faster than methyl *tert*-butyl ether (MTBE) because alcohols tend to react with oxygen more readily than ethers. Oxidation of ethers is a slow reaction: a GC MS analysis showed the presence of methyl *tert*-butyl ester after contact with oxygen.

Methyl esters of saturated acids are more stable than methyl esters of unsaturated acids (FAME). This is caused by the presence of unstable multiple bonds.

Oxidation of saturated compounds produces mainly alcohols and ketones. The reactions run at a slow rate, although the presence of such compounds is indicative of oxidation processes taking place.

Oxidation of unsaturated compounds leads to the formation of alcohols, ketones, aldehydes, and carboxylic acids.

Ethyl alcohol and methyl *tert*-butyl ether (MTBE) are oxidized to esters, although the reactions run at different rates.

The appearance of the carbonyl group as the result of accelerated oxidation of mixtures designed to imitate the composition of fuels, confirms the fact that oxidation has taken place, thereby, its initial properties have changed.

Motor gasolines with a content of ethanol have a lower oxidation stability, compared with those having a content of ether compounds. This is also confirmed by the fact that alcohols are oxidized more readily than ethers.

A diesel fuel with 7% (V/V) of FAME has a lower oxidation stability, compared with the diesel fuel containing less than 2% (V/V) of FAME; consequently, fatty acid methyl esters determine the stability of final products because of their different chemical structure (multiple bonds), among other things. The fact is confirmed by all oxidation stability analyses, including the Rancimat method, PetroOxy, and the weighing method to determine deposits formed by sample oxidation.

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References

[1] Ed.: Jan Surygała, Vademecum rafinera [*A refiner's guide*], Wydawnictwo Naukowo-Techniczne, Warsaw, 2006

[2] Baczewski K., Kałdoński T. Paliwa do silników o zapłonie samoczynnym [*Fuels for self-ignition engines*], Wydawnictwa Komunikacji i Łączności, 2004, 2008

[3] Baczewski K., Kałdoński T. Paliwa do silników o zapłonie iskrowym [*Fuels for spark-ignition engines*], Wydawnictwa Komunikacji i Łączności, 2005,

[4] Witkiewicz Z. Podstawy chromatografii [*Foundations of chromatography*], Wydawnictwo Naukowo-Techniczne, Warsaw

[5] Kęcki Z. Podstawy spektroskopii molekularnej [*Foundations of molecular spectroscopy*] (Pages 15-26, 56-80, 84-91, 143-155)

Chapter 9

Environmental Aspects in the Life Cycle of Liquid Biofuels with Biocomponents, Taking into Account the Storage Process

Izabela Samson-Bręk, Barbara Smerkowska and
Aleksandra Filip

Additional information is available at the end of the chapter

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1. Introduction

Environmental Life Cycle Assessment is a technique designed to assess the environmental risks associated with the product system or activity, either by identifying and quantifying the energy and materials used and the waste introduced into the environment, as well as the environmental impact of such materials, energy and waste. The assessment relates to the whole life cycle of the product or activity from the mining and mineral processing, product manufacturing process, distribution, use, re-use, maintenance, recycling up to the final disposal and transportation. LCA directs the study of environmental impact of the product system to the area of the ecosystem, human health and the resources used.

Results of studies on LCA were first presented by Harold Smith during the World Energy Conference in 1969. Interest in the usefulness of LCA was shown by Coca–Cola which commissioned an LCA of its beverage packaging products. On the other hand, theoretical foundations of LCA methodology were established as late as in 1990. Because of the growing interest in methods for LCA, works were commenced by the Society of Environmental Toxicology and Chemistry (SETAC) and ISO to harmonize and standardize the LCA methodology. The effort provided a definition of LCA and a number of standards (the series ISO EN 14040).

Even for same products, LCA can be performed at different levels of detail. Business purposes and executive decisions in management are well served by screening LCA (the shortest and simplest variant) or by simplified LCA; the latter is used, for instance, in decision-making processes concerning product development or in communication strategies. Detailed LCA is used for a full LCA and for comparative studies of products. It is based on detailed original data, obtained primarily by direct measurements, analyses, discussions, while also using latest literature data and statistical information after verification of their reliability. In R&D, the typical levels are the simplified LCA and detailed LCA.

In Poland, LCA remains to be a rather novel method in environmental management. It is used mainly for R&D purposes and is developed in R&D centers. In the light of the requirements regarding minimization of the adverse environmental impact of the fuel industry, imposed by the EU legislation, LCA seems a useful tool to fulfill such requirements. It may encompass the whole life cycle of a fuel, from the mining of raw materials, all the way through its manufacturing, use, and processes involved in the handing of those fuels which are below the applicable standards [2].

The use of LCA in the fuel industry enables the realization of and indicates relationships between human activities and their consequences for the environment. Moreover, it is an important source of information in making decisions intended to minimize the adverse impact of fuel production technology on the environment and to improve its condition. LCA enables identification of the processes of technology with the highest consumption of energy and highest emissions, as well as reduction of the costs of energy and raw materials, and efficient management of waste arising in technological processes.

This chapter presents Life Cycle Analysis as one of the methods enabling assessment of the environmental impact of the production of engine fuels and biofuels, especially their storage. A comparison of LCA and WtW analyses is made, and computer software is compared in the aspect of capabilities and justification for its use in assessing the environmental impact of the manufacturing and use of fuels and biofuels. The respective steps of LCA as well as the requirements and rules of assessment are discussed, taking into account their impact on the final result of LCA.

2. Relations between LCA and WTW

As pointed out earlier in this chapter, LCA enables the assessment of environmental risks over the whole life cycle of a product or process, starting from the mining and processing of raw materials, all the way through the manufacturing, distribution, use, re-use, maintenance, recycling, and final disposal and transportation. LCA directs the study of environmental impact of a product system to the area of the ecosystem, human health and the resources used [1].

Even for same products, life-cycle assessment may have different levels of detail, depending on the addressee of the results of the assessment and on its intended use. Essentially, three variants of LCA exist [3, 4]:

- *Screening LCA* – typically used within a single entity but also in circumstances requiring a fast analysis or low budget; screening LCA uses approximated secondary data from existing databases or statistical sources. a sensitivity analysis is recommended in this LCA variant in order to establish the actual impact of the results obtained on the key issues of the analysis;

- *Simplified LCA* – used in decision-making processes concerning product development and in communication strategies. Input data for the analysis may originate from existing databases but they should be supplemented with current literature data and with primary information obtained from suppliers, manufacturers or other product chain participants, or from direct discussions and measurements. A sensitivity analysis is indispensable to correct essential assumptions, if required;
- *Detailed LCA* – used for a full LCA of products and for comparative studies of products. It is based on detailed primary data, obtained by means of direct measurements, studies, analyses or discussions but also on latest literature data and statistical information after verification of their reliability. According to ISO EN 14040, an independent reviewer ought to be included in every step of the assessment process. It is necessary to describe all procedures, instances where data are incomplete, to carry out a thorough sensitivity analysis and justify choices.

A Well-to-Wheel analysis (from the fuel production to the energy that drives the vehicle) is a variant of LCA, dedicated to the assessment of the environmental impact of the life cycle of the production and use of transport fuels and vehicles. The WtW analysis is commonly used in assessing the consumption of energy or emissions of greenhouse gas (GHG) in the entire life cycle of a fuel, as well as for assessment of energy efficiency. The following variants of WtW are possible:

- „well-to-station" WtS (from fuel production to the filling station);
- „well-to-tank" WtT (from fuel production to the tank);
- „station-to-wheel" StW (from the filling station to the energy that drives the vehicle);
- „tank-to-wheel" TtW (from tank to the energy that drives the vehicle);
- „plug-to-wheel" PtW (from plug to the energy that drives the vehicle).

Relationships between LCA and WtW are shown in Figure 1.

The methodology of LCA and WtW according to ISO series 14040 [5, 6], involves four phases:

i. Goal and Scope definition;

ii. Life Cycle Inventory (LCI);

iii. Life Cycle Impact Assessment (LCIA);

iv. Life Cycle Interpretation.

i. Goal and Scope definition

The initial phase of LCA; decisions made in this phase determine the whole analysis. It is essential to precisely formulate the goal of LCA, justify its choice, specify the way the results of LCA are going to be used, and indicate the final user. The goal of LCA is defined in ISO EN 14040: the

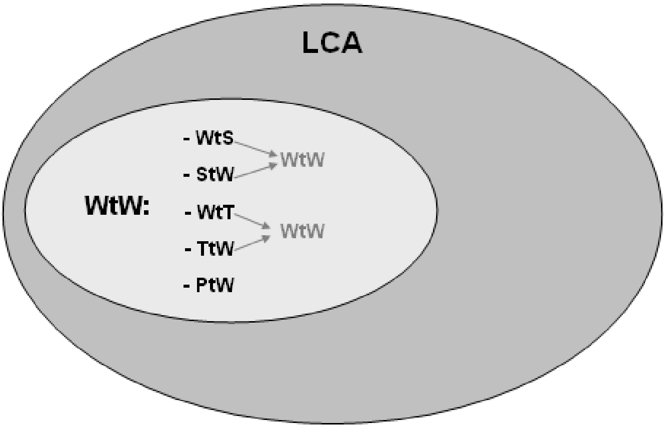

Figure 1. Correlation between LCA and WtW

goal ought clearly to indicate the intended use, the reasons for carrying out the LCA, and the potential user.

The scope of LCA will result from the established goal and ought to specify in detail the functions and the product system boundaries. The notion of system boundaries is understood as the contact area between the product system and the environment or other product systems. The system boundaries determine the framework of LCA. A function (or functional unit) is the quantitative effect of the product system, used as a reference unit in LCA. It is the task of the functional unit to provide a plane of reference for standardization of input and output data based on the mathematical approach [4].

As mentioned earlier in this chapter, WtW analyses are merely a variant of LCA, one applied in assessing the environmental impact of the production and use of fuels and vehicles. The scope of LCA is much broader and concerns freely selected products (Table 1).

The system boundaries for WtW comprise, fist of all, production and distribution of fuels, and emissions caused by their combustion in the vehicle's engine. In contrast, the system boundaries for LCA comprise processes, making up the entire life cycle of a product (Table 1).

Life cycle analysis dedicated to transportation comprises usually three phases: production, use, and recycling, as well as production and distribution of the appropriate fuel. Production of the infrastructure, both in LCA and in WtW analyses, is outside the system boundaries because of its lesser importance and lower impact on the outcome of the analysis.

ii. Life Cycle Inventory (LCI)

In the second phase, called Life Cycle Inventory (LCI), input/output data (concerning the inputs/outputs to/from the environment) are collected and analyzed. Such data are collected for every single unit process which is specified in a product system. The product system is understood as a set of materially and energetically connected unit processes which fulfill one or more specific functions. The unit process is the smallest part of the product system, for which data are collected when carrying out a life cycle analysis.

Specifications are prepared for the input/output quantities of materials and energy (side products, emissions, waste) to/from a given process. The LCI results are typically in the form of inventory tables, presenting quantitatively the consumption of natural raw materials, intermediate products, and generated waste. Important steps in data collecting include checking them for completeness and their validation.

In the case of WtW, the input data usually concern GHG emissions (mainly CO_2, N_2O and CH_4), consumption of energy, and energy efficiency (Table 1).

iii. Life Cycle Impact Assessment (LCIA)

The goal of the Life Cycle Impact Assessment (LCIA) is to establish the environmental relationships between all inputs/outputs covered by the LCA and to assess environmental impact.

During LCIA, the results of LCI are grouped into the appropriate categories of environmental impact based on the adopted environmental priorities taking into account local/regional conditions. Such classification consists in allocating the LCI results obtained by data inventorying into the respective categories of assessment of environmental impact [5]. A single result of LCI may be classified into more than one category of environmental impact. The way in which the single result is assigned into the appropriate category depends on the method of life cycle impact assessment and on the adopted goal of the analysis. The respective environmental impact categories are assigned weight coefficients, depending on their respective degrees of impact on the environment. This enables an assessment of the extent of impact of the various environmental loads forming the set of inputs/outputs in a given production system, and helps find out in which steps of the life cycle such impact takes place.

Owing to the use of available software, dedicated to LCA analysis, the classification process is automated. The LCI results are allocated into the appropriate categories of impact on the basis of lists of substances included in a software database and belonging with the calculation methods used.

LCIA comprises two groups of elements [5]:

- **compulsory elements**, including:
  - choice of category of the assessment of environmental impact, category indicators and characterization models;
  - allocation of LCI results to the respective categories of impact (classification);
  - calculation of the value of the category indicator (characterization).
- **optional elements**, which include:
  - standardization;

  - grouping;
  - weighting.

In the life cycle analyses of products based on the LCA methodology, it is possible to choose various categories of the assessment of environmental impact, depending on the goals and assumptions of the analysis and the analyzed product type. By contrast, impact categories in WtW concern, in the first place, emissions of GHG and air pollution.

iv. Life Cycle Impact Interpretation

Interpretation is the final phase of LCA. Its chief goal is to review and contemplate the results, make sure they are complete, coherent, and useful to the goal and scope. In this phase, final conclusions are formulated, limitations are explained and guidelines on how to reduce environmental impact are provided.

LCA enables management in manufacturing processes and their modification in the aspect of reduction and rationalization of the use of fuels and raw materials. That is why the Abiotic Depletion Potential (ADP) factor has been introduced in this analysis. ADP is based on the concentration of resources globally and on the rate of de-accumulation and is established for the mining of every type of fossil resources. Moreover, the collected information is processed to express the ratio of the quantity of resources used to the quantity that remains in nature, in order to achieve the required characterization factor.

Owing to the introduction of “ozone depletion” and “change of climate” factors, the LCA technique enables reduction of negative environmental impact for products, mainly by the exact analysis of carbon footprints and determination of the extent of reduction of carbon dioxide emission.

WtW	LCA
Goal: assessment of the environmental impact of the production and use of fuels and vehicles	**Goal:** assessment of the environmental impact of the production and use of any selected products and processes
Scope: production and distribution of fuels, emissions caused by fuel combustion in vehicle’s engine	**Scope:** all processes making up the whole life cycle of a product
Input data: emissions of GHG (mainly CO_2, N_2O in CH_4), consumption of energy, energy efficiency	**Input data:** all energy and material flows, waste and emissions (dust and gas) into water, air and soil
Impact categories: it is possible to choose between various categories of assessment of the environmental impact, depending on the goals and assumptions of analysis and on product type	**Impact categories:** impact categories mainly for emissions of GHG and air pollution
Standardization: no established methodology	**Standardization:** analyses according to ISO EN 14040, 14041, 14042, 14043

Table 1. Main differences between LCA and WtW analyses

3. Programs for environmental impact assessment

3.1. Programs for LCA analysis

There are more than 20 well known LCA software products in the international market. The first task faced by the potential user is to choose the proper tool for their particular problem. The choice has to be done based on a combination of the user's financial capabilities and functional requirements, on a case by case basis. The leading programs, as listed by subject, are the following:

- SimaPro 7 (and the recently released version SimaPro 8) by PRe Consultants, Netherlands;
- GaBi 4 (Ganzheitliche Bilanzierung – holistic balancing) by PE Europe GmbH and IBP University of Stuttgart;
- Umberto by the Institute for Environmental Informatics, Hamburg;
- GEMIS (Global Emission Model for Integrated Systems) by Oko-Institut. GEMIS is a LCA program and database for energy, material, and transport systems;
- IDEMAT by Delft University of Technology. IDEMAT is a tool for material selections in the design process;
- CMLCA (Chain Management by Life Cycle Assessment) by Centre of Environmental Science (CML) – Leiden University;
- Open LCA – open source software;
- Team by Pricewaterhouse Coopers Ecobilan Group;
- Wisard (Waste – Integrated Systems Assessment for Recovery and Disposal) by Pricewaterhourse Coopers Ecobilan Group;
- Greet by Argonne National Laboratory US;
- Solid Works by Solid Works Sustainability;
- SPOLD Data Exchange Software by The Society for Promotion of Life-cycle Assessment;
- BEES (Building for Environmental and Economic Sustainability) by the National Institute for Standards and Technology (NIST) Building and Fire Research Laboratory;
- The Environmental Impact Estimator – by the ATHENA Sustainable Materials Institute;
- LCAPIX by KM Limited;
- Windchill LCA by PTC.

Two commercial programs: SimaPro and GaBi, the universal LCA software for products and services, are the most widely used ones. Being professional LCA software tools, both SimaPro and GaBi use databases which are regularly updated by their respective publishers. What is important to mention-LCA software is only a kind of interface with which to upload and process data. The other essential part of the software are the inventory databases as well as impact assessment methods. One of the most extensive and well known databases is Ecoinvent, with its latest 3.0 version [http://www.ecoinvent.org/database]. Containing more than 4 000 inventories in different categories (e.g., energy, biofuels and biomaterials, transport, chemical products, waste treatment, building materials, agriculture and other ones) is one of the most comprehensive international LCI (Life Cycle Inventory) databases. The main data validity area is Western Europe and Switzerland, though it contains data also from other regions of the world. The database is included e.g., in SimaPro, GaBi, Umberto or IKE programs, and is continuously updated.

SimaPro, invented by the Dutch company PreConsultants, is a robust and thoroughly tested LCA tool, based on reliable, scientific data. The latest version of SimaPro (number 8) contains additionally water footprinting assessment and a much larger Ecoinvent 3.0 database. SimaPro contains multiple impact assessment methods as well as several inventory databases and approx. 10 000 processes available. The added value of this tool is the editing capability and expanding databases with own data without limitation and also adjusting existing and creating new impact assessment methods. This makes it a flexible tool, suitable for complex life cycles comparison and environmental performance analyzes. SimaPro offers a full review of the potential impact of the product. It is able to determine thr key environmental performance indicators (KePI) used for determining and assessment of the execution of adopted objectives. The KePI approach is fundamental in EU policy, as key indicators are easily understood and managed. Being a commonly used software, it enables analytical results to be shared with other researchers or companies throughout the world.

GaBi is a system based on three simple concepts: plans, processes, flows. The plan represents the analyzed life cycle; the processes apply to the plan, representing the actual steps occurring in real life; the flows connect the processes and represent the material and energy balance in the system. As GaBi can be integrated with some databases, it is possible to use predefined data for creating one's own models. The tool enables visual analysis: where the biggest impacts occur, and what are the largest opportunities for improvements in the processes. It is also possible to compare how the system's behavior is affected by changes implemented in flows – alternative models show how the changes affect the environmental, economic and social aspects in the system. Gabi has the option of easily creating the reports, e.g., concerning "if scenarios" as well as Environmental Product Declaration and ISO compliance reports. GaBi databases contain large internally consistent LCI datasets available (over 7 200 datasets). The database covers all essential fields of energy and material production as well as transportation, its contents can be extended in response to any client-specific demand. It can be combined with the Ecoinvent database as well. GaBi can be used in designing products with more environmentally friendly components (with lower GHG emissions and a reduced water footprint and waste use).

With SimaPro and GaBi it is possible to create complex models and use the software in highly complicated and expert analyses. More advanced analyses within SimaPro and GaBi, such as variation of parameters (comparing and modeling different scenarios), sensitivity analysis and

Monte Carlo simulations with uncertainty analysis giving the level of standard deviations, are possible.

Beside these two most popular tools, there are also other software products. Some of them are open source software products, such as Open LCA. It is a modular software for life cycle analysis and sustainability assessments. But the important thing when considering the use of free software is that no process data are included. Therefore, it is necessary to use external databases which is an extra cost [7].

The use of various software capabilities also depends on the region. For example, Greet, published by the Argonne National Laboratory, is a popular software product in the USA. It is sponsored by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) and, therefore, free of charge. The software is used for GHG, regulated emissions, and energy use in transportation modeling. It is dedicated to transport issues, enabling the assessment of energy and emission impacts of advanced vehicle technologies and new transportation fuels [8]. This kind of software is convenient for WtW analyses.

Some LCA tools are more specific LCA software programs; one of them is EASEWASTE (Environmental Assessment of Solid Waste Systems and Technologies) focused on waste management system analyses. It is an LCA tool, developed at the Technical University of Denmark, modeling “resource use and recovery as well as environmental emissions associated with waste management in a life-cycle context. The model is set up for municipal waste but can also be used for other waste types” [9]. Recently, its successive form has been released under the name EASETECH – Environmental Assessment System for Environmental Technologies.

The general rule for choosing the proper tool for LCA modeling is the goal and scope of analysis, the target group of the results of analysis, and financial capabilities. Moreover, it is based on individual choice of the most intuitive software interface, the databases contents and possibility of their expanding and personalization. Using a model always involves simplification of reality, which causes distortion. They key requirement for any modeling tool is to minimize such distortions. **

3.2. BIOGRACE as a tool for environmental analysis of biofuels

BIOGRACE (version 4) is one of the most useful tools, dedicated to the calculation of greenhouse gas emissions which accompany the manufacturing of biofuels, available in Europe at present. The calculator has been developed by an international consortium as part of the project named BIOGRACE “”Harmonized Calculations of Biofuel Greenhouse Gas Emissions” [10]. The calculator fully complies with the methodology for assessing greenhouse gas emissions caused by the production and use of transport fuels, biofuels, and biofluids, referred to in Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources, Annex V, Part C (RED). It was meant to be a scientific tool facilitating the implementation of those provisions of the Directive, concerning sustainable production of biofuels [11].

The BIOGRACE calculator is a tool which, at present, allows only the calculation of the emissions of greenhouse gases accompanying the production of 1st generation biofuels. As regards the biofuels obtained from lignocellulose raw materials and waste, the calculator can be used as well, although a number of assumptions are required, potentially making the final result too uncertain. Moreover, it is necessary to introduce own input data in the analysis.

According to the methodology referred to in Annex V, the total greenhouse gas emission in the life cycle of fuels and biofuels is made up of the following processes [11]:

- total emissions due to the use of fuel;
- emission due to the mining/cultivation of raw materials;
- annual emission caused by variations in the quantity of carbon stock due to changes in land use;
- emission due to processes of technology;
- emission due to transportation and distribution;
- the extent of reduction of emissions, caused by the accumulation of carbon stock in soils due to improvements in agricultural economy;
- reduction of emissions due to carbon dioxide capture and storage in deep geological structures;
- reduction of emissions due to carbon dioxide capture and substitution;
- reduction of emissions due to an increased production of electrical energy by co-generation.

According to the methodology recommended by the European Commission, emissions caused by the production of machinery and equipment are not taken into account in RED. The production of machinery and infrastructure on the total result of the life cycle impact assessment usually has a minimum effect [11].

The BIOGRACE calculator enables the assessment of agricultural emissions of GHG as well as emissions and reductions of emission in the entire life cycle of biofuels per 1 MJ of manufactured biofuel. The following steps are included in calculating GHG in the respective biofuel production pathways: cultivation of raw material, process of technology, transportation and distribution. Emissions are assessed for three principal greenhouse gases: CO_2, CH_4, and N_2O. It also is possible to show aggregate values of emissions, as expressed in carbon dioxide equivalent. When interpreting the results of analysis, it should be remembered that BIOGRACE does not take into account all types of emissions, or types of impact other than emissions of GHG (such as acidification, eutrophication, emission of solids etc.).

BIOGRACE enables the calculation of emissions of GHG which accompany the cultivation of 8 plants which are substrates for making biofuels, and 22 pathways for production of biofuels (Table 2) [11].

Substrate	Biofuel production pathway
1. wheat	1. ethanol from sugar beet
2. sugar beet	2. ethanol from wheat (not specified technological fuel)
3. corn	3. ethanol from wheat (brown coal as a process fuel in heat-and-power plants)
4. rape	4. ethanol from wheat (natural gas as a process fuel in conventional boilers)
5. sunflower	5. ethanol from wheat (natural gas as a process fuel in heat-and-power plants)
6. palm oil	6. ethanol from wheat (straw as a process fuel in heat-and-power plants)
7. soy	7. ethanol from corn made in the EC (natural gas as a process fuel in heat-and-power plants)
8. sugar cane	8. ethanol from sugar cane
	9. biodiesel from rapeseed
	10. biodiesel from sunflower
	11. biodiesel from soy
	12. biodiesel from palm oil (not specified technology)
	13. biodiesel from palm oil (technology with methane capture in the oil mill)
	14. biodiesel from spent vegetable or animal oils
	15. hydrorefined vegetable oil (HVO) from rapeseed
	16. hydrorefined vegetable oil (HVO) from sunflower
	17. hydrorefined vegetable oil (HVO) from palm oil (not specified technology)
	18. hydrorefined vegetable oil (HVO) from palm oil (technology with methane capture in the oil mill)
	19. pure vegetable oil from rapeseed
	20. biogas from organic municipal waste as compressed natural gas
	21. biogas from wet manure as compressed natural gas
	22. biogas from dry manure as compressed natural gas

Table 2. Substrates and biofuel production pathways included in the BIOGRACE calculation tool

The BIOGRACE methodology for assessing greenhouse gas emissions in the step of cultivation of raw materials comprises the following [11]:

- production of seed/seedling material;
- fertilization with nitrogen (N);
- fertilization with phosphorus (P_2O_5);
- fertilization with potassium (K_2O);
- fertilization with calcium (CaO);
- plant protection agents;
- consumption of fuels when carrying out all the necessary field works;
- field emissions of N_2O;

- annual emissions caused by changes in the quantity of carbon stock due to changes in land use;
- emissions caused by the soil accumulation of carbon stock due to improvements in agricultural economy.

Furthermore, the BIOGRACE calculator enables the use of standard values of emissions, specified in the Directive Annex V, as well as the introduction of values provided by other sources, such as studies or own estimates. Emissions which accompany the production of nitrogen-based fertilizers are an example of the application of non-standard values for calculations. BIOGRACE assumes that a standard value of emission for conditions prevailing in Europe is 5880.6 g $CO_{2_{eq}}$/kg N. However, the works carried out by IUNG State Research Institute (Institute of Soil Science and Plant Cultivation) in Puławy, Poland, indicate that in Poland, emission accompanying the production of nitrogen-based fertilizers is much lower: just 3414.2 g $CO_{2_{eq}}$/kg N [12]. Since the use of a value which is prevailing in Poland will result in a lower total emission caused by the production of raw material and of the biofuel itlsef, such lower emission value is more preferable in the calculations [13].

4. The quality of results and the methodological assumptions

4.1. Goal, scope and system boundaries

LCA analysis approach has always to be related to goal and scope as well as the analysis target group. The intended application has to be defined. Typical applications can be as follows [16]:

- Comparing products having the same function (usually used in marketing or regulation);
- Identifying environmental hot-spots in product life cycle;
- Identifying possibilities of improvement of product or its production process;
- Communication to customers.

A product system is a collection of materially and energetically connected unit processes which perform one or more defined functions and reflect the life cycle of a product [5]. A product system in LCA is typically understood as its production line. Established on this basis are system boundaries, defined as an “interface between a product system and the environment or other product system”. System boundaries determine the unit processes which are included in the LCA analysis. The choice of unit processes ought to result from the goal, as established previously, while criteria of choice of the adopted system boundaries ought to be clearly and precisely established. It is important to make a contribution analysis and establish whether all highest-load processes have been taken into account. Typically, about 10 processes are of significance to the results of an analysis. Decisions on which processes should be included in the analysis or which ones are not important enough can be taken using the cut-off method for processes of which the contribution, for instance, in the consumption of energy or materials does not exceed a certain value (percentage or quantity). As a matter of fact, subjective choices are inherent in this type of analysis, therefore, one ought to check whether the results of analysis and the conclusions depend on the choices made. One of the applicable methods is to make calculations after modifying the assumptions (sensitivity analysis). In a sensitivity analysis, it is possible, for instance, to change a data source (process or database), compare results for different values of parameters (such as distance, type of transportation, waste recycling method), allocation (mass, economic) or absence of allocation, assumption, and the impact assessment method. If the results of analysis have changed after such modification (for instance, Process A is better than Process B or vice versa), then the fact ought to be commented on and explained.

Product life cycles as usually complex. It is then essential to maintain balance between complexity (high costs) and simplification (lower costs, possibility of providing the results in an easily understandable way). Depending on the goal of analysis, the scope can be reduced, focusing on e.g., only energy or mass or CO_2 emission issues. Another potential solution is to use the KePI (Key environmental Performance Indicators) approach, based on identification of key parameters determining major impact.

For a given LCA analysis, the geographic boundaries depend on the assumptions of a specific analysis/project. They can be established at the local, national, regional or global level. If the geographic region of the analysis covers a given country, it is permissible in certain instances (e.g., data concerning means of transport) to use average data, for instance, for the region of Europe. However, it is always necessary to carefully examine the possibilities to use average data, for instance, in the case of production of electrical energy, differences in division by country are essential (energy mix) and may lead to understated or overstated results.

As regards areas of technology, data concerning innovative processes (such as evaluation of new processes of technology) ought to originate from actual research works dedicated to a given process. In the case of non-innovative, previously used processes it is permissible to use data from literature sources.

4.2. Input data

According to ISO EN 14040, in publicly available comparative analyses, it is necessary to establish data quality requirements. The scope of uncertainty of the input data will be reflected both in the results of analysis and in the method for their interpretation.

The quality of input data for an analysis is established on the basis of such parameters as: time interval, geographic region, area of technology, precision, completeness, representativeness, consistency, reproducibility, data source, and uncertainty. The parameters concerning data quality, described in ISO EN 14040, are characterized below:

- time interval of data: actual data ought to originate during the project execution; departures by several years are permissible for literature data if it is impossible to acquire real-time data;

- geographical coverage: data ought to originate from studies carried out in the territory of a given country; in certain cases (such as data concerning means of transport) averaged data for the region of Europe are permissible;
- area of technology: data concerning processes of technology ought to originate from studies conducted or from operating facilities; for processes and technology for which it is not possible to acquire real-time data, it is permissible to use literature data;
- precision: data ought to be characterized by as high a precision as possible;
- completeness: data ought to be as complete and as accurate as possible;
- representativeness: data ought be representative in as much as possible;
- consistency: qualitative assessment of how uniformly the study methodology is applied to the various components of the analysis;
- reproducibility: data ought to originate from suitably documented studies to enable their reproduction and verification, if required;
- data source: data ought to originate from own studies or actual data, obtained in an operating facility, in the first place; from the point of view of the results of analysis, such data have the highest value; it is permissible under certain circumstances to use literature data or data from available databases, including those originating from the SimaPro software, which is used for LCA analyses;
- uncertainty: data ought to be characterized by the least possible uncertainty; moreover, any uncertainty concerning the data ought to be clearly formulated.

In LCA analyses carried out for scientific purposes, it is important to establish the scope of uncertainty of input data and, on this basis, to carry out the Monte Carlo uncertainty analysis.

4.3. The choice of LCA method — Impact categories

In choosing impact categories and LCA method, one ought to keep in mind the goal and scope of analysis in the first place. When comparing the environmental impacts of the life cycles of biofuels and fossil fuels, they ought to be considered in similar impact categories (e.g., global warming). Moreover, system-specific categories ought to be taken into account: in the case of biofuel production, it will be, e.g., the use of land for cultivation of energy plants. A typical set of categories in which the environmental impact of a product system is calculated (method: Ecoindicator 99 from SimaPro) is shown below:

- Carcinogens;
- Respiratory organics;
- Respiratory inorganics;
- Climate change;
- Radiation;

- Ozone layer;
- Ecotoxicity;
- Acidification/Eutrophication;
- Minerals
- Fossil fuels;
- Land use.

Because SimaPro is a leading tool for LCA analyses globally, the criteria of choice of the most suitable method for the analysis have been characterized on the basis of SimPro. The tool offers a dozen or so methods for life cycle impact assessment and the differences between them are significant. Therefore, when choosing the suitable method, it is necessary to clearly state the priorities for the specific LCA analysis. To make it easier to choose the life cycle impact assessment method, SimaPro has the ″Method selector″ tool. It helps understand the major differences between the various life cycle impact assessment methods and select the most suitable method, depending on the assumed goal and scope of analysis of LCA. Selection of the suitable method using the tool include the following aspects: result presentation as single score (numerical value), weighting set, time perspective, geographic coverage, accuracy of the life cycle impact assessment method and the impact categories considered in the method.

Some methods enable presentation of results in the form of single scores. On the other hand, according to ISO EN 14040, this way of presentation of the results, as results of comparative analyses which are going to be made public, should be avoided because they are too subjective, and simplifications are significant. In public, scientific papers, mainly midpoint methods are used as they are more scientifically certain. In that case, the life cycle impact assessment method is preferable, being one that enables presentation of results as indicators which are characterized separately for every impact category. Also weighting (that is, the allocation of weight to the respective impact categories) is not permissible in life cycle analyses which are presented in public [6]. In such cases, the way it was carried out has no effect on the method selection. Weighting or endpoints can be shown in business to business analyses, but not in public ones. When comparing some results and methods – it is not methodologically correct to compare endpoint and midpoint methods, as the results are shown in different ways, also of high importance is comparing two products only when the system boundaries and all the life cycle stages are the same.

When selecting the suitable life cycle impact assessment method, it is necessary to decide whether the selected method is going to cover a short-or a long-term horizon. In long-term methods, more emphasis is placed on those substances which persist in the environment for many years (like heavy metals). Since human activities have a long-term environmental impact by nature, the approach often seems to be the most appropriate one.

In selecting the suitable method, its complexity ought to be considered as well: the simpler the method, the more general results are provided. Recently developed methods, based on latest scientific accomplishments, are much more complex and require more accurate data; on the other hand, the results they provide are much more reliable and precise.

Another important aspect in selecting the right life cycle impact assessment method is the method's geographic coverage. Some methods were intended for specific countries only and they are applicable to their specific conditions, while other ones are more general [17]. In analyses of technology used in Europe, it is extremely important to consider methods which are suitable in conditions which prevail in Europe.

It is recommended to carry out LCA analyses using several methods of life cycle impact assessment; this enables verification of the results obtained by a given method and more objectivity. Such approach enables a sensitivity analysis as well as adjustment of any analytical error that may occur. Checking the analysis by doing it with another method. It is to remember that it is a methodological error to compare midpoint and endpoint methods.

The most popular methods within SimaPro include: Eco-Indicator 99 and Impact 2002+. Special emphasis in the two methods is put on substances which persists in the environment for many years, therefore, a long-term horizon is taken into account. Eco-Indicator is intended for damage assessment and is available in three variants: egalitarian (E), individual (I) and hierarchic (H). The egalitarian variant covers a very long-term horizon (even as long as 200 years), while the individual variant applies to a short one (of about 20 years). The hierarchic variant covers a balanced time horizon, while taking into account the long-and short-term perspectives. Therefore, impact assessment is frequently carried out according to the hierarchic method. Established in the method are three endpoints: human health, quality of the ecosystem, and depletion of resources. The following impact categories are deemed to be destructive to human health: climate changes, ozone depletion, carcinogens, destructive respiratory substances, and radiation. Damage to human health is expressed in DALY (Disability Adjusted Life Years) [18], the unit is used by WHO and the World Bank for health-related statistics. According to the method, the following impact categories are deemed to cause damage to the quality of the ecosystem: acidification, eutrophication, land use, and ecotoxicity. Generally, such damage is expressed as a diversity of species. In the acidification, eutrophication, and land use categories, the size of damage is expressed as the fraction of species which are exposed to extinction (*Potentially Disappeared Fraction* PDF) [3]. Damage which causes depletion of resources is expressed, in MJ, as an extra amount of energy which will be required in future for mining mineral and solid fuels.

The method Impact 2002+combines the midpoint and endpoint approaches, allocating the results to fourteen categories which have an impact on four areas of damage (damage categories): human health, quality of the ecosystem, climate changes, and resources (Figure 2). In that method, climate changes are regarded as a separate final category.

CML2000 is an example of the midpoint method, limited only to impact categories, without using damage categories. It is based on the following impact categories: ozone depletion, human toxicity, three kinds of ecotoxicity (affecting inland waters, sea water, and soil), photochemical oxidation, global warming, acidification, eutrophication, and depletion of abiotic resources (minerals and fossil fuels). Land use is not taken into account in that method [20].

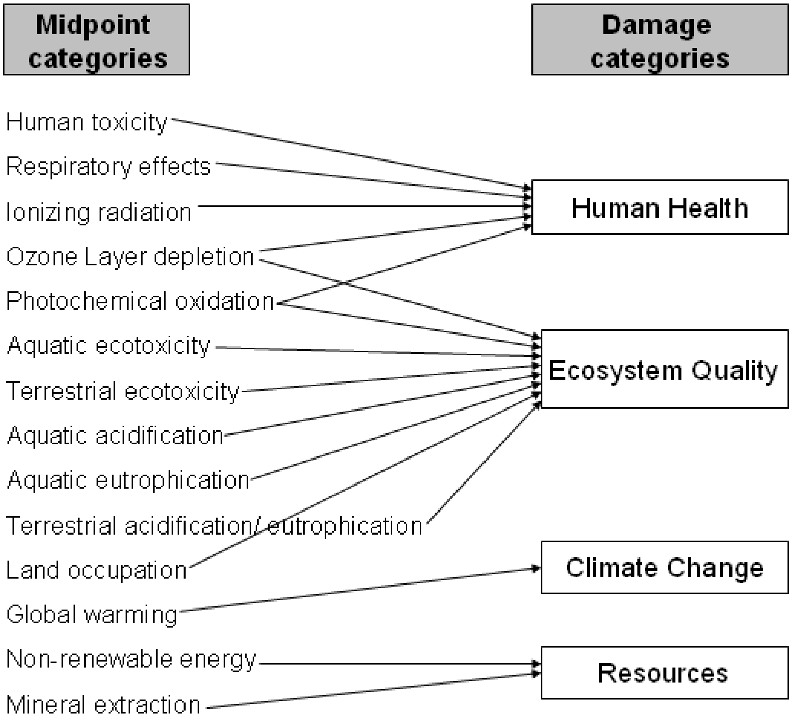

Figure 2. General diagram of the method Impact 2002+[19]

The methods referred to above are merely examples, showing the diversity and flexibility of software and methods for LCA analyses. The proper methodology always depends on the intended application, scope of analysis, the reasons for carrying out the study, as well as the intended audience [16].

5. Life cycle of engine fuels and biofuels

5.1. Steps of the life cycle of engine fuels and biofuels

Commonly used liquid fuels with biocomponents include the following [14]:

1. Fuels with the normative content of biocomponents:
   - a. gasoline with up to 5%(V/V) ethanol (PN-EN 228);
   - b. diesel fuel with up to 7%(V/V) of FAME (PN-EN 590);
   - c. 100%(V/V) FAME as a pure fuel (PN-EN 14214+A1).
2. Fuels with the non-normative content of biocomponents:

- **a.** gasoline with from 70 to 85%(V/V) of ethanol;
- **b.** diesel fuel with 20%(V/V) of FAME;

for use in vehicles having suitably adapted engines.

Essentially, five steps of life cycle exist both for the conventional fuels and biofuels: (Fig. 3):

1. Material acquisition (by mining or by cultivation of energy plants).
2. Transport.
3. Fuel production process.
4. Transport and distribution.
5. Use.

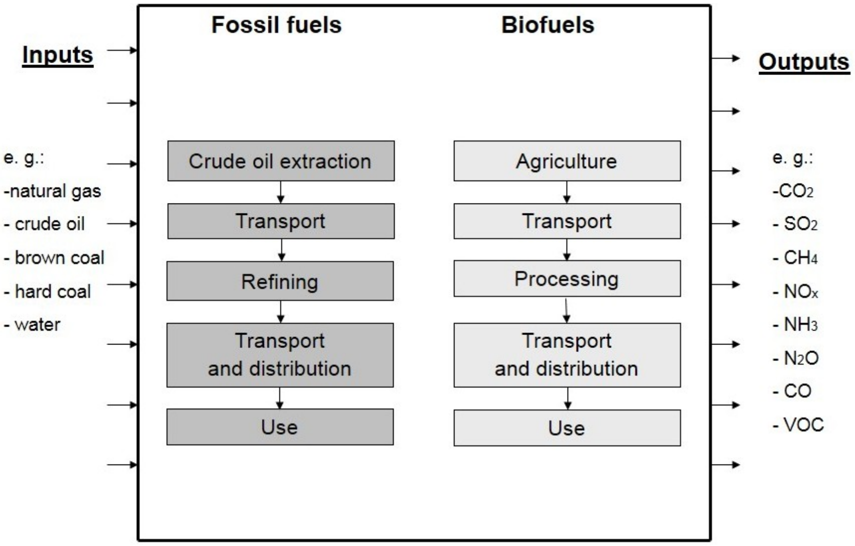

Figure 3. The process tree for petroleum-based fuels and biocomponents

Essential differences exist between the life cycle of fuels and biofuels at the steps of material acquisition and fuel production.

For the conventional fuels (gasoline, diesel fuel) the substrate they are made from is a fossil energy carrier in the form of crude oil, extracted from oil fields. Conventional extraction methods include drilling onshore or offshore wells; strip mining, in situ and other techniques are used, depending on the type of field or deposit.

By contrast, biofuels are typically made from biomass originating from dedicated plantations or from waste. 1st generation biodiesel is made from edible oil plants, such as soy, rape, sunflower; bioethanol is made from such plants as sugar cane, sugar beets, rye, corn, potatoes etc. [22] Biomass plantations often require the use of fertilizers and plant protection agents, involve high emissions and energy consumption (especially production of mineral nitrogen fertilizers). Additional emissions at this step involve combustion of fuel (mainly diesel fuel) during the field works connected with starting a plantation, its maintenance, harvesting, and liquidation [13]. Both factors may have a considerable impact on the end results of LCA analysis.

Transport takes place between the essential processes of the life cycle of fuels and biofuels. The transport of crude oil to refineries is typically long-term and uses pipelines (land transport) and tankers (marine transport). Vegetable raw materials for the production of biofuels are usually transported locally although, owing to the availability and prices of raw materials or intermediates, their transport can also be international (long-distance) (Fig. 4). Such basic differences in the types of transport means and distances must obligatorily be taken into account in LCA analyses.

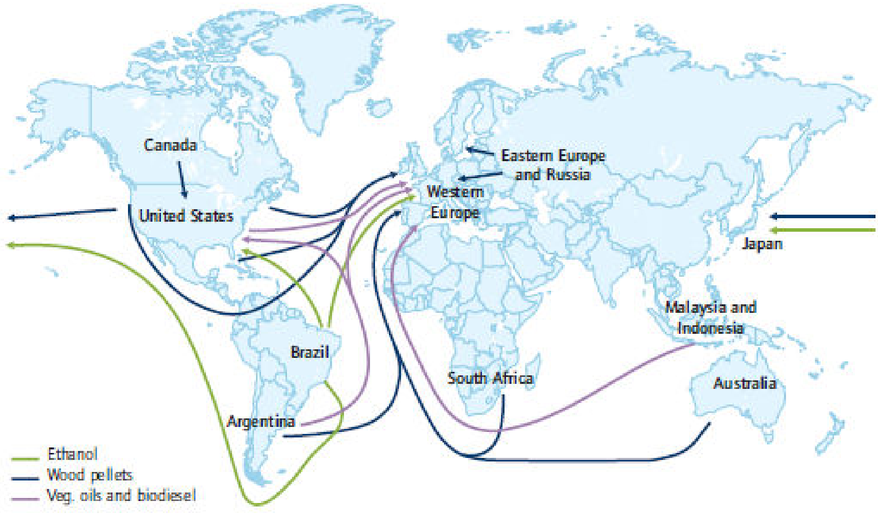

Figure 4. World biomass shipping today [21]

Important differences exist also between the processing of conventional fuels and biofuels.

Refinery processing is carried out by fractionation of raw material in the process of atmospheric distillation and vacuum distillation (for high-boiling components). In the subsequent steps, the fractions are converted (thermal cracking, catalytic cracking, hydrocracking), improved (catalytic reforming, isomerization, alkylation), refined (hydrorefining) and sent downstream to obtain specific compositions. For the purposes of LCA analyses, it is important to take into account allocations, because of the huge diversity of crude oil refining products.

For 1st generation bioethanol, the main steps of the production process include: preparation of raw material, mashing, fermentation, rectification, and dewatering (by azeotropic distillation, extraction distillation, or pervaporation), which is one of the most expensive and energy-consuming processes of the production of anhydrous ethanol intended for use as a fuel.

The production of 1st generation biodiesel involves the following steps: oil pressing or extraction (or the use of waste fats or oils), transesterification using methanol (or ethanol).

The two above-mentioned types of biofuels are the most popular ones globally and their manufacturing technologies are well known and understood. In the case of the consequent generations of biofuels, manufacturing technology is highly diversified, depending on the raw materials used, and these are highly various, including: non-edible biomass (energy plants, organic waste substances, or nonedible oilseeds). This group of raw materials comprises the following [22]:

- bioethanol, biobutanol and mixtures of higher alcohols, as well as their derivatives obtained by advanced hydrolysis and fermentation of lignocellulose based on biomass (other than raw materials for use as food);
- synthetic biofuels – obtained from biomass processing by gasification followed by a suitable synthesis technique to obtain liquid components for fuels in BtL (Biomass-to-Liquid) processes and those resulting from the processing of biodegradable industrial and municipal waste in WtL (Waste-to-Liquid) processes;
- fuels for spontaneous-ignition engines – obtained by the processing of lignocellulose from biomass in Fischer-Tropsch processes, including synthetic biodiesel based on a composition comprising lignocellulose products;
- biomethanol – obtained in processes involving the transformation of lignocellulose, including Fischer-Tropsch synthesis, also using waste carbon dioxide;
- biodimethylether (bio-DME) obtained by the thermochemical processing of biomass, such as bioethanol, biogas, syngas originating from biomass transformation;
- biodiesel as a biofuel or a component of fuels for spontaneous-ignition engines – obtained by refining with hydrogen (hydrogenation) of vegetable oils and animal fats;
- biodimethylfurane (bioDMF) – originating from the processing of sugars, including cellulose, in thermo-and biochemical processes;
- biogas – as a synthetically obtained natural gas-biomethane (SNG), obtained by gasification of lignocellulose, suitable synthesis, as well as by purification of biogas from agricultural sources, landfills, and effluents;
- biohydrogen – obtained by gasification of lignocellulose followed by the synthesis of gasification products, or in biochemical processes.

When carrying out a life cycle assessment for the production technology of the 2nd generation biofuels mentioned above, one should keep in mind that the technology may either be experimental (only bench or semi-technical scale) or it may be used in a limited number of commercial plants. This affects the quality, level of uncertainty, and possibility of input data verification, which ought to be taken into account during interpretation of the results of such analysis.

5.2. The role of storage in the life cycle of engine fuels and biofuels

From the point of view of the market, storage has an important role in the operations and functioning of enterprises. Among other things, storage helps avoid the negative impact of fluctuations in production/consumption, disturbances in production and supplies. Storage of liquid fuels is necessary for the accumulation of strategic reserves to guarantee national energy security. The strategic reserves are expected to guarantee the functioning of economy for 90 days. Long-term storage is essential nowadays for being able to avoid temporary energy crisis situations, resulting from disturbances in crude oil and gas supplies.

Industrial practice of storage of fuels has developed into long-or short-term storage. Long-term storage is a storage at the limit of manufacturer's guarantee and is called a maximum permissible period of storage. Storage on an as-needed basis is called short-term storage. Liquid fuels with a content of biocomponents may be stored for a short term only [15]:

- gasoline with ethanol – 6 months max.;
- diesel fuel with esters – 3 months max;
- FAME – 1 month max.

A life cycle assessment analysis of petroleum-based fuels enables locating those spots in the production chain of gasoline of diesel fuel which have the highest environmental impact. Besides, LCA helps find out the extent to which emissions are reduced by the use of biocomponents, by comparing the environmental impacts, caused in their entire life cycle. Moreover, it is possible to establish what kinds of environmental risks are caused by the acquisition of raw materials, their transport, production, and storage of transport fuels, compared with the environmental impact arising during the life cycle of petroleum-based fuels.

The life cycle of petroleum-based fuels or biofuels is extended to encompass the processes during which energy from nonrenewable sources is used and which generate emissions to all elements of the ecosystem in every step of their life cycle contemplated in the assessment.

A process tree for petroleum-based fuels and biocomponents is shown in Fig. 3 so as to illustrate the consequence of the storage of liquid fuels with biocomponents in the environmental aspect.

Storage is not included in the major process group. Each of the essential processes of the life cycle of petroleum-based and biofuels shown above comprises intermediate processes as well as auxiliary and side processes etc. Storage processes take place in every step of the life cycle of liquid fuels:

- storage of pre-refined crude oil (*Crude oil extraction*) (Fig. 5);
- storage of crude oil during transport by sea in tankers (*Transport*) (Fig. 6);

- storage before processing – crude oil (*Refining*) (Fig. 7);
- storage after processing – basic liquid fuels (*Refining*) (Fig. 7);
- storage after blending of base fuels with improvers (*Refining, Distribution*) (Fig. 7);
- storage after blending of base fuels with biocomponents (*Refining, Distribution*) (Fig. 8).

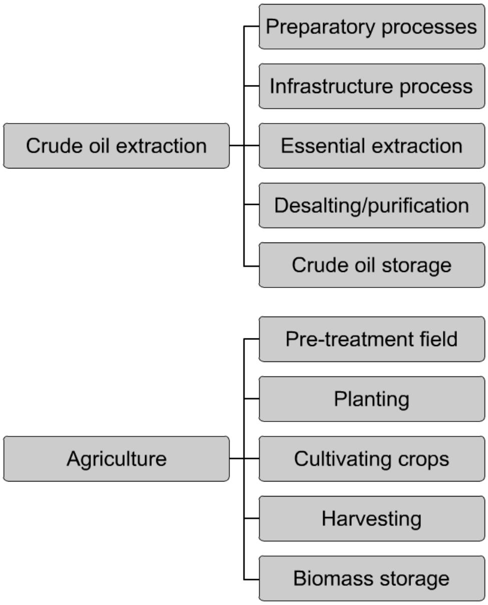

Figure 5. Storage in pre-refining of crude oil and biomass

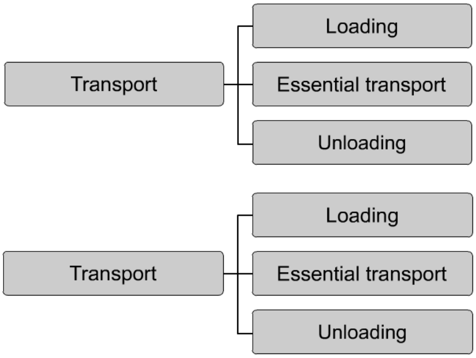

Figure 6. Storage in transport of crude oil and biomass

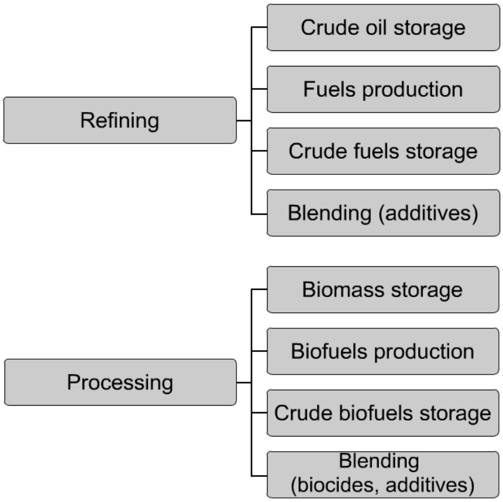

Figure 7. Storage in processing of crude oil/petroleum-based fuels and biomass/biofuels

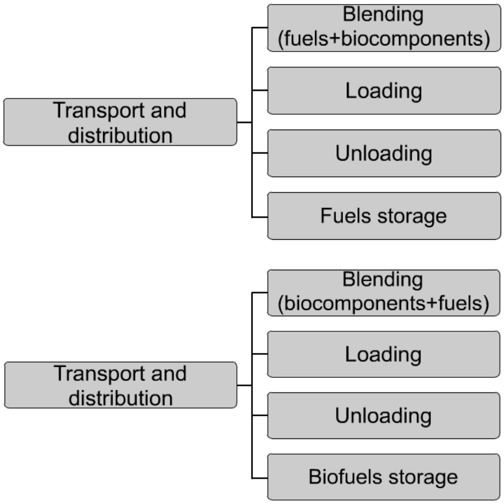

Figure 8. Storage in transport of petroleum-based fuels and biofuels

The importance of storage processes in the context of environmental protection depends on the potential pollution and on the physico-chemical properties of the products stored. Differences exist and should be noted, between hazard (natural chemical properties) and risk (probability that hazardous properties exist and will be released from stored products, causing damage to humans and the environment). Various products or substances create various risks due to their properties, such as low flash point, flammability, toxic effect on human health and on the environment.

In storage facilities, two operating conditions are identified in which emissions may be released when carrying out operations: normal operating conditions (including the handling of products to/from storage facility, and cleaning) and accidents or major failures.

Such emissions may occur in the following forms:

1. Emissions to the air – in normal operating conditions, significant emissions into the air in connection with storage of liquid fuels in industrial practice include the following groups:
   - those which occur in the process of filling/emptying the tanks;
   - those which occur during the tank breathing process, i.e., emissions caused by temperature increase due to vapor expansion, which is followed by emission;
   - temporary emissions from collar gaskets, connections and pumps;
   - those which occur during sampling procedures;
   - those which occur in effect of cleaning operations.

2. Discharge to water (direct/indirect via waste water system and treatment plants) – in normal operating conditions, significant emissions into water in connection with the storage of liquid fuels in industrial practice include the following groups:
   - effluent from chemical storage, tanks, leakage water, etc.
   - discharge from the waste water system;
   - washing effluents;
   - cleaning effluents.

3. Noise – in storage facilities essentially only in reloading processes:
   - emissions from pumping plants;
   - traffic of vehicles (receiver tanks) and vent valves.

4. Waste in the following forms:
   - residues or products below standard quality;
   - waste material from the vent cleaning systems;
   - spent containers;
   - deposits;
   - cleaning agents, where applicable.

Other than in normal operating conditions, emissions occur as a result of accidents and major failures of equipment. Emissions caused by accidents and failures typically take place over a short period of time and are much more intense than those taking place in normal operating conditions.

Storage processes also comprise transport and handling systems. Liquid fuels are transported by means of pipelines which are connected to the storage tank, but also by means of flexible hoses or marine loading arms to be attached to tanker trucks, railway tankers or tank ships. A liquid fuel handling system includes the fuel transfer by means of pipes to/from storage tanks, for instance, using pumps.

In the research practice, analyses assessing environmental aspects cover five major processes. Storage of fuels, even though it has an important role in the market, is not taken into account in LCA as a major process. Because of its low energy consumption and emission levels (emissions occur mainly by fuel evaporation from the storage tanks in the process of storage and tanker filling), storage is a mid-way process of low importance. Therefore, in most life cycle analyses, storage processes are either excluded from assessment or their accompanying emissions are included in the major processes.

6. Conclusion

A growing social awareness and more stringent legal requirements in environmental protection issues lead to arousing interest in activities and technologies with a potential to reduce the adverse environmental impact of man. In selecting the most suitable ones, it is convenient to use LCA – a comprehensive life cycle analysis, enabling the full assessment of the environmental impact of the entire manufacturing process, starting from the acquisition of raw materials and ending with the final step of disposal of waste arising in the process of product use. LCA offers numerous environmental and economic benefits. The method is potentially helpful in making investment decisions, enabling reduction of the consumption of materials and energy, as well as disposal of any byproducts and waste that arise.

Discussed in this chapter is the methodology for life cycle assessment (LCA), as a method enabling an assessment of the environmental impact of the production of engine fuels and biofuels, especially the storage process. A comparison between the LCA technique vs. WtW analysis, and of various types of computer software is made in the aspect of the capabilities and justification for their use in assessing the environmental impact of the manufacturing and use of fuels and biofuels. The respective steps of LCA and the requirements and rules of assessment are discussed, taking into account their impact on the final LCA result. Which specific method or software is selected depends on the goal and scope of analysis, end user, and the available input data. Moreover, it is necessary to take into account the various environmental impact categories which are specific for the given product system.

There are a number of tools in the market which facilitate the assessment of the environmental impact of products, although it is up to the user to choose the suitable tool for a particular problem. The most popular and most frequently selected tools include SimaPro (Dutch) and Gabi (German). Moreover, the most useful tool, dedicated to the calculation of greenhouse gas emissions accompanying the production of biofuels which are available in Europe now, is BIOGRACE – a calculator based on the methodology for assessing greenhouse gas emissions caused by the production and use of transport fuels, biofuels, and biofluids, referred to in the Directive 2009/28/EC, thereby facilitating the implementation of those provisions of the Directive, concerning sustainable production of biofuels.

Essentially, five steps of life cycle exist both for conventional fuels and biofuels: material acquisition, transport, fuel production process, transport and distribution, and use. Despite its important function in the market, storage is not taken into account in LCA as a major process because of its low energy consumption and emission levels. Therefore, emissions accompanying storage processes are contemplated as part of the major processes or are excluded from analysis in most life cycle analyses.

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References

[1] Fava J. 1991. *A Technical Framework for Life-Cycle Assessment*. In: SETAC and SETAC Foundation for Environmental Education, Washington.

[2] Samson-Bręk I., *Zastosowanie metody oceny cyklu życia (LCA) do oszacowania wpływu na środowisko procesu uprawy biomasy przeznaczonej na cele energetyczne*, [in:] the sci-tech monthly CHEMIK nauka – technika – rynek, 11/2012, ISSN 0009-2886.

[3] PRé Consultants; Goedkoop M., DeSchryver A. and Oele M., *Introduction to LCA with SimaPro 7*, 2008.

[4] Kowalski Z., Kulczycka J., Góralczyk M., 2007, *Ekologiczna ocena cyklu życia procesów wytwórczych (LCA)*, PWN, Warszawa 2007.

[5] ISO EN 14040, Environmental Management – Life Cycle Assessment – Principles and framework, 2006.

[6] ISO EN 14044, Environmental Management – Life Cycle Assessment – Requirements and guidelines, 2006.

[7] www.openlca.org

[8] http://greet.es.anl.gov/

[9] http://easewaste.dk/

[10] http://biograce.net/

[11] Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources.

[12] Faber A. et al., 2011. *Poziom emisji gazów cieplarnianych (CO_2, N_2O, CH_4) dla uprawy pszenicy, pszenżyta, kukurydzy i żyta przeznaczonych do produkcji bioetanolu oraz upraw rzepaku przeznaczonych do produkcji biodiesla*. Expert opinion, commissioned by the Ministry of Agriculture and Rural Development.

[13] Samson-Bręk I., Smerkowska B., *Evolution of environmental life cycle assessment in the context of biorefinery and biomass products*, Environmental Biotechnology Vol. 9 (1) 2013.

[14] Law of 16 February 2007 on the mandatory reserves of crude oil, petroleum products and natural gas and on the rules of procedure in circumstances of national fuel emergency and disruptions on the petroleum market (Dz.U. of 2007 No. 52 Item 343).

[15] Regulation of the Minister of Economy of 22.01.2009 in the matter of qualitative requirements concerning liquid biofuels (Dz.U. of 2009 No. 18, Item 98).

[16] *Effective LCA with SimaPro*, SimaPro course by Pre Consultants, workshop materials and proceedings, Netherlands, November 2011.

[17] SimaPro Method Selector http://www.pre.nl/wizard_link/method_selector/default.htm.

[18] Murray C. and Lopez A., *The Global Burden of Disease*, WHO, World Bank and Harvard School of Public Health 1996.

[19] Jolliet O., Margni M., Charles R., Humbert S., Payet J., Rebitzer G and Rosenbaum R., *IMPACT 2000+: A New Life Cycle Impact Assessment Methodology*. Int J LCA10(6) 2003: 324-330

[20] Frischknecht R., Jungbluth N., Althaus H.J., Doka G., Dones R., Hischier R., Hellweg S., Humbert S., Margni M., Nemecek T. and Spielmann M., *Implementation of Life Cycle Assessment Methods: Data v2.0. ecoinvent report No.3*, Swiss Centre for Life Cycle Inventories, Dübendorf 2007.

[21] Technology Roadmap Biofuels for Transport, IEA 2011 (based on Bradley et al., 2009).

[22] Bajdor K., Biernat K.: *Biopaliwa jako alternatywne nośniki energii w silnikach spalinowych, klasyfikacja i perspektywy rozwoju*, „Archiwum Motoryzacji” 1/2011.