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Chapter 8

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.

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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,

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- 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°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°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.

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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.

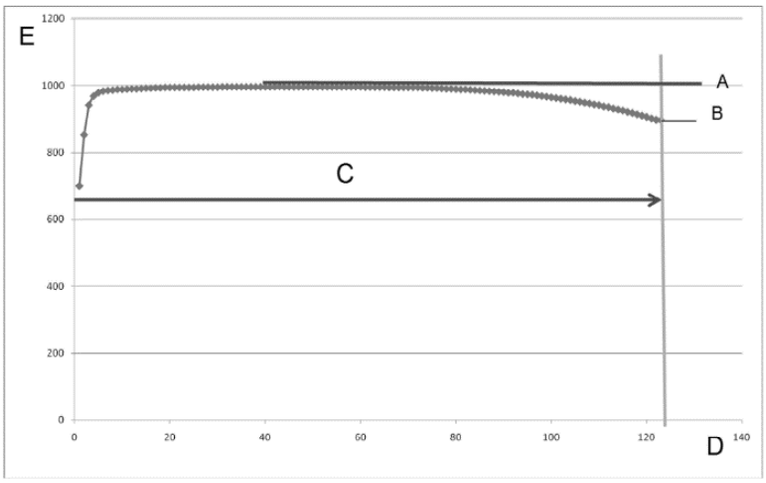


Figure 1. The rapid-oxidation test course diagram, **A** – the maximum pressure recorded, P_{max}, **B** – breakpoint, **C** – induction period (min), **D** – duration of test (min), **E** – pressure value recorded, kPa

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

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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.

$$T\left(\tilde{\nu}\right) = \frac{I}{I_0} \tag{1}$$

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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.

$$A\left(\tilde{\nu}\right) = \log\frac{I_0}{I} = -\log T \tag{2}$$

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).

$$R\left(\tilde{\nu}\right) = \frac{I}{I_0} \tag{3}$$

$$-\log R\left(\tilde{\nu}\right) = \log \frac{I_0}{I} \tag{4}$$

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-

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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.

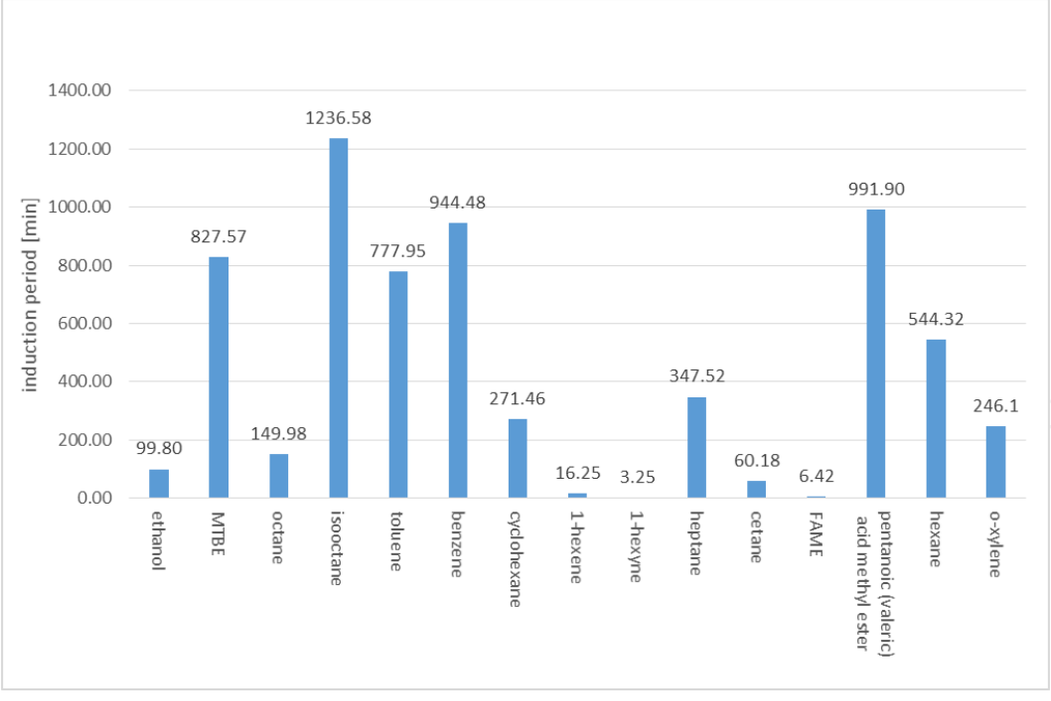


Figure 2. Results of oxidation stability tests of selected chemical compounds

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}).

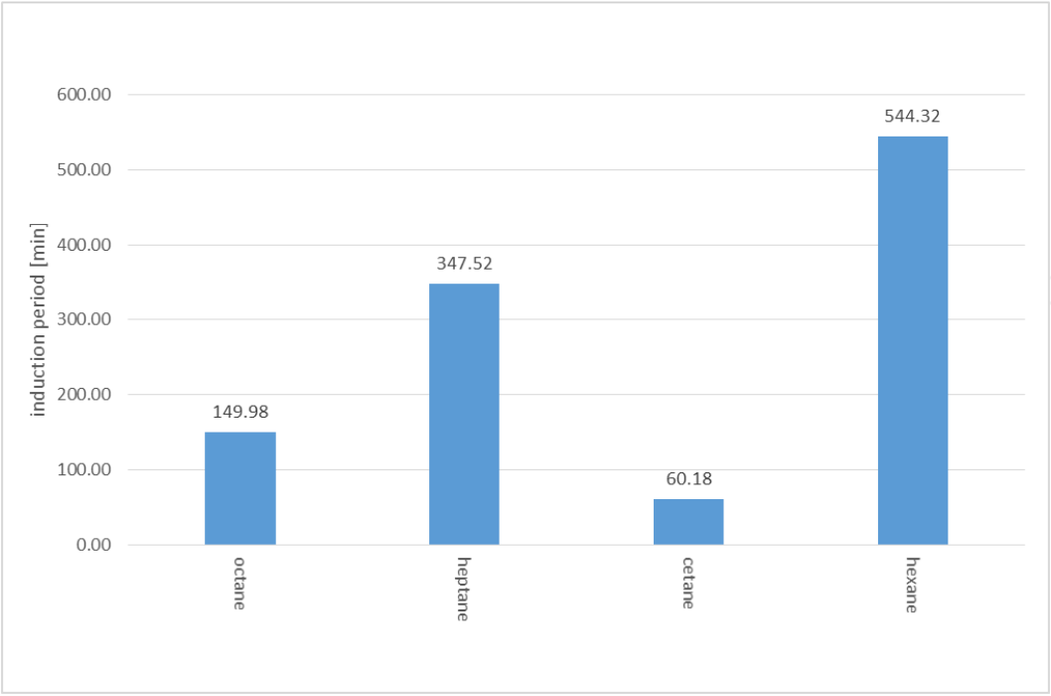


Figure 3. Carbon chain length vs. oxidation stability of hydrocarbons

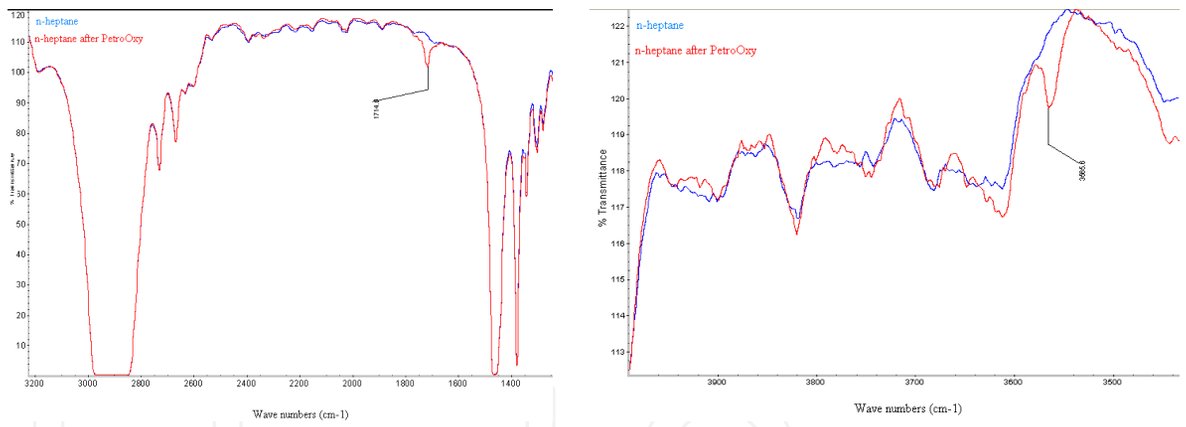


Figure 4. IR spectra for n-heptane before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

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.

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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).

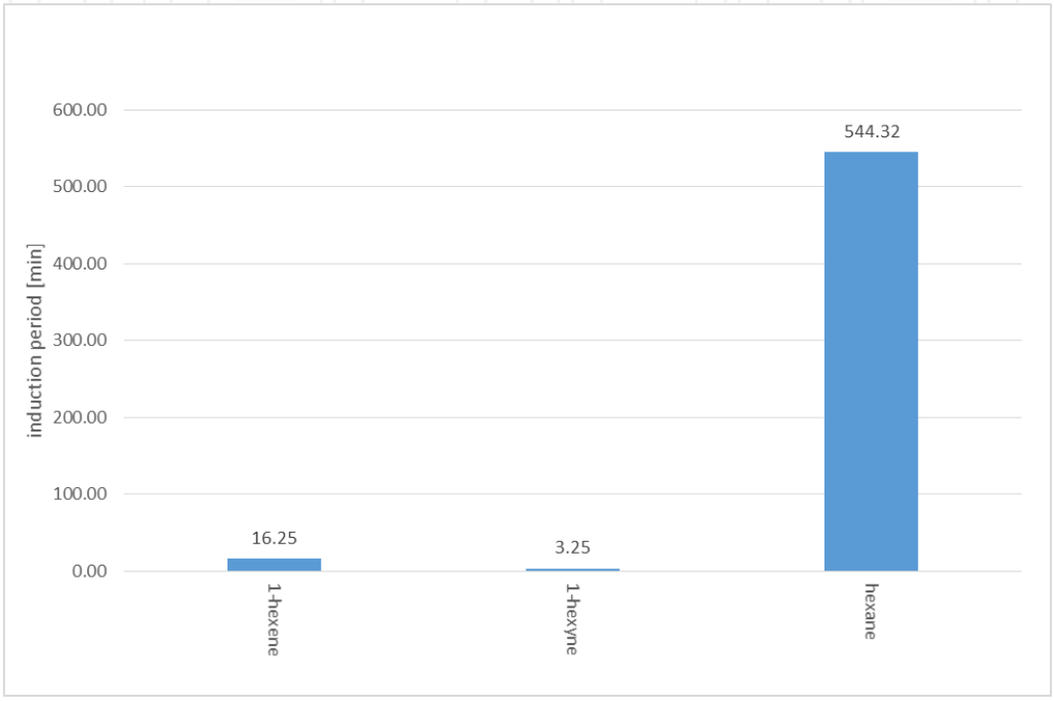


Figure 5. Type of bonds vs. oxidation stability of compounds.

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

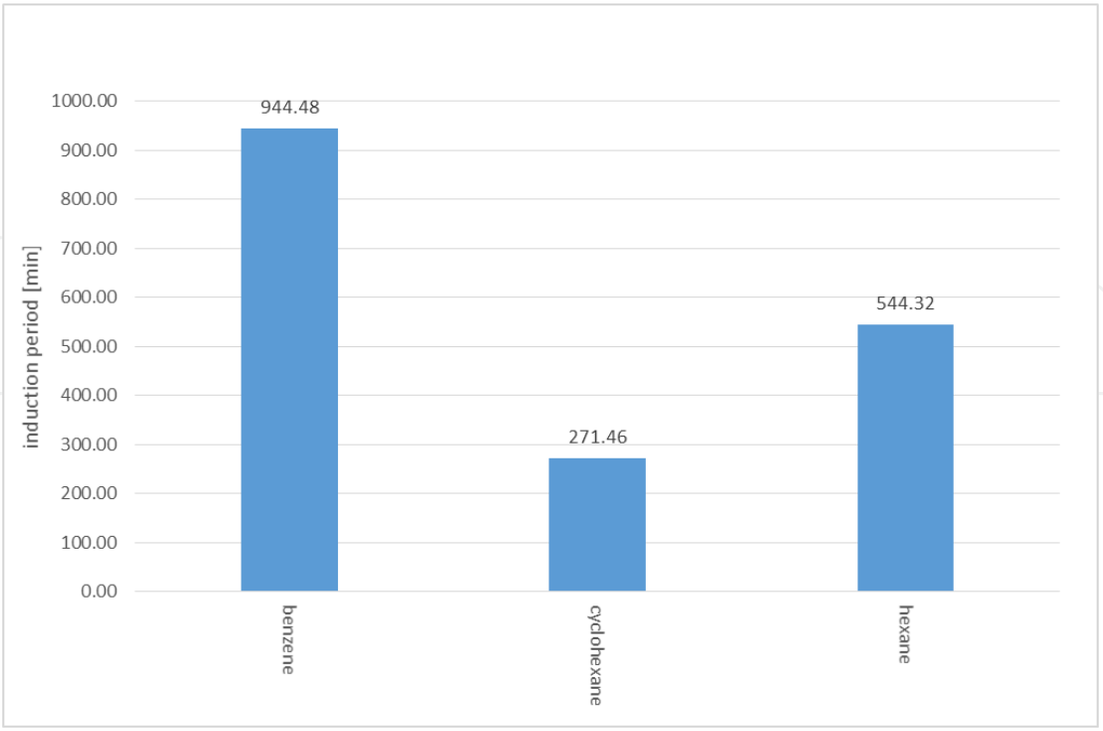


Figure 6. Structure vs. oxidation stability

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.

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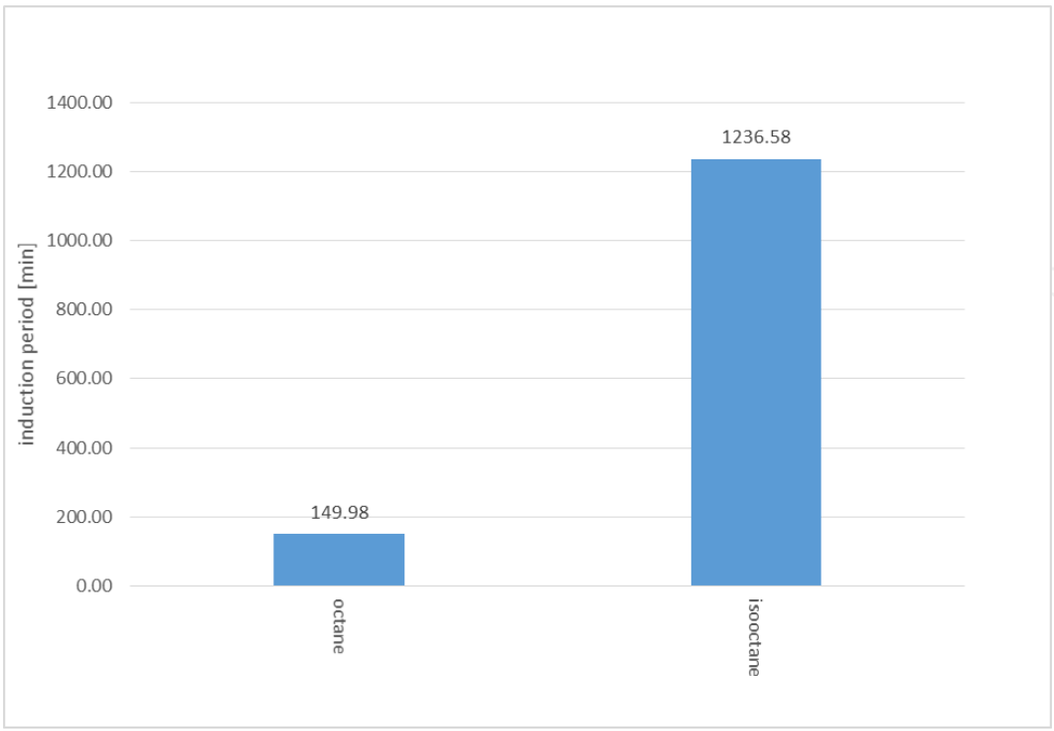


Figure 7. Isomerization vs. oxidation stability of hydrocarbons

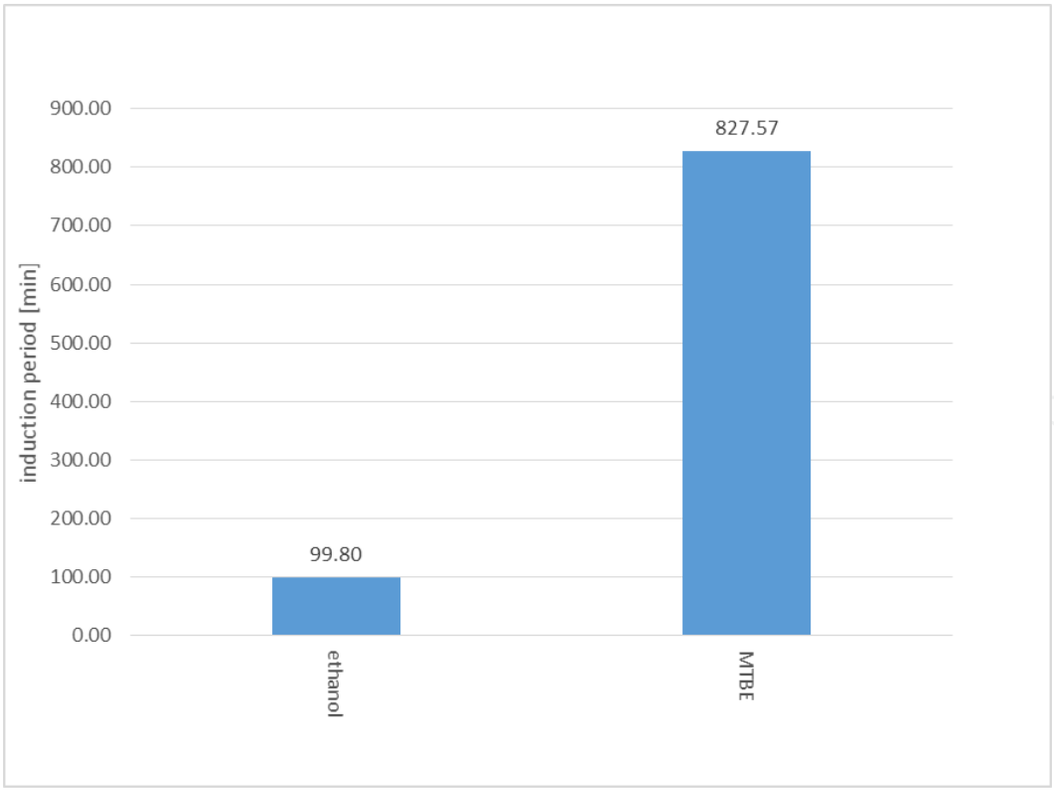


Figure 8. Results of oxidation stability tests for selected oxygen compounds

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.

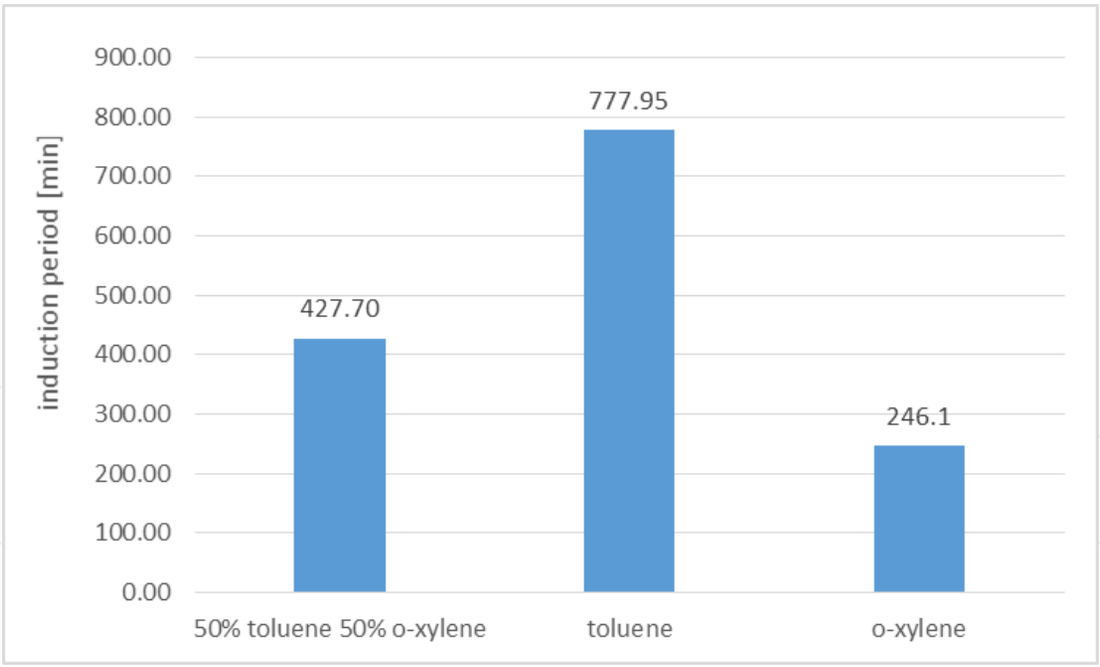


Figure 9. Oxidation stabilities for toluene and o-xylene and their 50/50 mixture

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.

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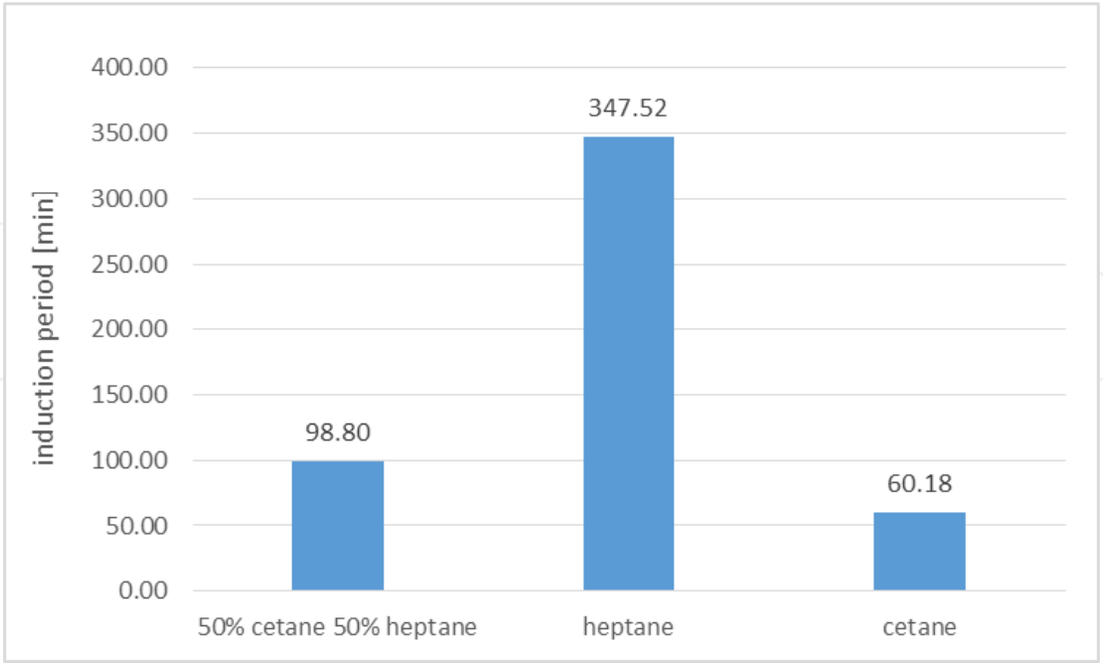


Figure 10. Oxidation stabilities for heptane and cetane and their 50/50 mixture

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.

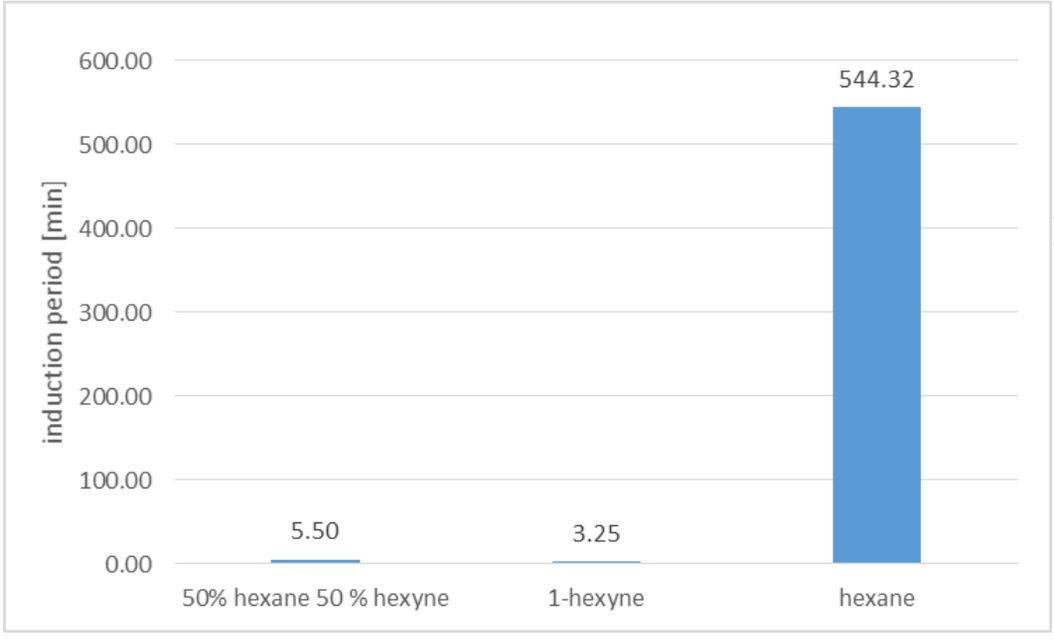


Figure 11. Oxidation stabilities for hexane and 1-hexyne and their 50/50 mixture

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.

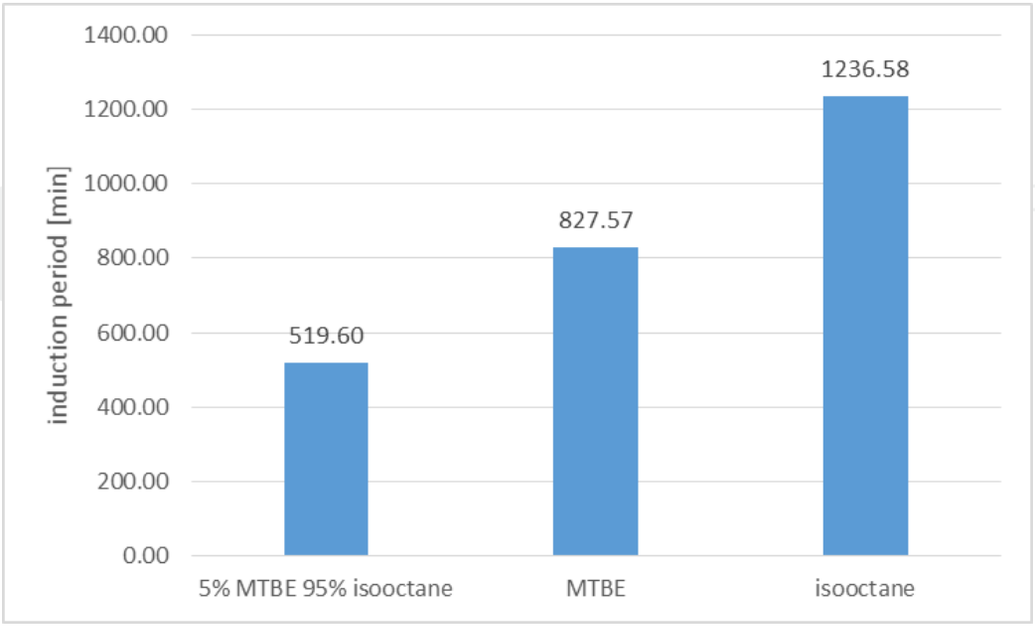


Figure 12. Oxidation stabilities for isooctane and MTBE and their 50/50 mixture

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

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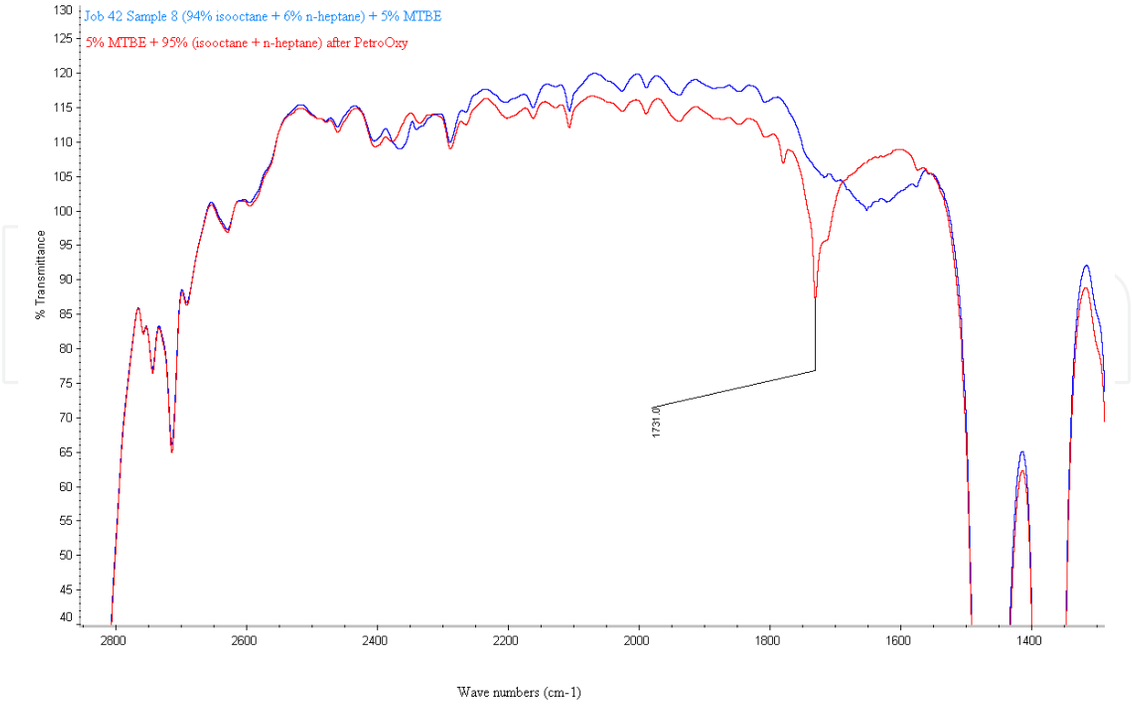


Figure 13. Superimposed IR spectra for 95% (94% isooctane + 6% n-heptane) + 5% MTBE before and after ageing (blue-spectrum before ageing, red-spectrum after ageing)

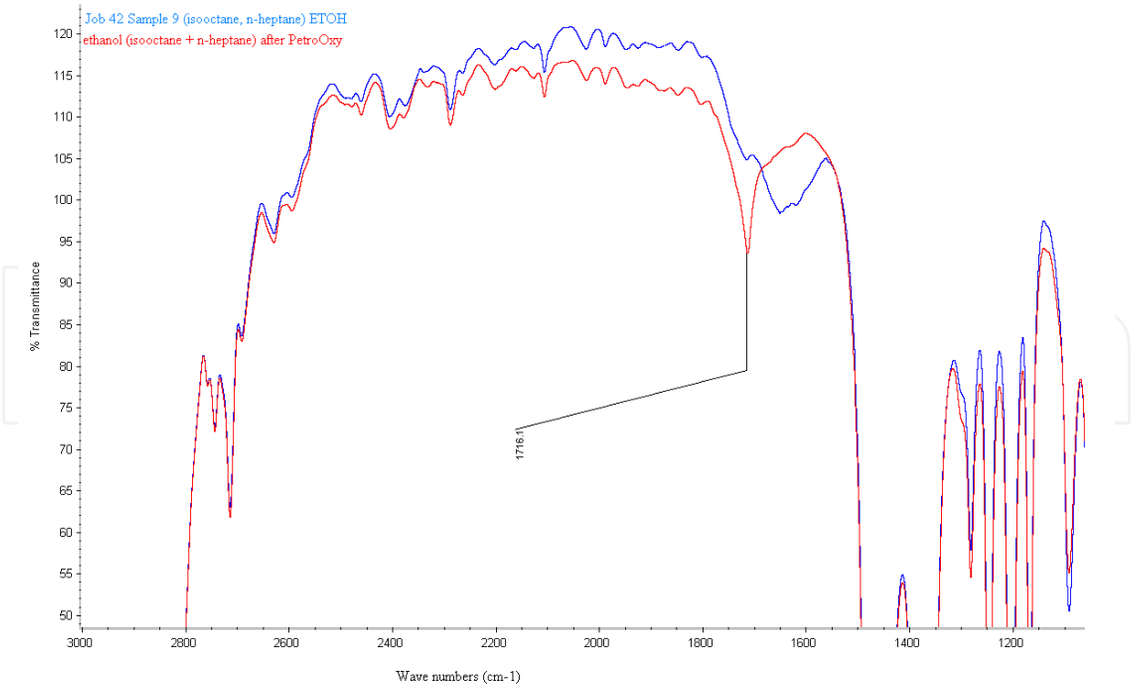


Figure 14. Superimposed IR spectra for 95% (94% isooctane + 6% n-heptane) + 5% ethanol before and after ageing (blue-spectrum before ageing, red-spectrum after ageing)

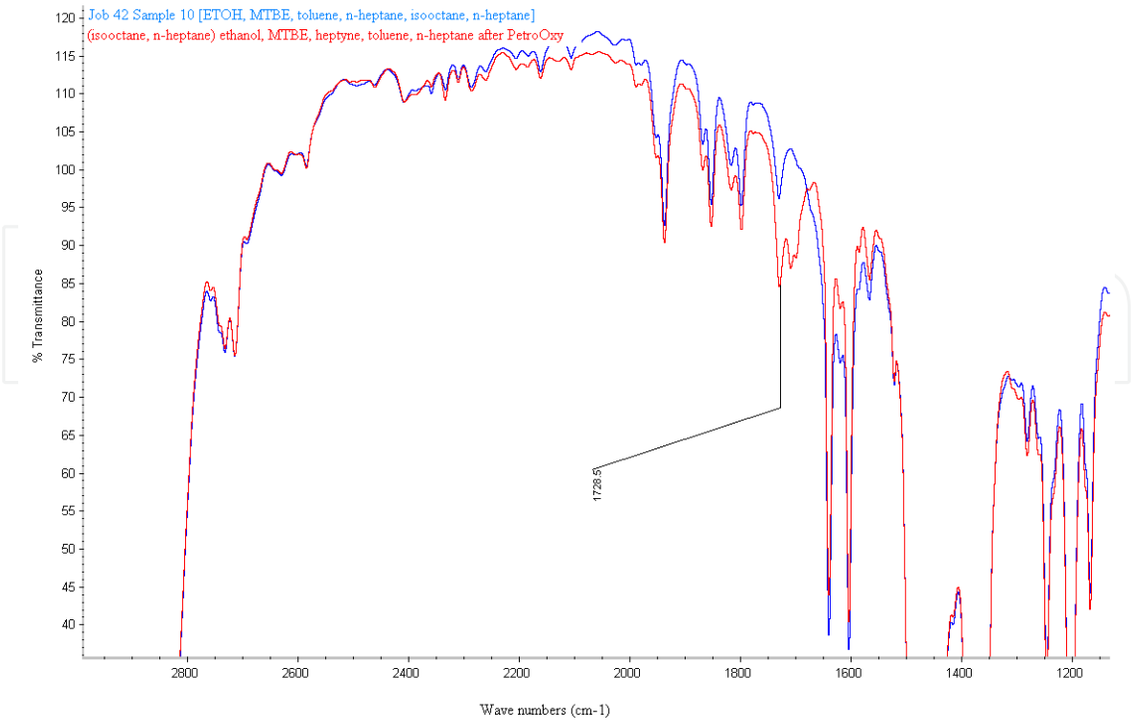


Figure 15. Superimposed IR spectra for 50% (95% isooctane + 5% n-heptane) + 5% ethanol + 5% MTBE + 15% 1-heptyne + 25% toluene before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

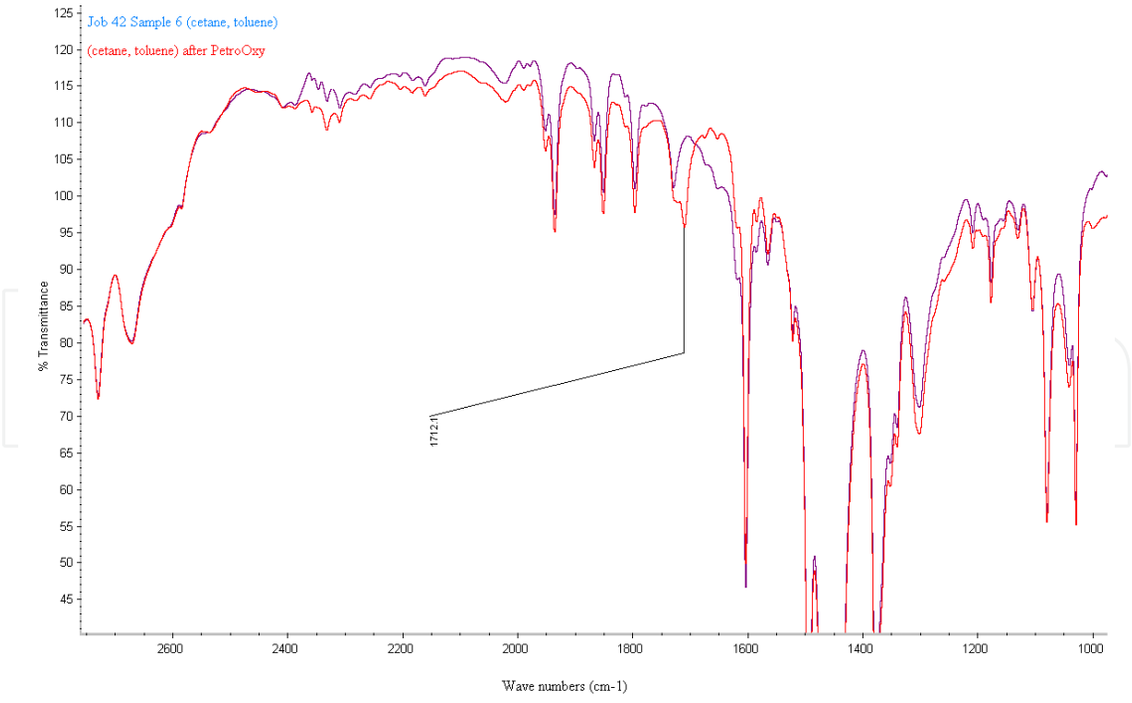


Figure 16. Superimposed IR spectra for 80% cetane + 20% toluene before and after ageing (blue-spectrum before ageing, red-spectrum after ageing).

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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.

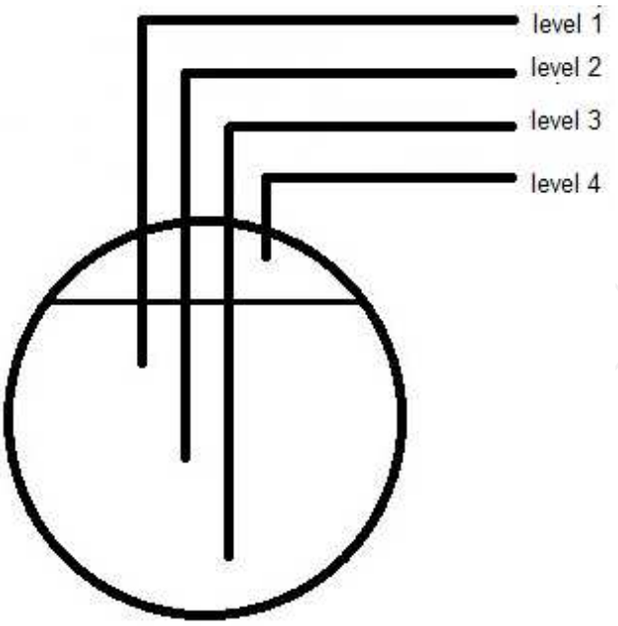


Figure 17. A diagram of the liquid fuel storage tank and the fuel sampling levels in the tank.



Figure 18. Liquid fuel sampling station.

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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°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

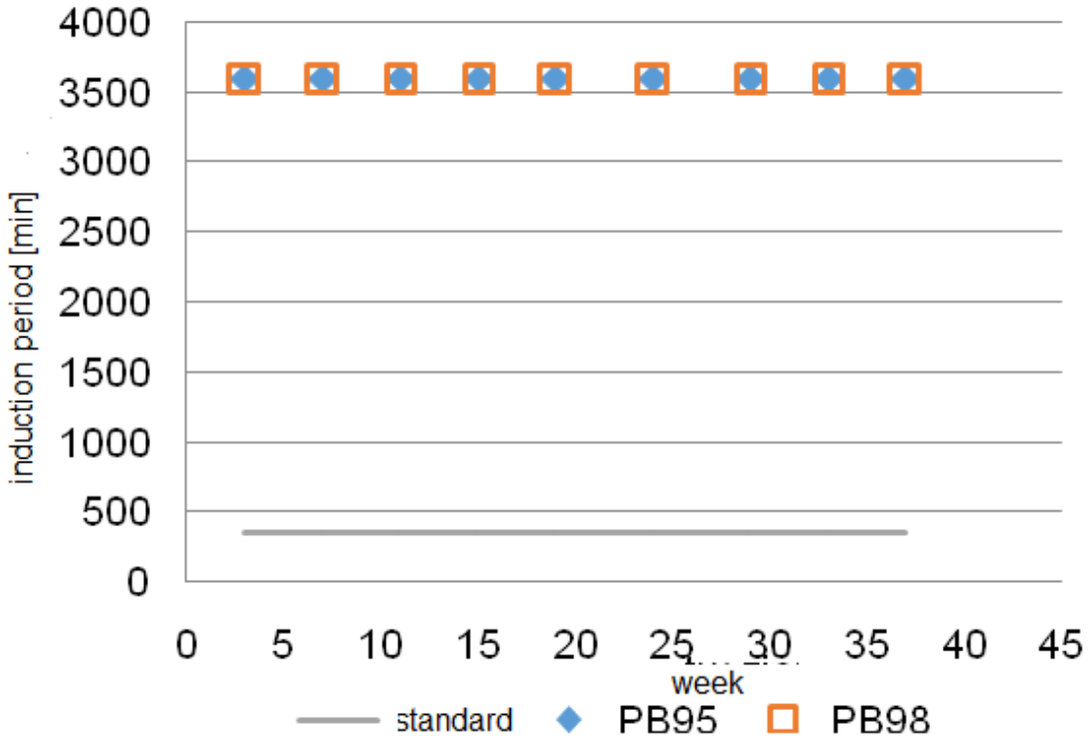


Figure 20. Graphical representation of findings for the test motor gasolines.

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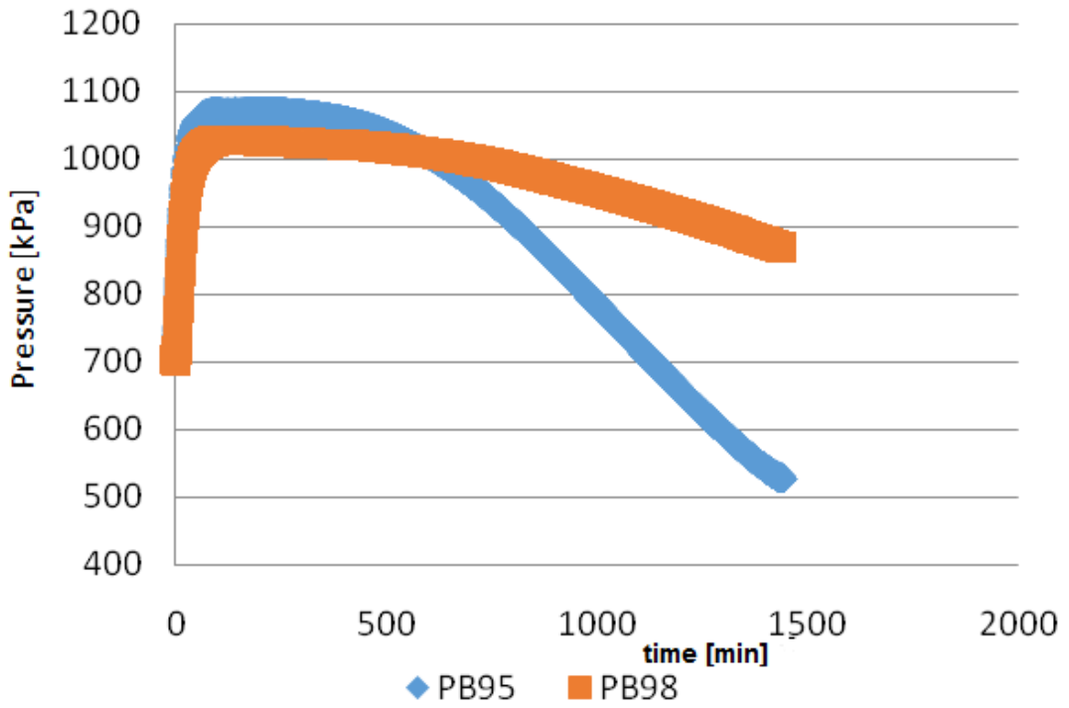


Figure 21. The course of oxidation of motor gasolines after 50 weeks of storage, as found by the induction-test method.

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.

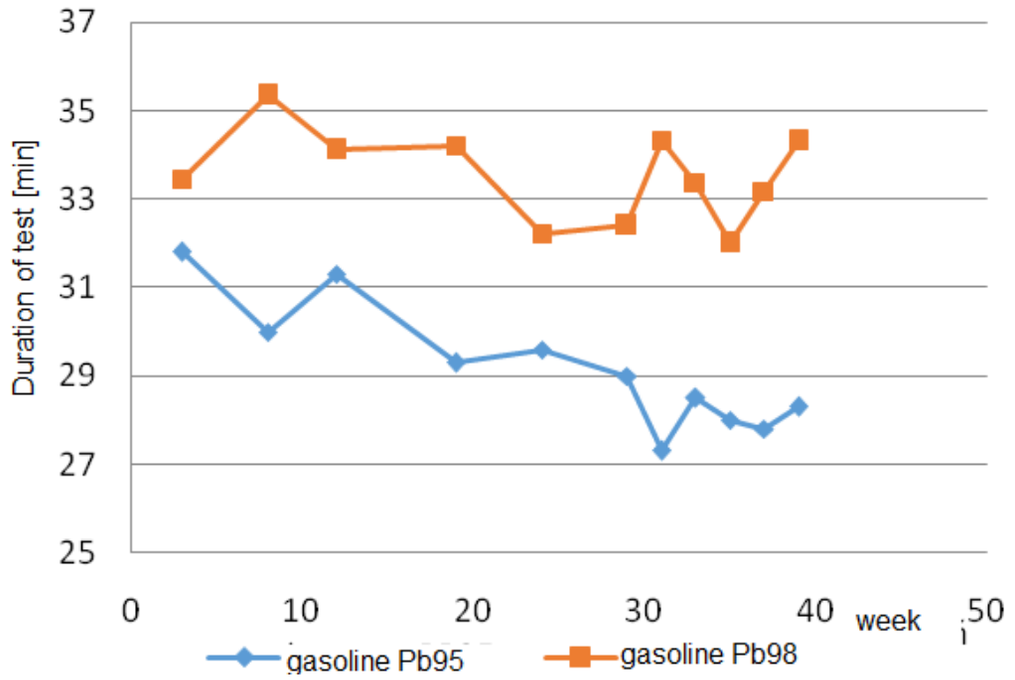


Figure 23. Results of the rapid-oxidation test for PB95 and PB98 gasolines.

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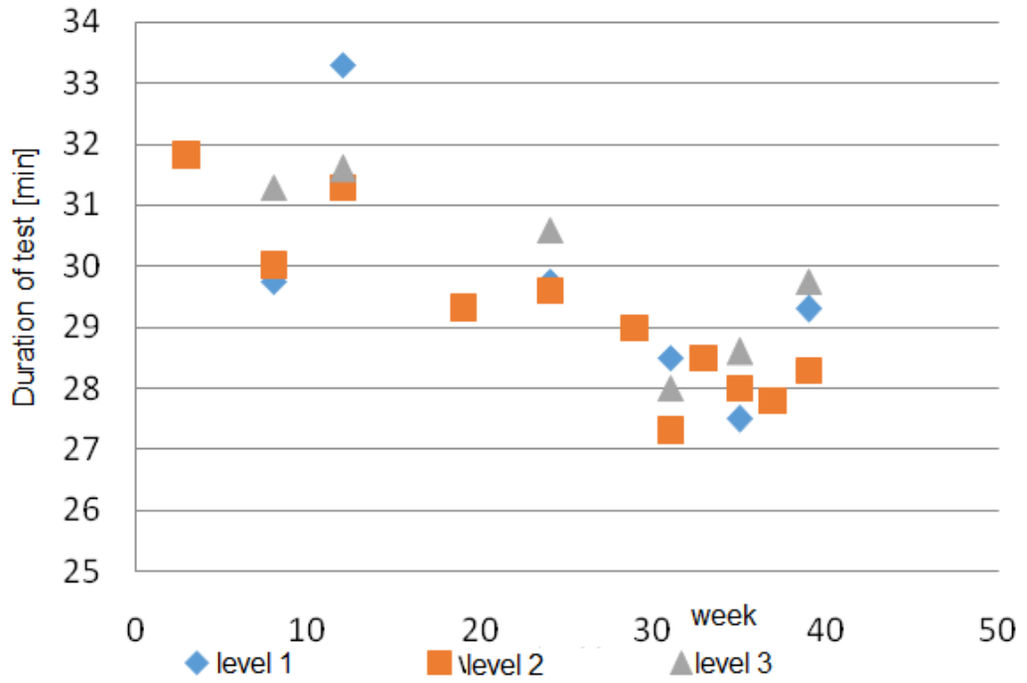


Figure 24. Results of the oxidation stability test for the PB95 gasoline, collected from various tank levels.

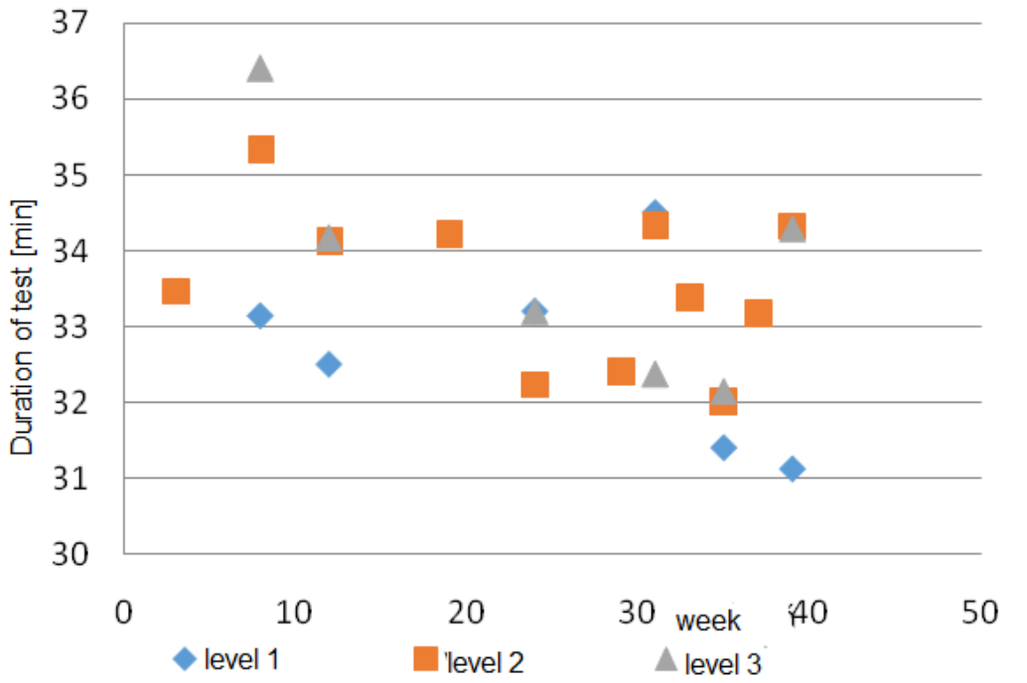


Figure 25. Results of the oxidation stability test for the Pb98 gasoline, collected from various tank levels

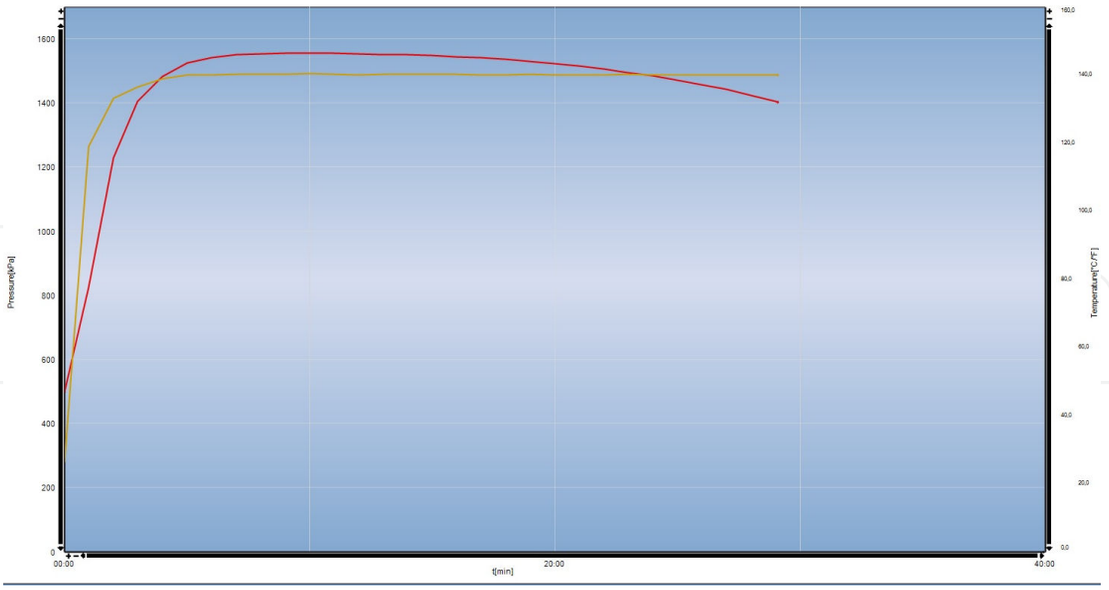


Figure 26. Graphical representation of oxidation of the test motor gasoline.

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.

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Figure 27. A test assembly for oxidation-stability tests of diesel fuels according to the standard EN 12205.

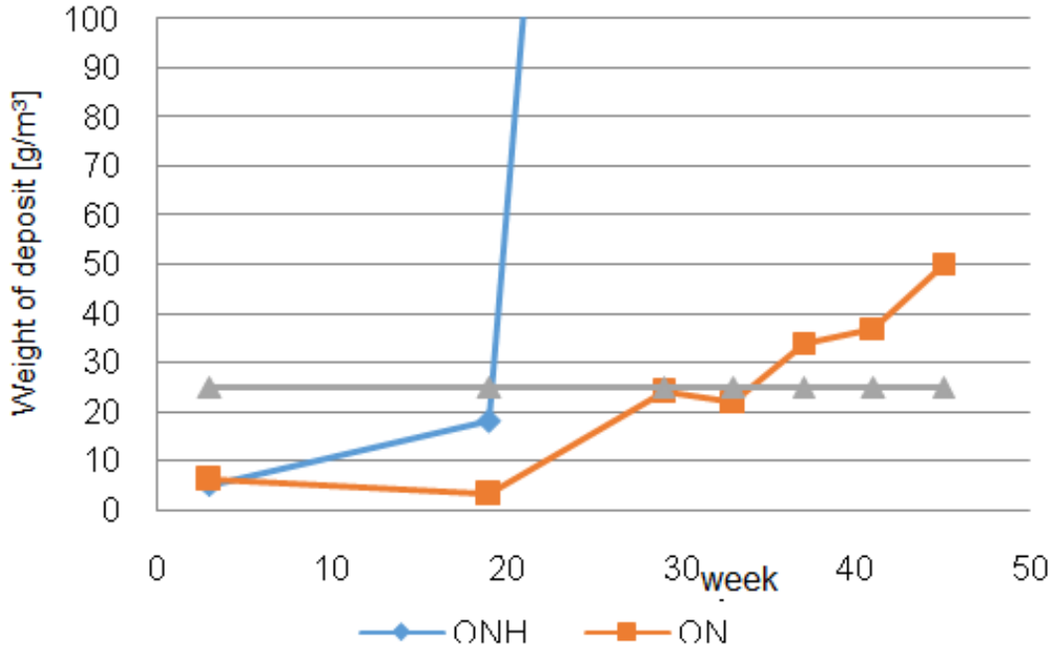


Figure 28. Results of oxidation stability tests.

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.

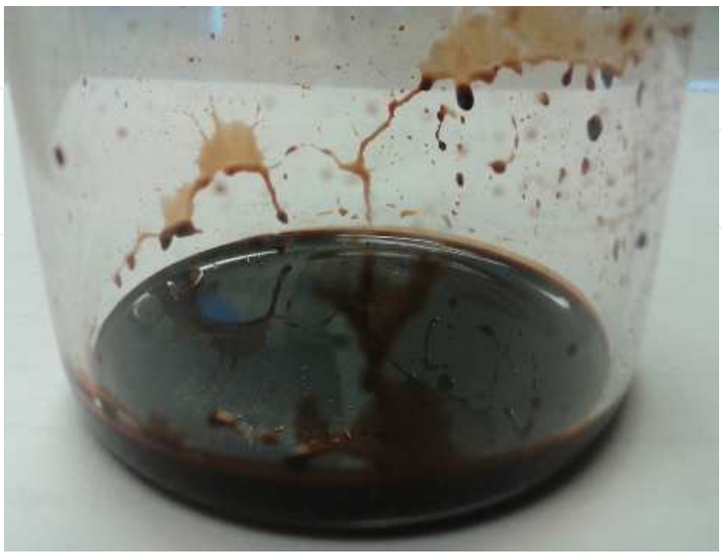


Figure 30. Solubles (gums), formed by oxidation during storage of diesel fuel with 7% (V/V) of a biocomponent.

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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^{o}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^{o}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).

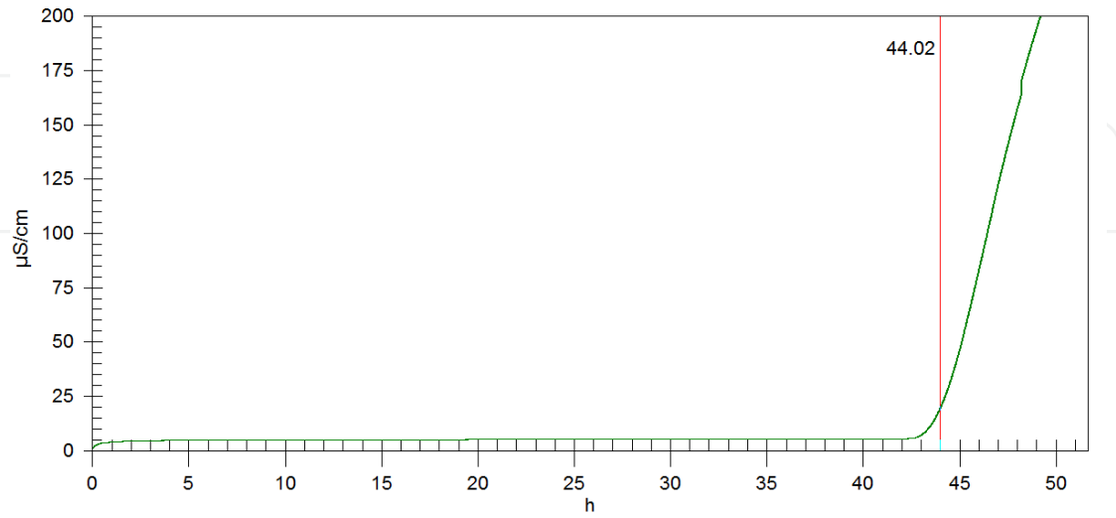


Figure 32. The course of oxidation of diesel fuel according to EN 15751 (Rancimat method).

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.

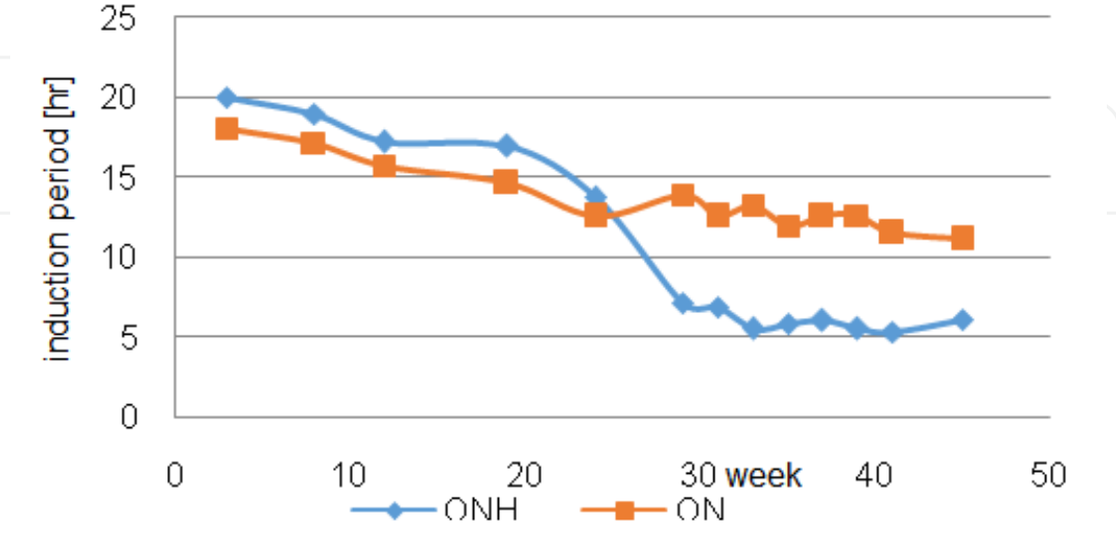


Figure 33. Results of ageing for diesel fuels during storage.

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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).

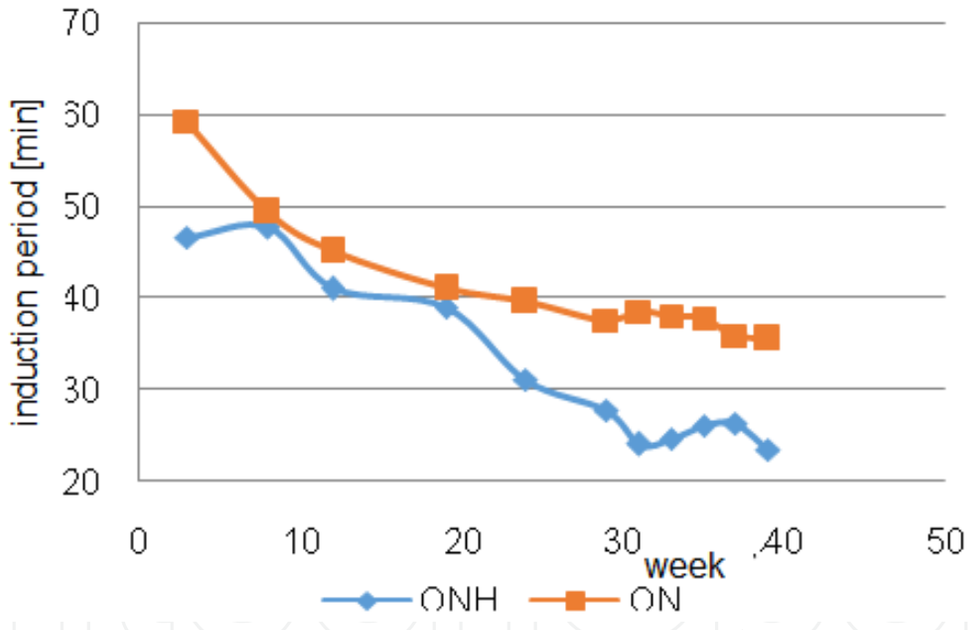


Figure 34. Results of oxidation stability tests for diesel fuels during storage.

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

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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)

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