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# Autoxidation of Fuels During Storage

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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].

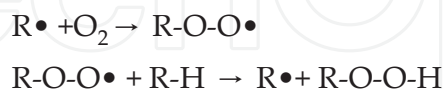
The theory is based on chain radical reactions with participation of peroxy and hydrocarbon free radicals, leading to the precipitation of substances which contaminate storage tanks, promote corrosion of transfer pipelines, cause filter plugging and similar problems in the fuel distribution system.

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]:

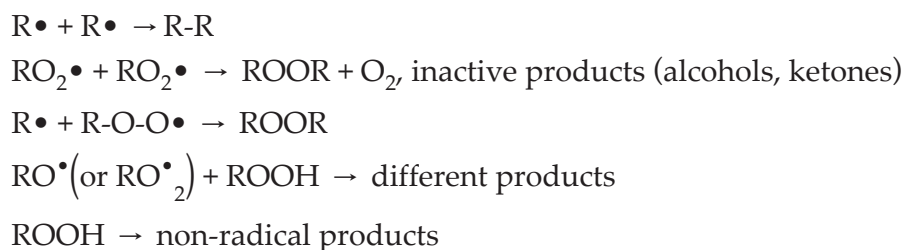
a. Initiation:



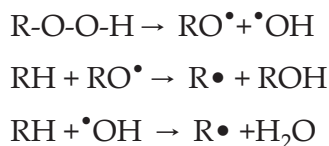
b. Propagation:



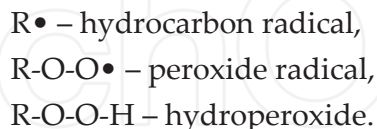
c. Termination:



d. Chain branching:



wherein: R-H – denotes hydrocarbon,



In the initiation step, the reactions generating hydrocarbon free radicals  $\text{R}\cdot$  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 resonance 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
RON 95 gasoline with TBHP	RON_95+PEROX	ISO 7536
RON 95 gasoline with cyclohexene	RON_95+OLEF	EN 16091 modified
RON 98 gasoline	RON_98	ISO 6246
RON 98 gasoline with TBHP	RON_98+PEROX	ASTM D 873
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

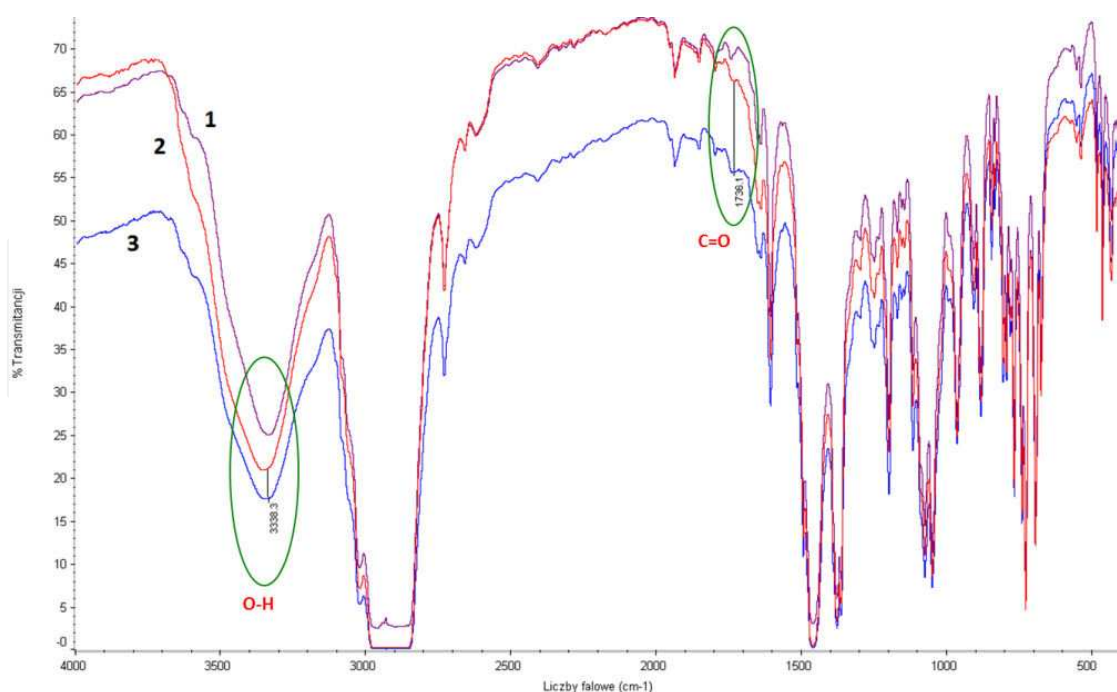
Infra-red spectroscopy enables examination of the structure of molecules. It helps determine what functional groups the analyzed compound has in it. Functional groups are a group of several atoms connected with one another by means of chemical bonds (for instance, carbonyl group  $\text{-C=O}$ , hydroxyl group  $\text{-OH}$ ). 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  $3300\text{ cm}^{-1}$ , while the carbonyl group gives a signal in the spectrum in the range from  $1750$  to  $1650\text{ cm}^{-1}$ , 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  $400\text{ cm}^{-1}$ , in a  $0.065\text{ mm}$  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).





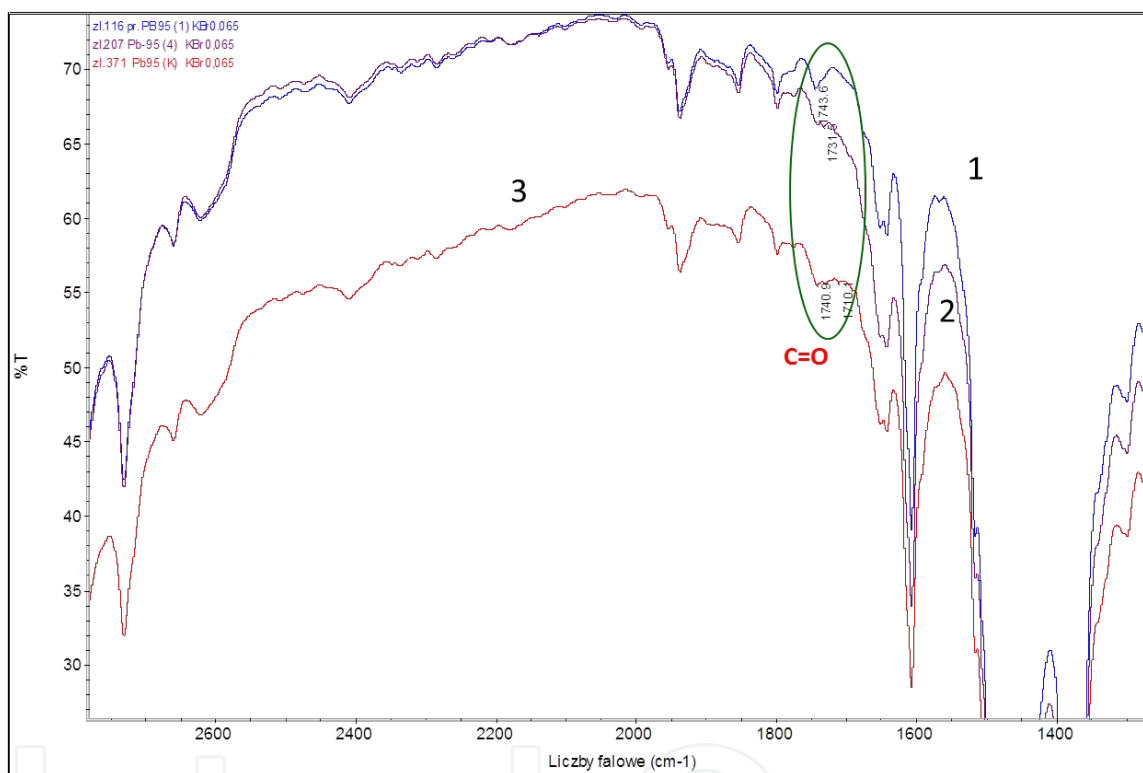
**Figure 1.** IR spectra, recorded for RON 95 gasoline samples: 1) fresh, 2) after 3 months of storage, and 3) after 6 months of storage.

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.  $3330\text{ cm}^{-1}$ , 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	$3330\text{ cm}^{-1}$ 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.  $1743\text{ cm}^{-1}$  – 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.



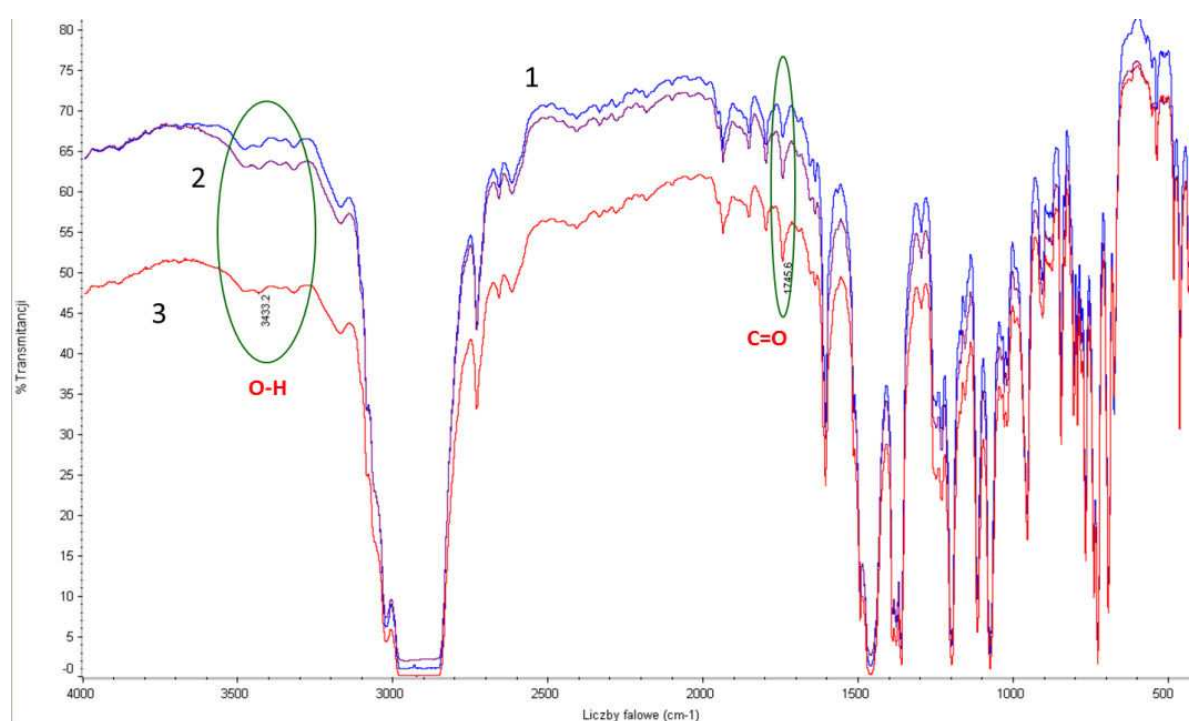
**Figure 2.** IR spectra in the range  $2700\text{--}1300\text{ cm}^{-1}$ , recorded for RON 95 gasoline samples: 1) fresh, 2) after 3 months of storage, and 3) after 6 months of storage

There was a small, narrow peak in the spectrum of the fresh gasoline sample, with its maximum at ab.  $1743\text{ cm}^{-1}$  (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  $1710\text{ cm}^{-1}$ ), 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 $\text{cm}^{-1}$	Band 1746 $\text{cm}^{-1}$
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  $1743\text{ cm}^{-1}$ , combined of low intensity peaks, combined to form a wider band. Similar changes as for the fuel without the compound were observed 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 involve 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 accelerated ageing.

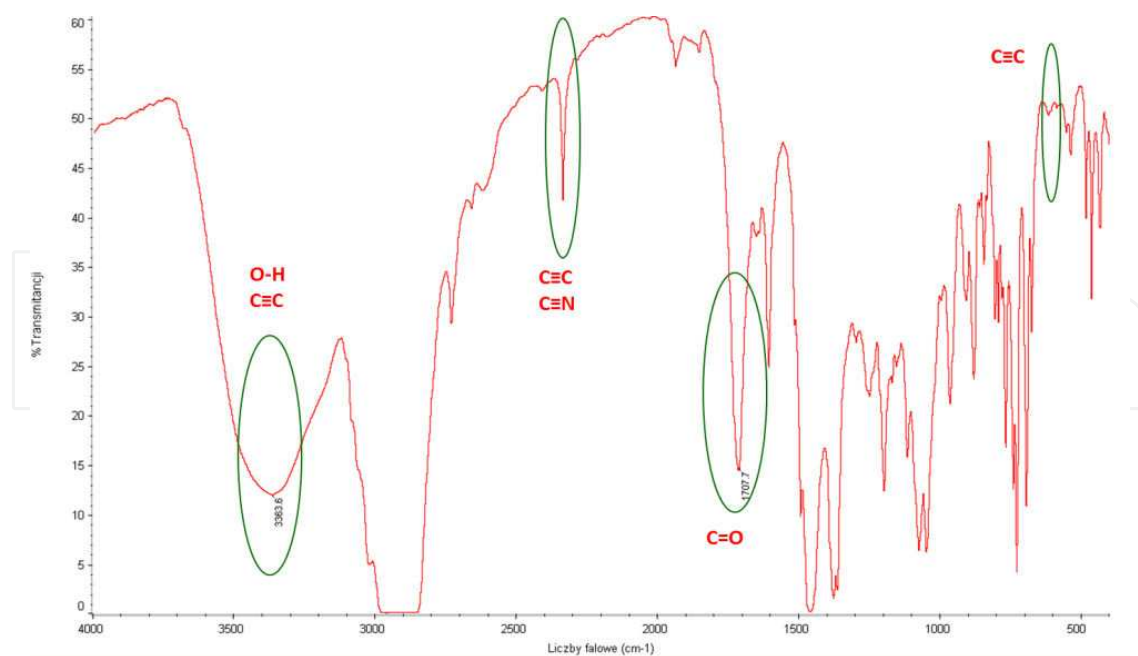
Oxidation stability is commonly evaluated by determination of induction period according to ISO 7536 [12].

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.  $1710\text{ cm}^{-1}$ .

The spectrum of the fuel subjected to the induction period tests showed a strong, sharp signal with its maximum at the wave number  $2332\text{ cm}^{-1}$ . The IR spectra recorded for samples collected after various times of storage and subjected to accelerated ageing indicate that the peak intensity at  $2332\text{ cm}^{-1}$  increases slightly with longer storage times. The peak is characteristic, for instance, for the triple bond in nitriles  $\text{C}\equiv\text{N}$ . In that range, the signal may also originate from the  $\text{C}\equiv\text{C}$  group, although the characteristic peak for that group in pure compounds is in the lower wave number range  $2100\text{-}2270\text{ cm}^{-1}$ . 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  $\equiv\text{C-H}$  group: a strong and sharp band of stretching vibrations at ab.  $3300\text{ cm}^{-1}$  and deformation bands in the ranges  $1220\text{-}1370\text{ cm}^{-1}$  and  $610\text{-}700\text{ cm}^{-1}$ . 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.  $620\text{ cm}^{-1}$ , 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.



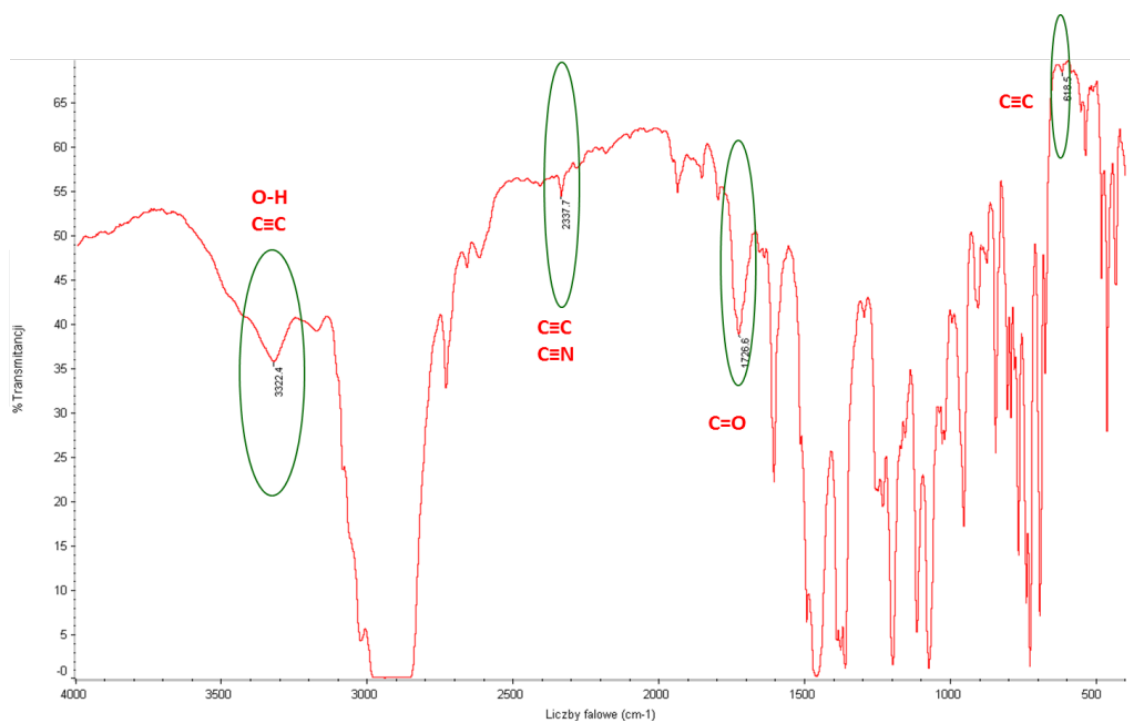
**Figure 4.** IR spectrum of RON 95 gasoline after 6 months of storage, after induction period tests

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  $1730\text{ cm}^{-1}$  and to the hydroxyl group at the wave number  $3322\text{ cm}^{-1}$  – 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  $2332\text{ cm}^{-1}$  and a weak signal at ab.  $620\text{ cm}^{-1}$  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  $2332\text{ cm}^{-1}$  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  $3300\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$  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.  $1720\text{--}1710\text{ cm}^{-1}$ , indicating the presence of compounds containing a carbonyl group. Moreover, the surface area below the peak ( $3300\text{ cm}^{-1}$ ) corresponding to the  $\text{--OH}$  group vibrations tended to increase. A band appeared which had its maximum at  $2332\text{ cm}^{-1}$ ; 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  $\text{--OH}$  and  $\text{C=O}$  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<sup>3</sup>. Findings for RON 95 are shown in Figure 6, those for RON 98 are shown in Figure 7.

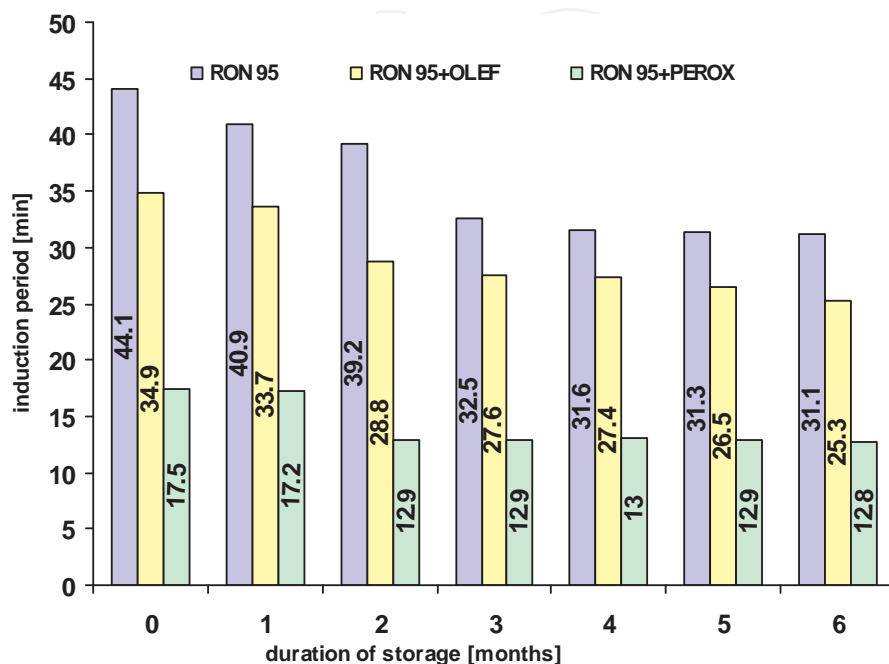


Figure 6. Induction period by micro method for RON 95 gasoline samples vs. duration of storage

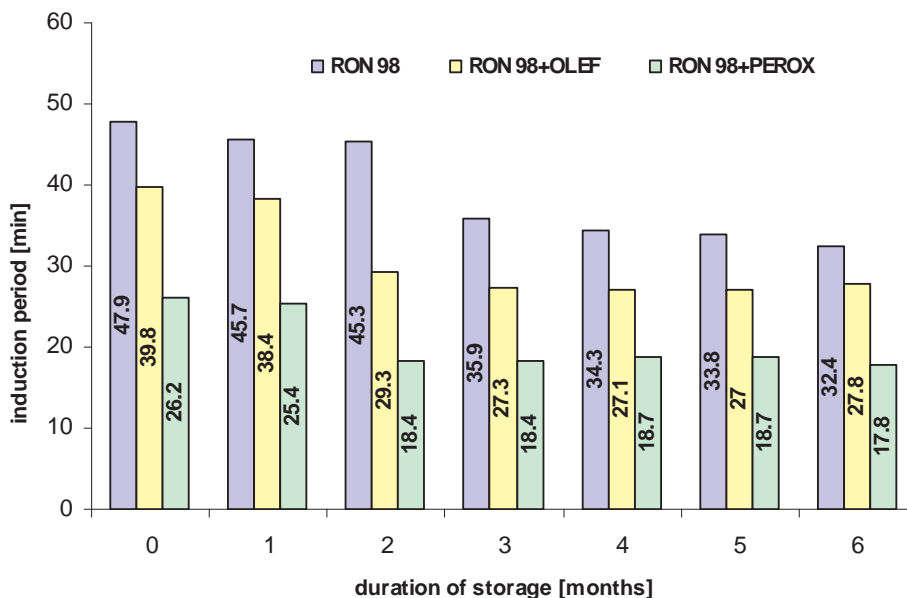


Figure 7. Induction period by micro method for RON 98 gasoline samples vs. duration of storage



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

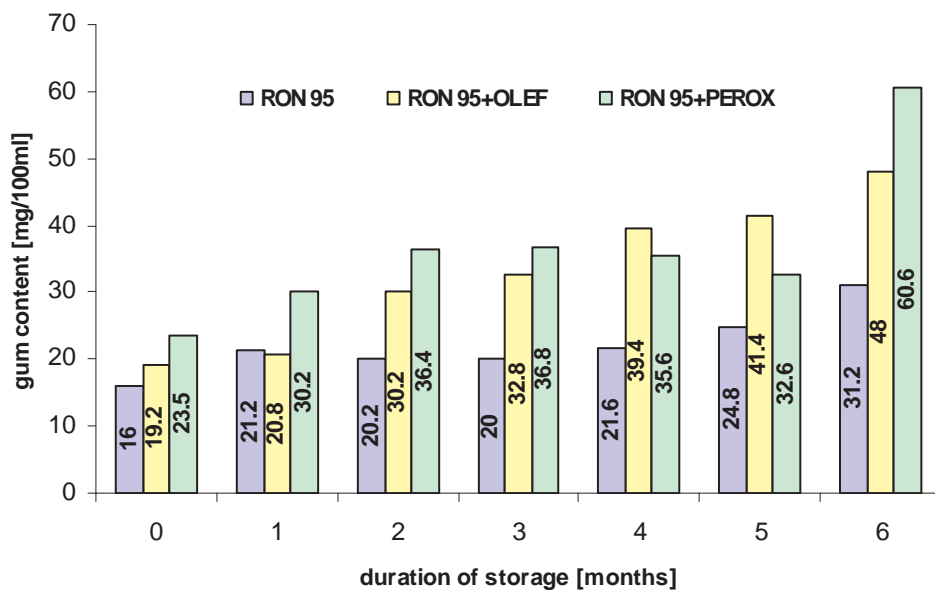


Figure 8. Gum content in the RON 95 gasoline vs. time of storage

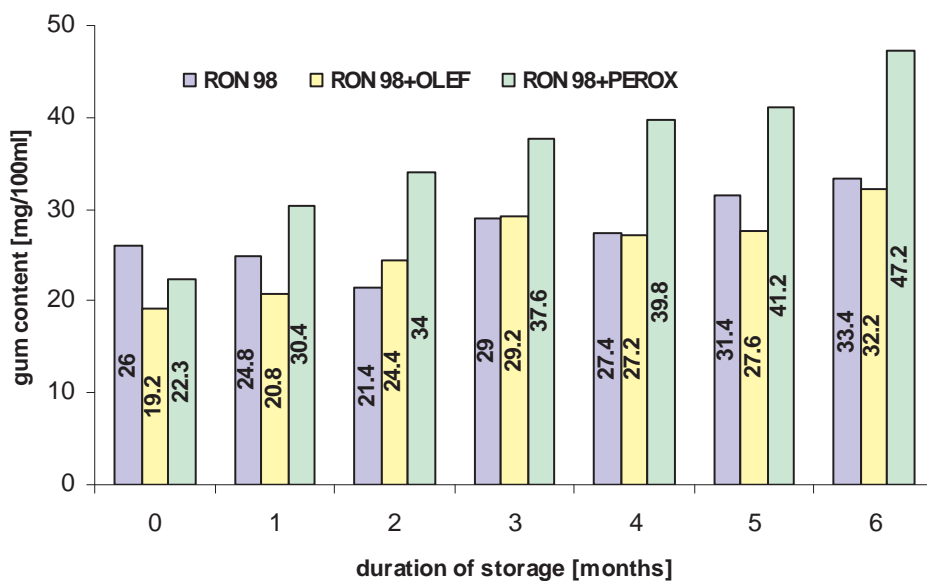


Figure 9. Gum content in the RON 98 gasoline vs. time of storage

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.

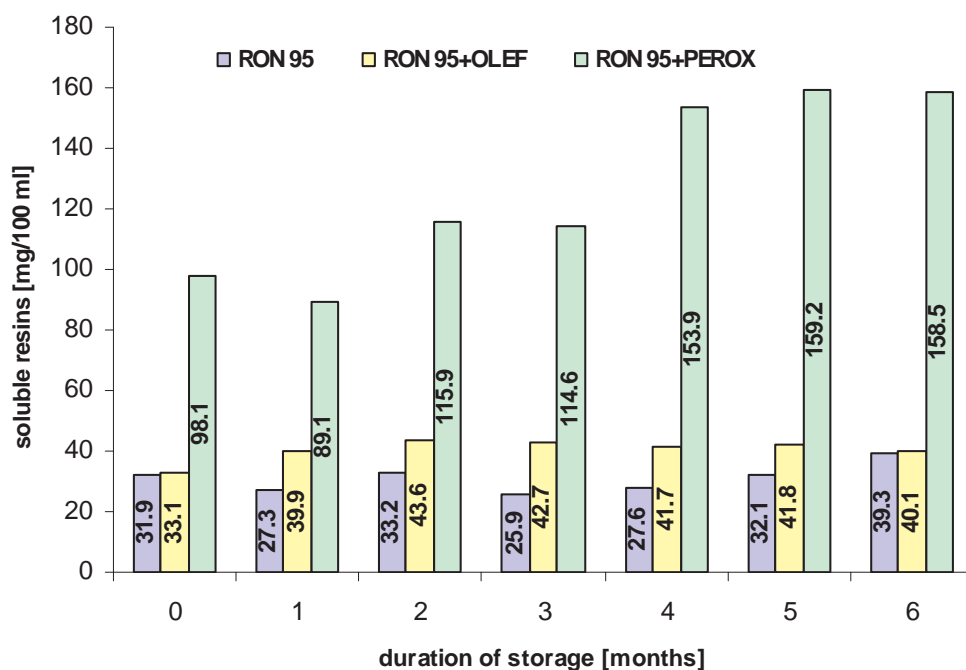


Figure 10. The soluble resins content according to ASTM D 873 in RON 95

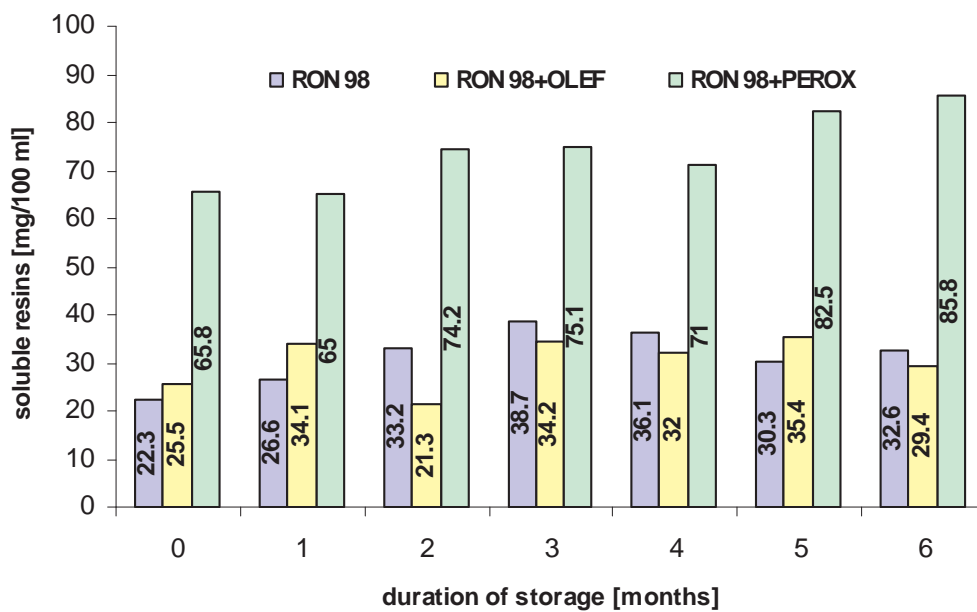


Figure 11. The soluble resin content according to ASTM D 873 in RON 98

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).

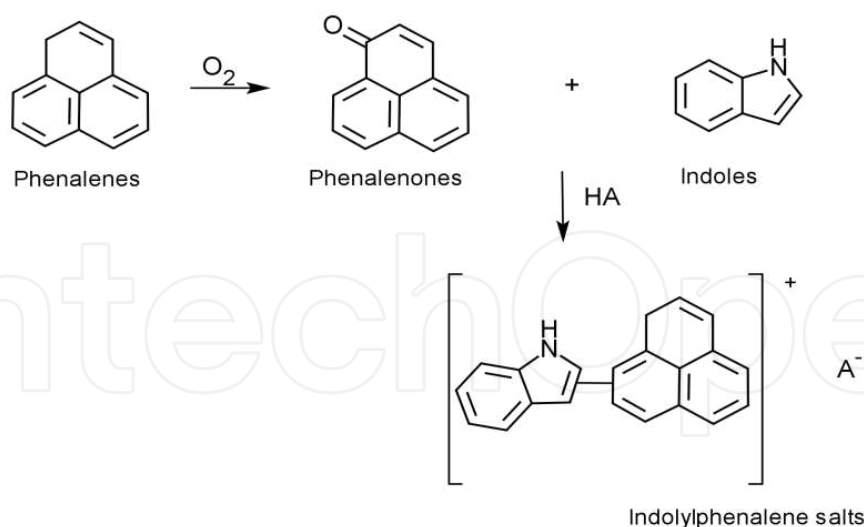
For alcohol-ether gasoline without admixtures and for that with an admixture of cyclohexene, the value of that parameter grows moderately with storage time while there is an observable tendency toward change in similar ether-based gasoline samples.

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  $4.0 \text{ mg}/100 \text{ cm}^3$ , and that of resins was  $6.9 \text{ mg}/100 \text{ cm}^3$ , with the initial value being less than  $0.1 \text{ mg}/100 \text{ cm}^3$ . 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 30<sup>th</sup> week of storage, and the total deposit was  $16.8 \text{ mg}/100 \text{ cm}^3$  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  $860 \text{ mg}/\text{l}$  to  $135 \text{ mg}/\text{l}$  in the 46<sup>th</sup> week of storage, while that of phenalenones increased from  $15 \text{ mg}/\text{l}$  to  $188 \text{ mg}/\text{l}$ . 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 aviation 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°C for 72 hours. For identification of the compounds being formed by oxidation, as well as to study the kinetics of decomposition 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  $\mu\text{m}$ . 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<sup>-1</sup>. 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

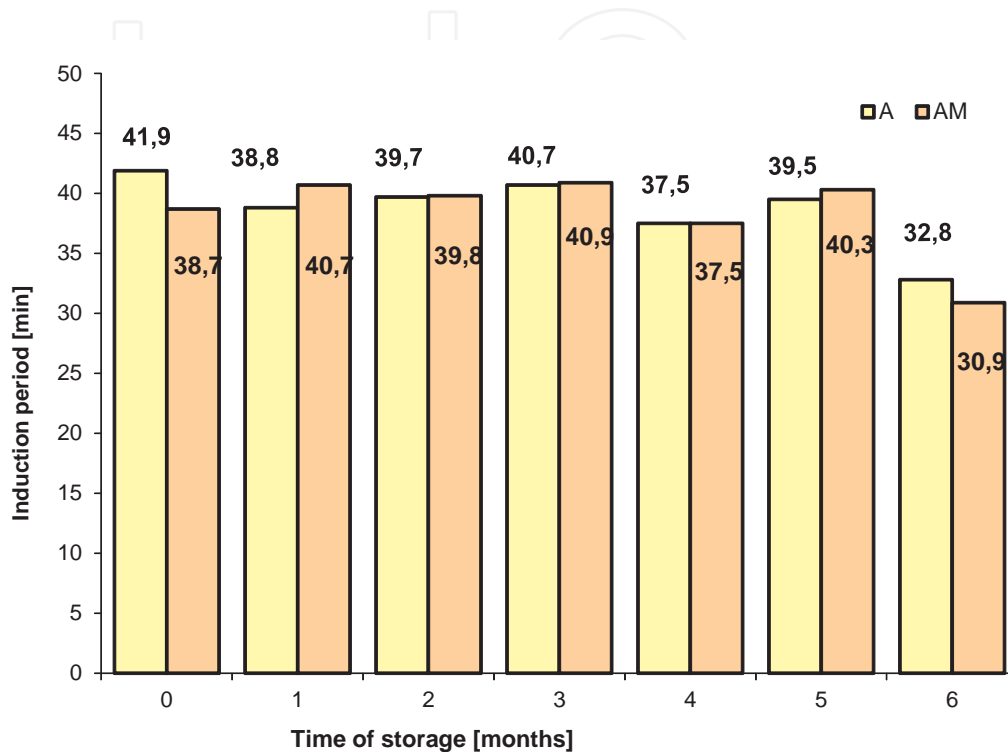
The test material consisted of two samples of diesel oil with different contents of fatty acid methyl esters. Each sample was doped with 130 mg/kg of 2-methylindole. The value was assessed based on literature reports. The samples were stored at a room temperature for 6 months in a dark place and were 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
Diesel oil with 1.3% (V/V) FAME + 130 mg/kg 2-methylindole	AM	EN 16091 FTIR spectra
Diesel oil with 7.2% (V/V) FAME	B	ISO 12205 EN 15751 ASTM D 5304
Diesel oil with 7.2% (V/V) FAME + 130 mg/kg 2-methylindole	BM	EN 16091 FTIR spectra

**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.

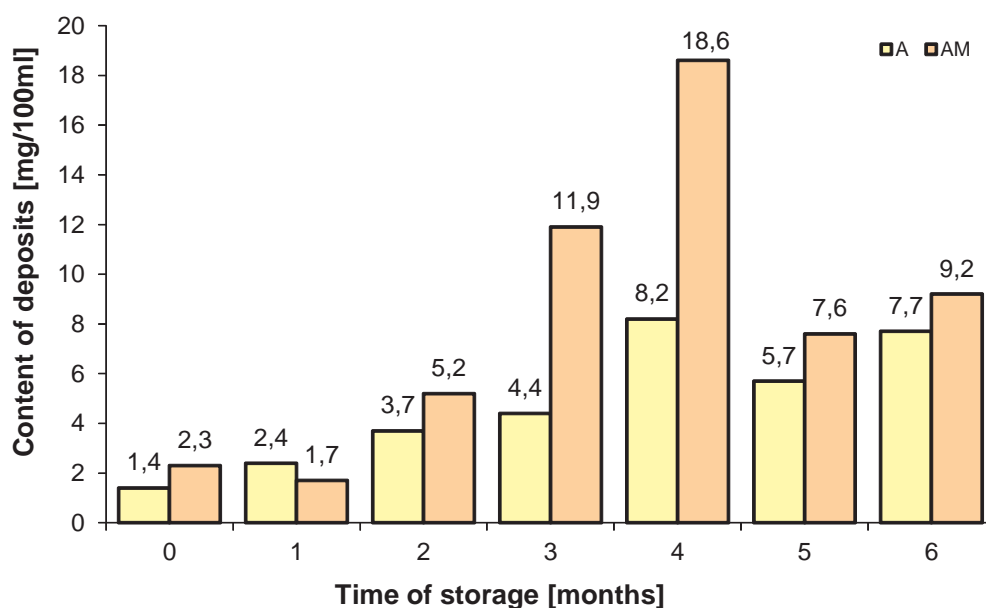


**Figure 13.** Induction period, as found according to EN 16091, for diesel oil samples containing 1.3%(V/V) FAME and methylindole.

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<sup>3</sup> of filterable deposits, 3 g/m<sup>3</sup> of adherent deposits, a total of 7 g/m<sup>3</sup>. After being stored for 6 months, the same sample contained 25 g/m<sup>3</sup> of filterable deposits and 2 g/m<sup>3</sup> of gum, a total of 27 g/m<sup>3</sup>. Very similar values were obtained for sample AM with a content of methylindole: initially, the content of filterable deposits was 3 g/m<sup>3</sup>, that of gum 2 g/m<sup>3</sup>; after 6 months, the sample contained 26 g/m<sup>3</sup> of deposits and 3 g/m<sup>3</sup> 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<sup>3</sup> and in the indole-free sample B - 11.5 mg/100 cm<sup>3</sup>. 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<sup>3</sup>.

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<sup>3</sup>, adherent deposits was 1 g/m<sup>3</sup>, giving a total of 8 g/m<sup>3</sup>; after being stored for 6 months, the same sample had 56.2 g/m<sup>3</sup> of filterable deposits and 2 g/m<sup>3</sup> of gum, a total of 58.2 g/m<sup>3</sup>. Different values were obtained for sample BM with methylindole:



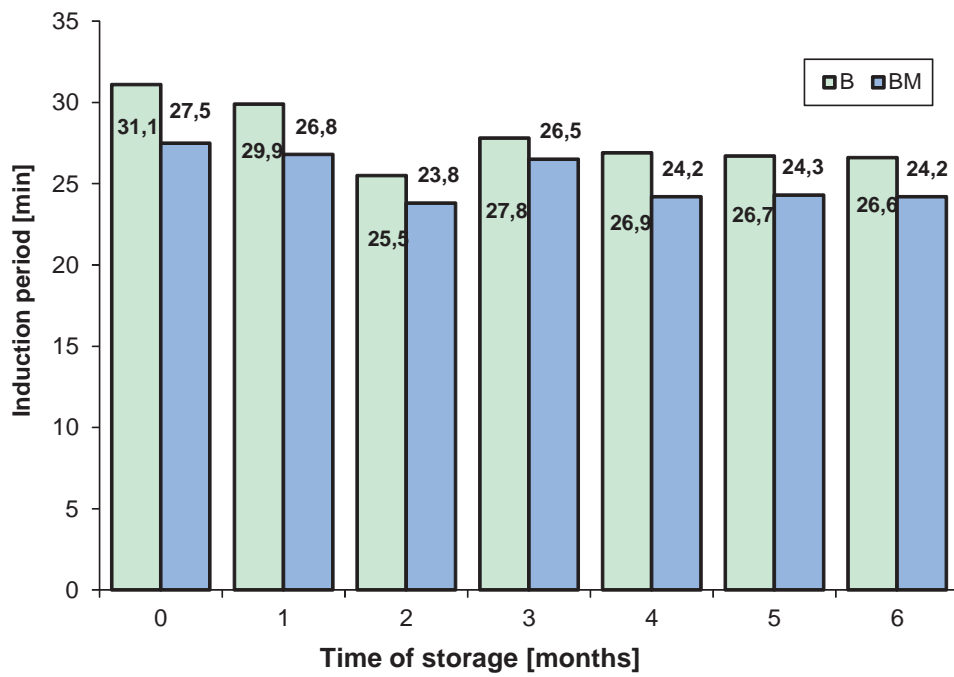


Figure 15. Induction period according to EN 16091 for diesel oil samples with a content of 7.2% (V/V) FAME and methylindole.

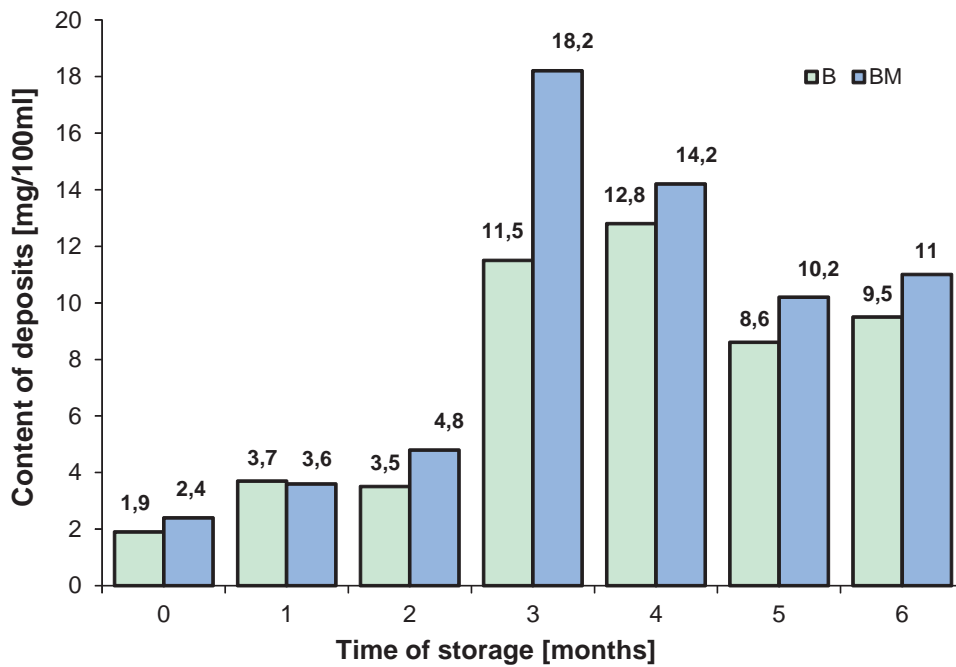
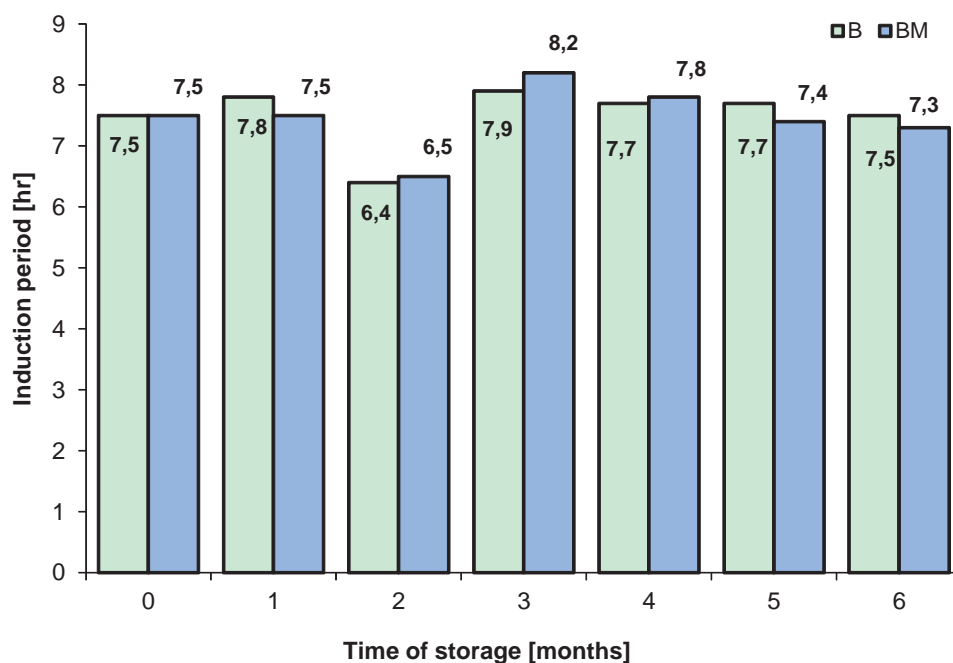


Figure 16. Total insolubles, as found according to ASTM D 5304 for diesel oil samples with a content of 7.2%(V/V) FAME and methylindole.



**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<sup>3</sup> of filterable deposits and 2 g/m<sup>3</sup> of gum; after 6 months of storage - 336 g/m<sup>3</sup> of filterable deposits and 13 g/m<sup>3</sup> 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 accordance 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.

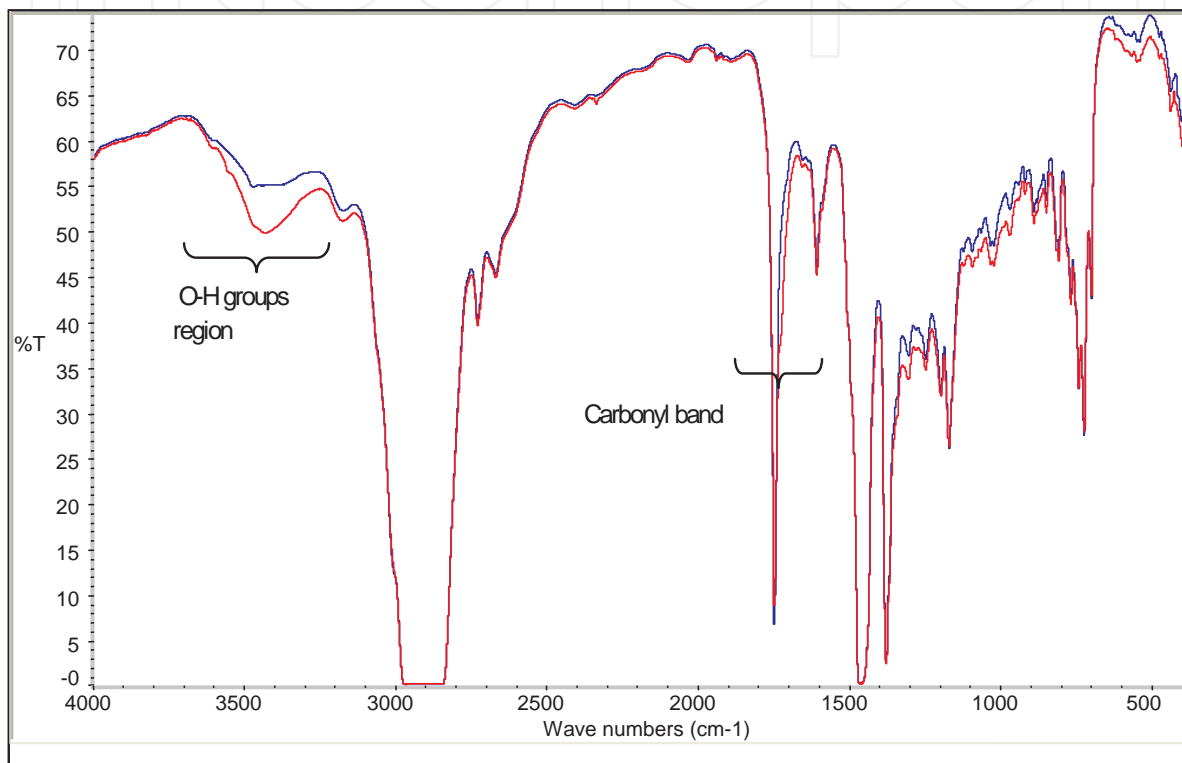
### 3.3. IR spectral analysis

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<sup>-1</sup> and 1800-1600 cm<sup>-1</sup>. For samples A and AM, which had negligible ester contents, changes were less

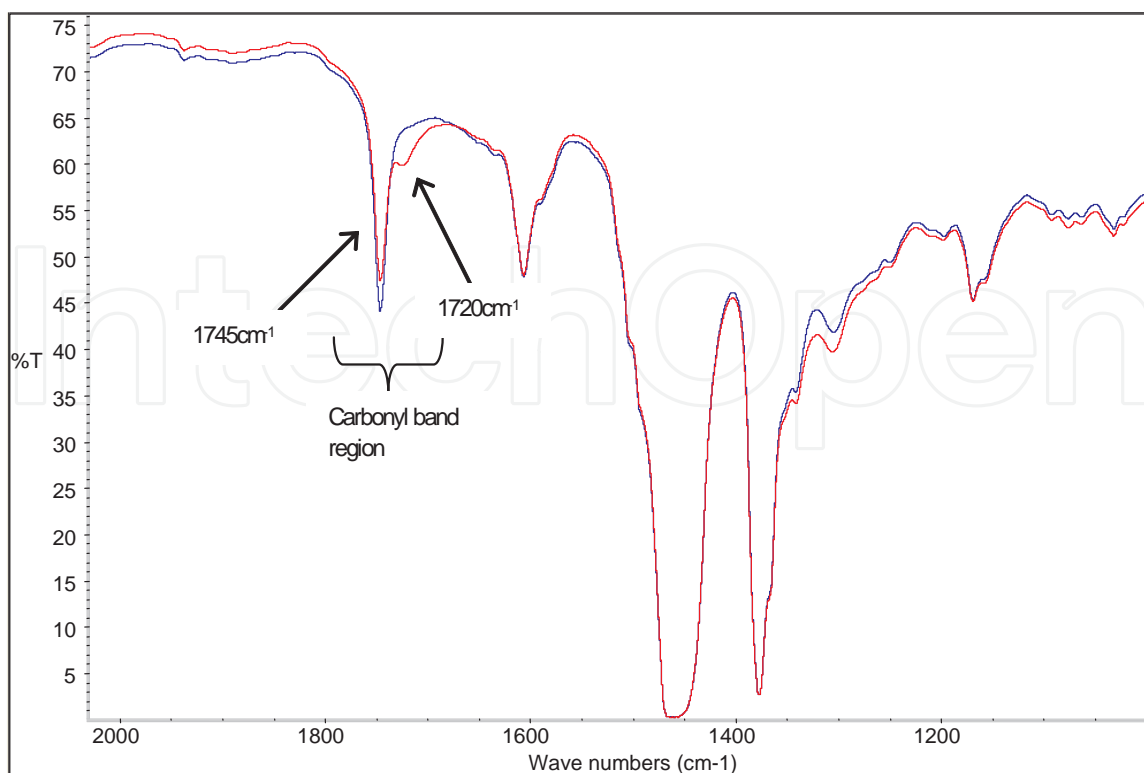
intense than for sample B and BM with a content of FAME of 7.2 % (V/V). In the spectral range 3600-3200  $\text{cm}^{-1}$ , there appears a wide absorption band, connected with valence vibrations for O-H groups. In the range 1800-1600  $\text{cm}^{-1}$ , there is a visible narrow carbonyl band, connected with the presence of fatty acid methyl esters (1745  $\text{cm}^{-1}$ ) 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  $\text{cm}^{-1}$  range, there appears a second band, at 1720  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$ , 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<sup>-1</sup> 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<sup>-1</sup> peak, another one is formed at 1720 cm<sup>-1</sup>, 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 3<sup>rd</sup> and 4<sup>th</sup> 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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