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Study of Stability Changes of Model Fuel Blends

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Abstract

Fuel during long-term storage, even at low temperatures, undergoes oxidation to various products, which are further converted into high molecular compounds precipitating from the liquid. The stability of the stored fuel depends on its chemical composition and storage conditions. Chemical conversions associated with the degradation of fuel are not well recognized, so it is difficult to predict the storage duration of such fuel and control the rate of ageing. Because of the variety of hydrocarbon composition of commercial fuels resulting from the diversity of crude oil and oil processing methods, surrogate fuels are used for simulating behaviour of commercial fuels in the various tests. In this paper, the type and dose of model components of fuel were chosen. To determine the degradation degree of model blends, few tests of accelerated ageing were selected. These methods were used to determine induction period, content of deposits and resistance to oxidation. Effect of inhibiting and catalyzing compounds on fuel oxidation was verified. An infrared spectroscopy analysis of the oxidized model blends was also performed. The results of this study showed slight changes of selected properties of the surrogate fuels. The most significant changes occurred for the model blends containing substances initiating radical autoxidation reactions and bio-components.

Keywords: model fuels, hydrocarbons, oxidative stability, induction period, accelerated ageing test

1. Introduction

Chemical stability of fuel, in terms of resistance to changes during storage and distribution, is an important parameter determining its quality. Processes deteriorating the fuel properties include, among others, oxidation. The oxidation products are chemically active substances and undergo further transformations to non-volatile macromolecular substance (resin), and the particulates precipitate in the form of deposits/sediments. Fuels, even under stable storage

conditions, can undergo autoxidation, where the hydrocarbon molecules react with atmospheric oxygen or with themselves [1].

There is an abundance of literature on fuel instability [2–13]. Nevertheless, reactions related with the degradation of the fuel are not well researched, so it is difficult to predict the rate and direction of changes of the fuel properties during storage and distribution. In addition, the diversity of the composition of hydrocarbon in commercial fuel species resulting from the variety types of processed crude oil and refinery technologies makes it difficult to determine the mechanisms of these changes. There are many theories describing the mechanisms of oxidation of petroleum products [14].

Generally, it is assumed that the fuels are oxidized by a radical mechanism, whereby the hydrocarbons are involved in radical chain reactions in the following sequence: initiation, propagation, branching and chain termination. The initiation reaction known as the initiation of an oxidative chain reaction begins with an attack of oxygen molecules from the air on the C-H bond in the hydrocarbon molecules. As a result, alkyl radicals (the radicals react with oxygen to hydroperoxides, which are aggressive oxidants) are formed. Decomposition products of peroxides are active alkoxy and hydroxyl radicals, which in the following reaction steps detach another hydrogen atoms from the hydrocarbons (propagation phase and chain branching). The last phase of hydrocarbon oxidation is termination, which is the completion of the reaction, where due to the recombination of hydrocarbon and peroxide, free radicals become deactivated creating non-radical products, for example, alcohols, ketones and acids, which can undergo further transformations to macromolecular substances. Among others, Denisov [15] described in detail oxidation of hydrocarbons in the liquid phase. However, we still do not know how an oxidation chain, in the absence of oxidation promoters such as sunlight, a source of free radicals and metal ions, is formed.

It is considered that the chemical structure of hydrocarbons has an influence on the rate of oxidation processes of petrol. The studies presented in the article [5] have shown that in petrol the tendency to produce resins depends on the amount and type of unsaturated hydrocarbons. In the case of petrol fractions from the cracking process, the presence of active radicals and trace amounts of metal ions originating from the catalyst was found. Pereira et al. [6] proved that not all of the olefins presented in the fuel are transformed equally to resins. Among tested olefins, those that formed the secondary allyl radicals (2,4-hexadiene and cyclohexene) had the largest share in the formation of macromolecular substances. These compounds are classified, respectively, to the unsaturated hydrocarbons with conjugated bonds and cyclic olefins. The considerations regarding to the stability of allyl and alkyl radicals and autoxidation reaction mechanism confirming the radical chain reactions were presented. Research of effect of ethanol and copper presence on the stability of petrol [7] showed that the addition of alcohol does not deteriorate fuel stability, whereas copper in the system is undesirable because it accelerates the oxidation processes.

However, in the case of diesel fuels, chemical instability is caused by the presence in the fuel compounds containing nitrogen and sulphur, reactive olefins and organic acids which are precursors of macromolecular structures having a limited solubility. One of the well-recognized mechanisms generating insoluble precipitates in the diesel fuel is conversion of

phenalenes and indoles to indole/phenalene salt complexes, described by Marshman and Davia [8]. An acidic environment is conducive to the reactions. Phenalenes are formed as a result of the oxidation of active olefins, and indoles are a natural component of the fuel. The organic acids (necessary to catalyze the reaction) are typically presented in the fuel components or are formed by oxidation of the mercaptans to sulfonic acids. Li et al. [10] conducted research on the thermo-oxidative stability of aviation fuel. Oxidation processes were followed by determination of hydroperoxides and FTIR spectral analysis. The results confirmed the theory presented by Zabarnick [11] that the fuel oxidation occurs according to the mechanism of free radical chain reactions in which the hydroperoxides can be considered as intermediates for subsequent reactions of hydrocarbon autoxidation. During the tests it was observed that the fuel that contains more polar components is more readily oxidized. Normally, the presence of polar components is the main factor of instability.

The complexity of the hydrocarbon fuel oil composition is a difficult in-depth analysis of the degradation process of the fuel components and consequently the finished fuel which is a mixture of hundreds of compounds. The chemical composition of the fuel determines the physicochemical properties and influences on the engine operating characteristics [16]. Commercial fuels, depending on a producer, may differ from each other in terms of composition and physicochemical properties. Fuel oxidation and its stability issues were studied by numerous scientists for simple systems using pure hydrocarbons, representative for each fuel type or model mixtures. A key decision about the composition of the model fuel is a selection of the individual compounds—most often pure components representing a hydrocarbon groups (it is assumed that their chemical interactions are typical of other similar chemical structures) are selected for the composing process.

Gernigon et al. [17] conducted a study aimed at recognition of the oxidation mechanisms of aviation fuel. The research was performed for model mixtures containing such mono-compounds as n-dodecane, 1,3-diisopropylbenzene, cyclohexylbenzene and 2,2,4,4,6,8,8-heptamethylnonane in characteristic proportions of the natural composition of the fuel. Studies of the decomposition kinetics of hydrocarbons showed that after 48 hours, test diminished from 40 to 80% of each of mono-compounds. For all hydrocarbons, two stages of degradation were recorded: the first is the rapid decrease in the hydrocarbon content during the first hour of the experiment; a second step, after approx. 8 hours, is characterized by slow 'consumption' of hydrocarbon and has an almost linear behaviour. IR spectrum analysis indicated that the new structures are formed, because with increasing time, the degradation of characteristic band intensity, for the compounds formed by the oxidation (OH, C-O, C=O), increases. The antioxidants used during the tests slowed down the hydrocarbons degradation.

Li et al. [10] used n-cetane of 99% purity as a reference fuel for spectroscopic studies of oxidized fuels. Natelson et al. [18] conducted a comparative study of aviation fuel and diesel reactivity with respect to mixtures of chemical compounds that have been selected as a model fuel (surrogate of diesel and aviation fuel). The studies described herein have focused on three substitutes, from three hydrocarbon groups (paraffins, naphthenes, aromatics), which are in the aircraft fuel and diesel. In order to maintain the small number of elements for modelling, one component from each of these groups was selected. N-decane ($C_{10}H_{22}$) was the

representative of paraffins, n-butyl cyclohexane ($C_{10}H_{20}$) was representative of naphthenes, and n-butylbenzene ($C_{10}H_{14}$) was a representative of aromatics. The surrogates have been used in respective proportions, depending on the structure and key features of the real fuel. The surrogate reactivity was compared to the average of ordinary aviation fuel and commercial diesel used in the United States.

The authors of following research conducted the study on the stability of diesel fuel during long-term storage and the results presented in the work [1]. In the case of petrol, after 6-month storage, in the IR spectra, slight change in the chemical composition was found. The oxidation-promoting substances, i.e. cyclic olefins and hydroperoxide intentionally added to the stored fuel, slightly influenced on intensification of transformation process. The study of induction period and potential resins content showed the potential adverse changes in petrol stability, which were poorly correlated with changes demonstrated by IR spectroscopy. However, in diesel fuel samples after 3–4 months of storage, there was a significant increase in the content of sediments. The IR spectra confirmed the changes in the chemical composition of the fuel. In the stored samples appeared degradation products of hydrocarbons, containing functional groups characteristic for acids, aldehydes, ketones and phenols, conducive to further reactions leading to the formation of indole/phenalenes.

Aforementioned studies were carried out for commercial fuels containing hundreds of chemical components of different elemental compositions and structures. Standard tests determining the petrol stability which include induction period [19] and resins content [20] are laborious and time-consuming. Also, the tests do not allow for early detection of changes in the fuel stability, which are visible on the IR spectra. The situation is similar in the assessment of stability of middle distillates; the scientists have much more methods to evaluate this parameter [21–24]. The authors have attempted to assess the stability of petrol using a quick and simple method of induction period at the micro level. To eliminate the influence of a large number of compounds presented in petrol and the interactions between them, the study was carried out for the model mixture replacing commercial petrol. Furthermore it was checked how the presence of the chemically unstable component (cyclohexene) changes the oxidation stability of model petrol. The induction period for the model mixture with the addition of oxygenated compound (ethanol) that improves the octane number was also determined. The studies relating to the stability was conducted for the model fuel replacing diesel. Due to the fact that during storage, middle distillates more rapidly degraded than petrol fractions, in addition to conventional ageing tests to assess the stability of the fuel at the time of storage, an accelerated ageing test at 45°C based on ASTM D 4625 [25] was conducted. The increased temperature helps to speed up the reactions occurring in the fuel during storage under conventional conditions.

2. Tests of chemical stability research of model blends

The induction period (micro method) based on the EN 16091 [24] standard was used to evaluate the chemical stability of model fuels (replacing petrol). In the micro method, induction period is defined as the time elapsed from the start of the study to the critical point

determined by the pressure drop of the test system by 10% compared to the maximum pressure registered during oxidation. The fuel ageing process was performed at 140°C, the initial oxygen pressure at 500 kPa and the amount of sample at 5 ml. The principle of measurement in the above-mentioned norm is similar to the principle used in the Standard ISO 7536 [19]. The micro method is less labour intensive than the ISO 7536 standard, which normally is used to assess the stability of commercial petrol.

The chemical stability of selected petrol model mixtures was also evaluated by the ASTM D 873 method [26]. It determines the fuel potential to create resins and sediments. In this method, petrol is oxidized by 4 hours at 100°C in oxygen atmosphere at a pressure of 690–705 kPa. The test result is given as the contents of potential resins (the total amount of insoluble and soluble resins). Insoluble resins—precipitate adjacent to the glass wall of the test cell, from which the oxidized fuel was removed, precipitation and soluble resins—are determined by weight gain of test cell after the study, compared to the mass of clean test cell before the examination. The oxidation products present in the fuel after ageing in dissolved form in the oxidized fuel or as deposits adhering to the walls of the test cell, soluble in toluene-acetone, are soluble resins.

Four most commonly used methods of testing the degree of diesel oils and their surrogate degradation were selected. All of them are methods of accelerated ageing. Since one of the characteristics of the fuel ageing process is the deposit formation, two of this type of tests were selected for the research, including ASTM D 5304 [21] and EN ISO 12205 [22], where the amount of insoluble filterable sediments precipitated during the test and retained on the filter and the resin adhering to the walls of the test cell is determined. At the same time, to verify the theory of the possibility of the fuel degradation without producing deposits, it was decided on two another oxidation stability tests EN 16091 [24] and EN 15751 [23], where the result is presented in minutes or hours. The EN 15751 test is dedicated to a fuel containing at least 2% v/v of fatty acids methyl esters, and the induction period measured by this method is the time from the start of measurement to the moment, where the formation of oxidation products recorded by changes in conductivity begins rapidly increase.

The tests conditions were as follows:

ASTM D 5304—temperature, 90°C; oxygen atmosphere at a pressure of 800 kPa; time, 16 hours

EN ISO 12205—temperature, 95°C; oxygen barbotage; time, 16 hours

EN 16091 (called PetroOxy test)—temperature, 140°C; oxygen pressure of 700 kPa

EN 15751 (called Rancimat test)—temperature, 110°C; air flow

Spectrophotometric analysis of model samples or their components, before and after accelerated ageing by PetroOxy test, was carried out using a Magna 750 FT-IR spectrophotometer (Nicolet). The spectra measurements were performed in KBr cuvette having a thickness of 0.065 mm in the range of 4000 to 400 cm^{-1} .

Long-term ageing test was carried out to determine the oxidative stability of the fuel during the long-term storage. The fuel samples were placed in a thermostatic chamber at 45°C in

vented glass bottles. At set intervals, another bottle with the fuel was removed from the chamber and deposit content was determined.

2.1. Model blend replacing petrol: stability test results

For the preparation of model petrol, the following hydrocarbons were used: n-heptane representing paraffins; isooctane, branched-chain alkanes; cyclohexane, cyclic alkane; toluene, aromatic compound; and cyclohexene, olefin. A non-hydrocarbon component—anhydrous ethanol—which is added to petrol to increase the octane number was also used. The organic peroxide (tertiary—butyl hydroperoxide TBHP) dosed in an amount of 50 mmol/l was used to prepare and simulate the oxidized fuel [27]. The two antioxidants, one being a mixture of sterically hindered phenols (AO-1) and the second—phenylenediamine (AO-2)—were used to improve the oxidation resistance of the selected compositions.

In addition, commercial petrol with research octane numbers 95 (95 RON) and 98 (98 RON) and fuel fractions used for petrol composing, i.e. cracked naphtha, alkylate and reformat were studied. Petrol 95 RON contained ethanol.

The composition of tested model petrol for ageing tests is shown in **Table 1**. Data concerning the major components of the commercial petrol in Europe presented in the publication [28] were used to determine the volume fractions of various hydrocarbons. The MP_2 mixture was prepared by mixing a volume ratio of 95:5 MP_1 petrol with anhydrous ethanol. Similarly, the MP_3 and MP_4 fuels were prepared, whereby cyclohexane was added instead of alcohol. The MP_5 fuel consisted of 90% v/v MP_1, 5% v/v ethyl alcohol and 5% v/v cyclohexene.

Symbol	Composition	Components (% v/v)					
		Heptane	Isooctane	Cyclohexane	Toluene	Cyclohexene	Ethanol
MP_1	–	14.5	36.5	11.7	37.3	–	–
MP_2	95% v/v MP_1 5% v/v Ethanol	13.8	34.8	11.1	35.4	–	5.0
MP_3	95%v/v MP_1 5% v/v Cyclohexene	13.8	34.8	11.1	35.4	5.0	–
MP_4	93%v/v MP_1 7% v/v Cyclohexene	13.5	34.0	10.8	34.7	7.0	–
MP_5	90%v/v MP_1 5% v/v Cyclohexene 5% v/v Ethanol	13.0	32.9	10.5	33.6	5.0	5.0

Table 1. Chemical composition of model petrol for ageing tests.

Induction period of hydrocarbons and ethyl alcohol is shown in **Table 2**. Among the tested compounds, the induction period using micro method was determined for cyclohexane, cyclohexene and ethanol. In the case of other pure compounds, after 360 min (6 hours) of test, there was no pressure drop meeting the criteria of the critical point. For comparison, induction period of fuel fractions, which are used for composing petrol, was determined. The tests were performed for three refinery fractions—the cracked fractions comprising about 20% v/v of olefins and aromatics, alkylate consisting only of paraffins and reformat— which the major component was aromatic compounds. The test results indicate that, among petroleum fractions, the cracked fraction containing unsaturated hydrocarbons undergoes the fastest oxidation.

Components	Induction period at 140°C, (EN 16091) min
Heptane	Not determined*
Isooctane	Not determined*
Cyclohexane	311.12
Toluene	Not determined*
Cyclohexene	11.31
Ethanol	298.17
Cracked naphtha	33.5
Alkylate	63.5
Reformat	79.9

*Recorded pressure drop was less than 10% after 360 min of the test.

Table 2. Induction period of pure hydrocarbons, ethanol and fuel fractions.

The values of the induction period for model mixtures determined by a micro method are shown in **Table 3**. Comparatively, the results for the commercial petrol of 95 research octane numbers (95RON) and (98RON), to which deliberately introduced 3% v/v cyclohexene (OLEF), were presented in the article. Petrol 95 RON contained 5% v/v ethanol.

	Model petrol					Commercial petrol			
	MP-1	MP-2	MP-3	MP-4	MP-5	95RON	95RON + OLEF	98RON	98RON + OLEF
Induction period, min	Not determ*	Not determ*	91.5	88.75	Not determ*	44.1	34.9	47.9	39.8

*Recorded pressure drop was less than 10% after 360 min of the test.

Table 3. Induction period determined by micro methods according to PN-EN 16091.

The MP-1 hydrocarbon fuel was chemically stable. The addition of cyclohexene, which, according to the literature [6], is easily oxidized, affects the chemical stability of the MP-1 model fuel. The higher the content of this compound, the shorter the induction period of MP-3 and MP-4 mixture. The effect of oxygen compound (ethanol) to this parameter was also

checked. Ethanol did not deteriorate stability of the MP-1 fuel, moreover positively affected the stability of the fuel comprising cyclohexene—the MP-3 mixture broke after 91.5 min, and for the mixture containing both cyclohexene and ethanol (MP-5), after 6 hours (360 min) of the test decrease in oxygen pressure in the system was less than critical 10%. In the case of commercial fuels, tested samples were characterized by a much shorter induction period than the model fuel. The addition of di-olefins (OLEF) in the amount of 3% v/v caused a sharp decline in the value of this parameter.

The obtained results of the induction period were confirmed by the tests of potential resins according to ASTM D 873, as shown in **Table 4**. As a result of the oxidation, the insoluble deposits have formed only in the case of MP-3 mixture (containing cyclo-olefin). The presence of soluble deposits has been found for all tested mixtures; the lowest value was observed for the base composition containing neither cyclohexene nor ethanol. Comparatively the oxidation of fuel samples available on the market was carried out.

Parameter	Unit	Model petrol				Commercial petrol			
		MP-1	MP-2	MP-3	MP-5	95RON	95RON + OLEF	98RON	98RON + OLEF
Soluble gum	mg/100 ml	0.1	0.3	0.3	0.2	31.9	33.9	22.3	25.5
Insoluble gum		0.0	0.0	0.4	0.0	0.2	1.1	0.3	1.2
Potential gum		0.1	0.3	0.7	0.2	32.1	35.0	22.6	26.7

Table 4. Content of potential resins in the model mixtures according to ASTM D 873.

Induction period of model petrol and the commercial petrol, where the oxidation effect was simulated by the addition of TBHP as a source of radical \cdot , was examined using micro method mixtures. The obtained results are shown below (**Table 5**):

Parameter	Model petrol				Commercial petrol			
	MP-1 + TBHP	MP-2 + TBHP	MP-3 + TBHP	MP-5 + TBHP	95RON	95RON + TBHP	98RON	98RON + TBHP
Induction period, min	Not determ*	Not determ*	22.3	52	44.1	17.5	47.9	26.2

*Recorded pressure drop was less than 10% after 360 min of the test.

Table 5. Induction period of model fuels and petrol with TBHP determined by the micro method.

The addition of peroxide to the model mixture resulted in a deterioration of oxidation resistance of samples containing the cyclic olefin (MP-3, MP-5). The samples without the addition of cyclohexene did not 'break' during the test run for 6 hours. In contrast, commercial fuels with intentionally introduced TBHP are characterized by significantly lower induction period when compared to fuel without the addition of this substance.

Two antioxidants were used in order to improve the oxidation resistance of the MP-3 sample. One of them, defined as AO-1, comprises a mixture of mono-*tert*-butylphenol, di-*tert*-butylphenol and tri-*tert*-butylphenol as active substance; the second (AO-2) comprises *N,N'*-di-*sec*-butyl-*p*-phenylenediamine as the active ingredient. The effect of antioxidants was evaluated by the induction period using the micro method. The activity of antioxidants in petroleum fractions was checked. The results, given in **Table 6**, clearly show that in the tested systems, the addition of an amine is more effective.

	Induction period, min				
	Without additives	+60 mg AO-1/1 kg MP-3	+100 mg AO-1/kg MP-3	+25 mg AO-2/1 litre MP-3	+43 mg AO-2/1 litre MP-3l
MP-3	91.5	Not determined*	–	Not determined*	–
Cracked naphtha	33.5	48.7	67.3	60.3	87.3
Alkylate	63.5	73.5	86.8	205	Not determined*
Reformate	79.9	114.4	149.4	Not determined*	Not determined*

*Recorded pressure drop was less than 10% after 360 min of the test.

Table 6. Induction period of MP-3 model mixture and petroleum fractions with addition of antioxidants.

The induction period of the MP-3 mixture with the addition of antioxidants, for which conditions of oxidized fuel were simulated by the addition of TBHP, was also studied. The tests were performed in two variants: (1) antioxidant and peroxide were added to the model mixture, and (2) an antioxidant was introduced to oxidized by peroxide sample. Similar results were obtained, regardless of the order of addition of the additive and peroxide. **Table 7** contains the induction period for option 2.

	Model fuel MP-3				
	+ TBHP	+ TBHP+60 mg/kg AO-1	+ TBHP+100 mg/kg AO-1	+ TBHP+25 mg/l AO-2	+ TBHP+43 mg/l AO-2
Induction period, min	22.3	22.5	23.5	32.1	36.0

Table 7. Induction period of MP-3 model mixture containing antioxidant additive and TBHP.

Antioxidants, both phenolic and amine, advantageously improved chemical stability of the fuel. However, their effectiveness was influenced by the presence of superoxide radicals, which is confirmed by the test results shown in the table above. It can be assumed that antioxidants introduced into the fuel, which is already occurring processes associated with oxidation, do not fulfil their protective function.

2.2. Model blend replacing diesel oil: stability test results

Diesel fuel, same as petrol, is a mixture of many hydrocarbons of various structural features. The following hydrocarbon groups are in the oil: n-alkanes, iso-alkanes, cycloalkanes, ole-

ins, aromatics and polyaromatics. Most of hydrocarbons have 15–17 carbon atoms in the molecule, the least hydrocarbons containing less than 9 and more than 23 carbon atoms in the molecule. Diesel fuel usually contains 40–50% by weight of paraffins, 20–30% by weight of cycloparaffins, 5–15% by weights of aromatics, 2–7% by weight of olefins and up to 7% by weight of fatty acid methyl esters (FAME). A disadvantage of esters is their low resistance to oxidation. In contrast to the ‘pure’ diesel fuel, esters added to the fuel make it more susceptible to oxidation or autoxidation during prolonged storage.

In the present study, n-hexadecane (n-cetane), n-butyl cyclohexane, n-butyl benzene and fatty acid methyl esters were used to compose the model diesel fuel.

The first stage of the study included accelerated oxidation tests of hydrocarbons and fatty acid methyl esters. An induction period examination (according to EN 16091 standard) has been used for this purpose. The analysis of possible changes in the quality of oxidized samples of mono-compounds on the basis of the IR spectrum was also conducted. The induction period results are shown in **Table 8**.

Component	Induction period at 140°C (EN 16091) min
n-Cetane	80.57
n-Butyl cyclohexane	61.83
n-Butyl benzene	175.55
FAME	27.33

Table 8. Induction period of pure ingredients and FAME.

For all the tested substances, there was a 10% decrease in oxygen pressure in the measuring chamber (on this basis the induction period was determined). N-butyl cyclohexane (saturated cyclic hydrocarbon) was the least resistant to oxidation at elevated temperature. N-butyl benzene (aromatic hydrocarbon with an aliphatic side chain) was the most stable compound. Among the four tested components, fatty acid methyl esters demonstrated the lowest resistance to oxidation. The changes that occurred as a result of accelerated oxidation of each model hydrocarbons were visible in IR spectrum. Products of hydrocarbons oxidation occurred in two spectral ranges. For a hydroxyl group, a broad band was from 3600 to 3300 cm^{-1} (with a maximum of about 3500 cm^{-1}), whereas for the carbonyl group, bands were in the range from 1750 to 1650 cm^{-1} (characteristic for oxidation products such as carboxylic acids, aldehydes, esters, ketones). Each position of the bands may undergo some shifts depending on the structure of the compound and the proximity of other groups. **Figure 1** shows an example of one of the tested hydrocarbon (n-cetane) spectra, before and after accelerated oxidation.

In the spectrum of n-cetane after oxidation, there are three peaks at a wavelength of 1710 cm^{-1} , 1714 cm^{-1} (area A) and 3558 cm^{-1} (area B). These peaks are not present in the spectrum of the n-cetane before oxidation. Peaks at 1710 cm^{-1} and 1714 cm^{-1} are characteristic for carbonyl groups (C=O) and are evidence of carbonyl compound formation in the n-cetane, while the third band at 3558 cm^{-1} indicates the formation of hydroxy compounds (–OH). A similar spec-

trum was obtained for the oxidized n-butyl cyclohexane, with the difference that was only one characteristic carbonyl peak. In the spectrum of the n-butyl benzene, changes were observed only in a range of the carbonyl band, and compounds with hydroxyl group were not formed. In the spectra of fatty acid methyl esters, there were no changes within the carbonyl band (the band is characteristic for esters), whereas area under the hydroxyl peak significantly increased.

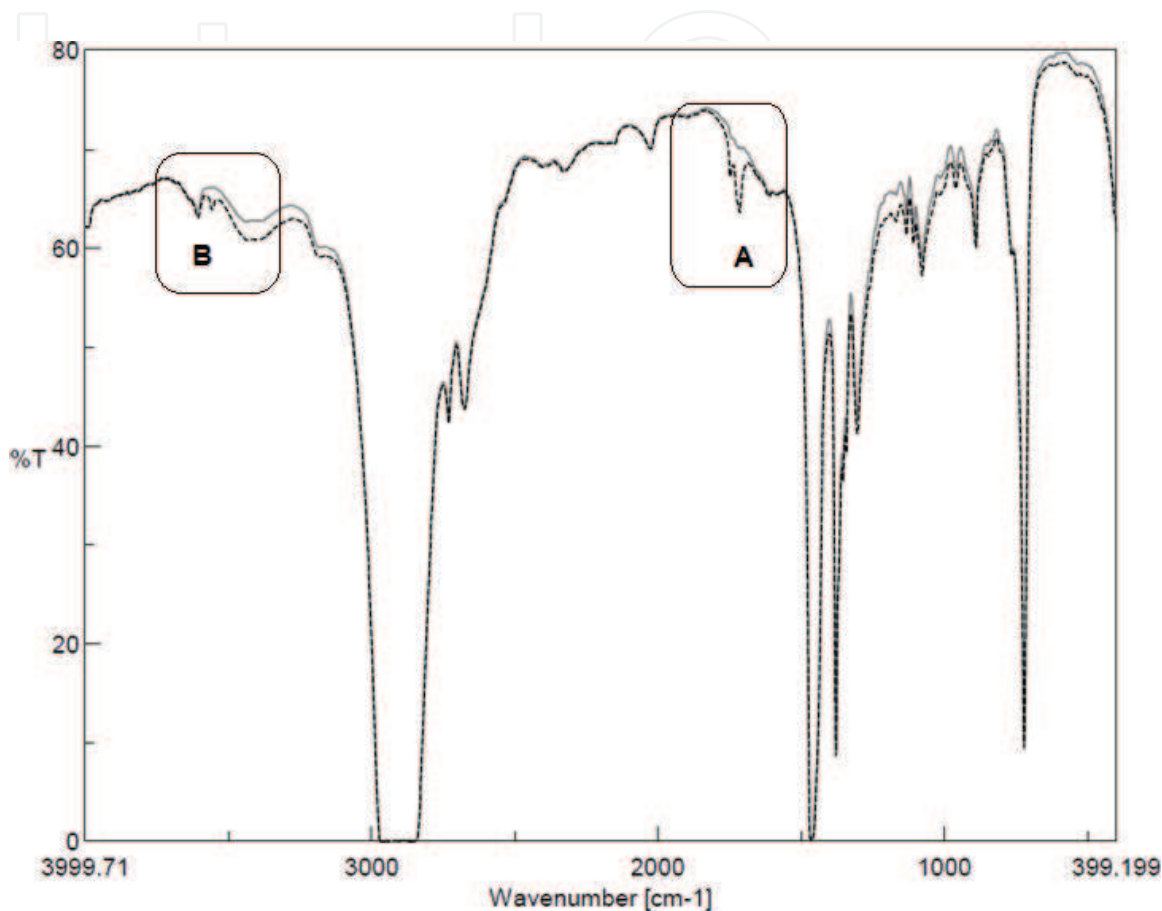


Figure 1. Comparison of the n-cetane before oxidation IR spectra (solid line) and after oxidation (dashed line).

The model mixtures (the composition is given in **Table 9**) were prepared for the tests of resistance to oxidation. Two mixtures were selected: the first mixture composed exclusively of hydrocarbons (M0) and the second one composed of hydrocarbons enriched with biocomponent—fatty acid methyl esters (M7).

Components	Model fuel M0, %(v/v)	Model fuel M7, %(v/v)
n-Cetane	50	46.5
n-Butyl cyclohexane	28	26.0
n-Butyl benzene	22	20.5
FAME	0	7.0

Table 9. Composition of the model blends.

The test of accelerated oxidation according to the previously described EN 16091 standard (PetroOxy test) was used for the mixture oxidation. In the case of the M7 mixture (containing FAME), additionally the oxidative stability examination according to EN 15751 (Rancimat test) was performed. The results are shown in **Table 10**.

Model fuel	Oxidative stability (EN 15751), h	Induction period (EN 16091), min
M0	–	110.90
M7	38.20	92.58

Table 10. Results of the oxidative stability of the blends of M0 and M7.

For the both studied mixtures, there was a 10% decrease in oxygen pressure in the measuring chamber; therefore, the induction period has been determined. The M7 mixture, due to the presence of methyl esters, was less resistant to oxidation than M0 blend. Comparative analysis of the IR spectra showed that in the M0 mixture after oxidation carbonyl compounds with characteristic bands 1715 cm^{-1} and 1743 cm^{-1} , shown in **Figure 2** within D area and wide, expanding bands characteristic for hydroxyl groups (C area). In the spectrum of oxidized M7 mixture containing fatty acids methyl esters are not substantially changed within the carbonyl band, because in this spectral range lies peak characteristic for esters. There was however a slight increase of the area of 1743 cm^{-1} the carbonyl band with a typical inflexion point of the peak at 1743 cm^{-1} , which indicates the formation of oxidation products. In **Figure 2** the spectra of the M0 mixture before and after oxidation are shown.

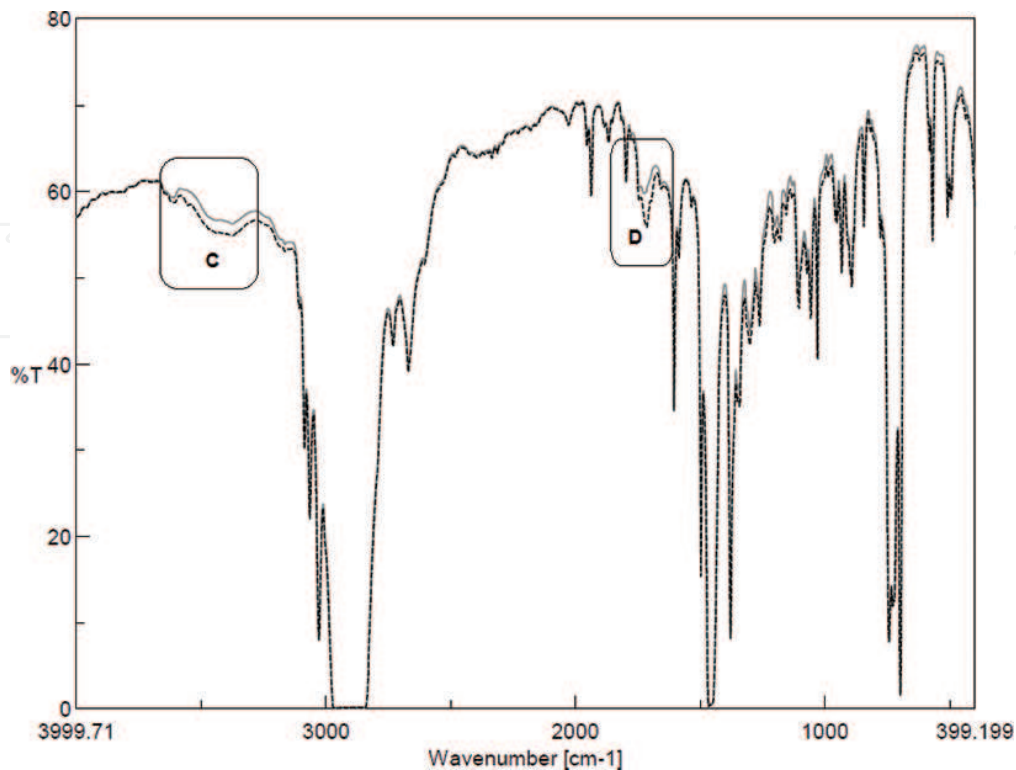


Figure 2. Comparison of the M0 mixture before oxidation (solid line) and after oxidation (dashed line) IR spectra.

2.2.1. Long-term ageing test

2.2.1.1. Model diesel oil

The M0 and M7 model mixtures were stored for 6 months. Every 30 days, measurements of oxidation stability (according to EN 16091 and EN 15751) have been performed, and the amount of sediment has been determined (according to ASTM D5304) for the batch of stored mixtures. The results are shown in **Table 11**.

Storage time, day	Model fuel M0		Model fuel M7		
	Induction period EN 16091, min	Deposit content ASTM D 5304, mg/100 ml	Induction period EN 16091, min	Oxidation stability EN 15751, hr	Deposit content ASTM D5304, mg/100 ml
0	110.90	0.6	92.58	38.2	0.9
30	109.45	0.4	91.90	38.0	0.7
60	110.25	0.6	91.25	37.7	1.1
90	108.83	0.8	90.84	37.8	1.5
120	108.30	0.7	88.55	37.3	2.8
150	107.15	1.0	88.05	37.1	2.6
180	105.52	0.9	86.62	36.4	3.5

Table 11. Results of model fuels storage stability test at elevated temperature.

The M0 and M7 model mixtures had a high stability during conducting long-term ageing test. Induction period measured by PetroOxy test varied slightly for both samples M0 and M7. At the end of the test, threefold increase of the total sediment for the M7 sample was observed. The M0 mixture (without FAME) contained the amount of sludge at a similar level. The M7 mixture had high oxidation stability, 38.2 hours, which decreased slightly during 180 days of storage to 36.4 hours.

2.2.1.2. Diesel oil with various content of FAME

Two samples of commercial diesel fuel containing various amounts of fatty acid methyl esters were examined. The sample A contained 1% by weight of FAME, while sample B, 7% by weight of FAME. The samples were stored at 45°C for 6 months in a dark place and at 30-day intervals were collected for testing in order to determine the amount of deposits formed during fuel storage (ASTM D 5304 test) and determine the induction period (EN 16091 test, EN 15751 test). The results are shown in **Table 12**.

In addition to the above-mentioned tests, the oxidation stability test (according to EN ISO 12205) was performed. The test was performed at the beginning and after 180 days of storage the samples A and B.

At the beginning of the study of the A sample, 7 g/m³ total sludge including 4 g/m³ filterable sludge and 3 g/m³ resins were produced while for the same sample after 6 months of storage, 25 g/m³ filterable sludge and 2 g/m³ resins, 27 g/m³ total.

Storage time, day	Sample A (diesel fuel with 1% FAME)		Sample B (diesel fuel with 7% FAME)		
	Induction period EN 16091, min	Deposit content ASTM D 5304, mg/100ml	Induction period EN 16091, min	Oxidation stability EN 15751, hr	Deposit content ASTM D5304, mg/100ml
0	41.9	1.4	31.1	27.5	1.9
30	38.8	2.4	29.9	27.8	3.7
60	39.7	3.7	25.5	26.4	3.5
90	40.7	4.4	27.8	27.9	11.5
120	37.5	8.2	26.9	27.7	12.8
150	39.5	5.7	26.7	27.7	8.6
180	32.8	7.7	26.6	27.5	9.5

Table 12. Results of commercial diesel oil storage stability test at elevated temperature.

The same for the B sample, at the beginning of the test, the amount of filterable sludge was 7 g/m^3 , and 1 g/m^3 resins, 8 g/m^3 total while for the same sample after 6 months of storage, 56.2 g/m^3 filterable sludge and 2 g/m^3 resins, 58.2 g/m^3 total. The presented data show that with the increase of the sample storage period, the total amount of deposits increases several times. The increase of sediments was mainly caused by the formation of filterable deposits, while the amount of resins did not change.

After 6 months of fuel storage, induction period determined by EN 16091 was lower than at the beginning of the study, for both samples A and B. For A sample the induction period dropped from 41.9 to 32.8 min and for the B sample from 31.1 to 26.6 min. The induction period measured by Rancimat test for B sample containing 7.2% FAME was constant during 180 days of storage fuel.

3. Conclusions

The model fuel as a petrol substitute composed of four hydrocarbons (heptane, isooctane, cyclohexane, toluene) was chemically stable at elevated temperature and oxygen pressure. The addition of a reactive olefin, i.e. cyclohexene caused a noticeable reduction in oxidation resistance determined by an induction period—the higher the content of this compound in the fuel, the lower the chemical resistance. The results of the induction period were confirmed by the study of potential resin content—as a result of oxidation, most deposits were formed in fuels with cyclohexene. Ethanol introduced in an amount of 5% v/v to the model fuel does not have a negative effect on the induction period, whereas the fuel with a cyclic olefin improved the value of this parameter. Antioxidants (phenolic and amine) added to the fuel with cyclohexene improved effectively oxidation resistance. The test of induction period of model fuels, where oxidation was simulated by the addition of TBHP as a source of reactive radicals, showed deterioration of the parameter sample cyclohexene.

Comparative studies conducted using commercial petrol have shown that the model fuel reflects behaviour of real fuel to a limited extent. The main drawback is the lack of a 'breaking'

of MP-1 model fuel designating the induction period of accelerated oxidation tests in micro-scale. It can be assumed that in the model, fuel lacked representative olefin susceptible to oxidizing agents but less reactive than cyclohexane.

The diesel fuel was replaced by the model mixtures, which were prepared from three to four compounds, representative for hydrocarbon groups presented in commercial fuel. Applied hydrocarbons are characterized by a high resistance to oxidation (the induction period was over 60 min). Fatty acid methyl esters, which have been used in studies as components from renewable sources, were the least resistant to oxidation. The IR spectrophotometric analysis of individual hydrocarbons and model mixtures showed that oxidized products with carbonyl or hydroxyl binding (carboxylic acids, aldehydes, ketones) were formed as a result of oxidation.

During long-term ageing tests at elevated temperature, the M0 and M7 model mixtures are characterized by high stability, and the induction period varied slightly with time. Only for the M7 mixture was an increase in the amount of deposits after 6 months of storage, which probably was related with the presence of fatty acid methyl esters in the studied system.

In the case of long-term ageing test of commercial A and B fuels, an increase in the amount of deposits according to ASTM D5304 after 4 months of storage was observed. In contrast, the oxidative stability study using EN ISO 12205 method showed a fourfold and sevenfold increase in amount of deposits, respectively, for A and B samples, indicating that the degradation proceeds more quickly in the fuels with the higher FAME. The oxidation stability of A and B samples decreased with increasing time of storage.

Based on the obtained results, it can be concluded that the model blends of diesel fuel of the composition shown in **Table 9** may be used to predict the oxidative stability of diesel fuels using the method of the induction period EN 16091, and for the samples containing fatty acid methyl esters, the EN 15751 method can also be used. However, model mixtures cannot be used to predict the rate of degradation of diesel fuel expressed as the amount of filterable sediments and resins. The model mixtures, during long-term ageing process, generate a small amount of sediments constant at the same level.

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