EVALUATION OF THE CHEMICAL STABILITY OF DIESEL OIL WITH USING TURBISCAN STABILITY INDEX (TSI)

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Abstract

For diesel oils containing fatty acid methyl esters (FAME), an important problem is their susceptibility to oxidation processes as this shortens the maximum storage time of such fuels and may result in deterioration of oil properties and thus affect the engine operation. One of the fuel ageing processes is the formation and release of resins from the fuel. The physical stability of mixtures may be evaluated by means of a physical stability index, determined with using a Turbiscan analyser [3, 19, 20]. The authors attempted to explore the possibility of using this index for evaluating the changes that take place during the ageing of diesel oil. Additionally, the impact of the presence of selected metals on the fuel ageing process was examined. Within the research, diesel oil samples containing various metals were prepared and subjected to the ageing process. Spectrophotometric tests were also carried out with using a Turbiscan instrument [4, 10, 11]. The samples were subjected to oxidation stability tests before and after the ageing process. The physical stability index and, additionally, the oxidation stability of the samples were examined by accelerated ageing methods.

Keywords: diesel oil; oxidation stability; TSI (Turbiscan Stability Index)

1. Introduction

The necessity of adding biocomponents had a negative effect on the chemical stability of diesel oil. Such problems become particularly well visible during distribution and long-term storage of this fuel. The accelerated deterioration of diesel oil quality chiefly results from the impact of external factors, e.g. contact with oxygen and solar radiation, as the said factors initiate the processes of oxidation and polymerization of the least-stable compounds (e.g. esters with unsaturated bonds), causing the formation of compounds with larger molecules, such as resins. The contact of diesel oil with metals (present e.g. in the construction materials used) may also contribute to the acceleration of oil ageing due to catalytic effects taking place in oxidation reactions.

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The chemical stability of diesel oil is most often expressed by "oxidation stability", i.e. the fuel resistance to oxidation. This is one of the most important parameters defining the fuel storability. Its determining is particularly important in consideration of the necessity of building required reserves and stockpiling of oil products. The impact of harmful external factors during long-term storage may cause the products to undergo ageing and, in consequence, changes in their physicochemical characteristics [15].

During storage, various chemical reactions take place in diesel oil and their rates depend on ambient temperature, storage tank material (metal), presence of moisture [6, 25], access of air, and exposure to sunlight [5, 14]. One of the main reactions observed is thermo-oxidation [13, 30]. Such reactions may cause changes in physicochemical characteristics of the oil, e.g. rise in the peroxide value, growth in the flash point, increase in the kinematic viscosity and acid number, or rise in the resin contents [5, 9, 15]. The thermo-oxidation stability of engine fuels may be improved at the production stage by adding anti-oxidation improvers, such as t-butylated hydroxyanisole (BHA) or 1,2,3-trihydroxybenzene (pyrogallol) [7, 8].

The process of deterioration of the thermo-oxidation stability of fuels, taking place during storage, causes a necessity for the fuel quality to be continuously monitored. This may be done by various analytical methods making it possible to determine the induction period, i.e. the time that elapsed from the start of the test to the instant when the reaction between the fuel and oxygen began: the longer the induction period, the better the chemical stability of the fuel. This may be examined by means of the Rancimat test or the PetroOxy test.

The Rancimat test is the basic diagnostic test employed for examining fatty acid methyl esters used as a fuel biocomponent or a self-contained biofuel. In the test, a fuel sample is subjected to oxidation by air at a constant temperature and the volatile organooxygen compounds formed as reaction products, chiefly carboxylic acids, are absorbed in demineralized water. This causes a change in the specific conductivity of the water, thanks to which the end of the test, i.e. the instant when the value of this parameter rises to a predefined level, can be identified [22]. In many cases, however, the correct carrying out of the test is time-consuming and takes several hours.

Another type of analytical instruments commercially available (PetroOxy) makes it possible to carry out a rapid oxidation stability test. The method of such a test has been described in detail in relevant US standards [1, 2]. However, no information has been provided in those standards about the interrelation between the test results obtained with using the PetroOxy and Rancimat instruments [18].

Both the Rancimat and PetroOxy instruments are intended for determining the chemical stability. The two test types differ from each other in the test duration time: the latter is definitely less time-consuming. However, only the Rancimat method is allowed by the Polish Standard PN-EN 590 for the oxidation stability testing [24] and laid down in the Regulation of the Minister of Economy of 9 October 2015 on the quality requirements for diesel oil. [26]

Another instrument that may be used for fuel stability testing is the Turbiscan analyser. In this case, however, physical rather than chemical stability is determined. More precisely, an answer is sought for the question how the changes that take place during the diesel oil ageing process affect the formation of particles in the oil that may be optically analysed in the Turbiscan instrument. The parameter referred to as TSI (Turbiscan Stability Index) is applicable to physical stability and is calculated by summing variations in the transmission or backscattering of light in successive measurements as a function of sample height [12].

$$d_i = \frac{\sum_h |scan_i(h) - scan_{i-1}(h)|}{H}$$

During the ageing process, resin-type compounds may be formed, which are composed of larger molecules and precipitate from the solution. The Turbiscan instrument is used to assess the stability of mixtures and makes it possible to detect the migration of particles, undetectable with a naked eye, in a solution. The authors wanted to find out whether the changes that take place during the ageing of fuel can be monitored and recorded with using the TSI values determined by means of the Turbiscan analyser.

2. Research methodology

Objects selected for testing

The tests were carried out on diesel oil samples containing up to 6.8% fatty acid methyl esters (FAME) of rapeseed oil, with no improvers. Selected metals, i.e. copper, zinc, and brass, prepared in the form of sheet plates, were put in the diesel oil. Moreover, a solution containing copper ions was added to the oil samples. To check the metal deactivator action, bis(salicylidene)-o-phenylenediamine solution was also added as the deactivator to some of the oil samples.

Synthesis of the metal deactivator

As mentioned above, bis(salicylidene)-o-phenylenediamine was used as a metal deactivator in the tests. This compound was synthesized in laboratory conditions, in a round-bottomed flask, into which 0.1 mole of o-phenylenediamine, 0.2 mole of salicylaldehyde and 100 ml of ethanol were added. The mixture was heated for 20 minutes in a system with a reflux condenser. The flask content was filtered in a funnel and left to reach the room temperature. The deactivator in the powder form was found not to dissolve in diesel oil, even if heated; therefore, 1% solution of the deactivator in toluene was prepared and added to the diesel oil samples.

Preparation of the metal plates

Before use, the test metal plates purchased from outside were thoroughly cleaned with abrasive paper and then washed with acetone in order to remove any contaminations

and oxidized metal surface layer. The appearance of the metal plates has been presented in Figure 1. A ready-made copper solution in oil, in a proportion of 1 000 µg of copper per 1 g of the solution, was purchased and used in the tests as well.

Fig. 1. Metal plates used in the tests: 1) copper; 2) brass; 3) zinc

Preparation of the fuel samples

The fuel to be tested was poured into eight bottles, about 500 ml into each, and the bottles were hermetically corked up. The fuel samples were arranged in pairs, with different metal plates or the copper-in-oil solution being added to individual pairs (the adding of the copper solution produced a metal concentration of 2 ppm in the fuel sample). Prior to applying the metal (plates or copper solution), the deactivator was added to one of the bottles in each pair, with the deactivator concentration being 10 ppm. The test samples have been shown in Figure 2 and the composition of each of them has been specified in Table 1.

Table 1. Composition of individual test samples

Sample symbols	Description of samples
Copper plate (Cu)	Copper plate + 10 ppm of deactivator in fuel (Cu + dea)
Zinc plate (Zn)	Zinc plate + 10 ppm of deactivator in fuel (Zn + dea)
Brass plate (Zn)	Brass plate + 10 ppm of deactivator in fuel (brass + dea)
2 ppm of copper dissolved (Cu r-r)	2 ppm of copper dissolved + 10 ppm of deactivator in fuel (Cu r-r + dea)

Fig. 2. Fuel samples prepared for the tests

The fuel samples prepared for the tests were kept in laboratory conditions in the room temperature (about 20°C) for two weeks. Once a day, the samples were poured into test vials, scanned in a Turbiscan instrument, and returned to the bottles. After 14 days, stability tests were additionally carried out with using Rancimat and PetroOxy instruments.

3. Test equipment

The Turbiscan LAB instrument made by Formulaction is designed for examining emulsions and dispersions and determining physical characteristics of such substances or, more precisely, for determining the size and concentration of particles in a sample [16, 17]. During a test, a cylindrical vial with the substance under test is placed in the instrument and a light beam with a wavelength of 880 nm is emitted from a light source and is analysed by two detectors: one of them, placed behind the sample, analyses the light beam transmitted through the sample under test and the other one, situated at an angle of 45° in relation to the light source, analyses the backscattered light. The instrument enables the sample temperature to be controlled within a range of (5-60)°C. The sample may be scanned over its entire height or the light beam may be analysed at a specific predefined level under interest [29]. A view of the instrument has been shown in Figure 3.

Fig. 3. Turbiscan analyser

When the samples are examined, it is important that the test vials (cells) should be adequately prepared and filled. The meniscus should be flat, free of foam, and always at the same level.

The Biodiesel Rancimat instrument manufactured by Metrohm is used for determining the oxidation stability by the rapid oxidation method in accordance with the relevant standard specifications [22]. During the measurement, an air stream is passed through a diesel oil or biodiesel sample at a temperature of 110°C. The oxidation process runs in accordance with the radical mechanism. The oxidation products are transported with the air stream to a measuring vessel containing distilled water, in which the conductivity is continuously measured. The conductivity vs time curve is an oxidation curve, whose point of intersection with a preselected conductivity level defines the induction period [22, 27]. A schematic diagram of the measuring system in the Rancimat instrument has been presented in Figure 4.
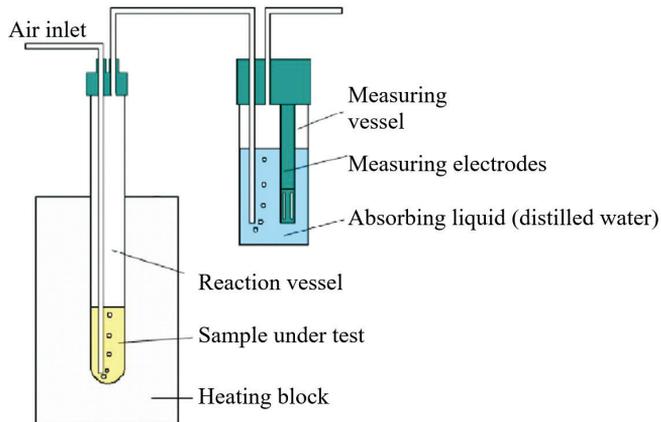
Fig. 4. Schematic diagram of the conductivity measuring system in the Rancimat instrument [28]

The PetroOxy apparatus manufactured by Petrotest is used for determining the oxidation stability by the rapid small-scale oxidation method. The oxidation resistance is evaluated by observing the oxygen pressure drop in a test chamber containing 10 ml of the fuel under test. The test chamber is pressurized with oxygen at 700 kPa (7 bar) at the ambient temperature and then heated to a predefined test temperature of 140°C, when the pressure rises to 1 000 kPa. The test is considered as completed when the oxygen pressure in the test chamber drops by 10% from the maximum pressure value recorded during the test [21, 23]. A view of the apparatus has been shown in Figure 5.

Fig. 5. PetroOxy apparatus

4. Test results and discussion

The authors decided to compare the Turbiscan test results with using TSI (Turbiscan Stability Index). This is a simple way to compare fuel samples with each other and to tell whose physical stability is better. The TSI value is calculated from the light backscattering (BS) and transmission (T) signals. The lower the TSI value, the more stable the sample under test is [29].

To examine the usefulness of TSI measurements for evaluating the stability of fuels, the TSI values recorded were compared with the corresponding PetroOxy and Rancimat test results. The PetroOxy and Rancimat measurement results have been juxtaposed in Table 2. Due to the small quantity of sample and a long time of analysis, the tests with the use of the Rancimat apparatus were carried out only after 14 days.

Table 2. Juxtaposition of measurement results obtained from the PetroOxy and Rancimat instruments

Fuel sample	PetroOxy [min]		Rancimat [h]
Reference (original) diesel oil	128.14	110.79	46.12
Diesel oil with metals (cf. Table 1):	After 7 days	After 14 days	After 14 days
Cu	67.02	64.28	11.05
Cu + dea	96.43	90.92	41.07
Cu r-r	21.45	21.42	1.25
Cu r-r + dea	55.43	42.77	9.51
Brass	33.01	25.38	3.96
Brass + dea	89.92	71.55	33.35
Zn	71.32	52.70	21.28
Zn + dea	90.68	74.78	38.81

As it can be seen from the data given in Table 2, all the diesel oil samples stored in contact with metals showed lower oxidation resistance in comparison with that of the original diesel oil sample. This resistance deteriorated with elapsing time of storage of the samples being in contact with metals and this deterioration reached the highest level after 14 days of storage. The least stable diesel oil sample was the one containing copper solution ("Cu r-r"). The presence of metal deactivator in the samples under test resulted in extended induction time compared with that of the samples with no deactivator; this shows that such an admixture slows down the catalytic action of metals in diesel oil.

Figure 6 shows a comparison of changes in the TSI values recorded for original diesel oil samples scanned for a week in one hour intervals at temperatures of 20°C and 40°C in order to check the impact of temperature on the oxidation stability. Only insignificant differences in the TSI values were recorded for the original diesel oil samples stored in different temperatures. The TSI values were observed to grow similarly for both fuel samples, which indicated that the diesel oil ageing process run for the 14 days in a similar way regardless of temperature.

Fuel destabilization vs time curves (global)
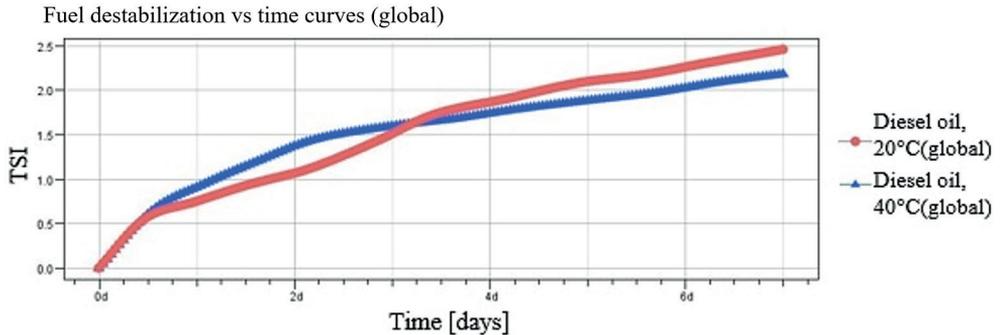
Fig. 6. Comparison of the TSI values recorded for original diesel oil samples stored for a week at temperatures of 20°C and 40°C and scanned in one hour intervals

Figure 7 shows a comparison of the TSI values determined for the samples that contained metal but did not contain metal deactivator. For all these samples, the TSI values increased, showing deterioration in their stability. The lowest stability was observed for the diesel oil sample with a copper plate while the best stability was showed by the sample stored in contact with a zinc plate. The impact of metals on the loss of diesel oil stability could be illustrated by the following ordered series, based on the experiments carried out:

copper > brass > copper solution > zinc.

Fuel destabilization vs time curves (global)
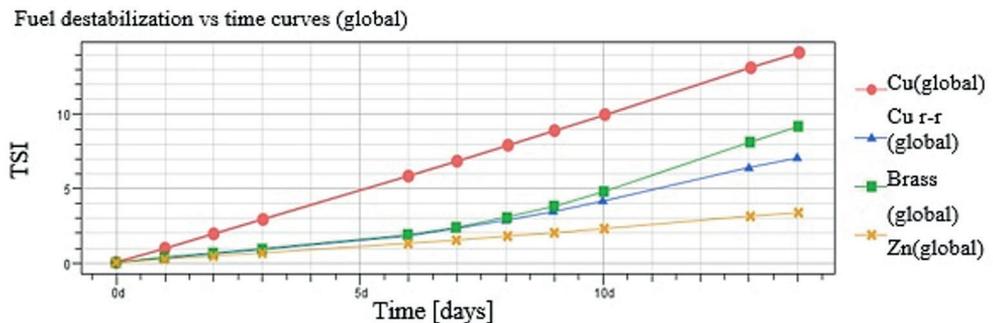
Fig. 7. Comparison of the TSI values recorded for diesel oil samples with metals, stored for 14 days

A comparison of the TSI values determined for the samples that contained metal and metal deactivator has been presented in Figure 8. A growth in the TSI values with time was observed in this case as well, but the nature of these changes differed from that observed for the samples with metal but without metal deactivator admixture. These data show that the least stable diesel oil sample was the one containing a copper plate ("Cu"). The impact

of metals on the loss of diesel oil stability in the presence of metal deactivator may be ranked as follows:

$$copper > copper\ solution > zinc > brass.$$

The deactivator lowered the TSI value, i.e. improved the fuel stability, only in the sample with brass. On the other hand, it raised the TSI value, i.e. spoiled the stability, for the samples with a zinc plate and coper solution.
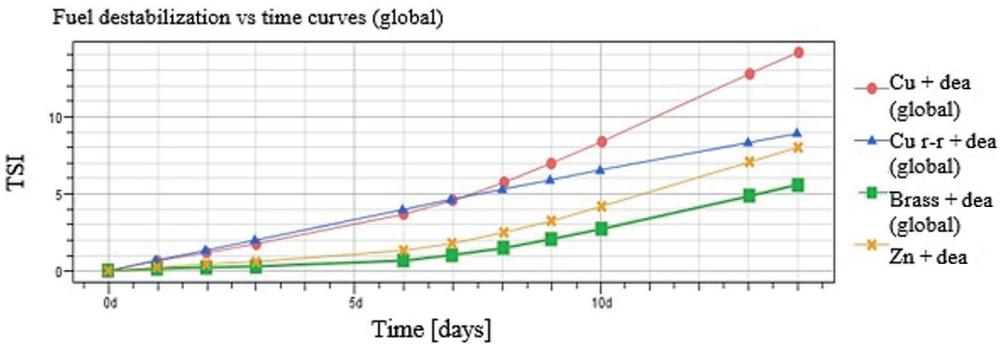
Fig. 8. Comparison of the TSI values for fuel samples with metals and metal deactivator, stored for 14 days

Figure 9 shows changes in the TSI values for the fuel samples with copper plates, with and without the deactivator. Only insignificant differences in the TSI values were recorded. Based on the course of these changes, a finding may be formulated that the deactivator used in the tests exerted a minor effect on the copper activity during the 10-day sample storage period and this impact declined with time, so that both curves began to coincide with each other at the end of the test.
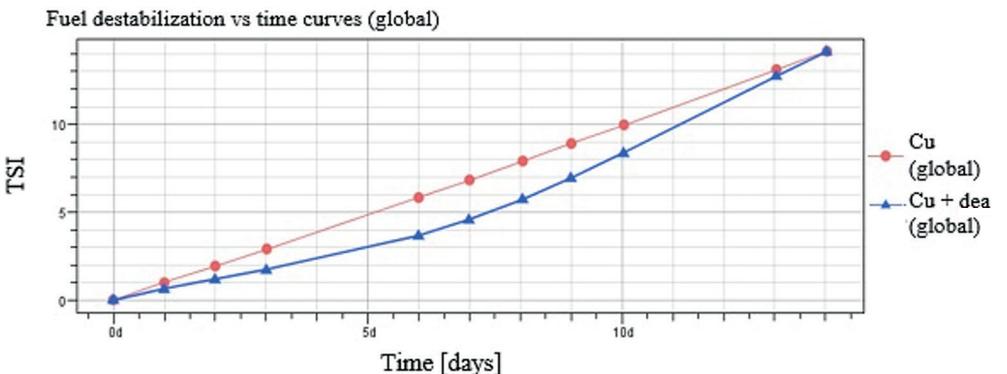
Fig. 9. Diesel oil samples with copper plates, with and without the deactivator, stored for 14 days

Figure 10 shows changes in the TSI values for the fuel samples with copper solution, with and without the deactivator. Here, the deactivator used in the tests was found not to affect the activity of copper (in the dissolved form) for the initial 8 days of the storage period and its effect could only be seen after the end of this stage, manifesting itself in the flattening of the TSI vs time curve. Hence, a statement may be made that the presence of the deactivator improved the stability of the fuel sample.
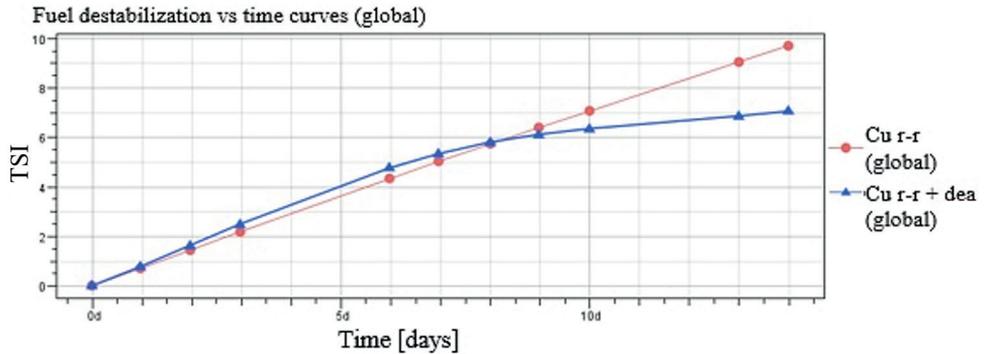
Fig. 10. Diesel oil samples with copper solution, with and without the deactivator, stored for 14 days

A comparison of the TSI values determined for the samples with zinc plates, with and without the deactivator, has been presented in Figure 11. The sample found to be more stable was the one without the deactivator, i.e. for the sample with a zinc plate, the deactivator used in the test impaired the sample stability.
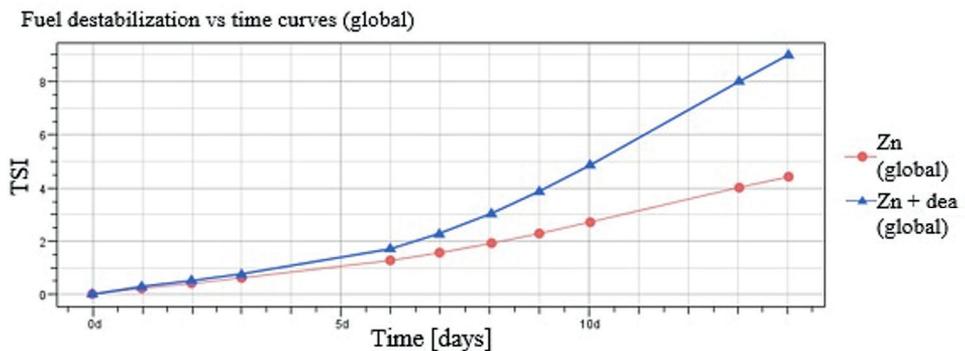
Fig. 11. Diesel oil samples with zinc plates, with and without the deactivator, stored for 14 days

Figure 12 shows changes in the TSI values for the fuel samples with brass plates, with and without the deactivator. The curves have similar shapes, but the TSI values were lower for the sample with the deactivator, which means that the presence of the deactivator improved the stability of diesel oil when the latter was in contact with brass.

Fig. 12. Diesel oil samples with brass plates, with and without the deactivator, stored for 14 days
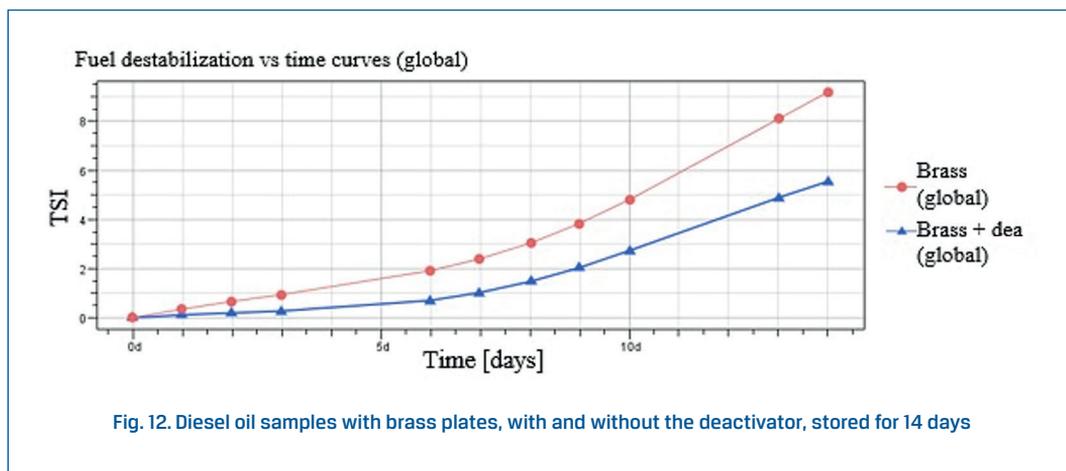
5. Summary and conclusions

Based on the Rancimat and PetroOxy test results (Table 2), an opinion may be formulated that the metal deactivator fulfilled its function and slowed down the catalytic action of metals in diesel oil. For the fuel samples to which the deactivator was added, longer time of the rapid oxidation test was attained. However, tests carried out with using the Turbiscan instrument showed that an opposite effect could be observed in some cases and a fuel sample with the deactivator added was less stable in comparison with a corresponding sample without that admixture. Such a situation took place when a diesel oil sample with a zinc plate was tested at a temperature of 20°C for 14 days. This could be caused by the impact of the deactivator (particle size) on the light transmittance and backscattering value recorded by the Turbiscan instrument, which directly reflects in the TSI value. Such a discrepancy between measurement results makes it difficult to correlate the data obtained from the Rancimat and PetroOxy oxidation analysers with the data obtained from the Turbiscan instrument.

In respect of the TSI values, the diesel oil sample found to be the least stable after 14 days of storage was the one with a copper plate. A comparison between changes in the TSI values recorded after 14-day storage for diesel oil samples with metals and containing metal deactivator shows that the more stable samples were, in ascending order, the samples with copper solution, zinc plate, and brass plate. The attempted use of the Turbiscan instrument does not reflect the impact of the deactivator and such a method should not be employed to assess the deactivating properties of the admixture. During the Rancimat and PetroOxy tests, the lowest stability was shown by the sample with copper solution.

The following conclusions may be formulated, based on the test results obtained:

- Metals have an impact on diesel oil and cause its ageing.
- The bis(salicylidene)-o-phenylenediamine used as a metal deactivator effectively inhibits the catalytic impact of metals.
- The Turbiscan instrument should not be used for examining the oxidation stability; the test results are not correlated with the results obtained from the Rancimat analyser (used in the oxidation stability testing method recommended by the requirements of Polish Standard PN-EN 590: 2013-12 and laid down in the Regulation of the Minister of Economy of 9 October 2015 on the quality requirements for diesel oil). The test results obtained from the Turbiscan instrument, if used for the evaluation of oxidation stability, are ambiguous and different from those obtained from the Rancimat and PetroOxy analysers.

6. Nomenclature

BHA t-butylated hydroxyanisole

BS   light backscattering signal

FAME   fatty acid methyl esters

PN-EN   Polish Standard introducing the European Standard

T   transmission signal

TSI   Turbiscan Stability Index

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