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THE NEW STAND FOR AGING OF BIOCOMPONENTS AND BIOFUELS PROCESS TESTING AT RELATIVELY SHORT TIME

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Abstract

In the paper, the concept of a model bench for accelerated ageing of bio-components and biofuels was presented. It is used to simulate the ageing process of biofuels and components of vegetable or animal origin, taking place during storage in the storage tanks. The construction of the bench's essential elements and its equipment were designed and implemented in such a way as to mostly reflect actual storage conditions in large capacity tanks. An additional and unprecedented function of the bench includes the possibility to simulate the product transport conditions. Furthermore, a method of the test, with the use of simultaneously performed traditional tests on the physical and chemical properties monitored in the process of storage was presented. An analysis of the relation between values of the parameters obtained with different methods (on the model bench and under laboratory conditions) was conducted. In addition, their usefulness to assess the impact of logistic processes on the product quality was presented.
In the paper, the results of the work executed within the framework of the project "Development of a prototype of the monitoring system the ageing rate and degree of bio-components and biofuels" within the Program Innovative Economy Operational Programme, Measure 1.4. "Support for goal-oriented projects" were used.

Keywords: *biofuels, biocomponents, ageing process, test bench, method of measuring*

1. Introduction

Storage is one of the important processes in the life cycle of fuel or a fuel component. During its course, significant changes in the physical and chemical properties of a stored product may occur. It is a multi-parameter process, whose nature and intensity depend on many factors related to, among others, the chemical composition and product initial properties, as well as the storage infrastructure construction and external factors, such as temperature, humidity, exposure to sunlight, etc. This diversity of forcing factors significantly makes it difficult to foresee the direction and intensity of changes during storage. The permissible storage period, i.e. time beyond which fuel loses its suitability to use in accordance with its intended purpose or requires additional treatment in order to restore its suitability, is especially difficult to predict.

The analyses of commonly used methods for determining the properties, which are or can be connected with the ageing process of fuels and components during long-term storage, were carried out. It was found that there are no reliable methods, which could be used to forecast the course and intensity of ageing processes. Traditional methods most commonly determine "suitability" for long-term storage on the basis of the assessment of the accelerated ageing effects under laboratory conditions, which do not reflect the actual storage conditions in any way. Hence, there is no possibility reliably to predict the permissible storage period.

In this regard, the works on development of the test bench that would allow simulating the storage process, in which the test conditions would be as close as possible to the actual conditions, were undertaken.

During storage of certain products, it was observed that the course of physical and chemical phenomena is not the same in the entire tank capacity [1-4]. It varies depending on the level. It is related to the fact that not all products remain homogeneous for a longer period. In part of them, the phenomena of formation of zones with different values of some parameters occur. It is not necessarily connected with possible stratification of phases of different physical and chemical nature.

In order to verify this phenomenon, the bench is designed to make it possible to analyse possible differences in the properties at various levels of a liquid column. According to the project assumptions, the bench's main purpose is to study biofuels and bio-components, and in particular fatty acid methyl esters (FAME). Fig. 1 shows a schematic diagram of the bench referred to the actual storage conditions.

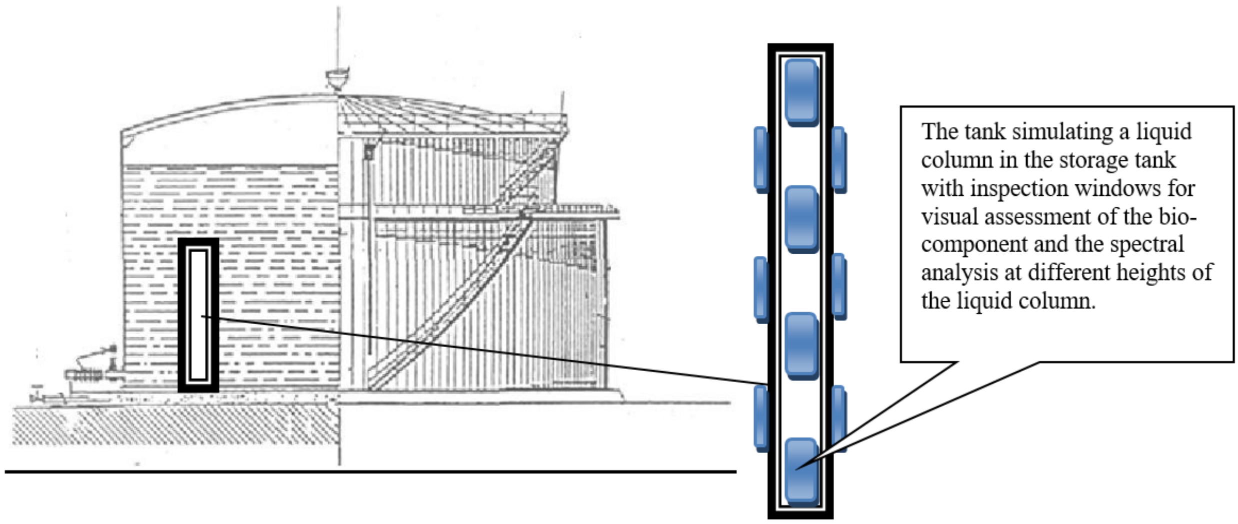

Fig. 1. Schematic diagram of the bench for testing the ageing degree and rate of bio-components during storage in the storage depots

2. Test bench description

The bench for monitoring the ageing rate and degree of bio-components and biofuels (Fig. 2) is equipped with:

- climatic chamber consisting of 3 working chambers which allow to store products at extremely different temperature conditions: in the heating chamber, it is possible to regulate the temperature from 0 to +65°C, in case of the cold chamber – from 0 to -40°C, and in the transition chamber, there should be the temperature of 0°C; in the chambers, wide doors allowing for the movement of tanks with biofuel on a rotating rack were installed,
- test tanks with a capacity of 10 – 15 dm^3, made of acid-resistant steel, and the holes for sight flows of borosilicate glass are made in them. They enable a spectroscopic analysis of samples with the use of an illuminator and a spectrometer equipped with a fibre optic. In the tanks, the connections that allow taking samples for analysis were also made.

  Additionally, the bench is equipped with:
- a system of taking samples of the tested fuel of any volume with the use of connections placed in the simulation tank, equipped with solenoid valves,

- a system of filling the simulation tanks with the use of a vacuum-pump,
- transport simulators – the entire rack with simulation tanks can be moved with back and forth motion, with adjustable frequency, which simulates the movement of fuel during transport in the rail tanker or tank truck,
- transport trolleys.

b)

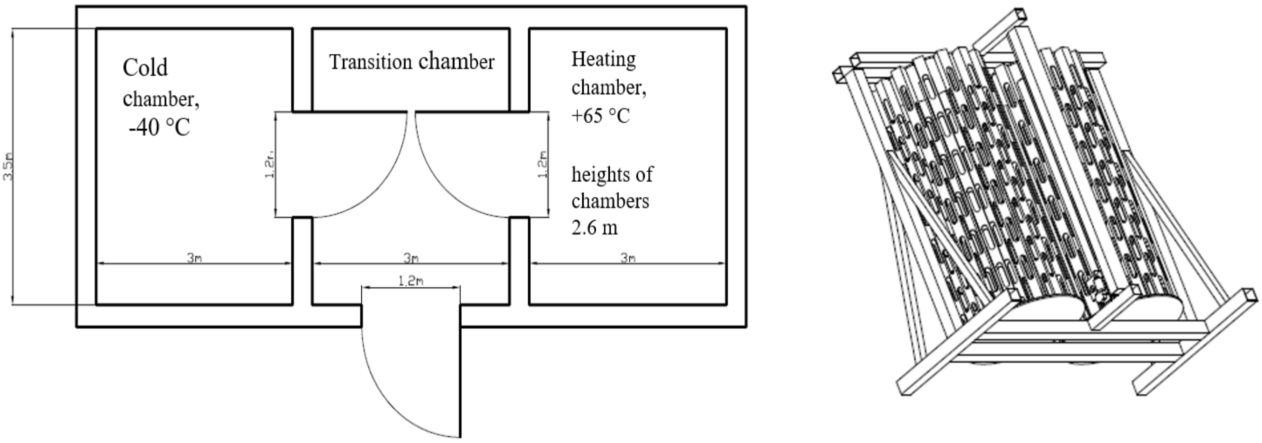

Fig. 2. Bench scheme: a) climatic chamber, b) a set of simulation tanks

An integral part of the model equipment for testing the ageing process of bio-components includes the absorption spectrometer. It is a precise measuring device used to measure the spectrum of light (intensity in a wavelength function). It is also possible to measure the light transmission (%) after the beam passing the tested object. The used spectrometer was built on the basis of the CCD lines of 2048 pixels. It is a reflection grating spectrometer, suitable for spectral measurements in the sub-ranges of 200 nm to 1150 nm. It allows operating in the range from visible light to near infrared (VIS-IR).

The bench can be operated in two systems:

- of direct removal of the spectrum of the bio-components stored in simulation tanks (Fig. 3a),
- of sampling the bio-component from the simulation tank and spectrum removal of the sample placed in the cuvette (Fig. 3b).

In the system of direct spectrum removal of the bio-component, radiation emitted by the illuminator passes through the bio-component layer with thickness equal to the tank's width. The strong absorption of radiation in such a thick layer results in the situation that in order to record the spectrum, it is important to significantly reduce the measurement sensitivity, which, however, finally does not eliminate the possibility of recording the changes in the band height, e.g. approximately 950 nm, resulted from acceleration of the reaction of creating the ageing precursors of FAME. By using this system, it is possible to conduct tests of the ageing process of bio-components in the increased temperature, e.g. 50°C, the container is then entered into the climatic chamber, and the radiation emitted by the illuminator is supplied to the inspection window in the container by the fibre optic. Radiation after passing through the bio-component's layer is also received by the fibre optic and supplied to the detector.

For the research purposes, it is important to remove the spectra with possibly high sensitivity, which is possible when the bio-component's layer is adequately thin, thus, when the bio-component is placed in the cuvette with appropriately selected thickness, which allows for the system presented in Fig. 3b. In this system, a sample of the bio-component is taken with the use of the release device from the container and is transferred to the cuvette.

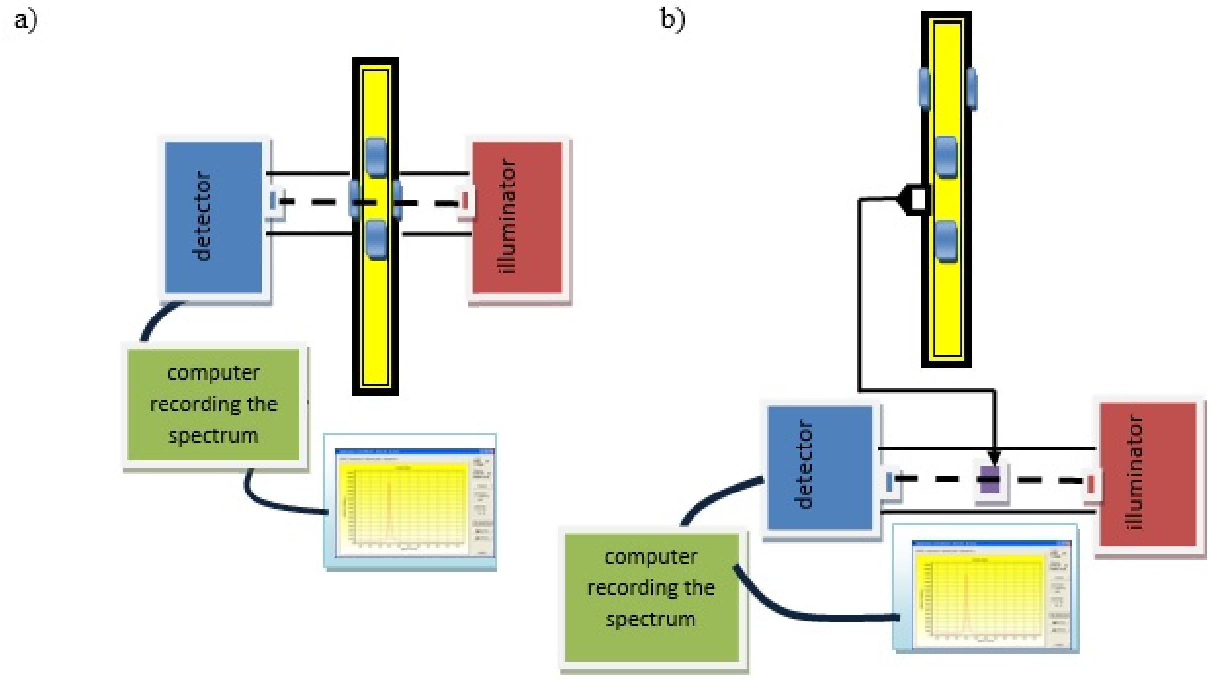

Fig. 3. Diagram of the bench for testing the ageing degree and rate of bio-components during storage: a) system of direct removal of the spectrum of the bio-component in the simulation tank, b) system of sampling and measurement in the cuvette

3. Conduct of simulated ageing tests of bio-components

The main purpose of the simulated ageing is to identify differences in the spectra obtained for fresh and aged bio-components, and in the long term, their linking with the results of tests of the selected physical and chemical properties. The basic functional elements, that is, the working chambers are used to invoke different kinds of ageing processes. For example, in the high temperature chamber, a bio-component in the simulation tank is subjected to heat in order to initiate radical reactions leading to the product ageing. In the low temperature chamber, a bio-components is frozen in order to carry out the changes in the physical-chemical structure (solidification of some of its components, stratification), which can lead to irreversible changes in the bio-component properties. If it is provided by the test programme, then pollution is added to bio-components, e.g. radical initiators or catalysts, the task of which is to accelerate the chemical transformation processes. If there is a research problem in determining the impact of heating and cooling of the bio-components on the change of its properties, then a sample is transferred from the external tank to the high temperature chamber, then it is moved to the low temperature chamber and back (simulation of the cyclic heating and cooling of a stored product).

Depending on the tested object and purpose of carrying out the simulation, the timetable and conditions for conducting the tests can be individually modified.

The exemplary range of activities necessary to assess the product storage estimated period might include:

- testing of the physical and chemical properties in the laboratory using standard methods for a given product, and with the use of non-standard methods, in terms of the parameters changing in the storage process (obtained results will provide reference results),
- preparation of the bench in terms of activation of the equipment for measuring and monitoring the environment,
- programming of the climatic chamber's working conditions (if necessary, one, two or three chambers),

- placing of the tested product in the tanks simulating a liquid column,
- placing of a set of tubes into the chamber selected for the first stage of simulation,
- launching the bench and starting the simulated ageing,
- conduct of the recording of changes in the chemical composition of a tested sample by the periodic (determined in the test programme) inspection of the spectrum with the use of the absorption spectrometer in the direct system (according to Fig. 3a), or with the use of the sampling system (according to Fig. 3b),
- depending on the test conditions – the movement of a set of tubes between the working chambers,
- conduct of the tests of physical and chemical properties of the product after the simulated ageing in the range corresponding to the research carried out at the beginning of the test.

There is a possibility of parallel testing of the samples stored in various conditions, in order to compare the intensity and nature of changes in the chemical composition.

The test results are composed of three parts:

- laboratory test results,
- results of the tests performed with the measuring head,
- measurement results of the parameters defining the storage conditions of the tested fuel (as results of an ancillary nature).

The results of standardised laboratory tests involve all or some of the parameters included in the product specification. The results of non-standardised tests include these parameters, which were not placed in the specification and can be important for interpretation of the ageing process. The tests of individual parameters are carried out in accordance with the relevant methodologies described in the documents of a normative nature. These results will provide input data for the model describing the biofuel ageing process.

The laboratory tests were carried out in two ranges: the first one – involving the tests defined in the product specification – in this case, it is the European standard for the biofuel or bio-component used to supply the diesel engines EN 14214 [5], and the second one – involving the test not included in the document, but closely related to the ageing process. It was found that in this case, while conducting the simulated ageing, most of the normative parameters remains the same or the changes are minor. However, it was decided that the work in this area will be continued, because in terms of practical and application matters, the reference of the chemical changes to the normative requirements, which are applied by users at all stages of using the bio-components (starting from their generation, through their storage, distribution, and possible blending with fuel of petroleum origin, and ending with combustion in the engine), is essential.

The results of the tests performed with the measuring head (absorption spectroscope) are recorded in the form of absorption spectra, and then digitally processed and recorded in the form of the absorption relationship of selected spectrum bands to the storage time. These results constitute input data for the model describing the biofuel ageing process. The measurement results of the parameters defining the storage conditions of the tested fuel, i.e. air temperature in the area of the storage tank's staying and in the climatic chamber, air humidity and temperature of the tested biofuel in the simulation tank are collected on a continuous basis throughout the test. These results are recorded in a function from the time of testing, and they are used during interpretation of the ageing process course.

In order to validate the adopted research methodology, a series of tests were conducted, on the basis of which the precision of determination of the bio-components' individual parameters was developed. The exemplary test results of the FAME samples, in which in order to determine the chemical composition changes that are responsible for changes in the physical and chemical properties, there were used the results obtained with the measuring head – absorption spectroscope and selected tests carried out in the laboratory (peroxide number and chromatographic analysis – GC: the content of hydrocarbons C18 and C18:2), were presented below. During their conduct, it was found that the most visible and reproducible changes are the ones characterised by IR spectroscopy: the peak heights for the wavenumber of 890 cm^{-1} and the peak heights for hydrocarbons C18:1 and C18:2 with the use of the gas chromatography method.

Figure 4 shows the distribution of results for the above properties, and Tab. 1 presents a summary of the parameters characterising the precision of methods.

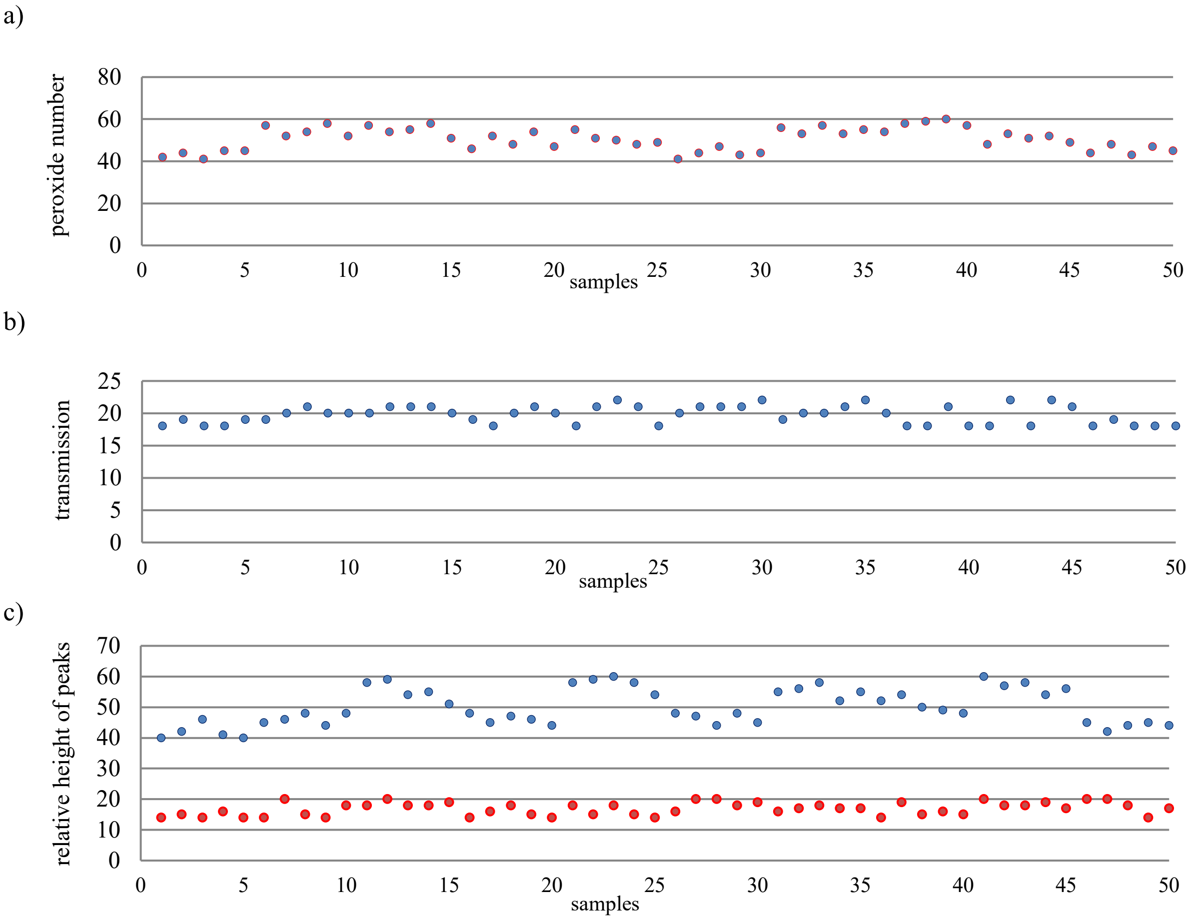

Fig. 4. Distribution of the FAME test results of: a) peroxide number, b) peak height for the wavenumber of 890 cm^{-1} (infrared spectroscopy method), c) height of the peaks C18:1 and C18:2 (gas chromatography)

Tab.1. Summary of parameters characterising the precision of methods

Parameter	Peroxide number	IR peak heights for the wavenumber 890 cm^{-1}	Gas chromatography heights of peaks	
			C18:1	C18:2
arithmetic mean of results, $x_{śr}$	50.52	19.74	50.0	16.84
minimum value of 50 measurements	41	18	40	14
maximum value of 50 measurements	60	22	60	20
range of 50 measurements	19	4	20	6
standard deviation of all measurements, s(x)	1.32	1.17	1.49	1.55
average deviation $S(x_{śr})$	1.04	1	1.24	1.24
confidence interval, ε	0.98	0.87	1.11	1.15
total uncertainty of results S(q)	**0.23**	**0.22**	**0.28**	**0.28**

On the basis of the tests carried out on the bench for testing the ageing degree and rate, and in actual conditions, it was found that the process of chemical reactions could be divided into at least two periods (Fig. 5).

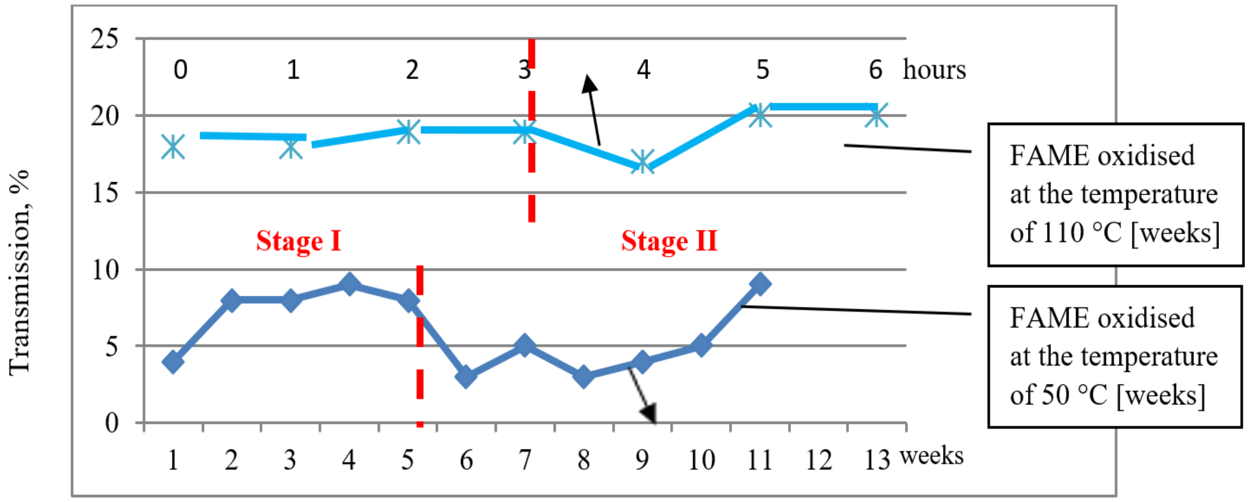

Fig. 5. Comparison of changes in the intensity of the 890 cm^{-1} band derived from peroxides during the FAME sample storage under different conditions

In the first stage, there is formation of the so-called ageing precursors, which then constitute substrates in the FAME ageing process. After reaching a certain level of concentration, while meeting other essential factors, the initiation of the reaction (the beginning of II stage) occurs, which results in an initial decrease in the concentration of precursors. Later, the precursors are used in the oxidation reactions, but at the same time, their formation takes place. As a result, the reactions can be continued. Some chemical changes, which in practice, corresponds to changes in some physical and chemical properties (e.g. oxidation stability, which is considered one of the main parameters associated with ageing processes, decreases) occur.

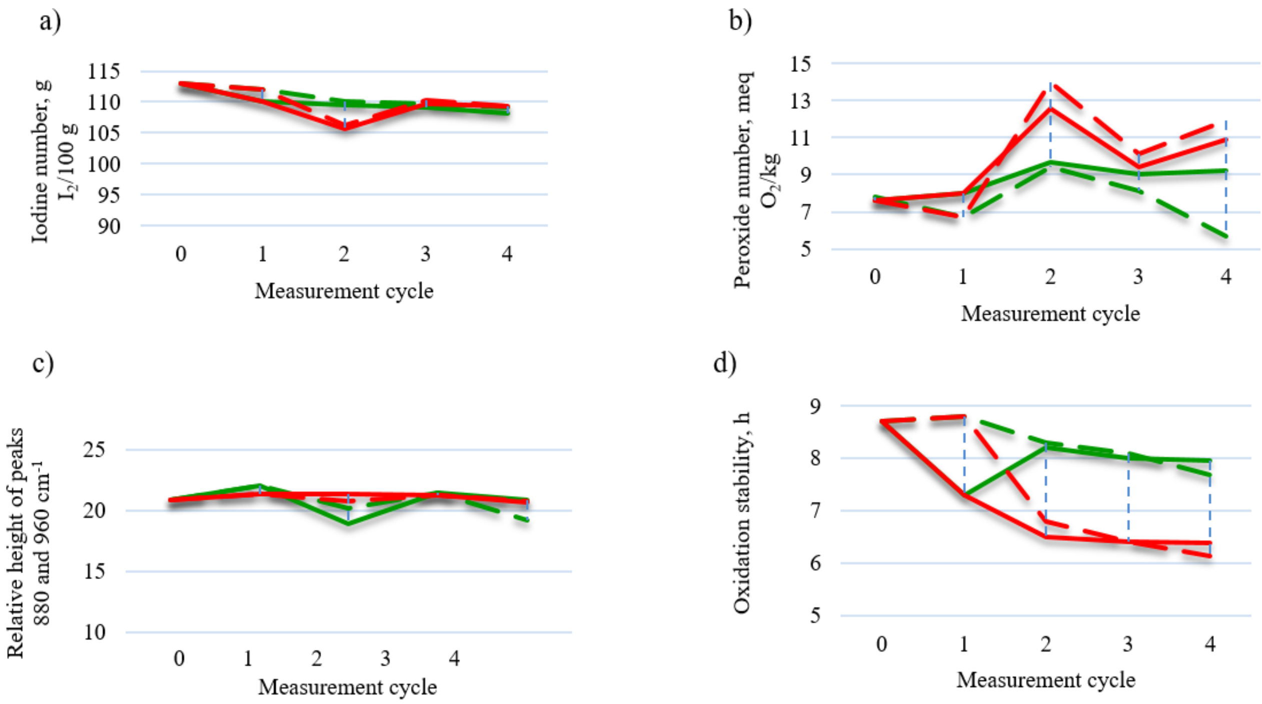

Fig. 6. Course of changes in values of the physical and chemical properties during ageing in simulation tanks: a) iodine number, b) peroxide number, c) relative height of peaks 880 cm^{-1} and 960 cm^{-1} in the UV-VIS spectrum, d) oxidation stability (—— upper sample without heating, – – lower sample without heating, —— heated upper sample, – – heated lower sample)

It was also illustrated in Fig. 6, where in case of the properties closely associated with the chemical composition (Fig. 6a, 6b and 6c), the changes in the concentration of precursors are visible, and Fig. 6d shows the consequence of it. Especially in case of the samples taken from the bottom of simulation tanks, the corresponding changes in the intensity of the oxidation stability decrease are visible.

Based on the results obtained during the fuel ageing with the use of the simulation station, a correlation programme, which allows determining the rate and degree of the bio-component ageing, was developed. Due to the manner, in which the ageing process is conducted and may be substantially similar to the actual conditions, it was assumed that although the chemical degradation of fuel during storage is complex, it can be treated as the weighted sum of less complex processes, and characterised with the use of a selected criteria parameter. The parameters that were presented earlier are the most useful for this purpose, because they show the greatest selectivity demonstrated by regular changes that are visible during the test conduct.

4. Conclusion

The work results presented in the paper show that it is possible to perform simulation tests that involve the accelerated ageing under laboratory conditions, the effect of which is determination of the expected storage of bio-components to liquid fuels. The test is based on the theory of formation and use of the ageing precursors.

During the tests, two periods were selected. In the first one, the phenomenon of formation of precursors occurred. At that time, the chemical composition, and hence the properties of a stored product are not affected. It means that the product is fully suitable for safe use. Only in the second period, there is activation of the previously generated precursors, as well as their use in the chemical reactions identified as ageing reactions, the result of which is a change in the physical and chemical properties of a stored product. Then, there is the possibility that the limit values of normative parameters will be exceeded, which will disqualify or restrict the applicability of the product in accordance with its original purpose.

The described bench and the principle of its use were used to develop the correlation programme, which allows determining the rate and degree of the bio-component ageing. In this paper, the mentioned programme was not presented because it is the subject of another development [5].

The bench and research methodology presented in the paper were reported to the patent protection. At the same time, they were shown, i.e. during innovation exhibitions, such as THE WORLD EXIBITIONS, SESEARCH and NEW TECHNOLOGIES, BRUSSELS INNOVA 2014 and awarded the gold medal.

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