Assessments of changes selected properties of fuels during their storage

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Introduction

The increase in demand for liquid fuels has caused the need for more efficient use of oil and contributed to the development of technologies of deep processing of petroleum fractions. As a result of these technologies are obtained components of fuel with different contents of paraffins, olefins and aromatics. Alkenes and aromatics are reactive compounds, easily undergo radical polymerization and oxidation, and therefore have a decisive influence on the properties of the finished fuel, in particular on their oxidative stability. The oxidative stability is the one of the most important parameters determining the suitability of fuel for storage and warehousing. This is particularly important given the need for mandatory reserves and reserve storage of petroleum products. Long-term storage causes aging of the product and thereby changing its physical and chemical parameters. The aging processes can also be catalyzed by chemicals which are included in the structural elements of the storage tanks or transmission lines. Currently, the fuel produced includes which, depending on the species, contain various bio-components, such as fatty acid methyl esters, alcohols, ethers. These compounds are usually additional factors initiating or intensified the aging of the fuel. As a result of these processes we can observe turbidity of the product, stratification and create sediments falling to the bottom of storage tanks.

In Institute for Fuels and Renewable Energy (at present Automotive Industry Institute) is led a project „On-line monitoring system of the degree and rate aging process of the liquid fuels while storage" (project co-financed by the European Regional Development Found). The project is intended to lead to the identification of changes occurring in today's aging stored fuels, to determine the time of their safe storage and to develop effective methods to control product quality.

Experimental and methods

Based on many years of research work at the Institute for Fuels and Renewable Energy of the aging process of stored fuels, and given the current trends in the development of biofuel market, to work of the project were selected three type of fuels: unleaded petrol containing 10%(v/v) ethyl alcohol (E10), diesel containing 7%(v/v) methyl esters of fatty acids (B7), diesel containing 20%(v/v) methyl esters of fatty acids (B20).

Tested fuels were stored in steel drums for a period of 6 moths, in a roofed room exposed on natural conditions, during the period from May to December.

The project uses the following methods of testing the stability of fuels:

1. The gasoline resistance E10 to oxidation was measured according to standard PN-ISO 7536 by the induction period method. Determination is done in the pressure bomb, which introduces a sample of gasoline, with the next filled with oxygen to a pressure of 600 kPa and heated to a temperature of 98°–102°C. Oxygen pressure is recorded continuously, until you reach the point of collapse, which is determined by the pressure drop of exactly 14 kPa within 15 minutes, followed by a further drop in pressure is not less than 14 kPa within the next 15 minutes. The time needed to reach this point is the designated period of induction.
2. The content of gums E10 was determined according to standard PN-EN ISO 6246 using the evaporation in air stream method. This method allows determine unwashed gums, or the sediments after the evaporation of gasoline is not subjected to further treatment and washed gums, the sediments after evaporation and washing with heptane. Usually as a result of the final determination shall be the amount of washed gums, because such requirements are prescriptive, but it can also be administered amount of unwashed gums.
3. Determination of oxidation stability B7 and B20 fuels was measured according to standard PN-ISO 12205. According to the procedure pre- filtered sample of the fuels is subjected to aging at a temperature of 95°C in the oxygen atmosphere for 16 h. After this process the sample is cooled to approximately room temperature and filtered in order to determine the amount of insoluble sediments. Filtration is used in filters with pore size 0.8 microns. Adherent insoluble are then removed from the oxidation cell and associated glassware with trisolvent. The sum of the filterable and adherent insoluble is reported as test result.
4. Assessment of fuel B7 and B20 storage stability was determined according to ASTM D 5304 Standards. A sample of fuel is placed in a borosilicate glass container, in the next the container is placed in a metal pressure vessel. The pressure vessel is pressurized with oxygen to 800 kPa and forced over 90° C for 72 hours. Throughout the course of the test is recorded pressure of oxygen in the tank.

Results

Analysis of selected parameters of E10 fuel during its storage

Induction period determined in accordance with the methodology of ISO 7536 is a measure of chemical stability of gasoline, and carried out during its long-term storage stability of gasoline indicates time. This parameter can also be used as an indicator of propensity of gasoline to create gums.

In our test for E10 gasoline, both the induction period at the beginning and after 6 months of storage was more than 360 minutes, which meets the requirements imposed normative gasoline engine (PN-EN 228). Because the test is not carried to the point of collapse, so we can not say anything about trends in the stability of gasoline during storage. This question requires a detailed analysis, which is as time consuming and therefore were not scheduled to perform in the first part of the project and will be implemented in its subsequent stages.

However, in the initial stage of the research project was carried out experiments to determine the effects of ethanol on the stability of gasoline. For this purpose it was used a measure methodology specific for storage stability tests in equivalent/special conditions, the oxygen overpressure and high temperatures action on a sample of fuel. Experiments were carried on the apparatus PetroOxy, at a temperature of 130°C and a pressure of 500 kPa. The process of aging was carried out until a 10% drop in oxygen pressure in the measuring chamber. It was assumed that the time when oxygen pressure has been dropped about of 10% will reflect the rate of oxidation of fuel. The gasoline containing from 0 to 10% by volume ethanol were tested, and the results are shown in Figure 1.

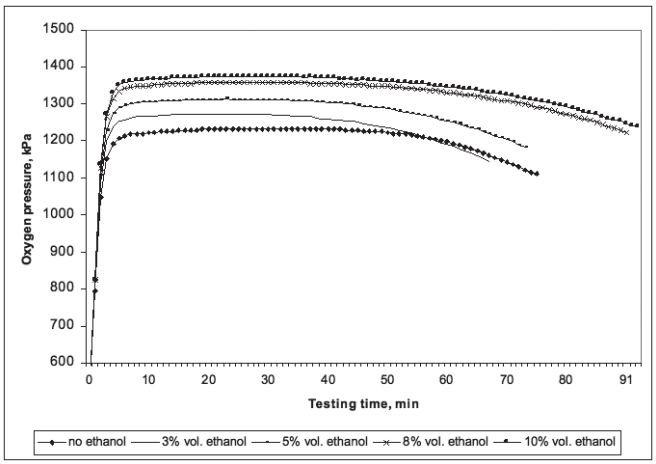

Fig.1. Experiments results for petrol with ethanol were carried on the apparatus PetroOxy

On the basis of our experiment can be concluded that the oxidation stability of gasoline containing 0.3 and 5% (v/v) ethanol is at a similar level, 10% of pressure fall has occurred after 65-70 minutes of the test, while for larger amounts of ethanol (8-10% (v/v) - after 93 minutes. A slow decrease in oxygen pressure during carried the test to indicate on a mild processes of oxidation. It can therefore be concluded that petrol containing 10% (v/v) ethanol has a high resistance to oxidation. The washed gums and unwashed gums are a very important parameter of quality of gasoline, because they inform about tendency to create sediments in the engine supply system and combustion chamber. The standard PN-EN 228 dictates that the gasoline engine should not be more than 5 mg of washed gums in 100 ml of fuel. The unwashed gums are not limited through these standards but standards regarding their quantity have been contained in the Worldwide Fuel Charter in 2006. For unleaded petrol in category 3 and 4 (with high demands on the emission of harmful substances emitted) limit the number of unwashed gums is 30 mg/100ml fuel.

In the present study measure of the level of washed and unwashed was performed for gasoline E10 in the 4-week intervals. The results obtained are shown in Figure 2.

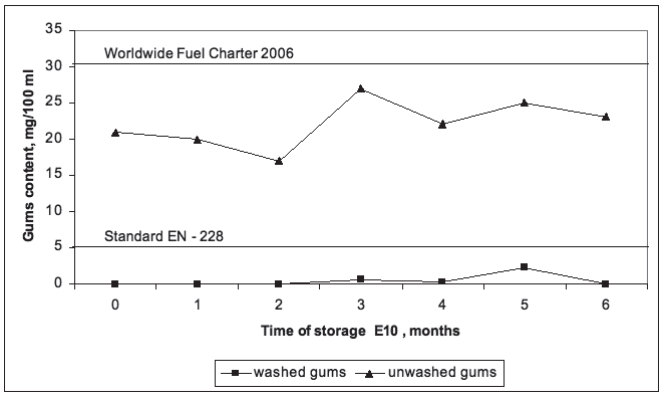

Fig. 2. The amount of washed and unwashed gums created during the storage

During 6 months storage E10 gasoline both the amount unwashed and washed of gums did not exceed the requirements applicable. The highest amount of washed gums was determined after 5 months of storage, whereas unwashed gums after 3 months. There has been no upward trend in the amount of gums. Therefore, it can be assumed that in the period of time, there were no visible changes in the quality of petrol.

Analysis of changes in fuel parameters for B7 and B20 biofuels during their storage

Test method for resistance to oxidation was used to determine the content of insoluble deposits that may occur during storage of the fuel. Monitoring of the amount of sediments forming is very important in the case of fuel containing FAME, because esters are particularly susceptible to oxidation and contribute to the accelerated degradation of the product. Determine the amount of sediments was performed according to method ISO 12205. However, due to the large amount of sediments passing through the upper filter, the results have been shown in Figure 3 are the sum of the masses of sediment retained on both filters dried to constant weight.

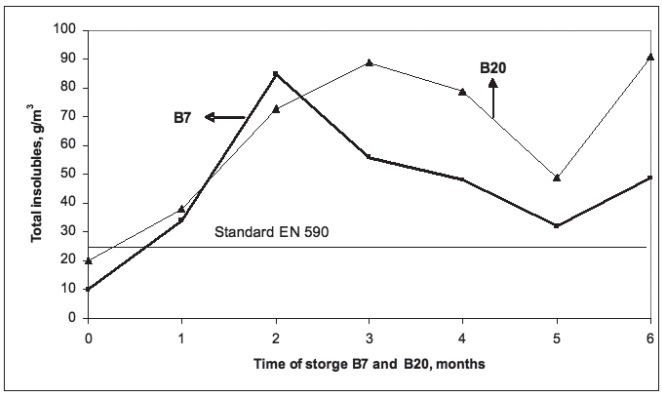

Fig. 3. The amount of insoluble sediments forming during the storage B7 and B20 biofuels

Research results have shown a significant increase in the amount of sludge after 2-3 months of storage, a decrease after 5 months and then increased again after the six-months storage. Already after one month storage the amount of insoluble deposits exceeded the allowable standards - 25 g/m3 for both B7 and B20. As expected, biofuel B20 is characterized by a greater tendency to deposit formation than fuel B7.

The results of measurements of fuel storage stability for biofuels B7 and B20 method of aging according to ASTM D 5304 have been showed to Figure 4 and 5. For diesel fuel samples B7 in the first months of storage, there has been a slow decrease in oxygen pressure, which would indicate a mild oxidation processes occurring. Research of fuel stored for six months showed a significant decrease in oxygen pressure in the final stage of the experiment. This decrease can be considered as the first symptom indicating the progressive aging of fuel and noticeable changes in its stability.

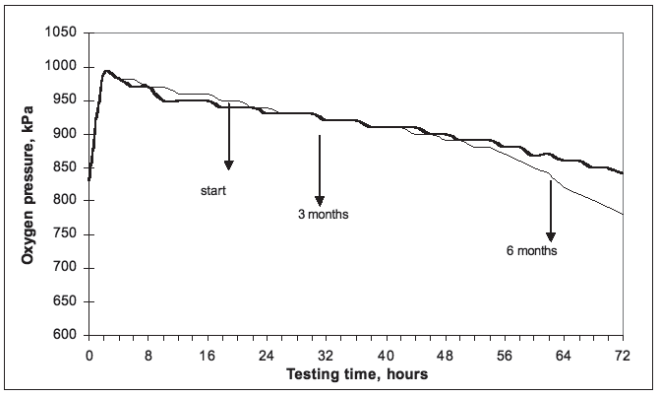

Fig. 4. The oxidative stability of biofuel B7 during 6 months of storage

Biodiesel B20 degrades more easily than B7 as shown by the course of the test performed. Accepted the conditions of experience, or high oxygen pressure and elevated temperature, make B20 biodiesel is rapidly oxidized. Jumping drop in oxygen pressure occurs already after 44 hours of research; in the case of B7 such a relationship has been noted. A similar trend of a sudden drop in oxygen pressure is observed for B20 samples tested after 3 and 6 months of storage. We observe the clear relationship: the longer it is stored biodiesel B20 this earlier and faster the drop of pressure of oxygen, so fuel is aging faster.

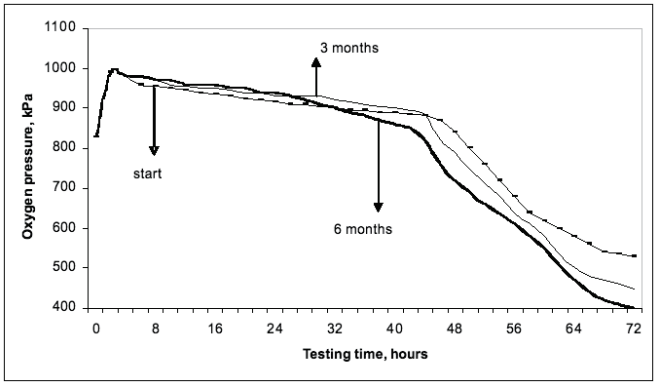

Fig. 5. The oxidative stability of B7 biofuel during 6 months of storage

Summary

Analysis of the results allows the following conclusions:

- The values of induction period (more than 360 minutes) indicate the possibility of storing gasoline E10 for at least 6 months
- When storing gasoline E10 not observed unwashed and washed gums in quantities determined by the standard PN EN 228 and the World Fuel Charter
- When storing biofuels B7 and B20 insoluble precipitates are formed, whose number exceeds the quality requirements in this regard
- The tests for storage stability in special conditions (short-term aging) performed on biofuel B20 confirmed its low resistance to oxidation.

Based on the above proposals in the latter part of the project will be continued testing of gasoline containing 10% vol. ethanol and diesel fuel containing 7% vol. FAME. Low resistance to oxidation and high sediment insoluble in biofuel B20 eliminates the them to of further studies.

Further information about our investigation we describe in next article.

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Translation into English by the Author

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