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THE METHOD, BASED ON STORAGE SIMULATOR AND IR – VIS SPECTROSCOPY, FOR PREDICTING THE ALLOWABLE TIME OF STORAGE OF BIOCOMPONENTS FOR CI ENGINES

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Abstract

The paper presents the results of investigations concerning a new method used for predicting the allowable time of storage of biocomponents – FAME. The method was based on laboratory research carried out with the use of a storage tank simulator. The aging process was carried out in the conditions increasing the reaction rate – at high temperature. There are several methods/procedures used for predicting the allowable time of storage of fuels and biocomponents – FAME, but all of them are based on tests at the temperature so high that the mechanism of aging process is different than the one observed in storage tanks. It was assumed that the aging process could be divided into two stages: at the first stage, the aging precursors are created and at the second stage, precursors are converted into the fuel aging products. These products lead to changes in fuel properties. The kinetics of precursor creation determines the rate of all reactions, which lead to the final aging products. It was found that the rate of reaction at the first stage of fuel aging can be effectively increased by an increase in temperature and even relatively high temperature does not change the mechanism of the creation of aging precursors. The method that has been worked out makes it possible to control the mechanism of aging process during quick laboratory tests. The products of aging processes were detected with the use of the IR-VIS spectrometry. The allowable time of storage was determined for several FAME samples on the basis of quick laboratory tests. The results of laboratory quick tests were verified by comparing them with the results of the aging process of FAME in storage tanks. On the basis of the test results, the algorithm of allowable time of FAME storage calculation was worked out.

Keywords *Fuel, fuel aging, Oils & Lubrication, biocomponents*

1. Introduction

The fuel aging process is very important for the logistics of fuels as well as for users that require fuels of good quality. Fuels, when distributed, are transported by pipelines, by train and by cars. There are usually several fuel storage plants in the distribution chain. Fuel is distributed from a refinery to an end user several weeks. This is a short time for mineral fuels, like gasoline and diesel fuel, and during this time, the aging cannot have influence on fuels quality, but if a given fuel is stored several years as a strategic reserve, the aging becomes very important. Fuel producers and/or logistic operators, responsible for the quality of stored fuel, are interested in the prediction of allowable time of fuels storage. There are several tests, developed by various oil companies and research units, but their usefulness is limited and they cannot be used for fuels produced from various crude oils by different refineries.

The reason for limited applicability of existing tests is that each of them is carried out at relatively high temperature, which accelerates chemical reactions of the aging process. The problem that there are many possible reactions that fuels may undergo, but some of them may occur only at high temperature. Consequently, when testing fuels at high temperature, the mechanism of the aging process is different than the one observed in a storage tank. The prediction of allowable time of fuel storage on the basis of such tests is highly biased or impossible.

The problem is much more difficult in the case of biocomponents and biofuels storage. They are usually stored for a few weeks, sometimes a few months. Their chemical structure, like in the case of FAME, is quite different from the structure of mineral fuels. This is why they undergo the aging process much faster than hydrocarbons of mineral fuels. The mechanisms of aging of FAME and mineral diesel fuels aging are different and new tests aimed at the prediction of allowable time of FAME storage should be developed.

The aim of the work was to develop a new method of predicting the allowable storage time of FAME.

2. Methodology

The experience in the field of bioethanol use shows that the main problems with the biocomponent distribution and storage is contamination by water and solid particles, but chemical aging is much less important. However, in the case of FAME, the chemical aging is very important, so research described in this paper was focused on the biocomponent aging.

There are a number of methods of fuel and biofuel aging simulation in laboratory tests [1-3, 5-7]. The common feature of all these methods is increasing the rate of fuel/biofuel aging by an increase in temperature. The aim of such methods is to obtain the information about tested fuel/biofuel propensity for aging in a relatively short time (a day or a week) while in the case of real storage this process is longer. Chemical aging is a complex process and there are many reactions, which are initiated under different conditions. An increase in the energy introduced into the fuel/biofuel as heat leads to the initiation of subsequent reactions. Some of these reactions are initiated at relatively high temperature, which cannot happen during real storage. Consequently, the temperature of tested fuel/biofuel that is too high changes the mechanism of the aging process when compared to real conditions (fuel/biofuel temperature). The results of tests carried out at the too high temperature do not correspond to fuel/biofuel changes observed during storage at normal temperature under real conditions.

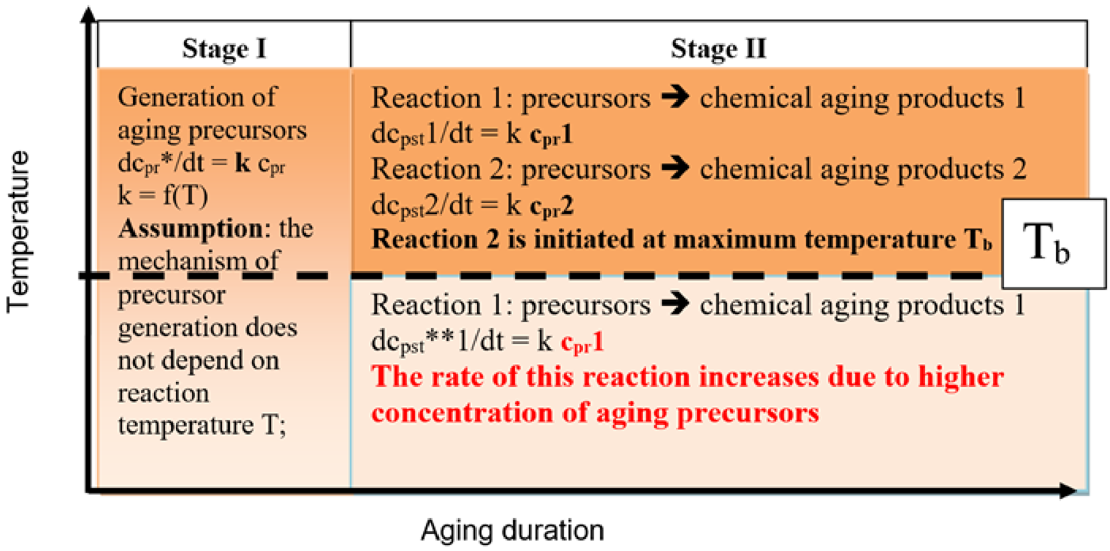

*Fig. 1. The diagram showing chemical aging processes under various conditions (temperature): *c_{pr} – the concentration of aging precursors, **c_{pst} – the concentration of aging products*

Predicting of aging process rate needs a new methodology, which:

- significantly increases the rate of aging process,
- ensures the same mechanism of aging in laboratory tests and during fuel/biofuel storage.

This new methodology is based on the kinetics of chemical reactions responsible for biofuel aging. The main problem which had to be solved was the determination of the mechanisms of FAME`s aging and the determination of the criteria for changing the mechanism during tests. The research included:

- determination of aging process precursors,
- determination of the mechanisms of biocomponents aging under different conditions.

The aging process can be divided into two stages: the first one (Stage I) consists of the production of aging precursors, and the second one (Stage II) comprises reactions leading to aging products [4]. During Stage I, some of fuel components create aging precursors, which are the substrate in further reactions leading to final products of fuel aging. What is important is the fact that the creation of precursors is the only possible reaction during Stage I. Consequently, during Stage I an increase in temperature should cause an increase in the rate of the precursor creation, but cannot cause any change in the mechanism of the precursor creation. Stage II is different. During this Stage, an increase in temperature can cause reactions with higher values of the activation energy.

Based on this assumption, the research described in this paper was focused on:

- identification of the precursors of FAME aging,
- determination of the influence of the concentration of precursors on the rate of the aging process of FAME.

Kinetic equations were formulated on the basis of the model of FAME aging shown on Fig. 1. It was assumed that the aging process consists of first-order reactions. The rate of these reactions is as follows:

$$dc/dt = k\ c, \tag{1}$$

where:
c – concentration of precursors,
k – reaction rate constant,
t – reaction duration.

After integration within t_n and t_0, the following relation is obtained:

$$\ln c_n - \ln c_0 = kt, \tag{2}$$

where:
c_n – concentration of precursors after a test,
c_0 – the beginning concentration of precursors. k values may be calculated by means of the equation (2).

The calculated k values will be used for:

- calculation of the activation energy E_a for reactions at various temperatures [$\ln k = \ln A + \exp(E_a/RT)$]; the same value of E_a for reactions at various T indicates the same mechanism of precursor creation,
- calculation of the critical storage duration – the time, after which the concentration of precursors will reach its critical value – the aging rate is so high that further storage of FAME is too risky.

Precursors were identified on a qualitative basis and their concentration in FAME was measured after aging at 20, 50 and 110°C.

The use of aging precursors, concentration as a measure of the critical duration of FAME storage is a new, innovative method used for the prediction of allowable times of storage of biocomponents/biofuels.

Tab. 1. The aging test conditions and sampling procedure

Temperature [°C]	Test duration	Sampling	Parameter measured in each sample
20	5 months	Every month	IR-VIS spectra; transmission at 962 nm related to transmission at 880 nm
50	10 weeks	Every week	IR spectra; transmission at 890 cm^{-1}
110	6 hours	Every hour	Peroxide number

3. The results

The selected sample of FAME-RME was tested by means of the above-described methodology. The obtained results are shown in Tab. 2, 3 and 4.

Tab. 2. The results of aging process of FAME at 20°C (IR-VIS spectra)

Test duration [month]	Transmission at 880 nm (Tr_{880})	Transmission at 962 nm (Tr_{962})	Δ transmission = Tr_{962}-Tr_{880}
0	43.9	90.5	46.6
1	43.4	94.8	51.4
2	42.8	94.8	52.0
3	44.2	95.7	51.5
4	43.1	96.3	53.2
5	37.8	93.4	55.6

Tab. 3. The results of aging process of FAME at 50°C (IR spectra)

	Test duration [week]	ln (transmission at 890 cm^{-1})
Stage I	0	1.39
	1	2.08
	2	2.08
	3	2.20
	4	2.08
Stage II	5	1.10
	6	1.61
	7	1.10
	8	1.39
	9	1.61
	10	2.20

Tab. 4. The results of aging process of FAME at 110°C (peroxide number)

Test duration [hour]	ln (peroxide number)
0	-1.61
1	-1.56
2	-1.05
3	-0.91
4	-0.80
5	-0.75
6	-0.36

On the basis of the above results, the k values were calculated:

- aging at 20°C up to 4 months: $k = 1.4 \times 10^{-5}$,
- aging at 20°C 4 and 5 months: $k = 5.5 \times 10^{-5}$,
- aging at 50°C Stage I: k = 0.0010,
- aging at 50°C Stage II: k = 0.0022,
- aging at 110°C: k = 0.20.

The following k values can be used to predict the allowable duration of FAME storage:

- $k = 1.4 \times 10^{-5}$ in a test at 20°C – test duration min. 1 month,
- $k = 0.0010$ in a test 50°C – test duration min. 2 weeks,
- $k = 0.20$ in a test at 110°C – test duration min. 3 hours.

The critical value of peroxides concentration, expressed as Δ transmission, was 53 (IR-VIS spectra) in a test carried out at 20°C. This value resulted from the analysis of the selected standard parameters of pure stored FAME.

4. The verification of the usefulness of the method developed for the prediction of the allowable time of FAME storage

To verify the kinetic model described above, the following three samples of FAME were used: Sample 1 – RME from supplier 1, Sample 2 – RME from supplier 2 and Sample 3 – PME from supplier 3. They were stored 5 months at 20°C. (RME – rapeseed methyl ester, PME – palm oil methyl ester). Each month small samples were taken and analysed with the use of IR-VIS spectra (transmission at 962 nm and 880 nm). This paper shows the results of the prediction of allowable storage duration on the basis of a test carried out at 20°C.

Tab. 5. The tests results of aging at 20ºC for Sample 1 of FAME

Storage duration at 20ºC [month]	Transmission at 880 nm	Transmission at 962 nm	□ Transmission
0	87.9	44.2	43.7
1	92.8	42.4	50.4
2	86.9	38.5	48.4
3	88.5	39.7	48.8
4	95.2	41.2	53.8
5	91.5	37.2	54.3

On the basis of the above results after the first month with $k = 1.4 \times 10^{-5}$, the allowable duration of storage of Sample 1 was calculated:

$$t = (\ln c_n - \ln c_0) / k = 4286 \text{ hours},$$

where:

c_0 – measured concentration of precursors after 1 month of storage of the FAME sample,

c_n – a critical value of concentration of precursors (Δ Transmission = 53).

Prediction: Sample 1 can be stored longer than 4 months. The results of Δ Transmission measurements show that Sample 1 can be stored longer than 4 months.

Tab. 6. The results of aging tests at 20°C for Sample 2 of FAME

Storage duration at 20ºC [month]	Transmission at 880 nm	Transmission at 962 nm	Δ Transmission
0	89.9	41.4	48.5
1	92.7	42.7	50.0
2	90.3	41.5	48.8
3	92.3	37.5	54.8
4	100	38.4	61.2
5	100	37.2	62.8

On the basis of the above results after the first month with $k = 1.4 \times 10^{-5}$, the allowable duration of storage of Sample 2 was calculated:

$$t = (\ln c_n - \ln c_0) / k = 2143 \text{ hours}.$$

Prediction: Sample 2 cannot be stored longer than 3 months. The results of Δ Transmission measurements show that Sample 2 reaches its critical value (c_n) after 3 months.

Tab. 7. The results of aging tests at 20°C for Sample 3 of FAME

Storage duration at 20ºC [month]	Transmission at 880 nm	Transmission at 962 nm	Δ Transmission
0	54.7	26.4	28.3
1	30.8	13.8	17.0
2	56.2	28.1	28.1
3	46.7	18.4	28.3
4	-	-	-
5	-	-	-

On the basis of the above results after the first month with k = 1.4 x 10^{-5}, the allowable duration of storage of Sample 3 was calculated:

$$t = (\ln c_n - \ln c_0) / k = 42857 \text{ hours.}$$

Prediction: Sample 3 can be stored longer than 3 months. The results of Δ Transmission measurements show that after 3 months Sample 3 does not reach its critical value (c_n,) which is much less than critical Δ Transmission = 53.

All the results presented above confirm that the new methodology developed for the prediction of allowable FAME storage duration gives acceptable results. Further investigations will be focused on verification by means of tests carried out at 50°C and 110°C.

5. The algorithm for the calculation of the allowable time of FAME storage

The results shown above made it possible to work out the algorithm for the prediction of the allowable time of FAME storage. The algorithm consists of the following steps:

1. sampling of test FAME,
2. storage of test FAME for 1 month at 20°C,
3. analysis of test FAME with the use of IR-VIS spectrum after one-month storage at 20°C (see Fig. 2.),
4. calculation of Δ Transmission for a test FAME sample after one-month storage,
5. calculation of the allowable time t of storage of test FAME using the following relation:

$$t = (\ln c_n - \ln c_0) / k,$$

where c_n – 53, c_0 – Δ Transmission for a test FAME sample after one-month storage; k = 1.4 x 10^{-5}.

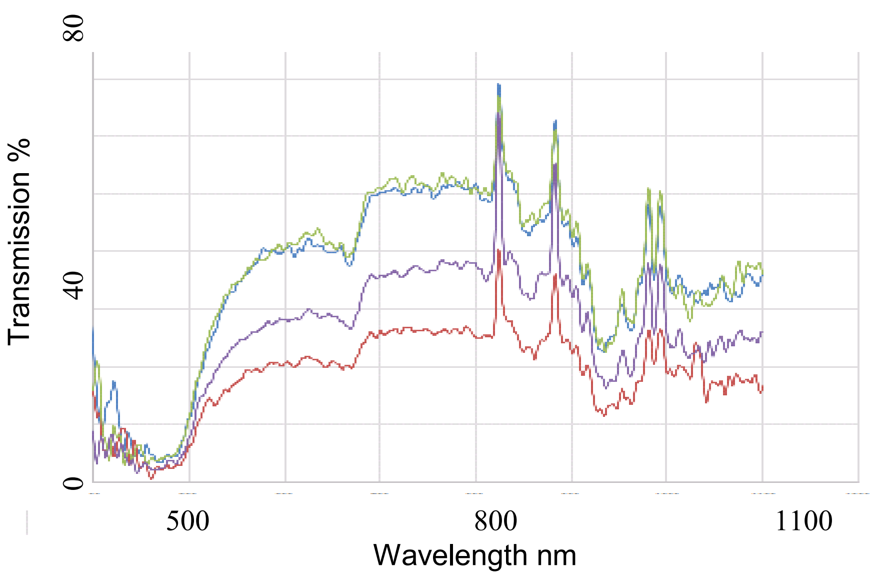

Fig. 2. Examples of IR-VIS spectra of FAME during aging at 20°C – graphical representation; numerical representation of spectra is much more useful for the analysis

6. Conclusions

The new methodology of the prediction of allowable FAME storage duration described in this paper is different from other methods that are currently used, developed mainly for mineral fuels. All the existing methods are based on an increase in the aging rate resulting from an increase in the reaction temperature. Excessive temperature may change the mechanism of aging. Consequently, the prediction of allowable time of storage of fuels/biofuels is based on a different process, not on the aging process in real storage conditions. The usefulness of such tests for the prediction of allowable time of storage of fuels/biofuels storage is limited. The new method allows a significant reduction of a test duration without changing the mechanism of FAME aging. FAME propensity for aging is determined on the basis of measurement of the concentration of aging precursors. The mechanism of precursor creation does not change at the temperature between 20 and 110°C. Three tests were developed for the purpose of prediction of allowable FAME storage duration: at 20°C, 50°C and 110°C. The predicted allowable time of FAME storage, with the use of the test carried out at 20°C, was verified empirically. It was observed that the predicted allowable FAME storage duration was measured in real storage conditions.

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