Forecasting indicators of thermal oxidative stability of lubricating oils

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Abstract. The results of testing partially synthetic Total Quartz 10W-40 SL / CF motor oil for thermo-oxidative stability in terms of optical density, volatility and coefficient of thermo-oxidative stability are presented taking into account the thermal energy absorbed by the products of oxidation and evaporation. The linear dependences of the decimal logarithm of thermal energy absorbed by the products of oxidation and evaporation and the total thermal energy absorbed by these products from the decimal logarithm of the test time in the temperature range from 160 to 190 °C are established. A graphical and analytical model is proposed for predicting the indicators of thermo-oxidative stability, determined by the dependence of the decimal logarithm of the thermal energy absorbed by the products of oxidation and evaporation on the temperature of thermostating.

1. Introduction
As a result of the study of the mechanism of oxidation of lubricating oils [1-3], it was found that the formation of water, resins, ester acids increases the acidity of the oil, which many authors have taken as a criterion for assessing the intensity of oxidation processes [4, 5]. In [6], a formula was proposed for calculating the time to reach the set value of the acid number at temperature $T_x$ based on data obtained at temperatures $T_1$ and $T_2$:

$$\lg \frac{t_x}{t_1 - t} = \frac{T_2 - T_x}{T_x - T_1} \cdot \lg \frac{t_1 - t}{t_2 - t},$$

where $t_x$ – the required time to reach the accepted values of the acid number at the test temperature $T_x$, h; $t_1$ – the time to reach the accepted values of the acid number at the test temperature $T_1$, h; $t_2$ – the time to reach the accepted values of the acid number at the test temperature $T_2$, h; $t$ – oxidation resistance time, h.

In the research work [7], an alternative method for predicting the indices of thermo-oxidative stability using photometry and an analytical model is proposed:

$$\frac{\lg t_1 - \lg t_2}{T_1 - T_2} = \frac{\lg t_x}{T_x},$$

(2)
where \( t_1, t_2, t_3 \) – the time to reach the set values of thermal oxidative stability at temperature \( T_1, T_2, T_3 \), h.

Using formula (2), it is possible to determine the established values of the optical density, volatility and coefficient of thermo-oxidative stability, taking into account the processes of oxidation and evaporation for the selected temperature \( T_3 \) based on these temperatures \( T_1 \) and \( T_2 \). It should be noted that lubricating oil cannot absorb thermal energy indefinitely. Therefore, its excess is discharged in the form of oxidation and evaporation products. The amount of thermal energy \( Q \) absorbed by the lubricating oil is determined by the product

\[
Q = T \cdot t,
\]

where \( T \) – test temperature, °C; \( t \) – test time at which excess thermal energy was released, h.

The amount of thermal energy absorbed by the oxidation products is determined by the product

\[
Q_D = T \cdot t \cdot D,
\]

where \( D \) – optical density of lubricating oil during the test \( t \).

Amount of thermal energy absorbed by evaporation products \( G \)

\[
Q_G = T \cdot t \cdot K_G,
\]

where \( K_G \) – evaporation coefficient;

The total amount of thermal energy absorbed by the products of oxidation and evaporation is determined by the formula

\[
Q_{Kv} = T \cdot t \cdot K_{tos},
\]

where \( K_{tos} \) – value of the coefficient of thermal oxidative stability during the test \( t \).

The purpose of this research is to substantiate a graph-analytical model for predicting thermal oxidative stability indicators based on data obtained at three test temperatures or a reduced temperature control time.

2. Materials and methods
The universal, all-weather partially synthetic Total Quartz 10W-40 SL/CF engine oil was chosen for the study. As a means of control and testing were used: thermostat, photometric device and electronic scales. A sample of constant weight oil (100 ± 0.1 g) was thermostated, sequentially at temperatures of 160 °C, 170 °C, 180 °C and 190 °C with stirring with a mechanical stirrer with a speed of 300 rpm. At regular intervals (10 hours), a sample of oxidized oil was weighed, the mass of evaporated oil was determined; a part of the sample (2 g) was taken for direct photometry and determination of optical density \( D \)

\[
D = \log \frac{300}{R},
\]

where 300 – photometer readings in the absence of oil in the cuvette, μA; \( R \) – photometer readings with an oil-filled cuvette, μA.

The coefficient of thermo-oxidative stability was calculated from the data of optical density and evaporation \( K_{tos} \)

\[
K_{tos} = D + K_G,
\]

where \( K_G \) – evaporation coefficient

\[
K_G = \frac{m}{M},
\]

where \( m \) – mass of evaporated oil during the study \( t \), g; \( M \) – mass of oil sample before testing, g.
3. Study of the optical density of lubricating oils

The investigated engine oil was tested at temperatures of 190 and 180 °C to a value of optical density equal to 0.5...0.6, and at temperatures of 170 and 160 °C the tests were carried out for 30 hours and after every 10 hours of testing, samples of oxidized oil were taken for determination of optical density, volatility and coefficient of thermo-oxidative stability, then, according to the data obtained, the indicators of thermo-oxidative stability were predicted after 10 hours to 90 hours of testing for a temperature of 170 °C and 140 hours for a temperature of 160 °C. At the same time, engine oil tests were continued to verify the convergence of experimental and calculation methods for determining the indicators of thermo-oxidative stability.

Figure 1a shows the dependences of the decimal logarithm of the thermal energy absorbed by the oxidation products on the decimal logarithm of the time and temperature of the engine oil test. At a temperature of 190 °C (direct 1), the oil was tested for 30 hours, and at a temperature of 180 °C - 60 hours (direct 2). These dependences are described by linear equations for temperatures:

\[
\begin{align*}
\lg Q_D &= 2.44(\lg t - 0.07), \\
\lg Q_D &= 2.37(\lg t - 0.21).
\end{align*}
\]

For temperatures of 170 °C (direct 3) and 160 °C (direct 4), the test oil was tested at the beginning of 30 hours, while the analysis was carried out after 10 hours. Based on the results of three values of the decimal logarithm of the thermal energy absorbed by the oxidation products, graphical dependences on the decimal logarithm of time are constructed, which are described by linear equations for temperatures:

\[
\begin{align*}
\lg Q_D &= 2.24(\lg t - 0.32), \\
\lg Q_D &= 2.20(\lg t - 0.49),
\end{align*}
\]

where 2.44, 2.37, 2.24 and 2.2 – coefficients characterizing the rate of change of the decimal logarithm of the thermal energy absorbed by the oxidation products from the decimal logarithm of the time and temperature of the test, h^{-1}; 0.07, 0.21, 0.32 and 0.49 – coefficients characterizing the start time of the change in the decimal logarithm of the thermal energy absorbed by the oxidation products, h.

According to the formulas 12 and 13, the values for \(\lg Q_D\) the test oil test time were calculated at a temperature of 170 °C up to 90 hours of testing (\(\lg t = 1.95\)) and a temperature of 160 °C up to 140 hours (\(\lg t = 2.14\)) with an increase of time by 10 hours and sampling of oils for analysis.

For example, at a temperature of 160 °C, it is necessary to determine the optical density during the test time of 50 hours (\(\lg t = 1.7\)) using the formula (13) or Figure 1. First, the decimal logarithm of the thermal energy absorbed by the oxidation products is determined

\[
\lg Q_D = 2.21(1.7 - 0.49) = 2.67,
\]

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As \( Q_o = T \cdot t \cdot D \) and antilogarithm 2.67 is 470.98, but \( 470.98 = T \cdot t \cdot D = 160 \cdot 50 \cdot D \), then \( D = 470.98 / 8000 = 0.06 \).

Comparing with the experimental data (table 1), at a test time of 50 hours, the optical density was 0.06. The relative error was 1.66%.

Further tests of the test oil at temperatures of 170 and 160 °C showed that the experimental data fell on lines 3 and 4.

In order to predict the values of thermal energy absorbed by the oxidation products and determine the optical density at other test temperatures, a graph-analytical model is presented, represented by the dependence of the decimal logarithm of the thermal energy absorbed by the oxidation products on the test temperature (Figure 1b).

This dependence is described by a linear equation

\[ \log Q_o = 0.0388(T - 131) \]  

where 0.0388 – coefficient characterizing the rate of change of the decimal logarithm of thermal energy from the test temperature, \( h^{-1} \); 131 - the value of the temperature of the onset of oxidation processes, °C.

Using formula (15), it is possible to determine the value of thermal energy absorbed by the oxidation products \( Q_o \) and the value of optical density at other temperatures. For example, at a test temperature of 150 °C, the decimal logarithm of thermal energy was 0.7372, and the amount of thermal energy absorbed by the oxidation products (antilogarithm of the number 0.7372) was 5.46, and since \( 5.46 = 150 \cdot 10 \cdot D \), then \( D = 0.0364 \).

For a temperature of 200 °C, the decimal logarithm of thermal energy was 2.6772, and the amount of thermal energy absorbed by the oxidation products was \( Q = T \cdot t \cdot D = 475.6 \), \( D = 0.238 \).

The dependences of the decimal logarithm of the thermal energy absorbed by the products of evaporation (Figure 2a) on the decimal logarithm of the test time are constructed in a similar way. These dependences are described by linear equations for temperatures:

\[
\begin{align*}
190 \degree C & : \quad \log Q_{K_o} = 1.8062 \log t + 0.1007, \\
180 \degree C & : \quad \log Q_{K_o} = 1.8743 \log t + 0.2661, \\
170 \degree C & : \quad \log Q_{K_o} = 1.9340 \log t + 0.6677, \\
160 \degree C & : \quad \log Q_{K_o} = 1.9675 \log t + 1.0834 .
\end{align*}
\]

where 1.8062, 1.8743, 1.9340 and 1.9675 – coefficients characterizing the rate of change of thermal energy absorbed by the evaporation products from the decimal logarithm of the time and temperature of the test, \( h^{-1} \); 0.1007, 0.2661, 0.6677 and 1.0834 – coefficients characterizing the value of thermal energy at \( \log t = 0 \), or the start time of the change in thermal energy absorbed by the evaporation products, h.

**Figure 2.** Dependences of the decimal logarithm of thermal energy, (a) absorbed by the evaporation products on the decimal logarithm of the time and temperature of the test (b) absorbed by the evaporation products after 10 hours of testing the partially synthetic engine oil Total Quartz 10W-40 SL/CF: 1 - 190 °C; 2 - 180 °C; 3 - 170 °C; 4 - 160 °C
Formulas 18 and 19 calculated the values \( \log Q_{K_G} \) for the test time of the test oil at temperatures of 170 and 160 °C. For example, at a temperature of 160 °C it is necessary to determine the value of volatility during a test of 50 hours (\( \log t = 1.7 \)) using formula (19) or Figure 2a. In this case, the decimal logarithm of the thermal energy absorbed by the products of evaporation is determined

\[
\log Q_{K_G} = 1.9675 \cdot 1.7 + 1.0834 = 2.2614, \tag{20}
\]

As \( Q_{K_G} = T \cdot t \cdot K_G = 2.2614 \), and antilogarithm 2.2614 is 182.6, but 182.6 = \( T \cdot t \cdot K_G = 160 \cdot 50 \cdot K_G \), then \( K_G = 182.6/8000 = 0.0228 \).

Comparing with the experimental data (table 1), at a test time of 50 hours, the volatility was 0.0227 g. The relative error was 0.44%.

To predict the values of thermal energy absorbed by the products of evaporation and to determine the volatility at other temperatures, we use a graph-analytical model represented by the dependence of the decimal logarithm of the thermal energy absorbed by the products of evaporation on the test temperature of the test engine oil (Figure 2b).

This dependence is described by a linear equation

\[
\log Q_{K_G} = 0.0337(\text{T} – 133), \tag{21}
\]

where 0.0337 – coefficient characterizing the rate of change of the decimal logarithm of thermal energy absorbed by the products of evaporation, g·°C; 133 - value of the temperature of the beginning of evaporation of the investigated engine oil, °C.

Using formula (21), it is possible to determine the decimal logarithm of the thermal energy absorbed by the products of evaporation and the value of volatility at other temperatures for 10 hours of testing. So, for example, at a test temperature of 150 °C, the decimal logarithm of thermal energy was \( \log Q_{K_G} = 0.0337(150 – 133) = 0.573 \), but \( Q_{K_G} = 3.7 \), as \( 3.7 = 150 \cdot 10 \cdot K_G \), then \( K_G = 0.0025 \).

At test temperature 200 °C \( \log Q_{K_G} = 0.0337(200 – 133) = 2.2579 \), then \( Q_{K_G} = 181.1 \), as 181.1 = 200 \cdot 10 \cdot K_G , then \( K_G = 0.0906 \).

The dependences of the decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation on the decimal logarithm of the test time are constructed in the same way (Figure 3a). These dependences are described by linear equations for temperatures:

\[
\begin{align*}
190 \, ^\circ\text{C} & \quad \log Q_{K_{\text{tot}}} = 2.5373(\log t - 0.06) \quad \tag{22} \\
180 \, ^\circ\text{C} & \quad \log Q_{K_{\text{tot}}} = 2.2990(\log t - 0.13) \quad \tag{23} \\
170 \, ^\circ\text{C} & \quad \log Q_{K_{\text{tot}}} = 2.1739(\log t - 0.22) \quad \tag{24} \\
160 \, ^\circ\text{C} & \quad \log Q_{K_{\text{tot}}} = 2.1570(\log t - 0.38) \quad \tag{25}
\end{align*}
\]

where 2.5373, 2.2990, 2.1739 and 2.1570 – coefficients characterizing the rate of change of the total thermal energy absorbed by the products of oxidation and evaporation from the decimal logarithm of the time and temperature of the test, h⁻¹; 0.06, 0.13, 0.22 and 0.38 – coefficients characterizing the decimal logarithm of the onset of oxidation and evaporation from the test temperature, h.

Using formulas 24 and 25, we calculate the values \( \log Q_{K_{\text{tot}}} \) for the test time of the test oil at temperatures of 170 and 160 °C. For example, at a temperature of 160 °C, it is necessary to determine the value of the coefficient of thermo-oxidative stability \( K_{\text{rot}} \) during a test of 50 hours (\( \log t = 1.7 \)) using formula (25) or Figure 3a. The decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation is determined

\[
\log Q_{K_{\text{tot}}} = 2.1570(1.7 - 0.38) = 2.85, \tag{26}
\]
As \( \lg Q_{K_{\text{tos}}} = T \cdot t \cdot K_{\text{tos}} = 2.85 \), and antilogarithm 2.85 equals 707.95, but 707.95 = \( T \cdot t \cdot K_{\text{tos}} = 160 \cdot 50 \cdot K_{\text{tos}} \), then \( K_{\text{tos}} = 707.95/8000 = 0.089 \).

Comparing the calculated data of the coefficient of thermal oxidative stability \( K_{\text{tos}} = 0.089 \) with experimental (table 1) \( K_{\text{tos}} = 0.09 \), found that the relative error was 4.5%.

![Figure 3](image)

**Figure 3.** Dependences of the decimal logarithm of thermal energy absorbed by the products of oxidation and evaporation on the decimal logarithm of the time and temperature of the test (b) absorbed by the products of oxidation and evaporation after 10 hours of testing the partially synthetic engine oil Total Quartz 10W-40 SL/CF: 1 - 190 °C; 2 - 180 °C; 3 - 170 °C; 4 - 160 °C

Using equations 10-25 thermo-oxidative stability values can be predicted \( D, G \) and \( K_{\text{tos}} \) for any test time, using the dependencies obtained over three test time ranges.

To predict the values of the total thermal energy absorbed by the products of oxidation and evaporation, and to determine the coefficient of thermal oxidative stability at other temperatures, we use a graph-analytical model represented by the dependence of the decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation on the test temperature of the test engine oil (Figure 3b).

This dependence is described by a linear equation

\[
\lg Q_{K_{\text{tos}}} = 0.033(T - 123.5),
\]

where 0.033 – coefficient characterizing the rate of change of the decimal logarithm of the total heat energy from the temperature of the test engine oil, °C; 123.5 – temperature of the start of conversion processes in lubricating oil, °C.

Using formula (27), it is possible to determine the values of the decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation, and the value of the coefficient of thermo-oxidative stability at other temperatures for 10 hours of testing. So, for example, at a test temperature of 150 °C, the decimal logarithm of thermal energy was \( \lg Q_{K_{\text{tos}}} = 0.033(150 - 123.5) = 0.956 \), but \( Q_{K_{\text{tos}}} = 9.045 \), as 9.045 = 150 \cdot 10 \cdot Q_{K_{\text{tos}}} \), then \( Q_{K_{\text{tos}}} = 0.26 \). At test temperature 200 °C \( \lg Q_{K_{\text{tos}}} = 2.7609 \), then \( Q_{K_{\text{tos}}} = 57.63 \), as 57.63 = 200 \cdot 10 \cdot K_{\text{tos}} \), then \( K_{\text{tos}} = 0.288 \).

4. Conclusion

The provided method for predicting the performance of a thermo-oxidative system takes into account thermal energy, which allows obtaining a graphical and analytical model for predicting the performance of thermo-oxidative stability for any temperatures obtained in three time values using the decimal logarithm of thermal energy and liquid temperature thermostating test oil tests.

The proposed forecasting method allows temperature studies being carried out without testing and determining the decimal logarithm of thermal energy, thermostating and the values of thermo-oxidative density studied by lubricating oil, as well as determining the temperature at which oxidation and evaporation processes begin.
Table 1. Test results and design data

| Time, h | lgt | D  | Q<sub>D</sub> T·D | Q<sub>G</sub> T·G | K<sub>G</sub> | Q<sub>K</sub> T·G | K<sub>loss</sub> |
|--------|-----|----|------------------|------------------|----------|----------------|----------------|
|        |     |    |                  |                  |          |                |                |
| Total Quartz 10W-40 SL/CF T<sub>test</sub> = 190 °C |
| 10     | 1.00| 0.102| 194.6            |                  | 2.29     | 0.0414          | 78.66          |
| 20     | 0.30| 0.278| 1056.4           |                  | 3.02     | 0.0765          | 290.57         |
| 30     | 1.48| 0.525| 2992.5           |                  | 3.48     | 0.1046          | 596.02         |
| 40     | 1.60| 0.843| 6406.8           |                  | 3.81     | 0.1245          | 945.90         |

Total Quartz 10W-40 SL/CF T<sub>test</sub> = 180 °C

| Time, h | lgt | D  | Q<sub>D</sub> T·D | Q<sub>G</sub> T·G | K<sub>G</sub> | Q<sub>K</sub> T·G | K<sub>loss</sub> |
|--------|-----|----|------------------|------------------|----------|----------------|----------------|
| 10     | 1.00| 0.041| 74.1            |                  | 1.87     | 0.0219          | 39.42          |
| 20     | 1.30| 0.103| 370.8           |                  | 2.57     | 0.0416          | 149.80         |
| 30     | 1.48| 0.180| 972.0           |                  | 2.99     | 0.0600          | 324.24         |
| 40     | 1.60| 0.272| 1958.4          |                  | 3.29     | 0.0771          | 555.43         |
| 50     | 1.70| 0.379| 3411.0          |                  | 3.53     | 0.0927          | 834.68         |
| 60     | 1.78| 0.500| 5400.0          |                  | 3.73     | 0.1067          | 1152.08        |

Total Quartz 10W-40 SL/CF T<sub>test</sub> = 170 °C

| Time, h | lgt | D  | Q<sub>D</sub> T·D | Q<sub>G</sub> T·G | K<sub>G</sub> | Q<sub>K</sub> T·G | K<sub>loss</sub> |
|--------|-----|----|------------------|------------------|----------|----------------|----------------|
| 10     | 1.00| 0.019| 31.6            |                  | 1.50     | 0.0108          | 18.36          |
| 20     | 1.30| 0.048| 162.5           |                  | 2.21     | 0.0214          | 72.87          |
| 30     | 1.48| 0.079| 400.9           |                  | 2.60     | 0.0303          | 154.75         |
| 40     | 1.60| 0.111| 754.1           |                  | 2.88     | 0.0399          | 271.22         |
| 50     | 1.70| 0.145| 1230.0          |                  | 3.09     | 0.0492          | 418.24         |
| 60     | 1.78| 0.180| 1836.0          |                  | 3.26     | 0.0584          | 595.28         |
| 70     | 1.85| 0.217| 2579.9          |                  | 3.41     | 0.0673          | 801.40         |
| 80     | 1.90| 0.255| 3469.4          |                  | 3.54     | 0.0760          | 1034.09        |
| 90     | 1.95| 0.295| 4512.0          |                  | 3.65     | 0.0846          | 1294.77        |

Total Quartz 10W-40 SL/CF T<sub>test</sub> = 160 °C

| Time, h | lgt | D  | Q<sub>D</sub> T·D | Q<sub>G</sub> T·G | K<sub>G</sub> | Q<sub>K</sub> T·G | K<sub>loss</sub> |
|--------|-----|----|------------------|------------------|----------|----------------|----------------|
| 10     | 1.00| 0.008| 13.5            |                  | 1.13     | 0.0049          | 7.84           |
| 20     | 1.30| 0.018| 58.9            |                  | 1.77     | 0.0093          | 29.91          |
| 30     | 1.48| 0.031| 148.3           |                  | 2.17     | 0.0138          | 66.38          |
| 40     | 1.60| 0.045| 290.6           |                  | 2.46     | 0.0183          | 116.80         |
| 50     | 1.70| 0.060| 480.8           |                  | 2.68     | 0.0227          | 181.67         |
| 60     | 1.78| 0.075| 720.0           |                  | 2.85     | 0.0272          | 261.18         |
| 70     | 1.85| 0.090| 1008.0          |                  | 3.00     | 0.0316          | 354.39         |
| 80     | 1.90| 0.105| 1344.0          |                  | 3.13     | 0.0361          | 462.24         |
| 90     | 1.95| 0.121| 1735.2          |                  | 3.24     | 0.0341          | 490.94         |
| 100    | 2.00| 0.136| 2174.4          |                  | 3.34     | 0.0449          | 718.02         |
| 110    | 2.04| 0.152| 2668.2          |                  | 3.43     | 0.0497          | 873.93         |
| 120    | 2.08| 0.167| 3212.2          |                  | 3.51     | 0.0546          | 1048.19        |
| 130    | 2.11| 0.183| 3812.6          |                  | 3.58     | 0.0586          | 1219.92        |
| 140    | 2.15| 0.199| 4466.6          |                  | 3.65     | 0.0631          | 1413.64        |

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