A complex of manometric methods for studying thermophysical, thermochemical properties and thermal stability of energy-intensive compounds

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A comprehensive manometric method for studying thermophysical characteristics and kinetics of thermal decomposition of components of fuels or lubricants for aircraft engines has been developed and tested, including a low-temperature unit of the Bourdon type and a new manometric unit for high temperatures and pressures. A comprehensive method has been developed for carrying out computational and experimental studies of the properties of new compounds on manometric installations. New data on thermophysical properties and kinetics of decane thermal decomposition for temperature and pressure ranges that are absent in the NIST information base was obtained [1].

1. Introduction

Currently, the problem of developing advanced aviation technologies requires a systematic approach to its solution. One of the important aspects is the search and study of the properties of new energy-intensive and thermostable compounds and their compositions, which can be used in the composition of fuels and oils in order to improve their performance properties. The problem is the limitation of existing experimental installations and research methods [2] of the kinetics of chemical reactions occurring with a change in the amount of gaseous compounds, as well as determining the temperature dependences of vapor pressures on temperature, enthalpies and entropies of evaporation, boiling points and critical temperatures of new compounds and materials at temperatures of up to 500 °C and pressures of up to 50 atm. In particular, this is reflected in the fact that most of them are not suitable for studying kinetic processes in the gas phase or have significant limitations when it comes to temperature and pressure in the experiment [3-4].

The aim of this paper is to develop and approbate a comprehensive technique for studying thermophysical characteristics and kinetics of thermal destruction of compounds - components of aviation fuel or lubricants by the manometric method. The methodology was approbated with the help of the dean, who partially knows the data from scientific and technical literature. A number of experiments were carried out as a result of which the rate constants of the thermal decomposition reaction in the temperature range 420 ÷ 450°C and its activation energy were determined. Also, the vapor pressure for the decan was discovered and compared with the data of other authors.

2. Design and principle of operation of experimental installations

The classical manometric method for studying the above properties of aviation fuels and oils can be called an installation based on the Bourdon device shown in Figure 1. The entire system is made of glass. A weighed portion - 1 is placed in the reaction vessel through the branch - 2, after which the branch is sealed. Then the sample is frozen and all air is pumped out from the reaction vessel and the compensation chamber - 4. The pressure in the compensation chamber - 4 is maintained so that the needle of the glass manometer - 5 does not deviate from the zero position, the pressure is determined by the mercury manometer - 6. The reaction vessel is heated in a thermostatic bath.
This method for determining the physicochemical properties of organic compounds is highly accurate, however, due to the glass chamber for pressure compensation and heating in a liquid thermostat, this method has a significant limitation in temperature and pressure: the maximum pressure in the experiment should not exceed 1 atm, as for the temperature -170 °C.

In the newly developed manometric installation, shown in Figure 2, the range of operating temperatures is up to 500 °C and the range of pressures expanded to 50 atm [5, 6]. A weighed portion of the test sample is placed in a glass reaction vessel - 1. If necessary, it can be frozen in liquid nitrogen. After the sample is loaded, air is pumped out of the vessel by a vacuum pump 12 and tube - 3 is sealed using a gas burner at the base of the membrane - 2. The reaction vessel with a sealed sample, a glass membrane and a soldered arrow is installed into the pressure compensation chamber - 5. Then from the pressure compensation chamber is evacuated by a vacuum pump - 12, and it is installed in the thermostat - 6. The temperature of the experiment is adjusted according to the indications of the thermocouple - 7, the signal from which enters the temperature control system - 8. The position of the arrow is determined visually by the deviation of the arrow from the zero position when using the eyepiece - 9. To determine the pressure inside the reaction vessel, nitrogen or air is supplied to the pressure compensation chamber from the cylinder 13 through the pressure control system 11 until the arrow takes a zero position, after which readings from the vacuum gauge or manometer are recorded - 10.

Figure 1. Manometric setup according to the Bourdon type for low temperature and pressure ranges
1 - branch for sample loading, 2 - reaction vessel, 3 - air evacuation tube, 4 - compensation chamber, 5 - glass sensitive membrane, 6 - mercury manometer.
3. Test methodology
During the study of thermophysical properties, the dependence of the vapor pressure of a liquid compound on temperature is recorded. The parameters of the Clausius–Clapeyron relation, the enthalpy and entropy of evaporation, the boiling point, and the critical temperature of the studied compound are determined from the obtained data.

The temperature dependence of the vapor pressure of a liquid is described by the Clausius-Clapeyron equation:

$$\frac{dP_v}{dT} = \frac{\Delta H_v}{T \Delta V_v} \text{ln} \frac{P_v}{P_c}$$ 

where $P_v$ – vapor pressure, atm; $\Delta H_v$ – heat of vaporization, cal/mol; $\Delta V_v$ – change in molar volume during vaporization, cm$^3$ / mol; $Z$ – compressibility factor; $Z = PV/RT$; $\Delta V_v = Z_g - Z_l$; $Z_g$ - for saturated steam; $Z_l$ – for saturated liquid.

By integrating equation (1), most of the known equations for calculating the vapor pressure are obtained. To calculate the vapor pressure in extended temperature ranges, it is proposed to use the Riedel-Planck-Miller equation [7]:

$$\ln P_{vpr} = -\frac{G}{Tr} (1 - Tr^2 + k(3 + Tr)(1 - Tr)^3)$$

where, $P_{vpr}$ – reduced vapor pressure; $P_{vpr} = P_v/P_c$; $Tr$ – reduced temperature; $Tr = T/T_c$; $T$ – temperature, K, $G$, $k$ – parameters; $G = 0.4835 + 0.4605h; h = T_{br}lnP_c/(1 - T_{br}); T_{br}$ – reduced boiling point; $T_{br} = T_b/T_c$; $k = (h/G - (1 + T_{br}))/3 + T_{br})/(1 - T_{br})^2$; $T_c$ - critical temperature, K; $P_c$ - critical pressure, atm.

The boiling points and critical temperatures of compounds are determined from the dependence of the vapor pressure of these compounds on temperature.
When studying the kinetics of gas evolution at different temperatures, the time dependences of the amount of gaseous compounds are determined from the pressure in the reaction vessel. Kinetic laws are established and the rate constants of chemical reactions are calculated through the obtained data. The gas evolution reaction can be described by various kinetic equations [8]. If the gas evolution reaction is described by a kinetic law of the 1st order, the rate constant is determined by the equation:

$$ P = P_{\text{fin}} + (P_0 - P_{\text{fin}})\exp(-kt) \quad (3) $$

where, $P_{\text{fin}}$ – final gas evolution pressure when extrapolated to an infinite reaction time; $k$ – reaction rate constant, $\text{sec}^{-1}$; $t$ – time, $\text{sec}$.

The obtained data is used to determine the Arrhenius dependences of the rate constants of gas evolution reactions on temperature:

$$ k = k_0 \cdot e^{-\frac{E}{RT}} \quad (4) $$

where, $k_0$ и $E$ – constant parameters; $R = \text{cal} / (K \cdot \text{mol})$; $T$ – absolute temperature, K.

The composition of gases was determined by chromatography. In the case of the macrokinetic nature of the thermal decomposition of a compound, which is an inseparable combination of chemical reactions and physical transformations, the thermal decomposition brutto-reaction may include gaseous and liquid products of thermal decomposition. The pressure of the decomposition products in this case is determined by many factors - the total pressure in the system, the partial pressure of each component, temperature, etc. The composition of the formed gases was determined as follows.

At the beginning, the molar fractions of individual compounds in the liquid phase are determined:

$$ X_i = Y_i \cdot \frac{P}{P_0_i} $$

where, $X_i$ - mole fraction of the $i$-th compound in the liquid phase; $Y_i$ – mole fraction of the $i$-th compound in the gas phase; $P$ – atmosphere pressure; $P_0_i$ - saturated steam pressure of the $i$-th connection.

Furthermore, for another vessel, aged under identical conditions, the mass composition of thermal decomposition products is determined by the gravimetric method:

$$ m_g = m_l - m_{II} + m_{air}; $$
$$ m_l = m_{II} - m_{III}; $$
$$ m_s = m_m - m_g - m_l $$

where, $m_g$ - total mass of products in the gas phase; $m_l$ - total mass of liquid products; $m_s$ – total mass of solids products; $m_l$ – weight of the vessel before opening, $m_{II}$ – weight of the vessel after opening; $m_{air}$ – air mass in the vessel after opening; $m_{III}$ – the mass of the vessel after keeping it under vacuum when heated to 200 °C; $m_m$ – weight of the sample of the original compound.

After that, the mass fractions of the identified substances are found:

$$ N_{ig} = \frac{Y_i \cdot M_{ri}}{\sum (Y_i \cdot M_{ri})}; $$
$$ N_{il} = \frac{X_i \cdot M_{ri}}{\sum (X_i \cdot M_{ri})}; $$

where, $N_{ig}$ – mass fraction of the $i$-th compound in the gas phase; $N_{il}$ – mass fraction of the $i$-th compound in the liquid phase; $M_{ri}$ – molecular weight of the $i$-th compound.

The total amount of a substance for the liquid and gaseous phases of the identified compounds is found using the obtained data:

$$ n_{i\sum} = \frac{(m_l \cdot N_{il} + m_g \cdot N_{ig})}{M_{ri}} $$

where $n_{i\sum}$ - the total amount of the substance of the $i$-th compound in liquid and gas phases. Next, the amount of the substance in the high molecular weight solid residue is calculated:

$$ n_s = \frac{m_s}{M_r} $$

And the stoichiometric yield of the reaction products is determined:

$$ W_i = \frac{n_{i\sum}}{(\sum n_{i\sum} + n_s)}, $$

where, $W_i$ – the mole fraction of each identified compound in the products of the thermal decomposition reaction, taking into account liquid and gas phases and the high-molecular-weight residue.

Some assumptions:
1) the vapor pressure of liquid compounds complies with Raoult's law,
2) in two parallel experiments carried out under identical conditions, the same composition of products is obtained,
3) all gaseous compounds are removed within half an hour of opening,
4) the contribution to the liquid mass of products of large molecular weight (compounds that are not detected on a gas chromatography-mass spectrometer (more than C9) is negligible,
5) in the absence of data on the molecular weight of the solid residue, it is taken as equal to 130 g/mol.

4. Approbation of the technique

The method was tested by determining the rate constants of thermal decomposition of decane in the temperature range 420 °C – 450 °C – the results are shown in Table 1.

Table 1. Rate constants of the reaction of thermal decomposition of decane

| T, °С | k, c⁻¹ |
|------|--------|
| 450  | 1.57·10⁻⁴±4.52·10⁻⁶ |
| 440  | 9.91·10⁻⁵±2.64·10⁻⁶ |
| 430  | 6.08·10⁻⁵±1.31·10⁻⁶ |
| 420  | 3.29·10⁻⁵±9.29·10⁻⁷ |

The Arrhenius equation for describing the rate of gas evolution during decomposition of decane in the vapor phase at temperatures of 420°C–450°C is as follows:

\[ k = 10^{12.0±0.1} \exp((-52.2±0.4) \times 10^3/RT), \text{ c}^{-1} \]  

(5)

The determined activation energy of the thermal decomposition of decane is 52.2±0.4 cal / mol. It should be noted that the rate constants established in [9] for the temperature range 645 °C – 685 °C have the same Arrhenius parameters, which indicates the correctness of the chosen method and the reliability of the results obtained (Figure 3). Data results [10] differ significantly from the established Arrhenius dependence, which casts doubt on them.

![Figure 3](image_url)

**Figure 3.** Arrhenius dependence of the decane decomposition rate constant on temperature

1 - constants established in this work; 2 - constants established in [9]; 3 - constants set by [10].
Another important parameter characterizing the decomposition process is the stoichiometric coefficient of gas evolution $\chi$ (Figure 4). It characterizes the amount of gas released during the decomposition of 1 mol of the starting substance and is determined by the formula:

$$\chi = \frac{n_\infty}{n_0} \quad (6)$$

where, $n_\infty$ - the final amount of gas (at the temperature of the experiment) released as a result of the thermal decomposition reaction, obtained by extrapolating the experimental data to an infinite reaction time, mo; $n_0$ – amount of starting compound, mol.

The vapor pressure of the decane sample was measured in the temperature range 40 - 100 °C. The dependence of vapor pressure on temperature is shown in Figure 4. To compare the results obtained, lines 1 and 3 are added to Figure 5, corresponding to the data of the authors [11] and [12].

The analytical dependence of the saturated vapor pressure of the sample on temperature is presented in the form:

$$P_{\text{sat}} = 10^{2.8 \pm 0.1} \exp((-6.8 \pm 0.2) \cdot 10^3/RT) \quad (7)$$
The enthalpies and entropies of evaporation determined from this equation are ΔH = -6.8±0.2 kcal / mol, ΔS = 12.8± 0.4 cal / (mol * K).

Data results [12] differ significantly from the established parameters, which casts doubt on them.

In the products of thermal decomposition of decane in the vapor phase at a temperature of 460 °C and a depth of η close to 100%, 30 compounds were identified by the gas chromatography-mass spectrometry method, the qualitative and quantitative composition of which, calculated according to the above procedure, is shown in Table 2.

Table - 2. The results of analyzing the composition of the products of decane’s thermal decomposition

| №  | Substance | Exit time, min | Mol. weight | Amount of substance in the experiment in the gas phase, mol | The amount of substance in the experiment in the liquid phase, mol | Share in the gas phase,% | Share in decomposition products,% |
|----|-----------|----------------|-------------|----------------------------------------------------------|---------------------------------------------------------------|-------------------------|----------------------------------|
| 1  | CH4       | 1.27           | 16          | 5.08×10^-6                                             | 1.69×10^-7                                                   | 2.97                    | 1.4                              |
| 2  | C2H6      | 1.29           | 30          | 4.78×10^-5                                             | 1.59×10^-6                                                   | 27.94                   | 13.19                            |
| 3  | C3H8      | 1.32           | 44          | 5.87×10^-5                                             | 5.46×10^-6                                                   | 34.32                   | 17.14                            |
| 4  | C4H10     | 1.35           | 58          | 1.47×10^-5                                             | 3.34×10^-6                                                   | 8.59                    | 4.82                             |
| 5  | C4H12     | 1.39           | 58          | 1.71×10^-5                                             | 6.36×10^-6                                                   | 9.99                    | 6.26                             |
| 6  | C4H8      | 1.42           | 56          | 7.19×10^-7                                             | 1.75×10^-7                                                   | 0.42                    | 0.24                             |
| 7  | C5H10     | 1.47           | 70          | --                                                     | --                                                           | --                      | --                               |
| 8  | C5H12     | 1.51           | 72          | 7.02×10^-7                                             | 1.57×10^-7                                                   | 0.41                    | 0.61                             |
| 9  | C5H10     | 1.54           | 70          | --                                                     | --                                                           | --                      | --                               |
| 10 | C5H12     | 1.56           | 72          | 6.16×10^-7                                             | 8.31×10^-7                                                   | 0.36                    | 0.39                             |
| 11 | C5H10     | 1.59           | 70          | --                                                     | --                                                           | --                      | --                               |
| 12 | C5H10     | 1.64           | 70          | --                                                     | --                                                           | --                      | --                               |
| 13 | C5H6      | 1.71           | 66          | --                                                     | --                                                           | --                      | --                               |
| 14 | C5H8      | 1.79           | 68          | 1.39×10^-6                                             | 2.16×10^-6                                                   | 0.81                    | 0.95                             |
| 15 | C5H10     | 1.85           | 70          | 1.36×10^-5                                             | 2.69×10^-5                                                   | 7.96                    | 10.83                            |
| 16 | C6H14     | 1.95           | 86          | --                                                     | --                                                           | --                      | --                               |
| 17 | C6H12     | 1.99           | 84          | --                                                     | --                                                           | --                      | --                               |
| 18 | C6H14     | 2.06           | 86          | --                                                     | --                                                           | --                      | --                               |
| 19 | C6H12     | 2.13           | 84          | --                                                     | --                                                           | --                      | --                               |
| 20 | C6H12     | 2.34           | 84          | 2.12×10^-6                                             | 1.12×10^-5                                                   | 1.24                    | 3.56                             |
| 21 | C6H10     | 2.61           | 82          | --                                                     | --                                                           | --                      | --                               |
| 22 | C6H6      | 2.75           | 78          | 6.42×10^-6                                             | 3.89×10^-5                                                   | 3.75                    | 12.09                            |
| 23 | C7H14     | 2.96           | 98          | --                                                     | --                                                           | --                      | --                               |
| 24 | C7H14     | 3.13           | 98          | --                                                     | --                                                           | --                      | --                               |
| 25 | C7H14     | 3.19           | 98          | --                                                     | --                                                           | --                      | --                               |
| 26 | C7H14     | 3.24           | 98          | --                                                     | --                                                           | --                      | --                               |
| 27 | C7H14     | 4.03           | 98          | --                                                     | --                                                           | --                      | --                               |
| 28 | C7H14     | 4.33           | 98          | --                                                     | --                                                           | --                      | --                               |
| 29 | C7H8      | 5.46           | 92          | 2.12×10^-6                                             | 4.24×10^-5                                                   | 1.24                    | 11.89                            |
| 30 | C8H10     | 11.75          | 106         | --                                                     | --                                                           | --                      | --                               |
| 31 | Other     | 130            |             |                                                         |                                                               |                         | 16.64                            |

The obtained data correlates with the data from [13, 14], which indicates that the method for determining the composition of the products of the decane’s thermal decomposition has been chosen correctly.
5. Conclusion

The developed complex of manometric methods makes it possible to determine the vapor pressure of hydrocarbon compounds with high accuracy as well as to study the kinetics of its thermal decomposition. The results obtained agree with the data published in the NIST database, which confirms the expediency of using the developed method to study the properties of new compounds.

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