Thermophysical properties of high energy synthetic hydrocarbons

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Abstract. The vapor pressure, enthalpy and entropy of evaporation, boiling point and critical parameters of four synthetic frame and spiranic hydrocarbons of interest for use as aircraft synthetic fuels or their components have been investigated.

1. Introduction
Synthetic fuels are alternative to petroleum fuels. Some synthetic aliphatic polycyclic hydrocarbons are of interest for use as synthetic aviation fuels and their components [1–5]. Currently, there are no data on the thermophysical properties of a number of such hydrocarbons. In addition, if the fuel before burning is supposed to be used as a cooling agent under high temperatures and pressures, then the data on thermophysical properties of these hydrocarbons in a critical or supercritical region are needed. A promising task is also the synthesis of hydrocarbon fuels with desired properties. In this regard, prior to carrying out work on the synthesis of fuels, it is necessary to carry out a calculated estimate of the properties of the proposed hydrocarbons and to compare them with hydrocarbons synthesized after. In the present work, the thermophysical properties of some frame polycyclic and spiranic hydrocarbons C9–C11 were investigated by experimental and computation methods.

2. Objects of Study
The objects of study were synthetic frame polycyclic and spiranic hydrocarbons of interest for use as components of aviation fuels [1–5], listed in table 1.

3. Experimental Setup
An experimental manometric installation including a thermostat, a pressure control system, a test chamber was used in the study (Figure 1). It allows to determine a vapor pressure of a sample under investigation at pressures from 0 to 45 atm and temperatures from 15°C to 500°C [6]. The study of the vapor pressure of the studied samples was carried out by measuring the equilibrium pressure during their isochoric heating.

The test is as follows. A portion of the test hydrocarbon is loaded into the reaction vessel, frozen in liquid nitrogen, then the air is pumped out from the reaction vessel with a vacuum...
Table 1. The test frame polycyclic and spiranic hydrocarbons.

| Name in the IUPAC | Molecular formula | Structural formula |
|-------------------|-------------------|--------------------|
| Spiro [tricyclo [4.1.0.0 (2.4)] heptane-5, 1'-cyclopropane] | C₉H₁₂ | ![Structural formula](image1.png) |
| Pentacyclo [3.3.1.1 (3.10) .0 (2.4) .0 (6.8)] decane | C₁₀H₁₂ | ![Structural formula](image2.png) |
| Exo-tricyclo[5.2.1.0(2,6)]decane | C₁₀H₁₆ | ![Structural formula](image3.png) |
| Tetracyclo[6.2.1.0(2,7).0(3,5)]undecane | C₁₁H₁₂ | ![Structural formula](image4.png) |

Figure 1. Test manometric installation: 1 – glass reaction vessel, 2 – glass manometric membrane, 3 – glass arrow, 4 – metallic pressure compensation chamber, 5 – pressure control system, 6 – pressure gauge, 7 – arrow position sensor, 8 – thermostat, 9 – controlling thermocouple, 10 – regulating thermocouple, 11 – signal converter, 12 – computer, 13 – vacuum pump, 14 – air bottle.
	pump, and the vessel is sealed. The reaction vessel with the glass membrane and brazed arrow is installed in pressure compensation chamber 4. The air is pumped out of the pressure compensation chamber, and the zero position of the arrow is fixed.

The vapor pressure above the liquid is fixed at different temperatures. In order to make sure
that the thermal decomposition reaction with the evolution of gases was not observed, the test chamber was kept at a given temperature for 2 hours at each vapor pressure determination and the pressure did not change.

4. Results and Discussion
To obtain the calculated values of critical temperatures $T_c$, pressures $P_c$, and volumes $V_c$ of the hydrocarbons tested, there are various methods [7–9]; in the present work, the Lindersen method [7] was used, since this method is highly accurate and there are necessary basic data for the computation – structural components of hydrocarbons. The calculation of critical properties is carried out according to the formulas:

$$T_c = T_b \left(0.567 + \Sigma \Delta T - \left(\Sigma \Delta T\right)^2\right)^{-1},$$  
(1a)

$$P_c = M (0.34 + \Sigma \Delta P)^{-2},$$  
(1b)

$$V_c = 40 + \Sigma \Delta V,$$  
(1c)

where $T_b$ is a boiling point, K; $M$ is molar mass, g/mol, $\Delta T$, $\Delta P$, $\Delta V$ are structural components calculated according to [7].

The calculated values of the critical properties of the hydrocarbons tested and their experimental boiling points by formulas (1) are given in table 2. The experimental boiling point at 1 atm was determined at the manometer installation from the curve of the vapor pressure.

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

$$\frac{dP_{vp}}{dT} = \frac{\Delta H_v}{T \Delta V_v} = \frac{\Delta H_v}{\left(\frac{RT^2}{P_{vp}}\right) \Delta Z_v},$$  
or  $$\frac{d \ln P_{vp}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_v}{R \Delta Z_v},$$  
(2)

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

By integrating the equation (2), most equations for calculation and correlation of a vapor pressure are obtained. To calculate the vapor pressure in a wide temperature interval in the present work the equation of Riedel-Plank-Miller was used [7]:

$$\ln P_{vpr} = -\frac{G}{T_r} \left(1 - T_r^2 + k(3 + T_r)(1 - T_r)^3\right),$$  
(3)

where $P_{vpr}$ is reduced vapor pressure; $P_{vpr} = P_{vp}/P_c$; $T_r$ is reduced temperature; $T_r = T/T_c$; $T$ is temperature, K; $G$, $k$ are parameters; $G = 0.4835 + 0.4605h$; $h = T_{br} \ln P_{cj}/(1 - T_{br})$; $T_{br}$ is reduced boiling point; $T_{br} = T_b/T_c$; $k = (h/G - (1 + T_{br}))/3 + T_{br})(1 - T_{br})^2$.

**Table 2.** Critical properties and boiling point of the hydrocarbons tested.

| Hydrocarbon | Boiling $T_b$, K | Critical temperature $T_c$, K | Critical pressure $P_c$, atm | Critical volume $V_c$, ml/mol |
|-------------|-----------------|-----------------------------|-----------------------------|-----------------------------|
| C$_9$H$_{12}$ | 421             | 635                         | 30                          | 433                         |
| C$_{10}$H$_{12}$ | 449             | 666                         | 26                          | 497                         |
| C$_{10}$H$_{16}$ | 453             | 699                         | 27.77                       | 401                         |
| C$_{11}$H$_{16}$ | 491             | 716                         | 25.5                        | 539.5                       |
To calculate the reduced vapor pressure of the hydrocarbons tested using equations (3), the following expressions are obtained:

\[ \ln P_{\text{vpr}C_9H_{12}} = -\frac{3.565}{T_r} \left( 1 - T_r^2 + 0.514(3 + T_r)(1 - T_r)^3 \right), \]  \hspace{1cm} (4)

\[ \ln P_{\text{vpr}C_{10}H_{12}} = -\frac{3.588}{T_r} \left( 1 - T_r^2 + 0.525(3 + T_r)(1 - T_r)^3 \right), \]  \hspace{1cm} (5)

\[ \ln P_{\text{vpr}C_{11}H_{16}} = -\frac{3.738}{T_r} \left( 1 - T_r^2 + 0.563(3 + T_r)(1 - T_r)^3 \right), \]  \hspace{1cm} (6)

\[ \ln P_{\text{vpr}C_{10}H_{16}} = -\frac{3.302}{T_r} \left( 1 - T_r^2 + 0.455(3 + T_r)(1 - T_r)^3 \right). \]  \hspace{1cm} (7)

Figure 2 shows the calculated (solid lines – recalculation from the reduced pressures by (4)–(7)) and experimental (points) temperature dependencies of the vapor pressures of the studied hydrocarbons. It can be seen that the dependence of the saturated vapor pressure of the studied hydrocarbons on the temperature in the considered temperature range is described quite well by the Riedel-Planck-Miller method.

The results of determination of the vapor pressure obtained after interpolation of the experimental data are presented in table 3.

**Figure 2.** Vapor pressure vs. temperature for the studied hydrocarbons: ◦ – C$_9$H$_{12}$, △ – C$_{10}$H$_{16}$, □ – C$_9$H$_{12}$, ◼ – C$_{11}$H$_{16}$ – experiment; solid lines – calculated by the Riedel-Planck-Miller equation.

**Table 3.** The vapor pressure of the compounds studied.

| Temperature, °C | P(C$_9$H$_{12}$), atm | P(C$_{10}$H$_{12}$), atm | P(C$_{10}$H$_{16}$), atm | P(C$_{11}$H$_{16}$), atm |
|----------------|-----------------------|--------------------------|-------------------------|-------------------------|
| 250            | –                     | 3.98 ± 0.02              | 3.49 ± 0.02             | 1.76 ± 0.02             |
| 200            | –                     | 1.62 ± 0.02              | 1.50 ± 0.02             | 0.721 ± 0.005           |
| 150            | 1.02 ± 0.02           | 0.534 ± 0.005            | 0.527 ± 0.005           | 0.239 ± 0.005           |
| 100            | 0.226 ± 0.005         | 0.131 ± 0.005            | 0.140 ± 0.005           | 0.059 ± 0.005           |

The heat of vaporization at normal boiling point (\(\Delta H_{vb}\)) is a constant of pure matter. For
its calculation the Riedel method gives good results—the calculation error is almost always less than 2% [6]:

\[ \Delta H_{vb} = 1.093RT_cT_{br}\ln\frac{P_c - 1}{0.930 - T_{br}}, \]  

(8)

where \( R \) is universal gas constant, equal to 1.987 cal/(mol·K).

The entropy of evaporation at normal boiling point can be calculated by the formula:

\[ \Delta S_{vb} = \frac{\Delta H_{vb}}{T_b}. \]  

(9)

The enthalpy and entropy of evaporation of the studied hydrocarbons at normal boiling point, calculated by formulas (8) and (9), as well as comparison with the corresponding experimental values obtained by equation (2) for the investigated temperature range are given in table 4.

Table 4. Calculated and experimental enthalpies \( \Delta H_{vb} \) and entropies \( \Delta S_{vb} \) of evaporation at normal boiling points of the studied hydrocarbons.

| Hydrocarbon | \( \Delta H_{vb}(\text{cal}) \) | \( \Delta H_{vb}(\text{exp}) \) | \( \Delta S_{vb}(\text{cal}) \) | \( \Delta S_{vb}(\text{exp}) \) |
|-------------|-----------------|-----------------|-----------------|-----------------|
| \( C_9H_{12} \) | 8.2             | 9.4 ± 0.2       | 19.5            | 22.3 ± 0.6      |
| \( C_{10}H_{12} \) | 8.6             | 8.8 ± 0.2       | 19.2            | 19.6 ± 0.1      |
| \( C_{10}H_{16} \) | 8.1             | 8.3 ± 0.3       | 17.9            | 18.4 ± 0.7      |
| \( C_{11}H_{16} \) | 9.8             | 8.7 ± 0.6       | 19.9            | 17.9 ± 1.3      |

The studied synthetic hydrocarbons are non-associated non-polar liquids, which is approximately satisfied Trouton rule, according to which \( \Delta S_{vb} = \Delta H_{vb}/T_b \approx 20 \text{ cal/(mol·K)} \).

\( C_{10}H_{16} \) is more volatile compared to \( C_{11}H_{16} \). To study the intermolecular interaction between \( C_{10}H_{16} \) and \( C_{11}H_{16} \), a model mixture containing 0.27 mole fractions of \( C_{10}H_{16} \) was prepared.

Figure 3 shows a comparison of the experimental values of vapor pressure and values calculated by Raoul’s law for ideal solutions over a mixture of \( C_{10}H_{16} \) and \( C_{11}H_{16} \).

The vapor pressure over the mixture of hydrocarbons was calculated by the formula:

\[ P_{vp\Sigma} = P_{vpC_{10}H_{16}}x + P_{vpC_{11}H_{16}}(1 - x), \]  

(10)

where \( P_{vpC_{10}H_{16}} \), \( P_{vpC_{11}H_{16}} \) and \( x \) are vapor pressure over pure substances at a given temperature and a molar fraction of \( C_{10}H_{16} \) in the mixture equal to 0.27.

As can be seen from the comparison of the experimental and calculated values of the vapor pressure over the mixture of \( C_{10}H_{16} \) and \( C_{11}H_{16} \), there is a negative deviation from the law of an ideal solution (10), which indicates stronger intermolecular interactions between \( C_{10}H_{16} \) and \( C_{11}H_{16} \) molecules, compared to the interaction energies between the same molecules in the initial hydrocarbons.

For the hydrocarbons under study, the kinetics of thermal decomposition was studied by the manometric method on the installation described above. Starting from a temperature of 400°C, the decomposition reaction of the studied hydrocarbons proceeds in the gas phase at a measurable rate. It is established that up to large conversions of decomposition the process is described by the first-order reaction equation. Figure 4 shows the Arrhenius dependences of the rate constants on temperature. It is seen that the critical temperatures of the hydrocarbons are in the range of temperatures at which they are subjected to thermal decomposition. Thus, it can be concluded that the considered hydrocarbons will not be stable in a critical state.
Figure 3. Vapor pressure above the mixture of C_{10}H_{16} and C_{11}H_{16}: △ – C_{10}H_{12} (experiment), ○ – C_{11}H_{16} (experiment), ◦ – the mixture C_{10}H_{12} and C_{11}H_{16} (experiment), — calculation of the vapor pressure of the mixture C_{10}H_{16} and C_{11}H_{16} according to the law of Raul.

Figure 4. The rate constants of thermal decomposition vs. temperature: ◦ – C_{9}H_{12}, △ – C_{10}H_{12}, □ – C_{10}H_{16}, ○ – C_{11}H_{16}.

5. Conclusion
For the studied samples of synthetic hydrocarbons, the dependences of vapor pressure on temperature, enthalpy and entropy of evaporation were theoretically computed and experimentally determined, boiling points were experimentally determined, and critical temperatures were calculated. The data obtained in the research are necessary both at the stage of creating new fuels and for improving existing fuel compositions.
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