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Stoichiometric model of forced ignition of flammable liquids and their binary mixtures

Controlling the characteristics of stable combustion and emissions during the combustion of alternative liquid fuels, reducing the carbon index is achieved through the use of oxygen-containing alcohols and hydrogen-containing substances (hydrogen, ammonia, water) as admixtures. The critical temperatures of forced ignition and spontaneous ignition of liquid fuels are important characteristics of stable flame combustion, which depend on the composition of the liquid and the oxygen-nitrogen gas mixture. This paper addresses the urgent issues of finding the temperature of spontaneous ignition of combustible liquids and their mixtures in an oxygen-nitrogen gas environment with a temperature lower than the temperature boiling of liquids as a result of short-term exposure of the liquid surface to a pilot flame (thermal ignition source). After the ignition source is removed from the droplet surface, the droplet continues to burn steadily. The model is based on the assumption that at liquid temperatures lower than the ignition temperature, the oxygen content in the saturated layer is much higher and the combustible vapours are less than the stoichiometric composition according to the chemical reaction equation. At the same time, the necessary condition for ignition is fulfilled − the self-acceleration of the exothermic reaction rate. As a result of heating and evaporation in a saturated gas layer at the ignition temperature, the concentrations of the components reach equivalent values, and the initial increase in the temperature of the gas layer leads to a stable burning of the droplet with its own diffusion flame Little attention is paid to the ignition temperature of liquids. There are very few experimental values. However, there is a Jones model, which is the basis for most of the works. We developed a stoichiometric model for forced ignition and spontaneous combustion have obtained analytical dependences of the ignition temperature for individual liquids, their aqueous solutions, and binary solutions of two flammable substances. These dependences are in satisfactory agreement with the available experimental data.

Keywords: *ignition temperature, combustible liquid vapour, droplet, stoichiometry, binary solutions.*

Introduction. Recently, the development of heat and power and environmental technologies has led to the creation of alternative liquid and solid fuels, mixtures with oxygen-containing biofuels (alcohols) to save or replace traditional combustible fuels. In this direction, as well as for the development of fire and explosion safety measures, studies of stable ignition and combustion of combustible biofuel mixtures, including those with the addition of water, for example, in the form of emulsions or foams, are relevant. Important indicators of the physicochemical properties of combustible liquid substances are flash point, ignition, and spontaneous combustion temperatures [1, 2]. Flash and ignition occur when the liquid is heated to temperatures significantly below the boiling point and at low air (oxygen-nitrogen mixture) temperatures that are lower than the boiling point of the combustible liquid, only under the short-term action of the ignition source on the surface of the

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combustible liquid. After the ignition source is removed from the surface of the liquid, the flame itself disappears during the flash, and a steady flame burning occurs during the ignition. The determination of the ignition temperature in scientific research is much less common [3, 4]. In Western countries, the ignition temperature is called the "fire point" - the critical temperature of a combustible liquid at which a steady flame occurs when a thermal ignition source, the next flame, is briefly raised [1, 2]. NFPA 3022 defines the flash point as: "The lowest temperature at which a liquid ignites and achieves sustained combustion when exposed to a test flame. A better definition is given by BSI23: "The lowest temperature at which a liquid emits sufficient flammable vapours into the air to ensure sustained combustion after the ignition source has been removed." The auto-ignition temperature (spontaneous ignition) according to ISO1 is defined as the lowest temperature at which ignition and sustained flame combustion of a liquid is achieved without an ignition source The fire point is slightly higher than the flash point: 1-5°C for flammable liquids (FL), 30-35°C for combustibles. Typically, empirical formulas are used to analytically estimate the flash point T fire, which relate the flash point to the boiling point of the liquid and the stoichiometric coefficient ν_{O2} , structural energy bond coefficients, saturated vapour pressure and concentration diffusion coefficient. Based on the Jones model [5], the ignition temperature corresponds to the ratio of vapour pressure to the stoichiometric value p_s/p_{st} from 0.78 to 1.92. This difference can be explained by different methods of experimental determination of the ignition temperature of individual liquids, as well as by not taking into account the relative mass composition in the saturated near-surface layer. In [6], a formula for the ignition temperature of an individual flammable liquid was derived taking into account the composition of the liquid and gas phases and the stoichiometric ratio between vapours and oxygen in the near-surface layer.

The aim of this work is to make analytical estimates of the flash point of individual flammable liquids, binary solutions of flammable liquids and flammable liquids with water.

Ignition model. Ignition is initiated by a heat source (a regular flame) and occurs in the cold gas phase near the surface of the combustible liquid. As the liquid is heated and vaporised, the oxygen concentration in the near-surface layer decreases and the concentration of combustible vapour increases, reaching its stoichiometric value at the ignition temperature. Evaporation equation $A_f(liq) \rightarrow A_f(g) - L_f$. The heating of the droplet to the ignition temperature is carried out with virtually no heat loss due to evaporation, because the mass fraction of saturated vapours near the surface is less than 0.1, and the rest (0.9) is nitrogen and oxygen. A further increase in the temperature of the liquid due to heated air leads to spontaneous combustion - a displacement of the surface of the stoichiometric chemical reaction from the surface of the droplet and an increase in the and rate of chemical heat release and self-acceleration, which ends in a transition to stable flame combustion. The equation of the exothermic chemical reaction between combustible vapours and nitrogen-oxygen mixture and can be represented as follows:

$$A_f\left(g\right)+\nu_{O_2}\left(O_2+\frac{1-x_{O_2}}{x_{O_2}}N_2\right)\rightarrow\nu_{CO_2}CO_2+\nu_{H_2O}H_2O+\nu_{O_2}\frac{1-x_{O_2}}{x_{O_2}}N_2+Q_f\,\cdot$$

The thermal effects of the reaction in terms of oxygen Q_{O_2} (J/kgO_2) and fuel Q_f are related $Q_{O_2}=\dfrac{Q_f\mu_f}{\nu_{O_2}\mu_{O_2}}$. Ignition and spontaneous combustion can only occur if the condition of self-acceleration is fulfilled

$$Q_{O_2}Y_{O_2,\infty}E\,/\,c_{p,g}RT_{g,\infty}{}^{2}>4\,,$$

where E is the activation energy of the reaction, J/mol, $c_{p.g}$ is the specific isobaric heat capacity of the reaction gas mixture, J/kg·K, $T_{g,\infty}$ is the air temperature at infinity, and in the case of convection, at the boundary of the reduced film. In the case of ignition, the air temperature, $T_{g,\infty}$ is less than the boiling point, and in the case of spontaneous combustion, it is greater.

The first step is to calculate the molar and mass composition of all components of the gas phase. The sum of the mole fractions of oxygen x_{O_2} and nitrogen x_{N_2}, the partial pressures for a dry mixture of nitrogen and oxygen satisfies the condition: $x_{O_2}+x_{N_2}=1$, $p_{air}=p_{O_2}+p_{N_2}$ $p_{N_2}=(1-x_{O_2})p_{air}$, $p_{O_2}=x_{O_2}p_{air}$. For air $x_{O_2}=0.21$, $x_{N_2}=0.79$.

In a saturated gas layer, at a combustible liquid temperature below the ignition temperature, the proportion of oxygen is much greater than the proportion of combustible vapours and is greater than the stoichiometric value. As the temperature of the liquid increases as a result of heating and evaporation of in the saturated gas layer , the proportion of combustible vapour increases and the proportions of oxygen and nitrogen decrease. The total pressure in the saturated gas phase layer, according Dalton's law, is equal to the atmospheric pressure

$$p_0=p_{f,s}+p_{O_2,s}+p_{N_2,s}=p_{f,s}+p_{air,s}\,.$$

The sum of the mole fractions

$$\overline{p}_{f,s}+\overline{p}_{O_2,s}+\overline{p}_{N_2,s}=1,\ \overline{p}_{O_2,s}=x_{O_2}\overline{p}_{air,s},\ \overline{p}_{N_2,s}=(1-x_{O_2})\overline{p}_{air,s}\,.$$

Sum of mass fractions $Y_{O_2,s}+Y_{N_2,s}+Y_{f,s}=1$.

At the ignition temperature near the surface of the liquid, the mass fraction of saturated vapours of the fuel $Y_{f,s}\big|_S$ reaches a value corresponding to the stoichiometric (equivalent) mass fraction $Y_f\big|_{Steh}$. That is

$$Y_f\big|_{Steh}=Y_{f,s}\big|_S\,. \tag{1}$$

Naturally, at the same time

$$Y_{O_2}\big|_{Steh}=Y_{O_2,s}\big|_S,\ Y_{N_2}\big|_{Steh}=Y_{N_2,s}\big|_S,\ Y_f\,/\,Y_{O_2}\big|_{Steh}=Y_{f,s}\,/\,Y_{O_2,s}\big|_S \tag{2}$$

According to the Clausius-Clapeyron law, the saturated vapour pressure of a combustible liquid increases with increasing temperature. At the same time, the heat of vapour decreases slightly between the normal and boiling points. At the critical temperature, the heat of vapour is zero. According to Watson's formula [7]:

$$L_f = L_{f,boil}\left(\frac{T_{cr,f}-T}{T_{cr,f}-T_{boil}}\right)^{0.38} \simeq L_{f,boil}\left(1-B_f\left(T-T_{boil}\right)\right),\quad B_f = \frac{0.38}{T_{cr,f}-T_{boil}}.$$

This allows us to represent the Clausius-Clapeyron law as

$$\bar{p}_{f,s} = \left(\frac{T}{T_{boil,f}}\right)^{\frac{-B_f L_{f,boil}\mu_f}{R}} \exp\left(\frac{L_{f,boil}\left(1+B_f T_{boil}\right)\mu_f}{RT_{boil,f}}\left[1-\frac{T_{boil,f}}{T}\right].\right)$$

Assuming that L f is independent temperature:

$$\bar{p}_{f,s} = \frac{p_{fs0}}{P_0} = \exp\left(\frac{L_f \mu_f}{RT_{boil,f}}\left[1-\frac{T_{boil,f}}{T}\right]\right). \tag{3}$$

Finding the concentrations of vapours, oxygen and nitrogen in a saturated layer near the surface of a combustible liquid

$$Y_{f,s} = \frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \mu_{air}\left(1-\bar{p}_{f,s}\right)},\quad Y_{O_2,s} = \frac{x_{O_2}\mu_{O_2}\left(1-\bar{p}_{f,s}\right)}{\mu_f p_{f,s} + \mu_{air}\left(1-\bar{p}_{f,s}\right)}, \tag{4}$$

where is the molar mass of the oxygen-nitrogen mixture $\mu_{air} = x_{O_2}\mu_{O_2} + (1-x_{O_2})\mu_{N_2}$.

For convenience, the chemical reaction equation for the interaction of a combustible gas with a dry nitrogen-oxygen mixture is presented as follows

$$\bar{p}_{f,s}\left[A_f + \nu_{O_2}(O_2 + \frac{1-x_{O_2}}{x_{O_2}}N_2)\right] = \bar{p}_{f,s}\left[\nu_{CO_2}CO_2 + \nu_{H_2O}H_2O + \nu_{O_2}\frac{1-x_{O_2}}{x_{O_2}}N_2\right].$$

Then the stoichiometric mass fractions of the components in the gas phase

$$Y_{f,Steh} = \frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \bar{p}_{f,s}\nu_{O_2}\left(\mu_{O_2} + \mu_{N_2}\left(\frac{1-x_{O_2}}{x_{O_2}}\right)\right)} = \frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \mu_{air}\frac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}}, \tag{5}$$

$$Y_{O_2,Steh} = \frac{\bar{p}_{f,s}\nu_{O_2}\mu_{O_2}}{\mu_f \bar{p}_{f,s} + \mu_{air}\frac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}},\quad Y_{N_2,Steh} = \frac{\bar{p}_{f,s}\nu_{O_2}\mu_{N_2}\left(\frac{1-x_{O_2}}{x_{O_2}}\right)}{\mu_f \bar{p}_{f,s} + \mu_{air}\frac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}}.$$

Using the condition for and equations (1), (4) and (5), we have

$$\frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \mu_{air}\frac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}} = \frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \mu_{air}\left(1-\bar{p}_{f,s}\right)}. \tag{6}$$

From (6) we find the saturated vapour pressure at the ignition temperature

$$\bar{p}_{f,s} = \frac{x_{O_2}}{\nu_{O_2}(1 + x_{O_2}/\nu_{O_2})} = \frac{1}{\nu_{O_2}/x_{O_2} + 1}. \tag{7}$$

From (7), taking into account (3), we have the ignition temperature:

Table 1. Flash points of pure flammable liquids

Рідина	T_{boil}, °C	ν_{O_2}	L_m, at T_{boil}, kJ/kg	T_{cr}, °C	T_{fire}, °C		T_i, °C
					for (8)	exp [10]	exp [9, 10]
acetaldehyde C_2H_4O	20.8	2.5	585	188.0	–35.1	–35	156, 172
ethyl acetate $C_2H_8O_2$	77.1	5	363	250.4	–1.4	6	400, 446
ethanol $CH_3(CH_2)OH$	78.4	3	838	243.0	19.5	18	404, 400
isopropanol $(CH_3)_2CHOH$	82.4	4.5	664	235.6	16.6	21	400, 430
1-propanol $CH_3(CH_2)_2OH$	97.2	4.5	691	263.7	28.6	30	370, 371
heptane $CH_3(CH_2)_5CH_3$	98.4	11	318	267.0	–4.7	–4	–, 223
1-butanol $CH_3(CH_2)_3OH$	117.0	6	585	288.6	38.7	43	410, 340
propylene glycol $C_3H_8(OH)_2$	188	4	645	351.0	101.7	110	–, 371
glycerol $C_3H_8O_3$	290	3.5	663	577.0	190	187	393, 400

$$T_{fire} = \frac{T_{boil.f}}{1 + \dfrac{RT_{boil.f}}{L_f \mu_f} \ln\left(1 + \dfrac{\nu_{O_2}}{x_{O_2}}\right)}. \tag{8}$$

Formula (8) coincides with the expression in our work [6], which used the condition $Y_f / Y_{O_2}\Big|_{Steh} = Y_{f,s} / Y_{O_2,s}\Big|_S$, and allows us to analyse the dependence of the ignition temperature on the physicochemical characteristics and composition of the nitrogen-oxygen mixture. The calculation results are presented in Table 1.

Let us assume the implementation of the empirical rule of Truton [8], according to which the ratio of the molar heat of vaporisation taken at the normal boiling point to the boiling point has the same value for non-polar liquids:

$$\Delta S_{vap} = \frac{L_f(T_{boil,f})\mu_f}{T_{boil,f}} = 88, \quad A_f = \frac{\Delta S_{vap}}{R} = \frac{L_f(T_{boil,f})\mu_f}{T_{boil,f} R} = 10.5,$$

and for polar liquids

$$\frac{L_f(T_{boil,f})\mu_f}{T_{boil,f}} = 110, \quad A_f = \frac{L_f(T_{boil,f})\mu_f}{T_{boil,f} R} = 13.$$

The ignition temperature can then be quickly estimated using a simplified formula

$$T_{fire} = \frac{T_{boil.f}}{1 + \dfrac{1}{A_f} \ln\left(1 + \dfrac{\nu_{O_2}}{x_{O_2}}\right)}.$$

The concentration of combustible vapour (mass fraction) decreases with increasing distance from the droplet surface, and the oxygen concentration increases. From formulas (3) and (4) we have:

$$Y_f = \frac{\mu_f \overline{p}_{f,s}}{\mu_f \overline{p}_{f,s} + \mu_{air}\left(1 - \overline{p}_{f,s}\right)} \left(\frac{r_s}{r}\right), \quad Y_{O_2} = Y_{O_2,\infty} - \left(Y_{O_2,\infty} - \frac{x_{O_2}\mu_{O_2}\left(1 - \overline{p}_{f,s}\right)}{\mu_f p_{f,s} + \mu_{air}\left(1 - \overline{p}_{f,s}\right)}\right) \frac{r_s}{r}. \tag{9}$$

The distance from the surface of the droplet where the stoichiometry is set is found from equation

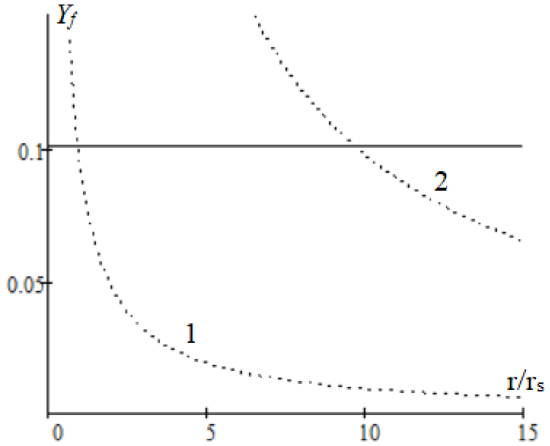

Fig. 1. Profiles near the droplet of ethanol vapour concentration (1- 291 K; 2- 350 K (T_{boil})) according to (9). The solid horizontal line characterises the stoichiometric value of the combustible vapour in the air. Calculation according to (5).

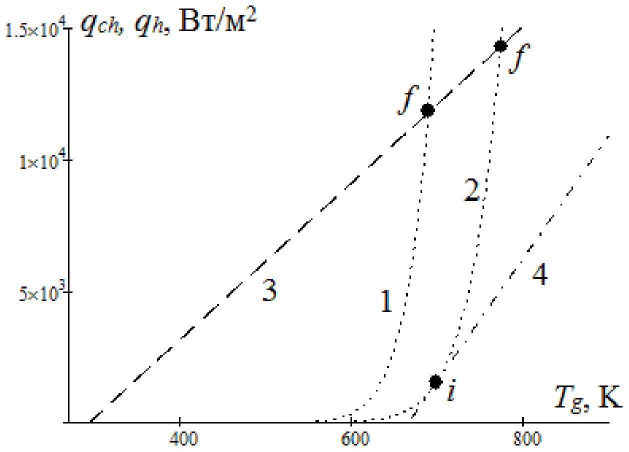

Fig. 2. Temperature dependences of heat output (droplet surface temperature 1 – $T_s = T_{fire} = 291$K, 2 – $T_s = T_{boil} = 350$K and heat loss (3 – $T = 291$K, 4 – $T = 665$ K) for an ethanol droplet with a diameter of 1 mm

$$\frac{\mu_f \bar{p}_{f,s}}{\mu_f \bar{p}_{f,s} + \mu_{air}\dfrac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}} = Y_{f,s}\frac{r_s}{r_{St}}.$$

In Fig. 1 shows the dependence of the concentration of combustible vapour on the distance from the surface of an ethanol droplet at the ignition temperature and the temperature close to the boiling point reached in heated air in the case of spontaneous combustion. From Fig. 1 shows that the stoichiometry is reached near the droplet surface and must be heated by an ignition source (pilot flame, for example) to ignite. When the temperature of the combustible liquid approaches the boiling point , the distance from the droplet r_{St}/r_s tends to

$$\lim_{\bar{p}_{f,s}\to 1}\frac{r_{St}}{r_s} = \lim_{\bar{p}_{f,s}\to 1}\frac{\mu_f \bar{p}_{f,s} + \mu_{air}\dfrac{\bar{p}_{f,s}\nu_{O_2}}{x_{O_2}}}{\mu_f \bar{p}_{f,s} + \mu_{air}\left(1-\bar{p}_{f,s}\right)} = 1 + \frac{\mu_{air}\nu_{O_2}}{\mu_f x_{O_2}}.$$

That is, the point where the stoichiometry between fuel vapours and air oxygen occurs, with increasing droplet temperature, moves away from the droplet surface (at the ignition temperature), but at a maximum distance of about 10 droplet radii. Fig. 2 shows the dependence of the ethanol vapour concentration on the distance from the droplet surface at the ignition temperature and the ethanol boiling point. Let's estimate the body temperature for the ignition of a liquid at the fire point. Assume that the reaction starts near the surface of the droplet, where the stoichiometry is observed. That is, the reaction is quasi-heterogeneous. The rate of chemical heat release of such a reaction should depend on the concentrations of fuel vapours and oxygen. But at low temperatures (fire point), there is more oxygen than vapour. Therefore, it is natural that we have a first-order reaction in fuel. The heat output per unit surface area of the droplet, taking into account the evaporation losses, is defined as:

$$q_{ch} = \left(Q_f - L_f\right)W_f, \quad W_{\text{f}} = k'\rho_g^2 Y_{f,s} Y_{O_2,s} \approx k\rho_{gs} Y_{f,s} Y_{O_2,\infty}, \quad k_1 = k_{1,0}\exp\left(-\frac{E_1}{RT_g}\right). \quad (10)$$

Here $k_0 = \rho_g \cdot 2\left\langle L_{fr}\right\rangle \cdot k_0'$ – is the pre-exponential factor of the quasi-heterogeneous reaction, which depends on the free path length of the vapour molecules. T_g is the temperature of the gas cell near the droplet, where combustion develops. It is the initial value of this temperature that defines a hot body. The surface vapour concentration is determined by the Clausius-Clapeyron equation and is determined by the droplet surface temperature T.

The rate of heat removal from the stoichiometric reaction zone is determined by the Newton-Richman law:

$$q_h = \alpha(T_g - T_s), \; \alpha = \beta c_{p,g}\rho_g, \; \beta = \frac{D_{O_2}Sh}{d}, \; D_{O_2} = D_{O_2,0}\left(\frac{T_g}{T_0}\right)^{1.8}. \quad (11)$$

Fig. 2 shows dependences (10) and (11). It can be seen that near 600 K there is a certain temperature above which chemical heat generation exceeds heat removal. This temperature corresponds to the minimum temperature of a raised heated body for the realisation of liquid ignition. This temperature is the critical temperature of forced ignition in a cold environment [11] - at higher initial temperatures, the chemical reaction accelerates, and at lower temperatures, the system cools down. Similar processes are possible in the so-called hysteresis region of heat and mass transfer.

Data from [12] were used for the calculation. This work considered the catalytic oxidation of ethanol over a platinum catalyst. It obtained a pre-exponential factor k_0= 4· 10^7 m/s and an activation energy E = 94 kJ/mol. In this case, the activation energy was chosen to be 50% higher than E = 141 kJ/mol at the same value of k_0.

Table 1 shows that the auto-ignition temperatures of most of the selected flammable liquids are in the order of 400 ºC. It is near this temperature that the temperature of the pilot flame (heated body) is also found. Fig. 2 shows that the auto-ignition temperature corresponds to the point of contact of the heat release and heat loss curves. Moreover, the temperature of the gas medium (air) for the selected kinetic parameters of the ethanol oxidation reaction is 390 °C. The identified agreement will allow us to further use the thermal explosion theory to estimate the ignition and spontaneous combustion temperatures of other flammable liquids.

Ignition of solutions of flammable liquids with water. For aqueous solutions of combustible substances, the molar composition of the liquid phase is first set $Z_f + Z_{H_2 0} = 1$.

The partial pressure of saturated vapours of the combustible component and water in the saturated layer in the gas phase according to Raoul's law is directly proportional to the mole fraction of the component in the liquid phase, i.e. $p_{fs} = Z_f p_{fs0}, p_{H_2O,s} = (1 - Z_f)p_{H_2O,so}$. According to Dalton's law, the total pressure in the saturated layer consists of the partial pressures of fuel vapour, water, oxygen and nitrogen:

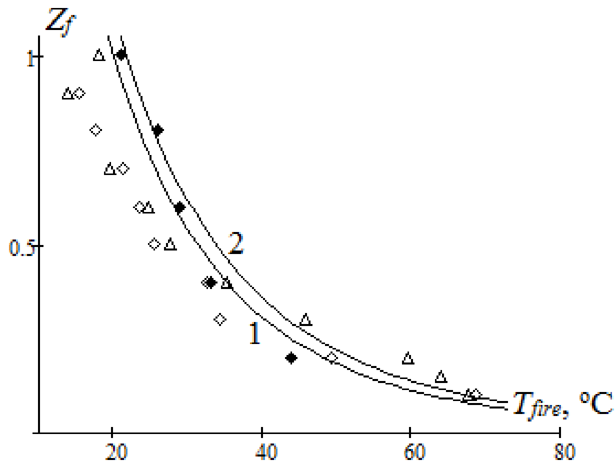

Fig. 3. Dependence of the mass fraction of a flammable liquid on the ignition temperature of its aqueous solution. Solid curves - calculation according to (14), dashed curves - calculation by Sabri [13], dots - experiment: 1 - ethanol, ♦,◊; 5 - isopropanol, Δ.

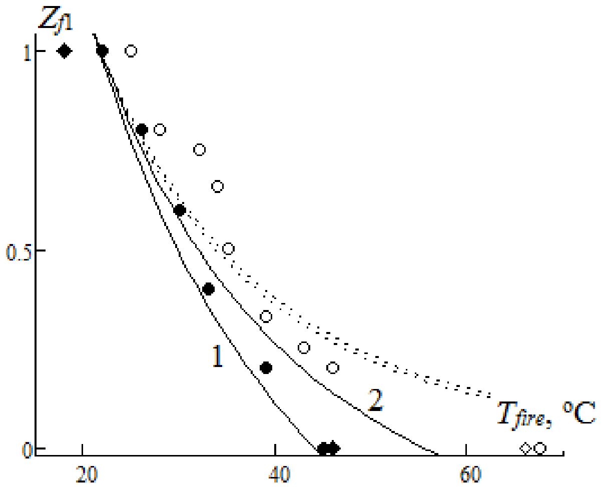

Fig. 4. Dependence of the mass fraction of the more volatile (first) component on the ignition temperature of a binary solution. Solid curves - calculation according to (15), dashed curves - calculation according to (14) (one of the components is inert), dots - experiment: 1 - n-octane/n-decane, ○, ◊; 2 - ethanol/butanol, ♦, ●

$$P_0 = p_{f,s} + p_{H_2O,s} + p_{O_2,s} + p_{N_2,s} = Z_f p_{fs0} + (1-Z_f) p_{H_2O,so} + x_{O_2} p_{air,s} + (1-x_{O_2}) p_{air,s}$$

Then the molar fractions of the gaseous components

$$\overline{p}_{f,s} + \overline{p}_{H_2O,s} + \overline{p}_{O_2,s} + \overline{p}_{N_2,s} = 1,\ \overline{p}_{N_2,s} = (1-x_{O_2})\overline{p}_{air,s},\ \overline{p}_{O_2,s} = x_{O_2}\overline{p}_{air,s},$$

$$Z_f \overline{p}_{fs0} + (1-Z_f)\overline{p}_{H_2O,so} + x_{O_2}\overline{p}_{air,s} + (1-x_{O_2})\overline{p}_{air,s} = 1$$

We find the mass fractions of saturated vapours and oxygen in the gas phase near the surface of a combustible liquid, taking into account the presence of water and nitrogen vapours:

$$Y_{f,s} = \frac{\mu_f Z_f \overline{p}_{f,s0}}{\mu_f Z_f \overline{p}_{f,s0} + \mu_{air}\left(1 - Z_f \overline{p}_{f,s0} - (1-Z_f)\overline{p}_{H_2O,so}\right) + \mu_{H_2O,s}(1-Z_f)\overline{p}_{H_2O,so}}, \quad (12)$$

$$Y_{O_2,s} = \frac{x_{O_2}\mu_{O_2}\left(1 - Z_f \overline{p}_{f,s0} - (1-Z_f)\overline{p}_{H_2O,so}\right)}{\mu_f Z_f \overline{p}_{f,s0} + \mu_{air}\left(1 - Z_f \overline{p}_{f,s0} - (1-Z_f)\overline{p}_{H_2O,so}\right) + \mu_{H_2O,s}(1-Z_f)\overline{p}_{H_2O,so}}.$$

The stoichiometric (equivalent) concentrations are calculated assuming that water vapour and nitrogen are not involved in the chemical transformation.

$$Y_{f,st} = \frac{\mu_f Z_f \overline{p}_{f,s0}}{\mu_f Z_f \overline{p}_{f,s0} + \mu_{H_2O,s}(1-Z_f)\overline{p}_{H_2O,so} + Z_f \overline{p}_{f,s0}\mu_{air}\dfrac{\nu_{O_2}}{x_{O_2}}} \quad (13)$$

$$Y_{O_2,st} = \frac{x_{O_2}\mu_{O_2}\left(1 - Z_f \overline{p}_{f,s0} - (1-Z_f)\overline{p}_{H_2O,so}\right)}{\mu_f Z_f \overline{p}_{f,s0} + \mu_{H_2O,s}(1-Z_f)\overline{p}_{H_2O,so} + Z_f \overline{p}_{f,s0}\mu_{air}\dfrac{\nu_{O_2}}{x_{O_2}}}$$

Using the ignition condition $Y_f\big|_{Steh} = Y_{f,s}\big|_S$, (11) and (12, we obtain the dependence of the mole fraction of the combustible liquid on the ignition temperature:

$$Z_f = \frac{\dfrac{x_{O_2}}{\nu_{O_2}}\left(1 - \exp\dfrac{L_{H_2 0}\mu_{H_2 0}}{RT_{boil,H_2 0}}\left[1 - \dfrac{T_{boil,H_2 0}}{T_{fire}}\right]\right)}{\left(1 + \dfrac{x_{O_2}}{\nu_{O_2}}\right)\exp\dfrac{L_f\mu_f}{RT_{boil,f}}\left[1 - \dfrac{T_{boil,f}}{T_{fire}}\right] - \dfrac{x_{O_2}}{\nu_{O_2}}\exp\dfrac{L_{H_2 0}\mu_{H_2 0}}{RT_{boil,H_2 0}}\left[1 - \dfrac{T_{boil,H_2 0}}{T_{fire}}\right]}. \quad (14)$$

The data of Sabri [13] on the fire point of aqueous solutions of acetone, methanol, ethanol, 1-propanol and 2-propanol were taken as objects for comparison.

Fig. 3 shows the calculated dependences of the ignition temperature for these aqueous solutions. In general, the dynamics of the increase in the ignition temperature with an increase in the proportion of water is in good agreement with the available experimental data and . It can be noted that the presence of 50% water in the solution increases its ignition temperature by 10 °C.

Ignition of binary solutions of combustible liquids. Initially, the molar composition of a binary mixture of combustible liquids is set $Z_{f1} + Z_{f2} = 1$. In the gas phase according to Raoul's law $\bar{p}_{f1,s} = Z_{f1}\bar{p}_{f1,so}$, $\bar{p}_{f2,s} = (1 - Z_{f1})\bar{p}_{f2so}$.

The saturated vapour pressures of combustible components are determined by the Clausius-Clapeyron law , if L f is taken constant, then

$$\bar{p}_{f1,s} = \frac{p_{f1,s0}}{P_0} = \exp\frac{L_{f1}\mu_{f1}}{RT_{boil,f1}}\left[1 - \frac{T_{boil,f1}}{T_{fire}}\right], \quad \bar{p}_{f2,s} = \frac{p_{f2,s0}}{P_0} = \exp\frac{L_{f2}\mu_{f1}}{RT_{boil,f2}}\left[1 - \frac{T_{boil,f2}}{T_{fire}}\right].$$

We find the mass fraction of saturated vapours[6]

$$Y_{f1,s} = \frac{\mu_{f1}Z_{f,1}\bar{p}_{f1,s0}}{\mu_{f1}Z_{f,1}\bar{p}_{f1,s0} + \mu_{air}\left(1 - Z_{f,1}\bar{p}_{f1,s0} - \left(1 - Z_{f,1}\right)\bar{p}_{f2,s0}\right) + \mu_{f2}\left(1 - Z_{f,1}\right)\bar{p}_{f2,s0}},$$

$$Y_{O_2,s} = \frac{\mu_{O_2}x_{O_2}\left(1 - Z_{f,1}\bar{p}_{f1,s0} - \left(1 - Z_{f,1}\right)\bar{p}_{f2,s0}\right)}{\mu_{f1}Z_{f,1}\bar{p}_{f1,s0} + \mu_{air}\left(1 - Z_{f,1}\bar{p}_{f1,s0} - \left(1 - Z_{f,1}\right)\bar{p}_{f2,s0}\right) + \mu_{f2}\left(1 - Z_{f,1}\right)\bar{p}_{f2,s0}}.$$

The stoichiometric concentrations are found from chemical equations, taking into account the mole fractions of combustible vapours

$$\bar{p}_{f,s} = Z_{f,1}\bar{p}_{f,s0} + \left(1 - Z_{f,1}\right)\bar{p}_{f2,s0},$$

$$A_{f,1} + \nu_{O_2,1}(O_2 + \frac{1 - x_{O_2}}{x_{O_2}}N_2) \to \nu_{CO_2,1}CO_2 + \nu_{H_2O,1}H_2O + \nu_{O_2,1}\frac{1 - x_{O_2}}{x_{O_2}}N_2$$

$$A_{f,2} + \nu_{O_2,2}(O_2 + \frac{1 - x_{O_2}}{x_{O_2}}N_2) \to \nu_{CO_2,2}CO_2 + \nu_{H_2O,2}H_2O + \nu_{O_2,2}\frac{1 - x_{O_2}}{x_{O_2}}N_2.$$

The stoichiometric concentration of fuel vapours is found from the chemical equations

$$Y_{f1,steh}=\frac{\mu_{f1}Z_{f,1}\bar{p}_{f,s0}}{\mu_{f1}Z_{f,1}\bar{p}_{f1,s0}+\frac{\mu_{air}}{x_{O_2}}\left(\nu_1 Z_{f,1}\bar{p}_{f1,s0}+\nu_2\left(1-Z_{f,1}\right)\bar{p}_{f2,s0}\right)+\mu_{f2}\left(1-Z_{f,1}\right)\bar{p}_{f2,s0}}.$$

We use the ignition condition ($Y_{f1,s}=Y_{f1,steh}$)and the formulas for $Y_{f1,s}$ and$Y_{f1,steh}$. As a result, the dependence of the mole fraction of the first component in a binary solution on the ignition temperature will be

$$Z_{f,1}=\frac{\frac{x_{O_2}}{\nu_{O_2,1}}-\left(\frac{\nu_{O_2,2}}{\nu_{O_2,1}}+1\right)\exp\frac{L_{f2}\mu_{f2}}{RT_{boil,2}}\left[1-\frac{T_{boil,2}}{T_{fire}}\right]}{\left(\frac{x_{O_2}}{\nu_{O_2,1}}+1\right)\exp\frac{L_{f1}\mu_{f1}}{RT_{boil,1}}\left[1-\frac{T_{boil,1}}{T_{fire}}\right]-\left(\frac{\nu_{O_2,2}}{\nu_{O_2,1}}+1\right)\exp\frac{L_{f2}\mu_{f2}}{RT_{boil,2}}\left[1-\frac{T_{boil,2}}{T_{fire}}\right]}. \quad (15)$$

For comparison, a solution of octane and decane, ethanol and 1-butanol were selected. The ignition temperatures of the components in these two pairs of coolants differ significantly, which will allow us to trace the dynamics of the influence of the solution composition. Fig. 4 shows the results of the calculation using formulas (14) and (15). A monotonic change in the ignition temperature value is observed when the composition of the binary solution changes. Pra significant difference in the ignition temperatures of the two components (more than 20 °C), the volatile component can be considered inert when its content in the solution is less than 50 %. The smaller the difference, the greater the error..

Conclusions. In this paper, a methodology for calculating the ignition temperature of individual liquids of flammable substances, their aqueous solutions and binary solutions is proposed. It is based on the assumption that at the ignition temperature near the droplet surface, the stoichiometric ratio between vapour and oxygen for each component must be fulfilled. This approach makes it possible to obtain an analytical dependence of the component fraction in a binary solution on the ignition temperature and thus take into account not only the temperature dependence of saturated vapour of a liquid, but also the temperature dependence of the specific heat of vapour formation. Comparisons with the experimental results give satisfactory results.

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Стехіометрична модель запалювання горючих рідин та їх бінарних сумішей

Управління характеристиками стійкого горіння та викидів при згоранні альтернативних рідких палив, зменшення вуглецевого індексу йде через використання в якості домішок кисневмісних спиртів та водневмісних речовин (водень, аміак, вода). Критичні температури вимушеного запалення і спонтанного запалення рідких палив є важливими характеристиками стійкого полум'яного горіння, які залежать від складу рідини та кисне-азотної газової суміші. В роботі вирішуються актуальні питання знаходження температури вимушеного займання горючих рідин і їх сумішей в кисне-азотному газовому середовище з температурою меншою за температуру кипіння рідин в результаті короткочасного впливу на поверхню рідини пілотного полум'я (теплове джерело запалювання). Після віддалення від поверхні краплі джерела запалювання крапля продовжує стійке полум'яне горіння. В основі моделі лежить припущення, що при температурах рідини, менших за температуру займання, в насиченому шарі зміст кисню набагато більше, а горючих парів менше стехіометричного складу згідно рівнянню хімічної реакції. В той же час виконується необхідна умова займання – самоприскорення швидкості екзотермічної реакції. У результаті прогрівання і випаровування в насиченому газовому шарі при температурі займання концентрації компонент досягають еквівалентних значень, а початкове підвищення температури газового шару приводить до стійкого горіння краплі з власним дифузійним полум'ям.

На температуру займання рідин дослідники мало звертають уваги. Експериментальних значень вкрай мало.На температуру займання рідин дослідники мало звертають уваги. Експериментальних значень вкрай мало. Але існує стехіометрична модель Джонса, на якій основані більшість робіт. Нами розвинута стехіометрична модель для вимушеного займання і самозаймання таотримані аналітичні залежності температури займання для індивідуальних рідин, їх водних розчинів та бінарних розчинів двох легкозаймистих речовин. Ці залежності задовільно узгоджуються з наявними експериментальними даними.

Ключові слова: *температура займання, пари горючої рідини, крапля, стехіометрія, бінарні розчини.*