COMPOSITION OF FLAMMABLE MATERIAL AND AIR MIXTURES CORRESPONDING TO MAXIMUM FLAME PROPAGATION RATE

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Abstract. Relationship between the important fire protection indices – flammable gaseous materials (or vapours arising from liquid flammable materials during a fire) concentrations in gas-air mixtures at maximum flame diffusion rate – and stoichiometric oxygen molecule number in combustion reaction equation were investigated.

The obtained equation combining the above mentioned factors were used to calculate especially dangerous flammable organic material concentrations in combustible mixtures. The obtained data will allow undertaking preventive measures and evaluating various stored materials which are fire hazards at construction and military sites.

Keywords: combustion reactions, flammable material concentrations, fire spreading rate.

1. Introduction

A large influence on the Earth’s climate is determined by the intensification of the greenhouse effect in recent years. This is caused by increase in CO₂ amount in the Earth’s atmosphere. CO₂ molecules absorb irretrievable part of the Sun’s energy reaching the Earth’s surface. As a result the Earth’s temperature is slowly but surely increasing.

One of the CO₂ paths into the Earth’s atmosphere is through the combustion process of organics.

Combustion is a complex physico-chemical process – a spontaneous chemical oxidation-reduction reaction, during which redistribution of reacting material atom valent electrons occurs. Heat and light as a flame is evolved during combustion [1–3].

Flammable materials and oxidators take part in the combustion process.

Various flammable materials are used in industry, technics and domestic fields. In our opinion the most important ones can be divided as follows:

1) elementary substances – metals (sodium, potassium, magnesium, aluminium) and non-metals (hydrogen, carbon, phosphorus, sulphur);
2) inorganic materials – hydrides (boron, nitrogen, silicon, phosphorus, sulphur); lower oxidation degree oxides (carbon monoxide); sulfides, nitrides, phosphides;
3) organic materials – hydrocarbons (alkanes – methane, ethane, propane, butane, octane, etc); alkene (ethylene and others), aromatic hydrocarbons (benzene, toluene, xylene, styrene, etc); alcohols (methanol, ethanol, butanol, etc); ethers (dimethyl as well as diethyl ethers); aldehydes (formaldehyde, acetaldehyde, etc);
ketones (acetone, etc); carboxy acids (acetic acid, etc); esters (ethyl acetate, etc); nitro compounds (nitrobenzene, etc); amines (ethylamine, etc);
4) natural organic combustible materials (crude oil, coal, lignite or brown coal, combustible shale, natural gas) as well as its refining products (gasoline, kerosene, diesel fuel, etc);
5) macromolecular organic materials – plastics and its articles, natural cellulose raw materials and its reprocessed products as well as production waste (wood, agricultural production products, peat, cultural and non-cultural vegetation, forests).

Organic materials, as a matter of fact, can be burnt, e.g industrial fuels, also fuels at factories, warehouses, auto parks and other organic assortments.

Oxidizers, like air, oxygen, ozone, hydrogen peroxide, sodium and other metal peroxides, halogens (fluorine, chlorine), nitric acid and its salts – nitrates (saltpetre), chlorates as well as perchlorates and other materials can be used.

Combustion can be homogeneous (natural gas combustion in air), heterogeneous (heavy oil droplets in air) and combustion of explosives.

A flame is a very important combustion process result. The flame temperature and brightness depends on the combustible materials and oxidator composition as well as its state. For example, the combustion temperature of hydrogen and air mixture is 1900 °C, in the case of acetylene-oxygen mixture it will reach 3000 °C, while for a cyanacetylene-ozone mixture – even 6000 °C [1].

The flame can propagate from its source at a certain rate. The flame propagation is connected with heat transmission due to thermal conductivity, and is called natural...
propagation, while its corresponding flame propagation rate – normal flame propagation rate, its dimension is m/s. This index depends on combustible material composition, combustible mixture composition, pressure, initial combustible mixture temperature and presence of admixtures.

Normal flame propagation rate (in m/s) differ widely for various combustible materials. For example, when paper burns in a roll, it is even to 0,3; for textile articles – 0,3–0,4; for synthetic rubber – 0,4; for wooden constructions – 1–4; for ethanol 8–20; for acetone – 32; for hexane – 32; for pentane – 35; for methane – 36; for diethyl ether, benzene – 38; for propylene – 43; for carbon monoxide – 46; for carbon disulfide – 48; for ethylene – 63°; for acetylene – 120; for hydrogen – 225 [1].

The combustion temperature during a fire varies: in dwelling quarters and public premises it is (800–900 °C); in quarters where fuel burns (1000–1400 °C); when magnesium or termite burns it reaches (2000–3000 °C).

Fumes from fires contain toxic gases – charcoal fumes, nitrogen oxide, phosgene, hydrogen cyanide [2].

As it is well known, living organisms are alive while they inhale oxygen from the air and when it circulates in the organism. Oxygen is transported and distributed in all parts of the organism. Oxygen and carbon dioxide are exhaled in呼出 gas.

As we can see from the equation, combustion of 1 l of octane requires 12,5 l of oxygen. Because the amount of oxygen in the air is only 20,947 % of the air volume (or 0,21 parts), then if we do not take into account the changes in gaseous volume with increase in temperature, we obtain the following equation:

\[ V_{v_{0}} = 100/(1 + 4,76 n_{O_{2}}) \%, \]  

(2)

where 4,76 – coefficient, which is the inverse of oxygen content in air by parts and even to 0,21; \( n_{O_{2}} \) – stoichiometric coefficient of \( O_{2} \) value in the equation.

According to equation (2), we find \( V_{v_{0}} \) values for a number of characteristic combustible organic materials (materials are arranged with an increase in \( V_{v_{0}} \) nomenclature) shows the \( V_{v_{0}} \) values found by (2), the denominator – determined from experimental curves [1]. The investigated group of materials is made up of the most important representatives of organic compounds from the practical usage point of view:

- hexane \( C_{6}H_{14} \) – 2,16/2,5;
- pentane \( C_{5}H_{12} \) – 2,56/3,0;
- benzene \( C_{6}H_{6} \) – 2,72/3,0;
- diethyl ether \( (C_{2}H_{5})_{2}O \) – 3,13/4,5;
- propane (propylene) \( C_{3}H_{6} \) – 4,46/4,7;
- acetone \( (CH_{3})_{2}CO \) – 4,46/6,2;
- ethane (ethylene) \( C_{2}H_{4} \) – 6,54/7,0;
- carbon disulfide \( CS_{2} \) – 6,54/8,5;
- methane \( CH_{4} \) – 9,51/10,5;
- acetylene – 8,60/10.

Correlation between the values found experimentally (from [1]) – \( V_{v_{0}}(\text{exp}) \) and values obtained from equation (2) – \( V_{v_{0}}(2) \) are shown in Fig 1.

As it can be seen from Fig 1, connection between experimental (actual) \( V_{v_{0}} \) values and calculated values can be expressed by the following equations:

1) in the case of C – H compounds –

\[ V_{v_{0}} = 111/V_{v_{0}}(2), \% \]  

(3)

or when \( V_{v_{0}}(2) \) value from equation (2) is used –

\[ V_{v_{0}} = 111/(1 + 4,76 n_{O_{2}}), \% \]  

(4)
2) in the case of C – O – H compounds –
\[ V_{\text{g}} = 1.11V_{\text{g(2)}} + 1.2, \% \]  

or when \( V_{\text{g(2)}} \) value from equation (2) is used –
\[ V_{\text{g}} = 111/(1+4.76 n_{O_{\text{c}}}) + 1.2, \% \]  

where 111 – coefficient obtained by multiplying the equation (2) value 1.11 by 100 \( \% \), which takes into account the influence of temperature coefficient with increase in reaction temperature; 1.2 – coefficient, which takes into account the presence of O and S atoms in the combustible material composition and influence on the increase in the amount of materials in a combustible mixture.

\[ V_{\text{g}} \] values obtained according to equations (4) and (6) – \( V_{\text{g(4,6)}} \) are very close to \( V_{\text{g(exp)}} \) values obtained from experimental data [1]. For the investigated materials, we obtained the following \( V_{\text{g(4,6)}} / V_{\text{g(exp)}} \) values:

- \( C_{4}H_{12} \): 2.40/2.5;
- \( C_{4}H_{12} \): 2.84/3.0;
- \( C_{4}H_{6} \): 3.02/3.0;
- \( C_{5}H_{12} \): 4.67/4.5;
- \( C_{6}H_{14} \): 4.95/4.7;
- \( C_{6}H_{14} \): 6.15/6.2;
- \( C_{7}H_{16} \): 7.26/7.0;
- \( C_{8}H_{18} \): 8.46/8.5;
- \( C_{9}H_{20} \): 10.56/10.5;
- \( C_{10}H_{22} \): 8.6/10.0.

The correlation coefficient reaches even 0.9998 (Fig 2).

So equations (4) and (6) give us a proper dependency of combustible material amount in mixtures with air at maximum flame propagation rates on combustible material composition.

\[ V_{\text{g}} \] values for \( C_{n}H_{2n+2} \) hydrocarbon series (CH, C2H6, ... ) can be also found also by using equation (7), which is an analogy of equation (2):
\[ V_{\text{g}} = 33.3/(1 + 2.15 n_{C}), \% \]

where \( n_{C} \) – number of C atoms in \( C_{n}H_{2n+2} \) series hydrocarbon formula.

2.2. Calculation results of combustible material and air mixture composition at maximum flame propagation rate

The information presented below include the most important organic combustible materials, which are used in plants, factories, construction sites as well as in shop warehouses, power utilities technical, transport, trade network as well as in households, \( V_{\text{g}} \) values, which we obtained according to (4) and (6) equations are given. The following is given in the list: material’s name, brutto formula and in brackets – physical state at room temperature (s – solid, l – liquid, g – gaseous; in case of solid or liquid materials, it boiling temperature, °C; \( V_{\text{g}} \) value):

1. **Hydrocarbons**

   - **Alkanes** (CnH2n+2):
     - methane \( CH_{4} \) (g) 10.56;
     - ethane \( C_{2}H_{6} \) (g) 6.28;
     - propane \( C_{3}H_{8} \) (g) 4.48;
     - butane \( C_{4}H_{10} \) (g) 3.47;
     - pentane \( C_{5}H_{12} \) (l, 36) 2.84;
     - hexane \( C_{6}H_{14} \) (l, 69) 2.40;
     - heptane \( C_{7}H_{16} \) (l, 98) 2.08;
     - octane \( C_{8}H_{18} \) (l, 125) 1.83.

   - **Alkenes** (CnH2n):
     - ethene (ethylene) \( C_{2}H_{4} \) (g) 7.26;
     - propene (propylene) \( C_{3}H_{6} \) (g) 4.95;
     - butene (butylene) \( C_{4}H_{8} \) (g) 3.76.

   - **Alkines** (CnH2n-2):
     - etyne (acetylene) \( C_{2}H_{2} \) (g) 5.54.

   - **Dienes** (diolefins), CnH2n-2:
     - 1,3-butadiene \( C_{4}H_{6} \) (g) 4.08;
     - isoprene \( C_{5}H_{8} \) (l, 34) 3.23.

   - **Cycloalkanes** (cycloalkanes), CnH2n:
     - cyclopropane \( C_{3}H_{6} \) (g) 4.95;
     - cyclobutane \( C_{4}H_{8} \) (l, 13) 3.76.

   - **Cycloalkenes** (cycloalkenes), CnH2n-2:
     - cyclopentene \( C_{5}H_{8} \) (g) 5.54.

   - **Aromatic hydrocarbons** (arenes):
     - benzene \( C_{6}H_{6} \) (l, 80) 3.02;
     - toluene \( C_{6}H_{5}CH_{3} \) (l, 111) 2.53;
     - o–xylene \( C_{6}H_{5}(CH_{3})_{2} \) (l, 144) 2.18.
2) C₆H₂₈: styrene C₆H₅CH = CH₂ (l, 145) 2,28.

- **Alcohols**
  1. Saturated monohydroxy alcohols, CₙH₂ₙ+1OH:
     - methyl (methanol) CH₃OH (l, 65) 14,84;
     - ethyl (ethanol) C₂H₅OH (l, 79) 8,46;
     - propyl (1–propanol) C₃H₇OH (l, 97) 6,15;
     - butyl (1–butanol) C₄H₉OH (l, 118) 4,96;
     - amyl (1–pentanol) C₅H₁₁OH (l, 138) 4,22.
  2. Alicyclo alcohols, CₙH₂ₙ-1OH:
     - cyclobutanol C₄H₇OH (l, 123) 5,28;
     - cyclopentanol C₅H₉OH (l, 141) 4,43;
     - cyclohexanol C₆H₁₁OH (l, 161) 3,88.
  3. Aromatic alcohols, CₙH₂ₙ-7OH:
     - benzyl alcohol C₆H₅CH₂OH (l, 205) 3,88.
  4. Bihydroxy alcohols, CₙH₂ₙ(OH)₂:
     - ethylene glycol (etandiol) C₂H₄(OH)₂ (l, 198) 9,80.
  5. Trihydroxy alcohols, CₙH₂ₙ-1(OH)₃:
     - glycerine (propantriol) C₃H₅(OH)₃ (l, 290) 7,48.

- **Ethers**
  - diethyl ether (C₂H₅)₂O (l, 35) 4,96;
  - dioxane C₄H₈O₂ (l, 102) 5,68.

- **Aldehydes**
  - formaldehyde HCHO (g) 20,47;
  - acetaldehyde CH₃CHO (l, 20) 9,80.

- **Ketones**
  - acetone (CH₃)₂CO (l, 56) 6,74.

- **Carboxylic acids (carbonic acids):**
  - formic (methane) acid HCOOH (l, 101) 34,04;
  - acetic (ethane) acid CH₃COOH (l, 118) 11,76;
  - acrylic (propene) acid CH₂ = CHCOOH (l, 140) 8,46.

  Analysis of all the data shows that the more C atoms (as well as H atoms) in the compound molecules, the more oxygen (as well as air) there should be in a combustible mixture. As a result, the flammable gas volume (%) in a gaseous mixture \( V\% \) is inversely proportional to C atom number (as well as to \( 2O \) n) in alkane molecules. All this is reflected in equation (2).

### 2.3. Combustible material and air mixture composition dependency on combustion enthalpy value

We can logically think, that value \( V\% \) can correlate with combustible material combustion enthalpies (combustion heat) \( \Delta H\text{comb} \).

To evaluate this proposition below we compared some combustible organic compound experimental \( V\% \) values (%) from [1] – \( V\%_{(\text{exp})} \) and (as a fraction) \( \Delta H\text{comb} \) (kcal/mol) values:

\[
\begin{align*}
\text{C}_6\text{H}_{14} & : 2,5/1032; \ 
\text{C}_6\text{H}_{12} & : 3,0/845; \ 
\text{C}_6\text{H}_{8} & : 3,0/819; \ 
\text{(C}_2\text{H}_5)_2\text{O} & : 4,5/652; \ 
\text{C}_3\text{H}_8 & : 4,7/522; \ 
\text{(CH}_3)_2\text{CO} & : 6,2/427; \ 
\text{C}_2\text{H}_6 & : 7,0/302; \ 
\text{CS}_2 & : 8,5/264; \ 
\text{C}_2\text{H}_4 & : 8,6/311; \ 
\text{CH}_4 & : 10,5/243. \ 
\end{align*}
\]

On the basis of these values we created a \( V\%_{(\text{exp})} \) – \( \Delta H\text{comb} \) relationship (Fig 3).

Fig 3. Relationship between experimental \( V\% \) values \( V\%_{(\text{exp})} \) and combustion enthalpies \( \Delta H\text{comb} \) (kcal/mol). Material numbers are the same as in Figs 1 and 2; 10 – \( \text{C}_2\text{H}_2 \)

The given correlation has a product \( V\% \cdot \Delta H\text{comb} \approx \text{const} \) meaning and could be expressed by the following equation:

\[
V\% \cdot \Delta H\text{comb} + 30 \approx 2560, \quad (8)
\]

where 30 – C–H as well as C–H–O type compounds combustion enthalpy high-temperature increase (kcal/mol), 2560 – product of \( V\% \) (\( \Delta H\text{comb} + 30 \)) value for mention e types of compounds (kcal/mol).

From equation (8) we can find the final correlation:

\[
V\% \approx 2560 / (\Delta H\text{comb} + 30) \quad (\%). \quad (9)
\]

Below we compared \( V\% \) values according to equation (9) \( V\%_{(\text{exp})} \) with (as a fraction) experimental \( V\%_{(\text{exp})} \) values:

\[
\begin{align*}
\text{C}_6\text{H}_{14} & : 2,41/2,5; \ 
\text{C}_6\text{H}_{12} & : 2,93/3,0; \ 
\text{C}_6\text{H}_{8} & : 3,02/3,0; \ 
\text{(C}_2\text{H}_5)_2\text{O} & : 3,75/4,5; \ 
\text{C}_3\text{H}_8 & : 4,64/4,7; \ 
\text{(CH}_3)_2\text{CO} & : 5,60/6,2; \ 
\text{C}_2\text{H}_6 & : 7,71/7,0; \ 
\text{CS}_2 & : 8,71/8,5; \ 
\text{CH}_4 & : 9,38/10,5; \ 
\text{C}_2\text{H}_2 & : 7,51/10. \ 
\end{align*}
\]

Relationship between \( V\% \) values obtained from equation (9) and experimental \( V\%_{(\text{exp})} \) values – \( V\%_{(\text{exp})} \) is given in Fig 4. As we can see, there is a very good correlation between these values (the correlation coefficient is equal to 0.9798).

This relationship can be explained by the fact that the larger the material combustion enthalpy, the lower the combustible material concentration in a combustible mixture.
Fig. 4. Correlation between $V_\%$ values obtained from equation (8) – $V_\%(\text{exp})$ and experimental $V_\%$ values – $V_\%(\text{exp})$

3. Conclusions

1. Equations were derived which described relationship between combustible material volume fractions, % of this material and air mixture ($V_\%$) on stoichiometric coefficient reaction values in equations (\textit{8}) –

- for C–H type compounds
  \[ V_\% = 111/(1 + 4.76n_{O_2}) \, (\%) \],

- for C–O–H type compounds
  \[ V_\% = 111/(1 + 4.76n_{O_2}) + 1.2 \, (\%) \],

where 4.76 – coefficient inversely proportional to the amount of oxygen in the air by parts (0.21).

2. $V_\%$ values for several tens of combustible organic materials were determined on the basis of these equations.

3. The knowledge of $V_\%$ values will allow to make apparent the most fire dangerous materials in households, production and other premises and allow to plan efficiently protection of human beings, animals as well as constructions and equipment against fires.

References

СОСТАВ СМЕСЕЙ ГОРЮЧИХ ВЕЩЕСТВ И ВОЗДУХА, СООТВЕТСТВУЮЩИЙ МАКСИМАЛЬНОЙ СКОРОСТИ РАСПРОСТРАНЕНИЯ ПЛАМЕНИ

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Резюме

Рассмотрена важная в отношении пожароопасности зависимость содержания газообразных горючих газов (или паров, образовавшихся из жидких горючих жидкостей в условиях горения) в их смеси с воздухом при максимальной скорости распространения пламени от стехиометрического количества молекул кислорода в уравнении реакции горения.

Получены уравнения, связывающие упомянутые факторы. На основании этих уравнений рассчитаны наиболее опасные концентрации горючих смесей для ряда органических веществ. Знание этих концентраций позволит оценить степень опасности веществ на производственных, строительных и военных объектах.

Ключевые слова: горючие вещества, концентрации горючих смесей.