

THE REGULARITIES IN FLAMMABILITY LIMITS OF ORGANIC SUBSTANCES IN AIR

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ABSTRACT

The physical nature of flammability limits was considered using some peculiarities of chemical kinetics of combustion of gaseous organic substances in air. New regularities in lower flammability limits and compositions of mixtures near peak points of flammability curves are revealed. These regularities are the following. Firstly, adiabatic temperatures T_{adCO} at combustion of gaseous mixtures up to CO and H₂O for fuel-air mixtures at lower flammability limits and fuel-air-diluent mixtures at peak points of flammability curves are in rather narrow ranges. Secondly, compositions of ternary fuel-air-diluent gaseous mixtures are close to stoichiometry in relation to combustion up to CO and H₂O. These regularities are important for the creation of new methods for an analytical evaluation of flammability limits of organic substances in air.

INTRODUCTION

Complex gaseous mixtures are used or formed during normal and emergency conditions in process industries. Such mixtures can also be formed by inertization of combustible mixtures by inert or chemically active agents. It is important to know flammability limits (FL) in such mixtures in order to evaluate fire and explosion hazards of technological processes and installations and to determine relevant measures for fire and explosion safety. In practice, flammability limits in complex gaseous mixtures are usually determined experimentally by standard methods (for example¹⁻³). There have been some investigations aimed at an analytical assessment of flammability limits (for example^{1,4-13}), but these methods are mainly empirical and often do not take into account the main regularities of

combustion of near-limit mixtures. Those methods are valid as a rule for burning in air and do not give any possibility to evaluate flammability limits in oxidizers, which differ from air (for example, oxidizers, which are mixtures of nitrogen and oxygen or nitrous oxide). The current methods are proposed mainly for the evaluation of lower or upper flammability limits and are not suitable for calculations of FL for combustible-oxidizer-diluent ternary mixtures. This study was aimed at analysing the regularities in FL of organic substances in air, based on the investigations of^{4, 7, 9, 11, 14-20}.

THE THEORETICAL BASIS FOR EVALUATION OF FLAMMABILITY LIMITS

The existence of FL of gaseous mixtures was probably discovered at the end of the 19th century²¹. Many investigations were aimed at revealing the nature of this phenomenon from the viewpoints of thermal^{22,23} and chain²⁴ theories of combustion. The thermal theory explains the existence of FL by heat losses from a flame front. Despite the significant successes of the thermal theory, it cannot satisfactorily explain some important physical phenomena (for example, inhibition of combustion). The chain theory explains the existence of FL by a competition of chain-branching and chain-termination reactions in a flame front. This theory did not receive as wide an application as the thermal theory, but some effects can be easily understood on its basis (for example, the influence of chemically active agents on combustion characteristics). In²² an attempt was made to combine the main concepts of both theories for explaining of the nature of FL, but the rather abstract character of that study does not allow practical applications to be made (for example, to create methods for estimation of FL). Numerical methods for the simulation of flame propagation in gaseous mixtures gained a wide distribution. These methods take into account diffusion, thermal conductivity, and up to several hundred elementary chemical reactions (for example²⁵⁻²⁷). But an interest in the explanation and analytical evaluation of FL remains^{7,15,16,28-41}.

According to a concept developed in³⁹, FL in a given gaseous mixture are determined both by chemical reactions in a flame front and interactions of the flame with surroundings (mainly radiation heat losses and a flame stretch). The initial composition of the gaseous mixture should be such that a flame should be able to generate radicals with a velocity sufficient for conversion of the whole fuel in a preflame zone into intermediate products. The most important reactions in hydrocarbon-air flames are the processes $H+O_2 \rightarrow OH+O$ and $OH+CO \rightarrow CO_2+H$. Lean and near-stoichiometric flames in principle can be characterized by flames of the system $H_2/CO/O_2/N_2/H_2O$. The chemical reaction in the flame front runs in two stages⁴². In the first stage, taking place in the preflame zone, fuel is converted due to interactions with radicals H, OH, O through a series of intermediate products into H_2 and CO. Carbon oxide is oxidized to CO_2 in the second stage. The analogous concept is described in⁴¹.

It was noted²³, that if an abrupt reduction in a heat release rate (one or two orders of magnitude) occurs at some critical content of fuel in a gaseous mixture, this fuel concentration will correspond to a flammability limit. The value of this limit will rather weakly depend on the magnitude of the heat losses. This viewpoint coincides qualitatively with results obtained in^{28, 29}. It was found by means of numerical modelling of a flame propagation²⁸, that values of FL rather weakly depend on the rate of heat loss, despite the fact that these heat losses stipulate an existence of these limits. This situation can take place in the case when a dependence on temperature (and therefore on a fuel concentration in the initial mixture) of a rate of a chemical reaction in a flame front is very abrupt. Consider, for example, a lean near-limit gaseous mixture of a combustible and air. Let the dependence of the rate of the chemical reaction on temperature, in a flame front, be characterized by an abrupt change at some temperature T_* . The temperature T_* in the flame front will be reached only at some minimum fuel

concentration C_{min} , and at an initial fuel content in the mixture $C_f < C_{min}$ the heat release rate W_h is very low and in general can be lower than the rate of heat losses W_l . But at $C_f > C_{min}$ the value of W_h increases rapidly and becomes higher than W_l , whose value has no abrupt change at $T = T^*$. In this case the value C_{min} will determine the value of lower flammability limit C_{LFL} , which will rather weakly depend on the rate of heat losses.

Now consider the question “what physical effect could be a cause of an abrupt change in the rate of a chemical reaction in a flame front with temperature?” The results³¹ concerning some peculiarities of non-isothermal regimes of chain-branching chemical reactions will be the basis of this discussion. According to³¹, some critical temperature T_{cr} exists, at which temperature a transition of the chemical reaction from a slow regime to a regime of a chain explosion occurs. After such a transition, a very rapid increase of concentrations of radicals takes place. At $T < T_{cr}$ (slow regime) the dependence of the heat release rate on temperature can be described rather well by the Arrhenius formula. But in the regime of the chain explosion this dependence is close to $\exp[\exp(-E/RT)]$. Combustion of organic substances in air is a chain-branching process, therefore some critical temperature exists, at which the rate of a chemical reaction and the appropriate heat release rate have an abrupt change. A possibility of reaching of this temperature determines the values of FL.

Consider the question “what is the physical nature of the value of T_{cr} for the combustion of organic substances in air?” In order to answer this question consider some peculiarities of chemical kinetics of the combustion of lean and near stoichiometric mixtures. As it was noted above, high-temperature zones of such flames can be simulated by flames of the system $H_2/CO/O_2/N_2/H_2O$. Consider an initial stage of a chain explosion, which is important for estimation of critical conditions for its origin. A simplified kinetic scheme of combustion of this system in the initial stage of chain explosion can be written in the following way:



Radicals of HO₂ formed in reaction (R6) can both continue a reaction chain (processes (R8) and (R10)) and can cause chain termination (processes (R9), (R11) and (R12)). For evaluation of conditions for the transition of the chain-branching process of CO oxidation into chain explosion it is necessary to calculate a probability of chain-branching through a HO₂ radical. It should be noted that the role of reactions (R11) and (R12) in chain termination will be negligible compared with the process (R9) in the initial stages of a chain explosion. At this stage a typical temperature is close to 1000-1200 K, and concentrations of radicals H, O, OH are very low. Concentrations of radicals O and OH are sufficiently lower than that of radical H because of their higher chemical activities^{39,40}. Rate constants of the reactions (R9) to (R12) are rather close to each other in the temperature range mentioned above^{39,40,43}. Therefore, a probability δ of chain termination through radical HO₂ can be described by the formula:

$$\delta = k_9 / (k_8 + k_9 + k_{10}) \quad (1)$$

where k_i are rate constants of the appropriate reactions.

In the remaining analysis only reactions (R1) to (R7) will be considered, taking into account that reaction (R6) is a chain termination process with an effective rate constant $k_{6eff} = 2k_6\delta$. The coefficient «2» in the last expression is due to the fact that recombination of two H atoms occurs as a result of a sequence of the reactions (R6) and (R9). On the basis of the method of quasi-stationary concentrations⁴⁴ the following critical condition for transition of the chain branching process of CO oxidation into chain explosion can be obtained:

$$\frac{k_2}{1 + \frac{k_7[O_2][M]}{k_4[H_2] + k_5[H_2O]}} = k_6[M] \frac{k_9}{k_8 + k_9 + k_{10}} \quad (2)$$

In the following analysis, experimental data⁴⁸⁻⁵⁰ will be taken into account on profiles of temperature, molecules and radicals in flame fronts of premixed hydrocarbon-air flames, and also rate constants of the reactions mentioned above from⁴³.

At temperature $T=1000$ K, which is typical for the initial stage of chain explosion, the following expressions take place: $k_7[M]/k_5 \approx 10^{-1}$, $k_7[M]/k_4 \approx 10^{-3}$.

At $[H_2] > 10^{-3}[O_2]$ or $[H_2O] > 10^{-1}[O_2]$ an influence of the term $k_7[O_2][M]/(k_4[H_2] + k_5[H_2O])$ on a root of Equation 2 in relation to temperature T_{cr} is negligible. In this case Equation 2 can be rewritten in the following way:

$$k_2 - k_6[M] \frac{k_9}{k_8 + k_9 + k_{10}} = 0 \quad (3)$$

which is close to the well known critical condition of autoignition of hydrogen on the second limit:

$$2k_2 - k_6[M] = 0 \quad (4)$$

Equation 3 has only one root $T_{cr} \approx 1000$ K. The value of T_{cr} determines the minimum temperature at which a chemical reaction in the system H₂/CO/O₂/N₂/H₂O can proceed in the regime of a chain explosion, that is at which an abrupt increase of the rates of chemical reaction and heat release occurs. Thus, the possibility of flame propagation in a gaseous mixture is determined at most by a regime of CO oxidation in a flame front. The values of FL should also be controlled by this factor. Therefore,

parameters related to the chemical kinetics of CO oxidation will be used in this study for the creation of methods for evaluation of FL. The Adiabatic temperature of the combustion of a gaseous mixture up to CO and H₂O (T_{adCO}) is an example of such a parameter^{7, 11, 14-20, 45}. In the following sections of the paper it will be shown how this viewpoint is correlated to the available experimental data on FL of gaseous mixtures.

AN ANALYSIS OF EXPERIMENTAL DATA

In this section, the most reliable published experimental data on FL for organic gases and vapours consisting of atoms C, H, O, N will be considered. Data on FL for combustible - oxidizer - diluent ternary mixtures will also be considered. Some of these data were taken from studies where experimental data available in international scientific literature have been evaluated (for example^{46,47,52,53}), other data was taken from original experimental studies (for example^{8,19-21,37,55}). But in all cases the reliability of experimental data was examined by an analysis of experimental procedures and comparison of obtained data with results of other investigations.

Lower flammability limits

There is a large array of experimental data in the literature on lower flammability limits (LFL) for mixtures of gases and vapours with air (for example^{8,10,19-21,37,46,47}). One of the main regularities, which has been revealed from analysis of these data, concerns the fact that adiabatic temperatures T_{ad} at the combustion of gaseous mixtures of organic substances, consisting of atoms C,H,O,N, and air at the lower flammability limit, are close to each other. The values of the adiabatic temperatures for mixtures at lower flammability limits are close to 1550 K⁽⁴⁾, but this empirical rule does not contain any reliable theoretical justification. The same can be noted for other empirical regularities for LFL described in the literature⁴⁻¹³. The most important correlations were obtained for a value of adiabatic temperature T_{adCO} ^{7,14-18}.

Table 1 shows results of calculations of T_{adCO} for organic substances of various classes at lower flammability limits. Average values of T_{adCO} for each class with appropriate mean square deviations are presented here (and further mean square deviations are shown as a measure of scattering). Experimental data on LFL needed for calculations were taken from^{46,47}, where the more reliable data are presented. Data for T_{ad} are shown for comparison. It can be seen that the mean square deviations for T_{adCO} within each class of organic compounds are, as a rule, lower than for T_{ad} . No regular change of T_{adCO} within each class of organic compounds was revealed.

Inertization points

It is well known from results of numerous experiments on various fuels, that a dependence of FL on diluent concentration in a combustible mixture is a typical curve, which restricts some region (in the form of a peninsula). This region is called a flammability region (Figure 1). The point, where lower and upper branches of the curve cross, is called a peak or inertization point. Mixtures at inertization points are as a rule rich^{8,21}, with the exception of hydrogen, methane and other not numerous

substances. An analysis of the compositions of ternary fuel - air - diluent mixtures at inertization points has been reported in^{4,45}. It was found⁴, that if nitrogen, carbon dioxide or steam are diluents, adiabatic flame temperature is in the range of 1400 to 1500 K. The important regularity was revealed in⁴⁵. It was found that for n-alkanes (or n-alcoholes) - air - nitrogen ternary mixtures, compositions at inertization points are close to stoichiometric in relation to combustion to CO and H₂O, and the values of T_{adCO} for these compositions are in the range of 1300 to 1400 K. A more detailed study of this regularity was carried out in¹⁶.

Concentration of fuel in the stoichiometric mixture, in relation to combustion to CO and H₂O, is connected with a diluent concentration by an expression:

$$c_f = (100 - c_d) / (1 + 100 \beta_{CO} / c_{O_2}) \quad (5)$$

where c_f, c_d are concentrations of fuel and diluent in the mixture, % (vol.); $\beta_{CO} = 0.5n_C + 0.25n_H - 0.5n_O$ is the stoichiometric coefficient of oxygen in the reaction of combustion to CO and H₂O; n_C, n_H, n_O are numbers of C, H, and O atoms in the fuel molecule; c_{O_2} is the oxygen concentration in the atmosphere (in the present case - in air , % (vol.).

In order to check how results of calculations of c_f (by means of the Equation 5) coincide with the experimental data for compositions of mixtures at inertization points, the data of⁸ was used. These are data for 21 organic substances and two chemically inert diluents (nitrogen and carbon dioxide). The values c_f calculated by Equation 5 were compared with the experimental data mentioned above. Relative mean square deviation was equal to 13%. Calculations of the T_{adCO} values were also carried out. It was found that these values are in the range of 1310 ± 90 K .

The testing of Equation 5 was also performed for mixtures containing halogenated diluents, with results presented in Table 2. Relative mean square deviation of the calculated C_f values from the experimental data is equal to 16%, that is in the case of halogenated diluent mixtures at inertization points that are also close to stoichiometric in relation to the combustion to CO and H₂O.

On a flammability curve (Figure 1) there is a point of tangency of a straight line, originating from the origin of coordinates, and the inertization curve. This line separates two regions. The region above the line corresponds to those ratios of fuel and diluent concentrations at which flame is able to propagate in the gaseous mixture at a determined air concentration. The region under the curve corresponds to mixtures in which the flame is not able to propagate with any air concentration within them. According to the definition given in²⁴, the mixture corresponding to the point of tangency is called a mixture "limiting on flammability". A correlation between fuel and diluent concentrations at this point determines a composition, which is safe from the viewpoint of explosions at a release of these mixtures into the atmosphere (for example, from technological equipment).

In¹⁵, on the basis of experimental data⁵³, effective oxidizer equivalence ratios α_{eff} in relation to burning up to CO and H₂O are found for mixtures limiting on flammability. 75 mixtures of various organic substances and diluents of various chemical nature have been considered: 49 mixtures with chemically inert diluents (nitrogen, carbon dioxide) and 26 mixtures with halogenated agents. The α_{eff} values were calculated by means of:

$$\alpha_{eff} = v_a / v_{as} \quad (6)$$

$$v_a = (100 - C_f - C_d) / C_f \quad (7)$$

$$v_{as} = (100 / C_{O_2}) (0.5n_C + 0.25n_H - 0.5n_O) \quad (8)$$

where ν_a and ν_{as} are numbers of moles of air per mole of fuel in the mixture limiting on flammability and the mixture stoichiometric in relation to burning up to CO and H₂O.

It was found that the α_{eff} values are in rather narrow limits. In the case of inertization by nitrogen and carbon dioxide $\alpha_{eff} = 1.40 \pm 0.15$, and for halogenated agents $\alpha_{eff} = 1.10 \pm 0.22$. For previously mentioned experimental data⁵³ the values T_{adCO} were calculated for fuel - air - chemically inert diluent (nitrogen, carbon dioxide) mixtures limiting on flammability. It was found that these values are in a rather narrow range (1170 ± 90 K).

CONCLUSIONS

It can be concluded that experimental data on LFL of organic substances in air and compositions of fuel - air - diluent mixtures near inertization points are correlated to the values T_{adCO} and the equivalence ratios in relation to mixtures stoichiometric to burning up to CO and H₂O. These correlations can be used for the creation of methods for estimation of FL for complex gaseous mixtures.

REFERENCES

1. Standard GOST 12.1.044 – 89, Fire- and-Explosion Hazard of Substances and Materials : List of Indexes and Methods for their Determination (in Russian).
2. NFPA 2001, Standard on Clean Agent Fire Extinguishing Systems.
3. DIN 51649, Teil 1, Bestimmung der Explosionsgrenzen von Gasen und Gasgemischen in Luft . Beuth Verlag GmbH, Berlin, 1987 (in German).
4. Monahov, V.T., Methods for Investigation of Fire Hazard of Substances, Moscow, Khimia, 1979 (in Russian).
5. Burgess, M.J., Wheeler, R.V., Journal of Chemical Society, 1911, v. 99, p. 2013.
6. Oehley, E., Chemie - Ingenieur - Technik, 1953, Bd. 25, No.7, s. 399.
7. Shustrov, N.I., Korolchenko, A.Ya., Bobkov, A.S., An Application of Kinetics Regularities of the Reaction of Carbon Oxide Oxidation for a Determination of Limiting Conditions of a Flame Propagation in Gaseous Mixtures, In: Problems of Combustion and Extinguishing of Fires. Abstracts of the 4-th All Union Scientific Conference, Moscow, VNIPO, 1975, pp. 61-62.
8. Zabetakis, M.G., Flammability Characteristics of Combustible Gases and Vapours. Bulletin 627. Bureau of Mines, Washington, 1965.
9. Guide for Calculations of Flammability Limits of Gases and Vapours in Various Atmospheres, No.12 r-83, Moscow, VNIPO, 1983 (in Russian).

10. Hilado, C.J., Cumming, H.J., Limits of Flammability of Organic Chemicals, *Journal of Fire and Flammability*, 1979, v. 10, July, p. 252 -260.
11. Shebeko, Yu.N., Zverev, E.N. An Analytical Estimation of Flammability Limits at Inertization of Organic Combustibles by Halogenated Agents, In: *Fire-and-Explosion Hazard of Substances and Materials*, Moscow, VNIPO, 1981, pp. 31-51 (in Russian).
12. Schroder, V., Schulz, S., Dietlen, S., Classification of Gas Mixtures for Application in Process Safety, Storage and Transport, An Experimental Method to Determine T_{ci} Values, In: *Loss Prevention and Safety Promotion in the Process Industries*, Proceedings of the 9-th International Symposium, Barcelona, Spain, 4 - 7 May 1998 , pp. 267 - 274.
13. Dvorak, O., The Determination and Calculation of the Lower and Upper Flammability Limits of NERATENS, In : *Fire - and - Explosion Hazard of Substances and Venting of Deflagrations*, Proceedings of the Second International Seminar, Moscow, 1997, pp. 189-195.
14. Korolchenko, A.Ya., Shebeko, Yu.N., Ivanov, A.V., Dmitrieva, T.M., On a Possibility of Elevation of Accuracy of Analytical Determination of Lower Flammability Limits, *Journal of Physical Chemistry*, 1981, v.55 , No.4 , p. 1071-1073 (in Russian).
15. Shebeko, Yu.N., On a Possibility of Prediction of Compositions of Mixtures of Fuels with Diluents Limiting on Flammability, *Journal of Physical Chemistry*, 1982, v. 56, No.2, pp. 304-306 (in Russian).
16. Shebeko, Yu.N., Korolchenko, A.Ya., Ivanov, A.V., A Study of Regularities of Combustion of Ternary Mixtures Fuel - Air - Diluent near Peak Points, *Physics of Combustion and Explosion*, 1981,v.17 ,No.6 ,pp. 130-133 (in Russian).
17. Shebeko, Yu.N., Ivanov, A.V., Kruglyakova, N.M., On a Regularity of Combustion of Lean Near - Limit Mixtures of Organic Gases and Air, *Journal of Applied Chemistry*,v.55 ,No.8 ,pp.1910-1912 (in Russian).
18. Korolchenko, A.Ya., Shebeko, Yu.N., Ivanov, A.V., Dmitrieva, T.M., Peculiarities of Chemical Kinetics of Combustion and Lower Flammability Limits, *Kinetics and Catalysis*, 1981, v.22, No.4, pp. 877-881 (in Russian).
19. Shebeko, Yu.N., Korolchenko, A.Ya., Iliin, A.B., Malkin, V.L., An Influence of Halons on Flammability Limits of Hydrocarbons at Combustion in Oxygen Enriched Atmospheres, *Physics of Combustion and Explosion*, 1985, v.21, No.1, p. 14-18 (in Russian).
20. Shebeko, Yu.N., Korolchenko, A.Ya., Iliin, A.B., Malkin, V.L., Flammability Limits in Mixtures Fuel - Diluent - Nitrous Oxide . *Physics of Combustion and Explosion*, 1988, v.24, No.3, pp. 48-51 (in Russian).
21. Coward, H.F., Jones, G.W., *Flammability Limits of Combustible Gases and Vapours*, Bulletin 503. Bureau of Mines, Washington, 1952.
22. Zeldovich, Ya.B., *Chemical Physics and Thermodynamics, Selected Papers*, Moscow, Nauka, 1984 (in Russian).
23. Williams, F.A., *Combustion Theory*. Addison Wesley Publishing Company, London, 1969.

24. Weinberg, F.J., *Proceedings of the Royal Society (London)*, 1955, v. A230, pp. 331-342.
25. Warnatz, J., *Combustion Science and Technology*, 1981, v. 26, pp. 203-213.
26. Basevich, V.Ya., Belyaev, A.A., Novozhilov, B.V., Posvyanskii, V.S., In: *Combustion of Heterogeneous and Gaseous Systems, Proceedings of the 8-th All Union Symposium on Combustion and Explosion, Chernogolovka, Institute of Chemical Physics, 1986*, pp. 8-11 (in Russian).
27. Westbrook, C.H., Dryer, F.L., *Combustion Science and Technology*, 1979, v.20, pp. 125-140.
28. Larshmisha, K.N., Paul, P.J., Murunda, H.C., In: *23-d Symposium (International) on Combustion. Pittsburgh, The Combustion Institute, 1991*, pp. 433-442.
29. Chen, Z.H., Sohrab, S.H., *Flammability Limits and Limit-Temperature of Counterflow Lean Methane-Air Flames. Combustion and Flame*, 1995, v. 102, No.1/2, pp. 193-199.
30. Jacobi, A.N., Sohrab, S.N., *Combustion Science and Technology*, 1990, v. 69, pp. 17-32.
31. Azatyan, V.V., *Physics of Combustion and Explosion*, 1979, v.15, pp. 62-70 (in Russian).
32. Azatyan, V.V., *Journal of Russian Mendeleev Chemical Society*, 1976, v. 21, pp. 426-433 (in Russian).
33. Baratov, A.N., *Journal of Russian Mendeleev Chemical Society*, 1976, v. 21, pp. 369-379 (in Russian).
34. Baratov, A.N., *Journal of Russian Mendeleev Chemical Society*, 1967, v. 12, pp. 276-284 (in Russian).
35. Law, C.K., Egolfopoulos, F.N., In: *23-d Symposium (International) on Combustion. Pittsburgh, The Combustion Institute, 1991*, pp.413.
36. Law, C.K., Egolfopoulos, F.N., In: *24-th Symposium (International) on Combustion. Pittsburgh, The Combustion Institute, 1992*, pp. 137.
37. Krivulin, V.N., Shebeko, Yu.N., Pavlova, V.L. et al., *An Investigation of Flammability Limits in Mixtures of Vapours of Halogenated Hydrocarbons and Air. Chemical Physics*, 1984, v. 3, No.12, pp. 1745-1749 (in Russian).
38. Shebeko, Yu.N., Korolchenko, A.Ya., Baratov, A.N., *A Mechanism of Influence of HCl and HBr on Chemical Processes at Combustion of Carbon Oxide, Chemical Physics*, 1984, v. 3, No.1, pp. 99-103 (in Russian).
39. Dixon-Lewis, G., *Flammability and Chemical Inhibition, In: Fire-and-Explosion Hazard of Substances and Venting of Deflagration. Moscow, 11-15 August 1997*, pp. 72-86.
40. Dixon-Lewis, G., *Laminar Premixed Flame Extinction Limits. 1, Combined Effects of Stretch and Upstream Heat Loss in the Twin-Flame Unburnt-to-Unburnt Opposed Flow Configuration. Proceedings of the Royal Society (London)*, 1996, v. A452, pp. 1857-1884.
41. Shebeko, Yu.N., Korolchenko, A.Ya., *On the Regularities of Flammability Limits of Combustible*

- Organic Substances in Air, In: Fire-and-Explosion Hazard of Substances and Venting of Deflagration. Moscow, 11-15 August 1997, pp. 602-619.
42. Sokolik, A.S., Auto-Ignition, Flame and Detonation in Gases. Moscow, Academic Publishing Corporation, 1960 (in Russian).
 43. Jensen, D.E., Jones, G.A., Reaction Rate Coefficients for Flame Calculations, Combustion and Flame, 1978, v.32, No.1, pp. 1-34.
 44. Semenov, N.N., On Some Problems in Kinetics and Reaction Capability, Moscow, Academic Publishing Corporation, 1958 (in Russian).
 45. Macec, A., Flammability Limits: A Re-Examination. Combustion Science and Technology, 1979, v.21, No.1/2, pp. 43-52.
 46. Monahov, V.T., An Investigation on Unification of Methods for Determination of Flammability Regions of Gases and Vapours in Air at Atmospheric Pressure, Thesis on a Scientific Degree of Doctor of Technical Sciences, Moscow, VNIPO, 1971 (in Russian).
 47. Monahov, V.T., Graschenkova, V.Ya., Estimated Values of Flammability Limits, In: Fire-and-Explosion Hazard of Substances and Materials. Moscow, VNIPO, 1978, pp. 134-148 (in Russian).
 48. Bechtel, J.H., Blint, R.J., Dasch, C.J., Weinberger, D.A., Atmospheric Pressure Premixed Hydrocarbon-Air Flames: Theory and Experiment. Combustion and Flame, 1981, v.42, No.2, pp. 197-213.
 49. Ksandopulo, G.I., Flame Chemistry, Moscow, Khimiya, 1980 (in Russian).
 50. Biordi, J.C., Lazzara, C.P., Papp J.F., Chemical Flame Inhibition Using Molecular Beam Mass Spectrometry, Bureau of Mines Report of Investigation RI-8307, Washington, 1979.
 51. Shebeko, Yu.N., Iliin, A.B., Ivanov, A.V., An Experimental Investigation of Flammability Limits in Mixtures Hydrogen-Oxygen-Diluent. Journal of Physical Chemistry, 1984, v. 58, No.4, pp. 862-865 (in Russian).
 52. Ermakov, B.S., Monahov, V.T., A Dependence of Flammability Limits of Combustible Gases on a Diluent Content in Ternary Mixtures, In: Fire-and-Explosion Hazard of Substances and Materials. Moscow, VNIPO, 1979, pp. 144-172 (in Russian).
 53. Monahov, V.T., Ermakov, B.S., Graschenkova, V.Ya. et al., Reduced Values of Flammability Potentials, Experimental Data, In: Fire-and-Explosion Hazard of Substances and Materials. Moscow, VNIPO, 1978, pp. 40-56 (in Russian).
 54. Guide for Calculations of Fire-and-Explosion Hazard Indexes of Substances and Materials. Moscow, VNIPO, 1985 (in Russian).
 55. Korolchenko, A.Ya., Tsap, V.N., Bobkov, A.S., A Dependence of Flammability Limits of Vapours of Organic Substances on a Diluent Concentration in Complex Mixtures, In: Fire-and-Explosion Hazard of Substances and Materials, Moscow, VNIPO, 1981, pp. 59-88 (in Russian).

Table 1: Values of T_{adCO} and T_{ad} for substances of various classes of organic compounds.

Class of compounds	Number of compounds	T_{ad} , K	T_{adCO} , K
Alkanes	24	1633±57	1082±32
Alkenes	9	1623±78	1056±35
Alcohols	12	1577±33	1030±28
Aromatic compounds	10	1623±39	961±31
Amines	9	1652±95	1164±94
Ketones	6	1567±50	986±29
Esters	17	1583±55	949±43
Simple ethers	7	1593±85	1030±30
Aldehydes	4	1596±32	980±20
Nitro-compounds	3	1571±92	1050±73

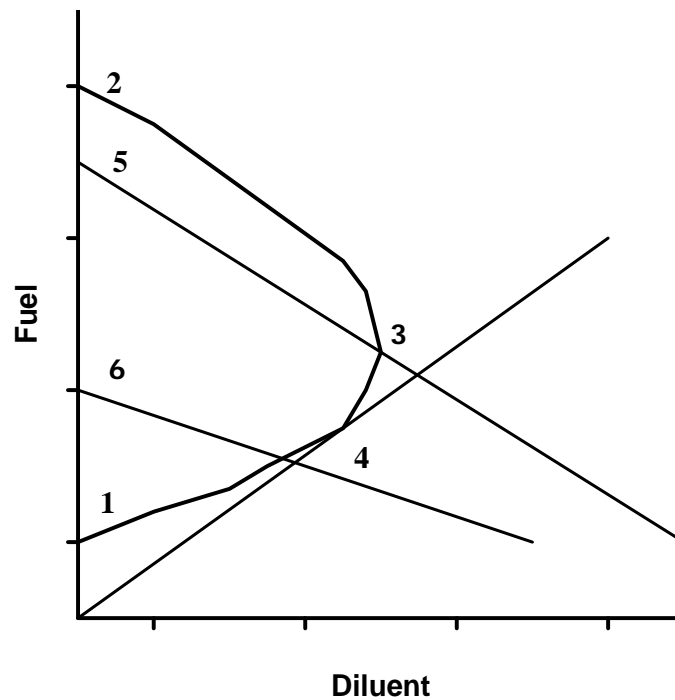


Figure 1: Typical flammability curve.

1- lower flammability limit ; 2- upper flammability limit ; 3- inertization (peak) point; point corresponding to mixture limiting on flammability ; 5- line of mixtures stoichiometric in relation to combustion up to CO and H₂O ; 6- line of mixtures stoichiometric in relation to combustion up to CO₂ and H₂O .

Table 2: Experimental and calculated data on concentrations of fuels and halogenated diluents at inertization points (experimental data were taken from^{8,52}).

Fuel	Diluent	Fuel concentration, % (vol.) (experiment)	Diluent concentration, % (vol.) (experiment)	Fuel concentration, % (vol.) (calculations)
Propane C ₃ H ₈	Difluorochloromethane CHF ₂ Cl	3.9	17.0	4.6
	1,1,2-Trifluorotrichloroethane C ₂ F ₃ Cl	5.2	11.3	4.9
	Fluorotrichloromethane CFCl ₃	6.5	14.7	4.8
	1,2-Dibromotetrafluoroethane C ₂ F ₄ Br ₂	5.8	3.1	5.4
n-Butane C ₄ H ₁₀	1,2-Dibromotetrafluoroethane C ₂ F ₄ Br ₂	4.6	3.2	4.3
Iso-Butane C ₄ H ₁₀	1,1,2-Trifluorotrichloroethane C ₂ F ₃ Cl	4.0	9.9	4.0
	Perfluorosulphur SF ₆	4.5	13.8	3.8
	Difluorochloromethane CHF ₂ Cl	3.0	16.0	3.7
Pentane C ₅ H ₁₂	Perfluorosulphur SF ₆	3.4	16.0	3.0
Pentane C ₅ H ₁₂	Tetrachlorocarbon CCl ₄	3.0	22.0	2.8
Ethanol C ₂ H ₆ O	Difluorodichloromethane CF ₂ Cl ₂	5.2	17.0	7.7
Iso-Butane C ₄ H ₁₀	1,2-Dibromotetrafluoroethane C ₂ F ₄ Br ₂	4.5	3.0	4.3