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The influence of $K_4[Fe(CN)_6]$ aerosol on the flame speed of methane-air flame

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Abstract

The influence of 1% aerosol of the water solution of potassium ferrocyanide $K_4[Fe(CN)_6]$ on the flame speed of stoichiometric methane-air flame, stabilized over the Mache-Hebra burner, has been studied experimentally and by computer simulation. The flame speed was measured at atmospheric pressure and the temperature 93 °C. Addition of the aerosol of the water solution of potassium ferrocyanide results in significantly greater reduction of the flame speed of stoichiometric methane-air flame, compared to aerosol addition without the salt. Modeling the flame speed with the mechanism GRI-Mech 3.0 shows this effect to be caused by the presence of potassium atoms in the composition of this salt. The results obtained account for effectiveness of applying fine aerosol of the water solution of $K_4[Fe(CN)_6]$ in extinguishing fires.

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Nomenclature

| | |
|----------------------|------------------------------|
| U_n | normal flame velocity (cm/s) |
| A | pre-exponential factor |
| b | temperature constant |
| E | activation energy |
| <i>Greek symbols</i> | |
| ϕ | stoichiometric coefficient |

1. Introduction

Finely dispersed water is widely used in the practice of extinguishing fires and preventing explosions. The main factor here is reduction of temperature in the combustion zone during evaporation of dispersed water. It is known that the effect of using finely dispersed water depends on the type of fire and on the dispersity of water droplets. In the methods described, the range of water droplets is wide, with the main amount of water being in the droplets larger than 100 microns. Therefore the disadvantage of this method is in the large consumption of water per one unit of flame volume. Raising the effectiveness of fire extinguishing with water may be reached both by improving water dispersity and by introducing various additives [1-

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12]. Recently a number of studies have been conducted, the purpose of which was to determine the effectiveness of flame suppression with aerosols of the water solutions of salts [1-12]. As additives, such compounds were investigated as NaCl, KCl, LiI, CH_3COOK , CoCl_2 , NiCl_2 , NaOH, NaHCO_3 , MgCl_2 , CaCl_2 , MnCl_2 , FeCl_2 and others. It has been found that some of the above compounds are more effective flame suppressors than the widely used CF_3Br , the production of which has been prohibited by the Montreal Convention. The principle of these additives' action consists in the fact that, when the aerosol of the water solutions of these salts is added into flame, evaporation of water, followed by decomposition of salts in flame, occurs. At that, labile compounds (metal oxides and hydroxides are formed), reacting with H and O atoms and OH radicals, accounting for chain reactions of combustion, leading to their loss (recombination). As a result, inhibition of the combustion processes occurs, up to flame extinction. According to the literature, potassium compounds [13] are the most effective (per mass) flame extinguishers. Therefore, the study of compounds containing the maximum number of potassium atoms is of interest because they exhibit the lowest mass extinguishing concentration [13]. One of such compounds is potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$. No studies of the impact of aerosols of the water solutions of this salt on the combustion of methane-air mixtures have been conducted.

The objective of the study is to investigate the impact of the aerosol of the water solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ on the burning velocity of CH_4/air combustible mixture at the pressure of 1 atm.

2. Experimental

To measure the laminar CH_4/air flame propagation velocity, the Mache-Hebra burner [14] was used. A schematic of the burner and of the system of supplying 1% water solution of potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ to the combustible mixture is shown in Fig. 1. The burner was a glass tube with the internal diameter of 2 cm and the length of 27 cm, tapering below to the diameter of 1 cm at the length of 3 cm. Such a shape of the burner allows flame of correct cone shape to be produced, as the gas flow velocity at the burner cross section at the exit from the burner is constant. The burner temperature was maintained to be permanent and was equal to 93 °C. With this temperature, the volume flow of the stoichiometric combustible mixture of methane and air was $104 \text{ cm}^3/\text{s}$.

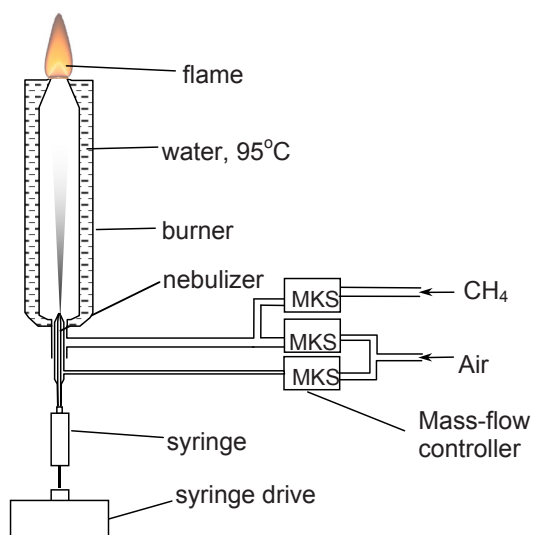


Fig. 1. Schematic of the experiment and a photo of flame with salt additive.

The aerosol of the water solution of potassium ferrocyanide was introduced into the flow of the combustible mixture with an atomizer, the design of which is shown in Fig. 2. The internal diameter of the atomizer nozzle was 0.1 mm, the width of the capillary walls was 0.04 mm, the annular gap at the exit was 0.05 mm. The solution was introduced with a syringe, the piston of which was moved by a mechanic drive with a step-by-step motor, which allowed the additive concentration to be changed in a wide range.

The burning velocity was measured with the PIV (particle image velocity) method [15-20]. Burning velocity was measured with an accuracy of $\pm 5\%$. The photographs taken were processed with a cross-correlation method using adaptive algorithms [19].

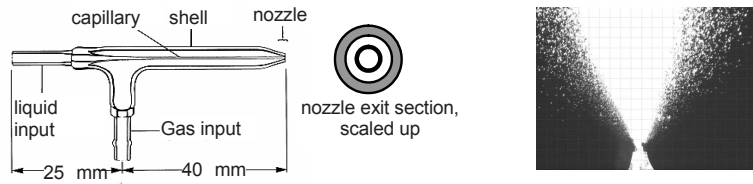


Fig. 2. Aerosol-producing atomizer.

Shown in Fig. 3 are the photographs of the laser-lighted flow at the exit from the burner. It can be seen that the salt particles get considerably smaller in size or completely disappear in the flame front. As the combustible mixture flows along the tube of the Mache-Hebra burner, the water aerosol gets practically evaporated. This can be seen in Fig. 4, showing the photographs of the combustible mixture at the exit from the burner in flame and without flame.

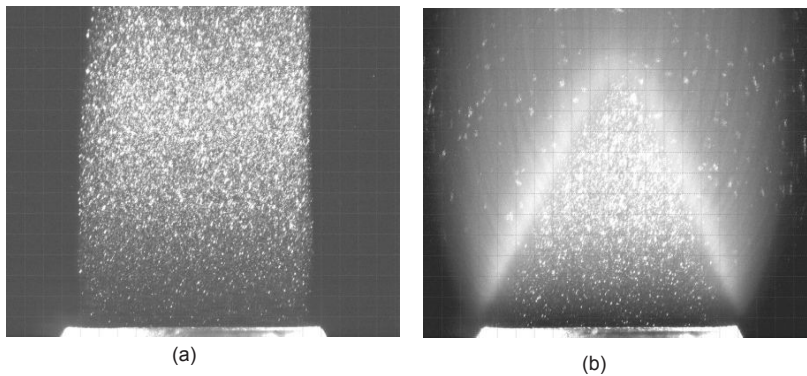


Fig. 3. Photographs of the flow of combustible mixture with salt aerosol without flame (a) and in flame (b).

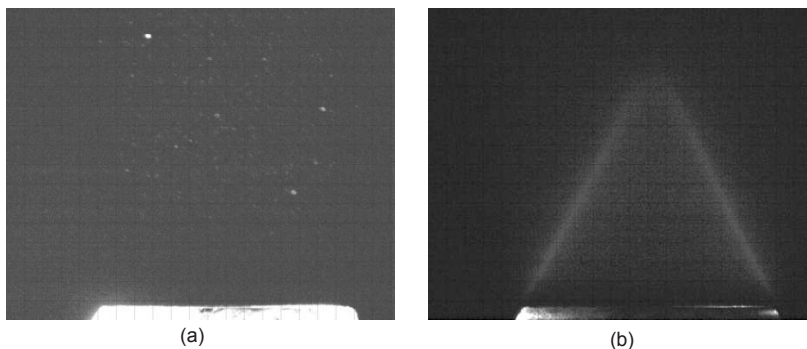


Fig. 4. Photographs of the flow of combustible mixture with water vapors without flame (a) and in flame (b).

Shown in Fig. 5 are the results of changing the burning velocity on the concentration of water additive and water solution of salt. The dots in the graph show the results of the experiment, the lines show the simulation results. The maximum concentration of the salt in the combustible mixture was 0.2 g/m^3 with water vapor concentration being 2.3 %, assuming its complete evaporation. Concentration of salt and the percentage of salt in water was calculated considering losses in the system of feeding the combustible mixture and on the burner walls.

To calculate the flame speed, the mechanism GRI-Mech Version 3.0 [21] was used, developed for modeling combustion of natural gas, including the nitrogen chemistry. It contains 325 reactions for 53 flame components. To consider the influence of $\text{K}_4[\text{Fe}(\text{CN})_6]$ on the flame speed, 22 gas phase reactions of transformation of potassium-containing particles were included into the mechanism [22]. The estimated value of the flame speed U_n without additive equal to 54 cm/s is

close to that measured in the experiment and equal to 55 cm/s. Table 1 shows the reactions included into the mechanism and their kinetic parameters. The results shown in Fig. 5 demonstrate qualitative agreement of the calculation results and of the experiment.

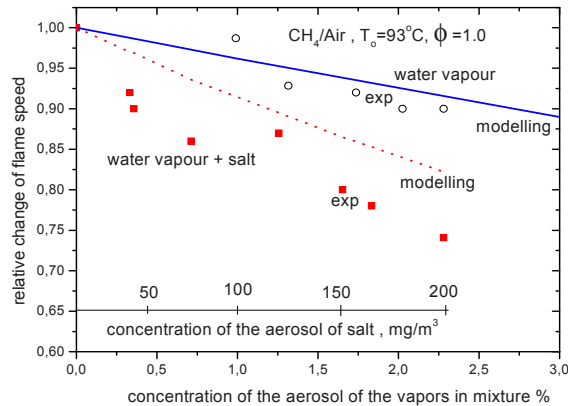


Fig. 5. The experimental results (dots) and modeling results (lines) of the dependence of the relative change in the CH₄/air flame speed on the concentration of the water vapors and on the aerosol of the water solution of the salt.

Table 1. Reactions and their rate constants for potassium-containing compounds, represented as $k=AT^m \exp(-E/RT)^*$. The reaction mechanism was borrowed from Marshall's study [22]

| Reaction | A | b | E |
|--|--------|-------|---|
| 1. K+HO ₂ = KOH+ O | 1.0E14 | 0 | 0 |
| 2. K+O ₂ (+M) = KO ₂ (+M) | 1.3E14 | 0 | 0 |
| 3. KO+H ₂ O = KOH+ OH | 1.3E14 | 0 | 0 |
| 4. KOH+H = K+ H ₂ O | 5.0E13 | 0 | 0 |
| 5. KO ₂ +CO = KO+ CO ₂ | 1.0E14 | 0 | 0 |
| 6. KO ₂ +H = K+ HO ₂ | 2.0E14 | 0 | 0 |
| 7. KO ₂ +H = KO+OH | 5.0E13 | 0 | 0 |
| 8. KO ₂ +H = KOH+O | 1.0E14 | 0 | 0 |
| 9. KO ₂ +O = KO+O ₂ | 1.3E13 | 0 | 0 |
| 10. KO ₂ +OH = KOH+ O ₂ | 2.0E13 | 0 | 0 |
| 11. K+O+M = KO + M | 1.5E21 | -1.50 | 0 |
| 12. K+OH+M = KOH+ M | 5.4E21 | -1.55 | 0 |
| 13. K+HO ₂ = KO + OH | 3.0E13 | 0 | 0 |
| 14. K+H ₂ O ₂ = KOH+ OH | 2.5E13 | 0 | 0 |
| 15. K+H ₂ O ₂ = KO+ H ₂ O | 1.6E13 | 0 | 0 |
| 16. KO+H = K +OH | 2.0E14 | 0 | 0 |
| 17. KO+O = K +O ₂ | 2.2E14 | 0 | 0 |
| 18. KO+OH = KOH+O | 2.0E13 | 0 | 0 |
| 19. KO+HO ₂ = KOH+ O ₂ | 5.0E13 | 0 | 0 |
| 20. KO+H ₂ = KOH+H | 1.6E13 | 0 | 0 |
| 21. KO+H ₂ = K+ H ₂ O | 3.1E12 | 0 | 0 |
| 22. KO+CO = K +CO ₂ | 1.0E14 | 0 | 0 |

* m – reaction order. A [(cm³/mol)^{m-1}c⁻¹]; E [cal/mol].

On adding 2.2 % water vapor, the flame speed decreases by 8 % in the experiments and in modeling. On adding 2.2 % water vapor and 0.2 g/m³ salt, reduction of the flame speed is observed - 15 % reduction in calculations and 25 % reduction

in the experiments. It can be seen that small additions of $K_4[Fe(CN)_6]$ essentially influence the flame speed of the methane-air stoichiometric mixture both in the calculations and in the experiment. At the same time, there is some disagreement between calculation and the experiment, which may be attributed to the fact that the reactions of radicals with other active products of salt decomposition (for example, with iron and its oxides) were not taken into account, as well as the heterogeneous reactions of the loss of active centers on the surface of the salt particles and condensed products of its decomposition, and possible incorrectness of the rate constants of the reactions. Earlier authors demonstrated that the suppression effectiveness of $K_4[Fe(CN)_6]$ is higher than we expected on the basis of number of K atoms [23-25]. Therefore, the presence of Fe atom in the molecule may be responsible for the disagreement between measured and simulated speed of the doped flames.

3. Conclusions

Small concentrations of the aerosols of the water solution of $K_4[Fe(CN)_6]$ significantly reduce the methane-air flame propagation velocity. The mechanism of this impact is qualitatively described with the mechanism GRI-Mech 3.0 by entering the transformation reactions of potassium-containing species there. In the experiments, the degree of the salt influence on the flame propagation velocity has been shown to be higher than that in the calculations. This may be attributed to both insufficient precision of the values of the kinetic parameters of reactions with participating potassium-containing species, with possible influence of heterogeneous reactions on the surface of the particles, and to possible reactions of radicals with the other active salt decomposition products (for example, iron and its oxides).

References

- [1] Mawhinney, J. R., 1993. "Design of Water Mist Fire Suppression Systems for Shipboard Enclosures," Proceedings of the International Conference on Water Mist Fire Suppression Systems. Boras, Sweden, pp. 16-44.
- [2] Moore, T. A., Weitz, C., McCormick, S., Clauson, M., 1996. "Laboratory Optimization and Medium Scale Screening of Iodide Salts and Water Mixtures," Proceedings of Halon Option Technical Working Conference. Albuquerque, NM, USA, pp. 477-498.
- [3] Shilling, H., Dlugogorski, B. Z., Kennedy, E. M., Leonardi, E., 1996. "Extinction of Diffusion Flames by Ultra Fine Water Mist Doped with Metal Chlorides," Proceedings of the Sixth Australasian Heat and Mass Transfer Conference, Begell House, New York, p. 275-282.
- [4] Zheng, R., Rogg, B., Bray, K. N., 1997. Effect of Sprays of Water and NaCl-water Solutions on the Extinction of Laminar Premixed Methane-air Counterflow Flames, *Combustion Science and Technology* 126, p.389.
- [5] Lazzarini, A. K., Krauss, R. H., Chelliah, H. K., Linteris, G. T., 2000. Extinction Conditions of Non-premixed Flames with Fine Droplets of Water and Water/NaOH Solutions, *Proceedings of the Combustion Institute* 28, p. 2939.
- [6] Mesli, B., Gokalp, I., 2000. Extinction Limits of Opposed Jet Turbulent Premixed Methane Air Flames with Sprays of Water and NaCl-water Solution, *Combustion Science and Technology* 153, p. 193.
- [7] McDonnell, D., Dlugogorski, B. Z., Kennedy, E. M., 2002. "Evaluation of Transition Metals for Practical Fire Suppression Systems," Proceedings of Halon Option Technical Working Conference, Albuquerque, NM, USA, pp. 117-124.
- [8] Hirst, R., Booth, K., 1977. Measurement of Flame Extinguishing Concentrations, *Fire Technology* 13, p. 296.
- [9] Hamins, A., Gmurczyk, G., Grosshandler, W., Rehwoldt, R. G., Vazquez, I., Cleary, T., 1994. "Evaluation of Alternative In-flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays," Proceedings of Halon Option Technical Working Conference, Albuquerque, NM, USA, pp. 345-465.
- [10] Hamins, A., 1998. Flame Extinction by Sodium Bicarbonate Powder in a Cup Burner, *Proceedings of the Combustion Institute* 27, p. 2857.
- [11] Linteris, G. T., Katta, V. R., Takahashi, F., 2004. Experimental and Numerical Evaluation of Metallic Compounds for Suppressing Cup-burner Flames, *Combustion and Flame* 138, p. 78.
- [12] Liu, J., Cong, B., Liao, G., 2008. "Experimental Study on CH₄/Air Fire Suppression Effectiveness of Water Mist with Metal Chloride Additives," Book of abstracts of 32th International Symposium on Combustion, McGill University, Montreal, Canada, 1F03
- [13] Shmakov, A. G., Korobeinichev, O.P., Shvartsberg, V.M., Yakimov, S.A., Knyazkov, D.A., Komarov, V.F., Sakovich, G.V., 2006. Testing Organophosphorus, Organofluorine, and Metal-containing Compounds and Solid-propellant Gas-generating Compositions Doped with Phosphorus-Containing Additives as Effective Fire Suppressants, *Combustion, Explosion and Shock Waves* 42(6), p. 678.
- [14] Mache, H., Hebra, A., 1941. Zur Messung Der Verbrennungsgeschwindigkeit Explosiver Gasemische. *Sitzungsber. Osterreich, Akad. Wiss. Abt.IIa* 150, p. 157.
- [15] Adrian, R. J., 1984. Scattering Particle Characteristics and Their Effect on Pulsed Laser Measurements of Fluid Flow: Speckle Velocimetry vs. Particle Image Velocimetry, *Applied Optics* 23, p. 1690.
- [16] Adrian, R. J., Yao, C. S., 1984. "Development of Pulsed Laser Velocimetry (PLV) for Measurement of Fluid Flow," Proceedings of the 8th Biennial Symp. On Turbulence, Rolla, Missouri, USA, pp. 170-186.
- [17] Willert, C. E., Gharib, M., 1991. Digital Particle Image Velocimetry, *Experiments in Fluids* 10, p. 181.
- [18] Stella, A., Guj, G., Kompenhans, J., Raffel, M., Richard, H., 2001. Application of Particle Image Velocimetry to Combusting Flows: Design Considerations and Uncertainty Assessment, *Experiments in Fluids* 30, p. 167.
- [19] Tokarev, M. P., Markovich, D. M., Bilsky, A. V., 2007. Adaptive Algorithms for PIV Image Processing, *Journal Computational Technologies* 12(3), p. 109.
- [20] Dulin, V. M., Kozorezov, Yu. S., Markovich, D. M., Stork, S. I., Tokarev, M. P., 2008. "Stereo PIV Diagnostics of Swirling Propane Flames," ISFV13 - Proceedings of 13th International Symposium on Flow Visualization, Nice, France, pp. 1-10.
- [21] Frenklach, M., Wang, H., Goldenberg, M., Smith, G. P., Golden, D. M., Bowman, C. T., Hanson, R. K., Gardiner, W. C., Lissianski, V.: Gas Research Institute Report GRI-95/0058; http://www.me.berkeley.edu/gri_mech/
- [22] Glarborg, P., Marshall, P., 2005. Mechanism and Modeling of the Formation of Gaseous Alkalisulfates, *Combustion and Flame* 141, p. 22.

- [23] Korobeinichev, O. P., Shmakov, A. G., Chernov, A. A., Shvartsberg, V. M., Rybitskaya, I. V., Makarov, V. I., Nifantev, E. E., Kudryavtsev, I. Y., Goryunov, E. I., 2004. "Study of Effectiveness of Flame Suppression by Organophosphorus Compounds in Laboratory and Scaled-Up Tests," Proceedings of Halon Option Technical Working Conference, Albuquerque, NM, USA.
Available from: http://www.nist.gov/el/fire_research/upload/R0401176.pdf
- [24] Korobeinichev, O. P., Shmakov, A. G., Shvartsberg, V. M., Yakimov, S. A., 2005. "Study of Fire Suppression Effectiveness of Organophosphorus Compounds and Compositions on their Base- Proceedings of Halon Option Technical Working Conference, Albuquerque, NM, USA.
Available from: http://www.nist.gov/el/fire_research/upload/R0501570.pdf
- [25] Korobeinichev, O. P., Shmakov, A. G., Shvartsberg, V. M., 2012. Chemical Transformations in Inhibited Flames over Range of Stoichiometry, in "Stoichiometry and Materials Science - When numbers matter" Dr. Alessio Innocenti and Norlida Kamarulzaman, Editors, InTech, Rijeka, Croatia p. 436.
Available from: <http://www.intechopen.com/books/stoichiometry-and-materials-science-when-numbers-matter/chemical-transformations-in-inhibited-flames-over-range-of-stoichiometry>.