EFFECT OF ORGANOPHOSPHORUS COMPOUNDS ON NON-PREMIXED COUNTERFLOW $CH_4/O_2/N_2$ FLAME AND STUDY OF ITS STRUCTURE BY EXPERIMENT AND MODELING

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ABSTRACT

Effect of number of novel organophosphorus compounds (OPC) on non-premixed counterflow $CH_4/O_2/N_2$ flame was studied. The high effective nebulizer for OPC loading in gas stream was used. Following OPC was studied: $(CH_3O)_2(CH_3)PO$, $(C_3F_7CH_2O)_3PO$, $(C_3F_7CH_2O)_2(CH_3)PO$, $(HCF_2CF_2CH_2O)_2(CH_3)PO$, $(HCF_2CF_2CH_2O)_3PO$, $(C_2H_5O)_2(H)PO$, $(CF_3CH_2O)_2(H)PO$, $(C_3F_7)_3PO$, $(CH_3O)_3P$, $(C_2H_5O)_3P$, $(CF_3CH_2O)_3P$, $(HCF_2CF_2CH_2O)_3P$. The tested OPC were ranked on their effectiveness. The temperature and concentration profile of stable species in the doped flame (added to oxidizer flow) was obtained by using thin microthermocouple technique, mass spectrometry with a microprobe sampling. The modeling of the structure of non-premixed counterflow $CH_4/O_2/N_2$ flame using OPPDIF code and kinetic model elaborated earlier by the authors and calculation of extinction strain rate was performed. Comparison of the experimental and calculated results demonstrated a satisfactory agreement.

INTRODUCTION

Interest in combustion chemistry of organophosphorus compounds (OPC) derives from the need to search novel fire suppressants for replacement of ozone-depleting halon compounds such as CF_3Br and CF_2ClBr [1]. Although halon production has been banned under the terms of the Montreal Protocol, alternative fire retardants have not yet been found. One of the perspective candidates for halon replacement are OPC including those compounds containing halogenated alkyl groups. Because these substances represent the large chemical family, there are some screening criteria defining the most appropriate suppressants for practical use [2]. These criteria are: fire suppression effectiveness is comparable to halons or higher, non-inflammability, atmospheric lifetime short, to keep out ozone depletion, high volatility, low toxicity, good materials compatibility. The esters of phosphoric and phosphonic acids, phosphonitriles and phosphorus halides have the greatest interest for further study [2]. Fluorination of alkyl groups in esters is expected to further decrease the boiling point and flammability [2, 3]. For the screening of halogenated OPC different technique to determine suppression effectiveness are used: the methods of the Bunsen burner, cup-burner, non-premixed counter flow burner - the Potter burner, cylinder method and others [3-9]. Though there are few works on determination of OPC suppression effectiveness by extinction strain rate in non-premixed counterflow burner [8,9].

The goal of present research consist in evaluation and study of suppression effectiveness of non-premixed diffusion counterflow $CH_4/N_2 – O_2/N_2$ flame by number of OPC including those containing fluorine atoms in alkyl radicals. Another objective of this research is to check out the possibility of application of TMP inhibition mechanism earlier developed for description of non-premixed counterflow flame doped with TMP. This problem is supposed to be resolved through comparison of modeling and experimental results on suppression effectiveness and structure of diffusion counterflow methane flame doped with TMP additives.

EXPERIMENTAL

Study of OPC fire suppressants effect on extinction strain rate of atmospheric diffusion counterflow $CH_4/N_2 – O_2/N_2$ (0,2/0,8 – 0,4/0,6 mole fraction) flame was performed. The opposed-jet burner was designed in accordance with recommendations of [10] and its construction was described earlier in [8]. Figure 1 shows the schematic of experimental set-up. The inner diameter of burner nozzles was 6.8 mm, the distance between nozzles was 6.7 mm. The nitrogen flow was used as a sheath. The oxidizer temperature was maintained equal 100 °C to prevent OPC condensation on the tube walls. The oxidizer and fuel flow rates were set and controlled by mass flow controllers (MKS Instruments), which were operated by PC. OPC were added from oxidizer side through nebulizer, which design is described elsewhere [11]. The OPC consumption through nebulizer was controlled by syringe pump. The procedure of the evaluation of extinction strain rate was described earlier in [8].

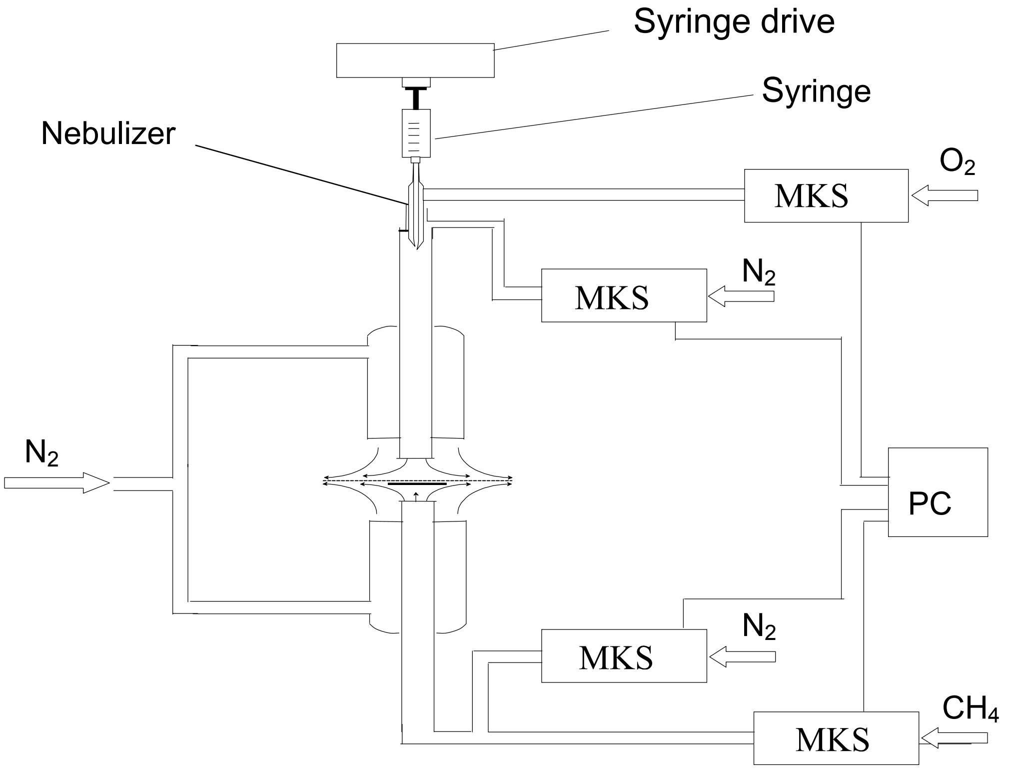

Fig. 1 Scheme of experimental set-up

Extinction measurements of diffusion counterflow methane flame were carried out for the compounds presented below:

Phosphate esters – $(CH_3O)_3PO$ (TMP), $(CH_3CH_2O)_3PO$, $(CF_3CH_2O)_3PO$, $(HCF_2CF_2CH_2O)_3PO$ $(C_3F_7CH_2O)_3PO$;

Phosphonate esters – $(CH_3O)_2(CH_3)PO$, $(CH_3CH_2O)_2(CH_3)PO$, $(CF_3CH_2O)_2(CH_3)PO$, $(HCF_2CF_2CH_2O)_2(CH_3)PO$, $(C_3F_7CH_2O)_3(CH_3)PO$;

Phosphites - $(CH_3O)_3P$, $(CH_3CH_2O)_3P$, $(CF_3CH_2O)_3P$, $(HCF_2CF_2CH_2O)_3P$, $(CH_3CH_2O)_2PHO$ $(CF_3CH_2O)_2PHO$; and phosphorus halide - $POCl_3$

The suppression effectiveness of diffusion counterflow methane flame by above mentioned phosphates and phosphonates was already tested, but the tests were performed at low concentrations of additives [8]. Pt – Pt/10% Rh Π-type 20-micron thermocouple was used for study of thermal structure of pure and doped with 1200 ppm TMP flame. The total diameter of coated with SiO_2 thermocouple was 50 micron [12]. The total length of thermocouple shoulders was 1 cm (more then external diameter of burner nozzles) in order to minimize flame deformation. Concentration profiles of the stable species (CH_4, O_2, CO_2, H_2O) of pure and doped with 1200 ppm TMP flames were obtained using quadrupole mass-spectrometer MS 7302. The flame was sampled by quartz microprobe (inner diameter (ID) was 40 micron, opening angle was 20^0), connected to the inlet system of mass-spectrometer, and sonic probe (ID was 80 micron, opening angle was 40^o) of molecular beam mass-spectrometric setup (MBMS) [12].

MODELING

Modeling of the flame was made using the opposed-flow flame code OPPDIF from the CHEMKIN II Suite [13]. GRI-MECH 3.0 mechanism of methane oxidation [14] was employed. Calculations of the flame doped with TMP were performed using TMP destruction mechanism presented earlier in [15, 16]. Mixture averaged diffusion velocities were used, thermal diffusion was neglected. The model was run for potential flow boundary conditions.

RESULTS

EXTINCTION STRAIN RATE IN A NON-PREMIXED CH_4/N_2 - O_2/N_2 FLAME

Normalized extinction strain rate dependencies for counterflow CH_4/N_2 – O_2/N_2 flame versus OPC loading are presented in fig. 2. As well this figure shows data for CF_3Br and $Fe(CO)_5$ (iron pentacarbonyl data were obtained by Linteris [17]). The fire suppression effectiveness in terms of extinction strain rates was defined as the fractional reduction in global extinction strain rate divided by the mole fraction of phosphorus χ_P in the flame [18]:

$$\text{Effectiveness}_q = \frac{a_{q,0} - a_q}{a_{q,0}} \frac{1}{\chi_P}.$$

The subscript q indicates that the strain rate measurement is made at extinction conditions, and the subscript 0 denotes the value for the undoped flame. All tested OPC show similar fire suppression effectiveness (in the range of experimental errors) at low OPC loading (up to 1000 ppm). For this flame and for 0 – 1000 ppm concentration range all tested OPC are approximately

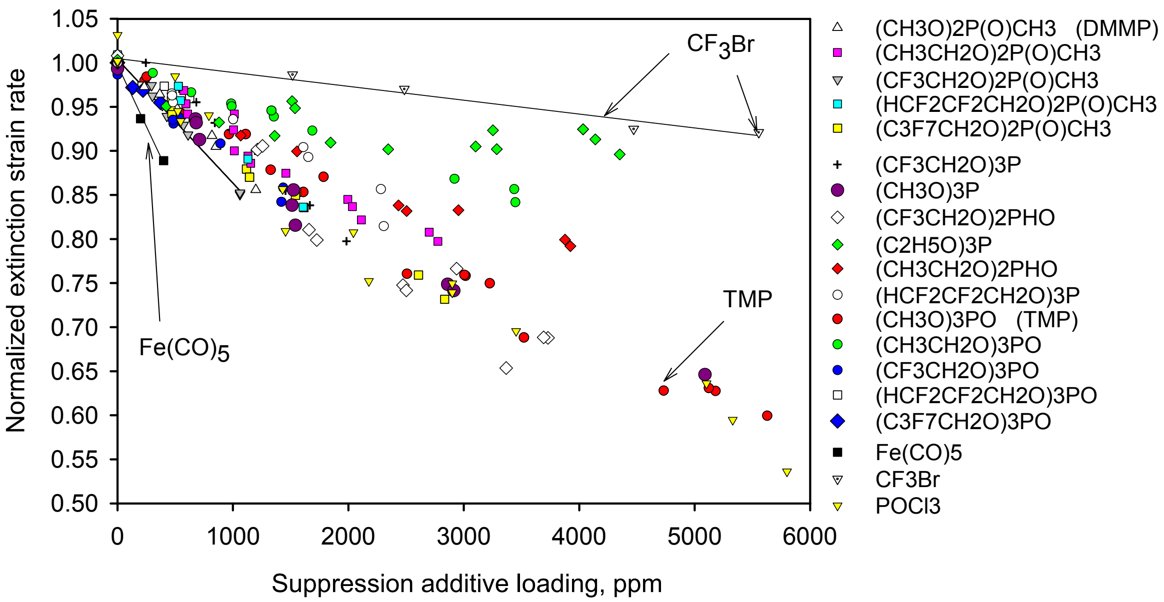

Fig.2. Normalized extinction strain rate of the flame as a function of OPC and other suppression additives loading

7 times more effective fire suppressants than Halon 1301 and about 3 times less effective than $Fe(CO)_5$ However, there are visible discrepancies between the curves for different compounds at concentrations are higher 1000 ppm. Thus, fire suppression effectiveness of such compounds as $(C_2H_5O)_3P$, $(C_2H_5O)_3PO$ and $(C_2H_5O)_2PHO$ becomes weaker. It may be connected with the contribution of ethyl radicals presented in these compounds to fuel excess, which may cause extinction strain rate increasing. The slopes of the curves corresponding other chemicals do not have any changes. Thus, most of studied OPC demonstrate a similar fire suppression effectiveness on a per phosphorus atom. This result supports the suggestion that fire suppression effectiveness is determined by concentration of phosphorous oxides, which does not depend on OPC molecule structure.

The results of numerical modeling of maximum temperature versus strain rate dependencies for the flames doped with 1200 and 2500 ppm TMP are presented in figure 3. Similar calculations were made before in [9,19]. These calculations allow to evaluate the normalized extinction strain rate values for these TMP concentrations and to compare with experimental data. The experiment shows decrease of extinction strain rate on 10 and 20 percents for TMP concentrations 1200 and 2500 ppm correspondingly, while numerical calculations demonstrate 4 and 8 percents respectively. This discrepancy between experiment and modeling is supposed to be related, with heat losses into the burner and by radiation, which the model does not take into account.

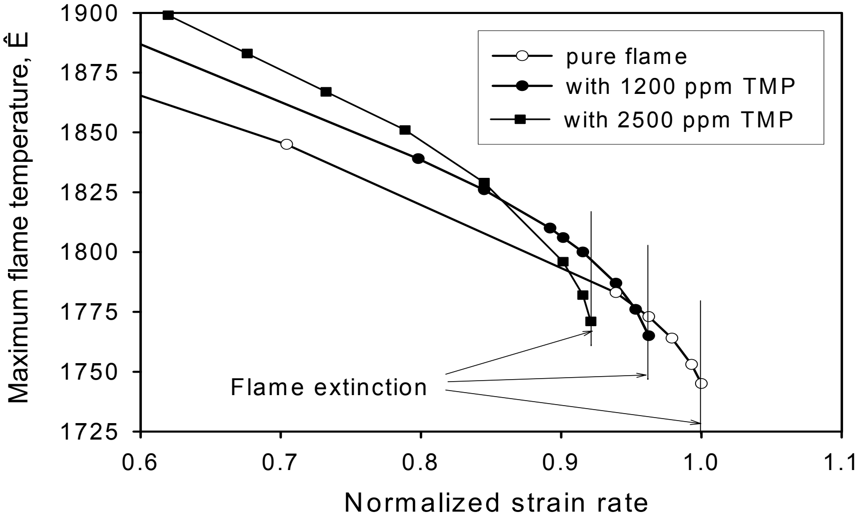

Fig. 3. Calculated dependence of a maximum flame temperature (pure and doped) vs normalized global strain rate. Potential flow boundary conditions

EFFECT OF TMP ON FLAME STRUCTURE. EXPERIMENT AND MODELING

Concentration and temperature profiles of stable species (CH_4, O_2, CO_2) of both flames doped with 1200 ppm TMP and without additive, obtained by microprobe technique, are presented in figure 4. Symbols are experimental data, lines - modeling. The strain rate value was 358 s^{-1}. This value was chosen in order to minimize microprobe and thermocouple affect on the flame, because thermal and hydrodynamic perturbations of the probe and thermocouple at higher strain rate become unacceptable great. The concentration and temperature profiles obtained experimentally at the burner axis and at the distance 3 mm from the burner axis demonstrate the coincidence within experimental errors. This result demonstrates validity of basis presumption of OPPDIF Code. Both experimental and modeling data show that within experimental errors TMP additive

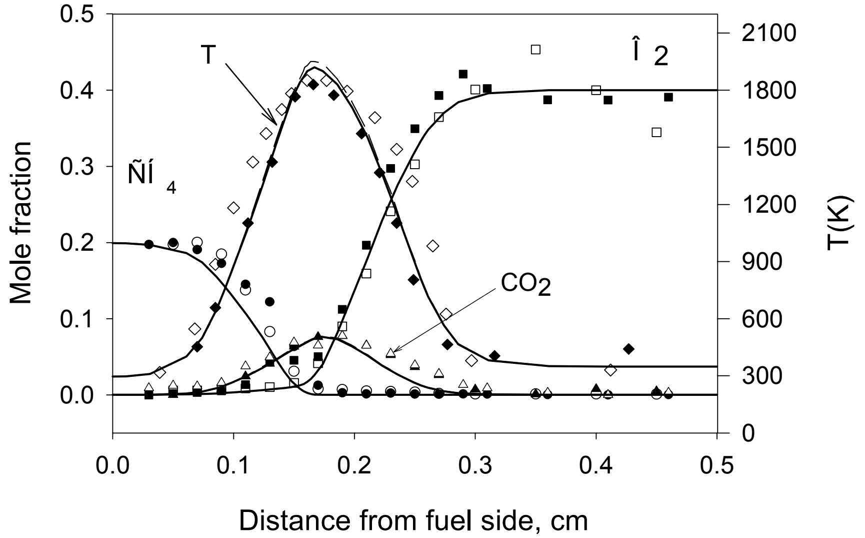

Fig. 4. Concentration and temperature profiles in diffusion counterflow CH_4/N_2 – O_2/N_2 flame doped with 1200 ppm TMP (filled symbols – experiment – microprobe sampling at the distance 3 mm from the burner axis, dashed line - modeling) and without additive (open symbols – experiment, solid lines - modeling). Strain rate is 358 s^{-1}

does not have any noticeable influence on temperature and species concentration profiles widths. Experimental maximum temperatures of pure and doped flames have weak discrepancies between each other while the difference between calculated ones is about 30°C. The experimental species concentration profiles widths demonstrate a good agreement with modeling data. However, represented at this figure calculated concentration and temperature profiles are shifted along the burner axis on 0.139 cm towards the fuel side to reach the coincidence with experimental profiles. Numerical calculations indicate weak sensitivity of the flame position to the flow rates, unlike experimental flame position that was found to have high sensitivity to the flow rates. This fact has been noted as well elsewhere [20] and it is supposed to be associated with burner heat losses, which are not considered by model. Concentration profiles of stable species (CH_4, O_2, CO_2 and H_2O) in pure flame, obtained by MBMS technique, are presented in figure 5. Symbols are experimental data, lines - modeling. The strain rate value was 358 s^{-1} too. The concentration profiles of stable species obtained with MBMS sampling system agree with those obtained with microprobe sampling system.In the table 1 below the calculation results of concentrations of basic phosphorus containing species in the doped with 1200 ppm TMP flame at the maximum temperature are presented.

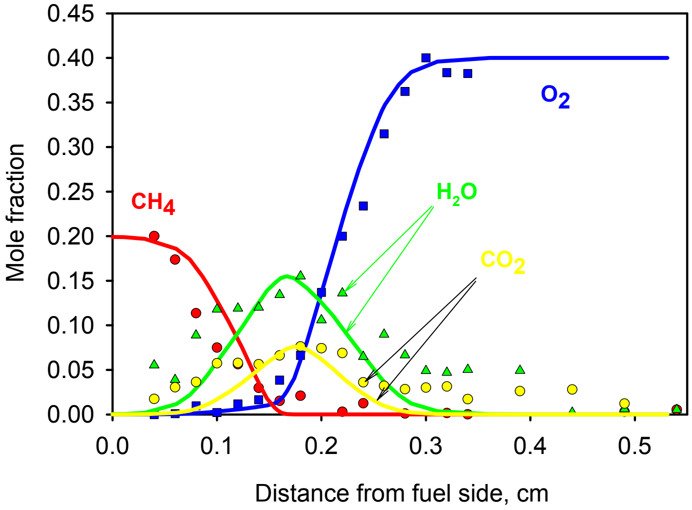

Figure 5. Concentration profiles in diffusion counterflow CH_4/N_2 – O_2/N_2 flame. Symbols – experiment obtained with MBMS system - sampling at the distance 3 mm from the burner axis , line - modeling - along the burner axis

Table 1. Mole fraction of a phosphorus-containing products at maximum temperature of non-premixed $CH_4/N_2 – O_2/N_2$ flame doped with 1200 ppm TMP calculated using OPPDIF Code and for thermodynamical equilibrium

№	Species	OPPDIF Code	Thermodynamical equlibrium (1851 K)
1.	$PO(OH)_3$	4.44×10^{-6}	15.5×10^{-6}
2.	$PO(OH)_2$	3.58×10^{-8}	2.3×10^{-8}
3.	HOPO	1.43×10^{-4}	1.45×10^{-4}
4.	$HOPO_2$	2.83×10^{-4}	3.72×10^{-4}
5.	PO	3.03×10^{-6}	0.47×10^{-6}
6.	PO_2	1.86×10^{-4}	0.63×10^{-4}

The computations were performed for equilibrium state and using OPPDIF Code. One can see, that thermodynamic equilibrium is not achieved in atmospheric counterflow diffusion flame, as well as in atmospheric premixed flames [21].

CONCLUSION

Influence of number OPC (fluorinated and non-fluorinated phosphates, phosphonates phosphites) on extinction strain rate of atmospheric diffusion counterflow $CH_4/N_2 – O_2/N_2$ flame was studied. The obtained data demonstrate that all tested OPC are more effective fire suppressants than CF_3Br. Furthermore, all fluorinated and non-fluorinated OPC show within experimental errors the same suppression effectiveness. It is also in a good agreement with the experimental results carried out using cup burner and Bunsen burner technique [11]. Calculation of extinction strain rate of the flame doped with 1200 and 2500 ppm TMP demonstrate the discrepancy with experimental results (experiment shows higher inhibition effect). This discrepancy is suggested to be connected with the fact that the model does not consider heat losses into the burner and by radiation. At the same time a satisfactory agreement was obtained between experimental (using microprobe and MBMS techniques) and calculated (for potential flow boundary condition) temperature and concentration of stable species profiles of non-premixed methane flame doped with 1200 ppm TMP and without additive. Calculation of concentrations of basic phosphorus containing species in the doped with 1200 ppm TMP flame at the maximum temperature demonstrates that the thermodynamic equilibrium have not been achieved in this flame.

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REFERENCES

1. Grosshandler, W. L., Gann, R. G., and Pitts, W. M., National Institute of Standards and Technology, Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays, NIST SP 861 (1994).
2. Tapscott, R. E., Sheinson, R. S., Babushok, V., Nyden, M. R. and Gann, R. G. Alternative Fire Suppressant Chemicals: A Research Review with Recommendations, NIST, Tech. Note 1443, 84 pages (December 2001).
3. Riches, J., Grant, K., and Knutsen, L., "Laboratory Testing of Some Phosphorus-Containing Compounds as Flame Suppressants," *presented at the 1999 Halon Options Technical Working Conference, Albuquerque*, NM, April, 27-29, 1999.
4. Nyden, M.R., Yang, J.C., Mather, J.D. "Screening of Candidate Fire Suppressants", *Proceeding of Halon Options Technical Working Conference*, 2000, pp. 104-114.
5. Babushok, V., Tsang, W., "Influence of Phosphorus-Containing Fire Suppressants on Flame Propagation", *Proceedings of the Third International Conference on Fire Research and Engineering*, Society of Fire Protection Engineers, Bethesda, 1999, p.257.
6. Kaizerman, J. A., Tapscott, R. E. Advanced Streaming Agent Development, Vol. 3., Laboratory-Scale Streaming Tests, NMERI, UNM, Albuquerque, NM, 1996.
7. Skaggs, R.R., Daniel, R.G., Miziolek, A.W., and McNesby, K.L., "Spectroscopic Studies of Inhibited Opposed Flow Propane/Air Flames," *Proceeding of Halon Options Technical Working Conference*, 1999, pp. 117-131.
8. A. G. Shmakov, O. P. Korobeinichev, T. A. Bolshova, V. M. Shvartsberg, D. A. Knyazkov, "Study of effect of organophosphorus fire suppressants on premixed C_3H_8/air and diffusive counterflow CH_4/Air flames", *Proceeding of Halon Options Technical Working Conference*, 1999, http://www.bfrl.nist.gov/866/HOTWC/HOTWC2002/pubs/24_Korobeinichev_et_al.pdf
9. Wainner, R.T., McNessby, K.L., Daniel, R.G., Miziolek, A.W., Babushok, V.I., "Experimental and Mechanistic Investigation of Opposed-Flow Propane/Air Flames by Phosphorus-Containing Compounds", *Proceedings of Halon Option Technical Working Conference*, Albuquerque, 2000, p.141.
10. MacDonald, M.A., Jayaweera, T.M., Fisher, E.M., and Gouldin, F.C., "Variation of Chemially Active and Inert Flame Suppression Effectiveness with Stoichiometric Mixture Faction", *27th Symp.(Int.) on Combust*., pp. 2749-2756 (1998).
11. Korobeinichev, O.P. et al., "Study of Effect of Aerosol and Vapour of Organophosphorus Fire Suppressants on Diffusion Heptane and Premixed C_3H_8/Air Flames", *Proceedings of Halon Option Technical Working Conference*, Albuquerque, 2003, p. ?.
12. Korobeinichev O.P., Il'in S.B., Mokrushin V.M., Shmakov A.G., "Destruction Chemistry of Dimethyl Methylphosphonate in H_2/O_2/Ar Flames Studied by Molecular Beam Mass Spectrometry", Comb. Sc. & Tech., 1996, 116-117, 1-6, pp.51-67.
13. Andrew E. Lutz, Robert J. Kee, Joseph F. Grcar, Fran M. Rupley, Chemkin Collection, Unlimited Release, Sandia National Laboratories, Livermore, CA (1997)

14. Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., Bowman, C. T., Hanson, R. K., Song, S., Gardiner, W. C. Jr., Lissianski, V. V. and Qin, Z. GRI Mech 3.0 (1999), http://www.me.berkeley.edu/gri_mech/
15. Korobeinichev, O.P., Ilyin, S.B, Bolshova, T.A., Shvartsberg, V.M., Chernov, A.A., " The Destruction Chemistry of Organophosphorus Compounds in Flames - III: The Destruction of DMMP and TMP in a Flame of Hydrogen and Oxygen", *Combust. Flame* 121: 593 (2000).
16. Korobeinichev, O.P., Mamaev, A.L., Sokolov, V.V., Bolshova, T.A., Shvartsberg, V.M., " Experimental Study and Modeling of the Effect of Phosphorous-Containing Compounds on Premixed Atmospheric Methane-Oxygen Flame Structure and Propagation Velocity", *Proceedings of Halon Option Technical Working Conference*, Albuquerque, NM, 2001, p.173.
17. Reinelt, D., Linteris, G.T., "Experimental Study of the Inhibition of Premixed and Diffusional Flames by Iron Pentacarbonyl", *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, 1996, pp. 1421-1428.
18. M. A. MacDonald, F. C. Gouldin, and E. M. Fisher, Combustion and Flame 125:668 –683 (2001)
19. Jayaweera, T. M., Ph.D. thesis "Flame suppression by aqueous solutions", Cornell University, May, 2002.
20. MacDonald, M.A., Jayaweera, T.M., Fisher, E.M., and Gouldin, F.C., Combustion and Flame 116: 166–176 (1999)
21. Korobeinichev, O.P., Bolshova, T.A., Shvartsberg, V.M., Shmakov, A.G., " Inhibition Effect of Organophosphorus Compounds on Structure of Atmospheric Premixed $C_3H_8/O_2/Ar$ and $CH_4/O_2/Ar$ Flames", Book of Abstracts of Twenty-Ninth International Symposium on Combustion, The Combustion Institute, Pittsburgh, 2002, p.262.