International Conference
on Combustion Physics and Chemistry

(Samara, Russian Federation, July 24-28, 2018)

TECHNICAL PROGRAM
AND
BOOK OF ABSTRACTS

“Insoma-Press”
Samara, 2018

УДК 544.45, 544.18
ББК 24.54, 22.317
M43

Edited by A.M. Mebel & V.N. Azyazov

**International Conference on Combustion Physics and Chemistry (Samara, Russia, 24-28 July): **Proceeding of the conference/ Edited by A.M. Mebel and V.N. Azyazov/ Samara University – Samara: Publishing OOO “Insoma-Press”, 2018 – 116 p.

ISBN 978-5-4317-0298-3

This collection presents the program and abstracts of presentations at the International Conference on Combustion Physics and Chemistry (ComPhysChem’18) held at Samara National Research University on Jul. 24-27, 2018. The presentations covered a broad range of fundamental and applied areas in combustion physics and chemistry including fundamental physical-chemical processes, quantum chemical studies of potential energy surfaces of chemical reactions in flames, kinetics and dynamics of elementary processes, mathematical modeling of processes in combustion, laser and optical diagnostics, chemical, plasma, and laser initiation of combustion, flame structure, formation and destruction of polycyclic aromatic hydrocarbons (PAH), soot, graphene, and carbonaceous nanoparticles, chromatography and measurement methods, and ecological issues related to combustion.

The Conference was supported by the Russian Foundation for Fundamental Research (Grant No. 18-03-20026) and the Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0020).

Intended for graduate students in the areas of physical chemistry, chemical physics, combustion science and technology, and for researchers and university professors.

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Foreword

Dear Participants:

We are happy to welcome you in Samara at the International Conference on Combustion Physics and Chemistry (**ComPhysChem'18**). Breakthrough combustion technologies of air-fuel mixtures can be developed on the basis of new fundamental knowledge on combustion physics and chemistry, including detailed mechanisms of elementary atomic and molecular processes involved in the formation and destruction of harmful emissions and in the initiation and sustainment of burning in combustion chambers of various types. In 2017-2019, Samara National Research University has been awarded a megagrant from the Ministry of Education and Science of the Russian Federation to create a laboratory for the purpose of development of physically justified models of combustion on the basis of new spectroscopic and kinetic data on chemical processes in combustion and flame characteristics. The objectives of this project include measurements and calculations of kinetic constants for the processes involved in initiation and sustainment of combustion, formation and destruction of pollutants (PAH, nitrogen oxides) and active species (radicals, intermediates, excited atoms and molecules, ions) and development of gas-dynamic and kinetic models of combustion based on physically proved rate constants and their validation on laminar model flames. Within this laboratory, a pyrolytic microreactor is being created with universal mass spectrometric detection of products of chemical reactions and with distinction of different isomers based on their photoionization cross sections. The reactor is planned to be commissioned in the second half of 2018 or in the beginning of 2019.

We have organized this **ComPhysChem'18** meeting with the goal to facilitate the development of the new laboratory and to promote scientific exchange and collaboration between combustion chemists and physicists around the world. The main topics of **ComPhysChem'18** include

- Fundamental physical-chemical processes in combustion
- Quantum chemical studies of potential energy surfaces of chemical reactions in flames
- Kinetics and dynamics of elementary processes
- Mathematical modeling of processes in combustion
- Laser and optical diagnostics of processes in combustion
- Chemical, plasma, and laser initiation of combustion
- Flame structure
- Formation and destruction of polycyclic aromatic hydrocarbons (PAH), soot, graphene, and carbonaceous nanoparticles
- Chromatography and measurement methods
- Ecological issues related to combustion

We are looking forward your interesting and exciting presentations as well as open, encouraging, and facilitating scientific discussions at the meeting. We also hope that you will enjoy the post-World-Cup city of Samara during and after the conference.

With our very best wishes,

Alexander M. Mebel, on behalf of the Organizing Committee

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TECHNICAL PROGRAM

July 23, 2018		July 24, 2018 Tuesday	July 25, 2018 Wednesday	July 26, 2018 Thursday	July 27, 2018 Friday		July 28, 2018
	8.30-9.00	Registration					
Arrival of participants	**9.00-9.20**	Opening Remarks	Invited M. Frenklach	Invited F. Qi	Invited V. Gubernov	**9.00-9.40**	Departure of participants
	9.20-10.00	Invited M. Ahmed	Invited S. Robertson	Invited A. Miyoshi	Invited O.Korobeinichev	**9.40-10.20**	
	10.00-10.40	Invited S. Anderson					
	10.40-11.00	Y. Medvedkov	Invited Ch. Zhou	Invited F. Zhang	Invited N. Smirnov	**10.20-11.00**	
	11.00-11.20	**Coffee Break**	**Coffee Break**	**Coffee Break**	**Coffee Break**		
	11.20-11.40	I. Antonov	A. Morozov	Invited A. Boldyrev	Invited A. Mebel		
	11.40-12.00	A. Chichinin	A. Sharipov				
	12.00-12.20	A. Thomas	E. Mikheyeva	A. Shmakov	S. Muppala		
	12.20-12.40	D. Porfiriev	D. Lopaev	R.Shaimukhametov	A. Drakon		
	12.40-13.00	A. Stolyarov	V. Perminov	P. Maryandyshev	Closing remarks		
	13.00-14.30	**Lunch**	**Lunch**	**Lunch**	**Lunch**		
	14.30-15.10	Invited A. Eskola	Invited A. Konnov	A. Krikunova	Ferry trip along the Volga River 15.30-19.30	**14.30-14.50**	
				A. Badernikov		**14.50-15.10**	
	15.10-15.30	I. Kosarev	Invited O.Vasyutinskii	A. Molokanov			
	15.30-15.50	B.Loukhovitski		V. Prokof'ev			
	15.50-16.10	N. Titova	D. Kozlov	City Excursion (3 hours)			
	16.10-16.30	**Coffee Break**	**Coffee Break**				
	16.30-16.50	V. Kobtsev	V. Smirnov				
	16.50-17.10	A.Chukolovsky	A. Volynets				
	17.10-17.30	M. Bulat	R. Joarder				
	17.30-17.50	E. Filimonova	E.Shchepakina				
	17.50-18.10	V. Upyrev	A. Nigay				
	18.10-18.30	S. Torokhov	Poster (18.15-20.00)				
	18.30-18.50	S. Golovastov					
Registration	**18.50-19.10**	M. Al-Jaboori					
Welcome party 19.30- 21.30				Conference dinner (is not included in the conference fee) 19.30- 22.00			

24 July, Tuesday

9.00-9.20 Opening Remarks

Andrey Prokofiev (Samara National Research University, Russia)
Michael Heaven (Emory University, USA)
Ralf Kaiser (University of Hawaii, USA)
Alexander Mebel (Florida International University, USA)

Session 1.1
Chair: Michael Heaven (Emory University, USA)

9.20-10.00 Musahid Ahmed (LBL, USA) *(Invited)*
Probing Combustion Chemistry with molecular beams and synchrotron radiation

10.00-10.40 Scott Anderson (University of Utah, USA) *(Invited)*
Carbon Oxidation Kinetics by Single Nanoparticle Mass Spectrometry

10.40-11.00 Iakov Medvedkov[1], V. Azyazov[1], A. Mebel[1,2], R. Kaiser[3] ([1]Samara National Research University, Russia, [2]Florida International University, USA, [3]University of Hawai‘i at Mānoa, USA)
Design of a New Generation Molecular Beam Machine

11.00-11.20 **Coffee Break**

Session 1.2
Chair: Oleg Vasyutinskii (Ioffe Institute, Russia)

11.20-11.40 Ivan Antonov, L. Sheps *(Northwestern University, USA)*
Developing novel PIMS apparatus to study oxidation kinetics at engine-relevant pressures

11.40-12.00 M. Poretskiy[1], Alexey I. Chichinin[1,2], C. Maul[1] and K.-H. Gericke[1] **(**[1]Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Germany, [2]Institute of Chemical Kinetics and Combustion and Novosibirsk State University, Russia)
Double-arm three-dimensional ion imaging apparatus for the study of ion pair channels in resonance enhanced multiphoton ionization

12.00-12.20 Aaron M. Thomas[1], M. Lucas[1], L. Zhao[1], J. Liddiard[1], R. Kaiser[1], A. Mebel[2] ([1]University of Hawai’i at Manoa, Honolulu, [2] Florida International University, Miami, USA)
Reaction Dynamics of Radical Intermediates formed during Hydrocarbon Combustion

12.20-12.40 M. Zagidullin[1,2], Denis P. Porfiriev[1,2], R. Kaiser[3], V. Azyazov[1,2], A. Mebel[1,4] ([1]Samara National Research University, Russia, [2]Lebedev Physical Institute, Samara, Russia, [3]University of Hawaii at Manoa, USA, [4] Florida International University, USA)
Pyrolysis of $C_{10}H_7Br$ in high temperature microreactor: experiment and modeling

12.40-13.00 A.V. Zaitsevskii, A.A. Medvedev, Andrey V. Stolyarov (Lomonosov Moscow State University, Russia)
Relativistic and quasirelativistic electronic structure calculations on the alkali metal - rare gas molecules

13.00-14.30 LUNCH

Session 1.3
Chair: Chongwen Zhou (Beihang University, China)

14.30-15.10 Arkke J. Eskola (University of Helsinki, Finland) *(Invited)*
Time-Resolved Kinetic Experiments Utilizing Photo-Ionization Mass-Spectrometers

15.10-15.30 Ilya N. Kosarev, S.V. Kindysheva, V.D. Grigorenko, S.O. Belov, A.Yu. Starikovskiy *, N.L. Aleksandrov (MIPT, Russia, *Princeton University, USA)
Shock tube study of plasma-assisted dimethyl ether ignition at temperatures near self-ignition threshold

15.30-15.50 Boris I. Loukhovitski, A.S. Sharipov (CIAM, Russia)
Influence of internal molecular degrees of freedom on their electric and optical properties

15.50-16.10 I.V. Arsentiev, V.A. Savelieva, Nataliya Titova (CIAM, Russia)
Numerical study of H_2S-H_2O-air mixture conversion to hydrogen via activation of air by an electric discharge

16.10-16.30 **Coffee Break**
Session 1.4
Chair: Nikolay Smirnov (Moscow State University, Russia)

16.30-16.50 Vitaly D. Kobtsev[1], S. Kostritsa[1], V. Smirnov[1,2], N. Titova[1], S. Torokhov[1] ([1]CIAM, [2]A.M. Prokhorov General Physics Institute, RAS, Russia)
The experimental study of the enhancement of hydrogen-air mixture ignition promoted by the singlet oxygen molecules

16.50-17.10 A. Volynets, D. Lopaev, Alexander Chukalovsky, T. Rakhimova, Yu. Mankelevich, N. Popov (Skobeltsyn Institute of Nuclear Physics, Lomonosov State University, Russia)
N_2 dissociation and kinetics of $N(^4S)$ atoms in nitrogen DC glow discharge

17.10-17.30 P. Bulat[1], M. Bulat[1], I.Volobuev [2] ([1]Baltic State Technical University "Voenmeh", [2]ITMO University, Russia)
Concept of low emission combustion chamber with using streamers discharge to increase combustion speed

17.30-17.50 Elena Filimonova, A. Bocharov, V. Bityurin (JIHT of RAS, Russia)
Formation of combustion wave in a hydrocarbon-air mixture in near high-voltage electrode of surface dielectric barrier discharge

17.50-18.10 P.V. Bulat[1,2], L.P. Grachev[3], I.I. Esakov[3], Vladimir V. Upyrev[1,2] ([1]Baltic State Tech. Univ. "Voenmeh", [2]ITMO University, [3] Moscow Radiotechnical Institute of the RAS, Russia)
Stabilization of combustion front in supersonic flow using streamer's discharge

18.10-18.30 K. Vereshchagin[1,2], S. Volkov[1,2], V. Kobtsev[1], S. Kostritsa[1], V. Smirnov[1,2], A. Starik[1], N. Titova[1], Sergey Torokhov[1] ([1]CIAM, [2]Prokhorov General Phys. Inst., RAS, Russia)
The numerical study of hydrogen-air mixture ignition under laser photo dissociation of O_2 molecules

18.30-18.50 Sergey Golovastov, G. Bivol, V. Golub (JIHT, Russia)
Detonation decay and flame propagation through a channel with porous walls

18.50-19.10 Muthana Al-Jaboori (Oman)
Extinguishing Oil Well's Fires

25 July, Wednesday

Session 2.1
Chair: Fei Qi (Shanghai Jiao Tong University, China)

9.00-9.40 Michael Frenklach (University of California at Berkeley, USA) *Invited*
Modeling of Soot Oxidation

9.40-10.20 M. Blitz, Ch. Morley, M.J. Pilling, Struan H. Robertson, P. Seakins, H. Wang, X. You (University of Leeds, UK) *Invited*
Obtaining the Phenomenological Rate Coefficients from Direct Analysis of Experimental Data

10.20-11.00 Chong-Wen Zhou (Beihang University, China), *Invited*
Combustion Chemistry for Alkenes: What Have We Learned from Butene Isomers?

11.00-11.20 Coffee Break

Session 2.2
Chair: Alexander Boldyrev (Utah State University, USA)

11.20-11.40 Alexander Morozov[1], A. Mebel[1], R. Kaiser[2] ([1]Florida International University, [2]University of Hawaii at Manoa, USA)
A Theoretical Study of Pyrolysis of exo-Tetrahydrodicyclopentadiene and its Primary and Secondary Unimolecular Decomposition Products

11.40-12.00 A.V. Pelevkin, Alexander S. Sharipov (CIAM, Russia)
Reaction kinetics of H_2 *with* O_2 *in highly excited electronic states*

12.00-12.20 A. Eremin[a], Ekaterina Mikheyeva[a,b], I.Selyakov[a,c] ([a]JIHT RAS, [b]Bauman Moscow State Technical University, [c]Lomonosov Moscow State University, Russia)
Soot formation in pyrolysis of acetylene with hydrocarbon additions

12.20-12.40 Dmitry Lopaev, A. Volynets, T. Rakhimova, O. Proshina, A. Chukalovsky (Skobeltsyn Institute of Nuclear Physics, Moscow State University, Russia)
Features of oxygen metastable molecules kinetics in O_2 *plasma with increasing pressure*

12.40-13.00 Valeriy Perminov, V. Marzaeva (Tomsk Polytechnic University)
Mathematical modeling of the impact of forest fires on buildings and structures

13.00-14.30 LUNCH

Session 2.3
Chair: Michael Frenklach (UC Berkeley, USA)

14.30-15.10 Alexander A. Konnov (Lund University, Sweden) *Invited*
Data consistency of the burning velocity measurements

15.10-15.50 Oleg S. Vasyutinskii (Ioffe Institute, Russia) *Invited*
Vector Correlations in Molecular Photodissociation: Femtosecond Stereodynamics

15.50-16.10 Dmitry Kozlov[a,b], V. Kobtsev[b], V. Smirnov[a,b] ([a]Prokhorov General Physics Institute RAS, [b]CIAM, Russia)
Local Optical Diagnostics of High-Temperature Gas Media Using Laser-Induced Gratings

16.10-16.30 **Coffee Break**

Session 2.4
Chair: Natalia Titova (P.I. Baranov Central Institute of Aviation Motors, Russia)

16.30-16.50 K. Vereshchagin[1,2] ,V. Kobtsev[1], S. Kostritsa[1], Valery Smirnov[1,2], N. Titova[1], S. Torokhov[1] ([1]CIAM, [2]Prokhorov General Physics Institute, RAS, Russia)
CARS and Fluorescent Study of Ignition of H_2-O_2 Mixtures upon Photo-Dissociation of O_2 Molecules

16.50-17.10 Andrey Volynets[1], D. Lopaev [1], A. Rakhimov[1] (Skobeltsyn Institute of Nuclear Physics of Lomonosov Moscow State University, Russia)
Actinometry of O atoms with Kr at elevated pressures (10 - 100 Torr) in pure O_2 discharge

17.10-17.30 Ratan Joarder, A.P. Singh (Indian Institute of Technology, Kharagpur, India)
LES of Laser Initiation of Combustion of Gaseous Fuel-Air Mixture

17.30-17.50 Elena A. Shchepakina (*Samara National Research University, Russia)*
A Geometric Approach to the Modeling of Critical Phenomena in Combustion Models

17.50-18.10 Aleksandr G. Nigay, D.O. Glushkov (Tomsk Polytechnic University, Russia)
Experimental investigation of the gel fuel combustion process initial by the hot particle

18.20-20. 00 Poster Session

P1. M.Y. Orlov, V.M Anisimov., O.V. Kolomzarov, M.Y. Anisimov (Samara University, Russia),
Maturation of workflow of combustion chamber with toroidal recirculation mixing zone

P2. V.N. Azyazov[1], M.V. Zagidullin[1,2], M.C. Heaven[1,3], A.M. Mebel[1,4] ([1]Samara University, [2]Lebedev Physical Institute, Samara, Russia, [3]Emory University, [4]Florida International University, USA)
Active oxygen species in combustion

P3. M. Lucas[a], A. Thomas[a], R. Kaiser[a], E. Bashkirov[b], V. Azyazov[bc], A. Mebel[bd] ([a]University of Hawai'i at Manoa USA, [b]Samara University, [c]Lebedev Physical Institute, Samara, Russia, [d]Florida International University, USA)
Products distribution in the reaction of atomic carbon with pyridine: theory and experiment

P4. A. Razuvaev, V. Biryuk, E. Blagin (Samara National Research University, Russia)
Increase of the energy plant efficiency in special conditions of its operation

P5. A.K. Chernyshov ([1]Lebedev Physical Institute, Samara, [2]Samara University, Samara, Russia)
Thermometry in a sealed discharge cell with noble gas

P6. A. Chichinin[1,2], O. Ott[1,3], Ch. Maul[1], K.-H. Gericke[1] ([1]Technische Universität Braunschweig, Germany;[2] Institute of Chemical Kinetics and Combustion and Novosibirsk State University, Russia, [3]Physikalisch-Technische Bundesanstalt, Experimental Physics, Nuclear Physics, Germany)
Photodissociation dynamics of SCl_2: resonance enhanced multi-photon ionization/time-of-flight mass spectroscopy study

P7. V. Azyazov[1], A. Demyanov[2], I. Kochetov[2], P. Mikheyev[1] ([1]Samara branch of P.N. Lebedev Physical Institute of RAS, [2]SRC RF Troitsk Institute for Innovation and Fusion Research, Russia)
Simulation of plasma initiation of ignition of methane-air mixtures under atmospheric pressure

P8. M. Evseev[1], E. Bashkirov[1], V. Azyazov[1], A. Mebel[1,2] ([1]Samara National Research University, Russia, [2]Florida International University, United States)
Formation Mechanisms of Phenanthrene and Anthracene

P9. Sh. Gabdrashova [1], M. Tulepov[1], M. Korchagin[2], B. Elouadi[3] ([1]al-Farabi Kazakh National University, Kazakhstan, [2]Institute of Solid State Chemistry and Mechanochemistry, Siberia Branch of the RAS, Russia, [3]Université de La Rochelle, France)
Study of pyrotechnic delay composition using reinforced composite material with carbon nanotubes

P10. G. Galimova [1,2], V. Azyazov[1,2], A. Mebel[1,3] ([1]Samara National Research University, [2]Lebedev Physical Institute, Samara, Russia, [3]Florida International University, USA)
Reaction mechanism for the oxidation of $C_{15}H_9$ *with hydroxyl*

P11. A. Ghildina [1], A. Mebel[2], V. Azyazov[1,3] ([1]Samara National Research University, Russia, [2]Florida International University, USA, [3]Lebedev Physical Institute, Samara, Russia)
The rate constants calculations and the potential energy surface for indenyl $C_9H_7 + O_2$ *reaction by ab initio methods*

P12. O.G. Glotov[1], G.S. Surodin[1], V.E. Zarko[1], M.A. Korchagin[2] ([1]Voevodsky Institute of Chemical Kinetics and Combustion, [2] Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia)
Combustion characteristics of model composite propellants with aluminum diboride

P13. V. Azyazov[1], A. Demyanov[2], I. Kochetov[2], P. Mikheyev[1] ([1]Samara branch of P N Lebedev physical Institute of RAS, [2]SRC RF Troitsk Institute for Innovation and Fusion Research, Russia)
Simulation of ozone formation in an electric discharge in mixtures of methane with air

P14. M. Orlov, V. Anisimov, O. Kolomzarov, N. Gurakov, N. Mironov (Samara University, Russia)
Substantiation of the expediency of using the combustion chamber with a toroidal recirculation zone in the small GTE

P 15. A. Korotchenko, M. Evseev, E. Bashkirov, V. Azyazov N., A. Mebel ([1] Samara National Research University, Russia, [2]Florida International University, United States)
Formation mechanism of triphenylene and 4- vinylacephenanthrylene in the interaction of 9-phenanthryl and vinilacetylene

P 16. V. Fabelinsky[1], V. Kobtsev[2], S. Kostritsa[2], D. Kozlov[1,2], V. Smirnov[1,2],K. Vereschagin[1,2] ([1]Prokhorov General Physics Institute, [2]Baranov Central Institute of Aviation Motors, Russia)
Methane-air flame thermometry using Planar Laser-Induced Fluorescence (PLIF)

P17. S.S. Matveev[1], I. Chechet[1], S.G. Matveev[1], A. Konnov[2] ([1]Samara University, Russia, [2]Lund University, Sweden)
Laminar burning velocities of n-decane with ethanol additions

P 18. V. Malikov [1], A. Ishkov[2], S. Dmitriev[1], A. Sagalakov[1] ([1]Altay State University, [2]Altay State Agracultural University, Russia)
Research materials and structures of space vehicles by multifrequency measuring system on the basis of eddy current transducers

P 19. D. Miftyakhova, M. Evseev, E. Bashkirov, V. Azyazov, A. Mebel ([1] Samara National Research University, Russia, [2] Florida International University, United States)
Formation mechanism of benzo(c)phenanthrene

P 20. A. Eremin[a], M. Korshunova[a,b], E. Mikheyeva[a,b] (*[a]JIHT RAS, [b]Bauman MSTU, Russia)*
Experimental study of chemiluminescence in UV and VIS range at hydrogen-oxygen mixtures ignition

P 21. G. Nyashina, (National Research Tomsk Polytechnic University, Russia)
Environmental advantages of composite fuels based on industrial wastes and different ranks of coal

P 22. A. Oleinikov[1], V. Azyazov[1,2], A. Mebel[1,3] ([1]Samara National Research University, [2]Lebedev Physical Institute, Samara, Russia, [3]Florida International University, USA)
The reaction of 1-naphthyl with 1,3-butadiene: a theoretical study

P 23. A.A. Pershin, A.P. Torbin, V.N. Azyazov (Samara University, Russia)
Ozone recovery in the presence of nitrous oxides

P 24. L. Petrov[1,2], N. Kortsenshteyn[2] ([1]G.M. Krzhizhanovsky Power Engineering Institute, [2]National Research University «Moscow Power Engineering Institute», Russia)
Modeling of the formation of ultrafine particles as coals burning

P 25. D. Porfiriev[1,2], V. Azyazov[1,2], A. Mebel[1,3] ([1]Samara National Research University, [2]Lebedev Physical Institute, Samara, Russia, [3]Florida International University, USA)
Kinetics of the 1-acenaphthyl + O_2 Reaction: A Theoretical Study

P 26. D. Rybakov, Kh. Lamazhapov (Samara State Transport University, Samara, Russia)
Percolation model of combustion

P 27. V. Saleev, A. Shipilova (Samara National Research University, Russia)
Ab initio study of magnesium surface oxidation

P 28. A. Savchenkova[1], A. Semenikhin[1], I. Chechet[1], S. Matveev[1], A. Konnov[2], A. Mebel[1,3] ([1] Samara University, Russia, [2]Lund University, Sweden, [3] Florida International University, USA)
Rate constants calculations of the CH_2 + CH_2CO reactions in triplet and singlet states by ab initio methods

P 29. A.S. Sharipov, A.V. Pelevkin (Central institute of aviation motors, Moscow, Russia)
Quantum chemical study of the reactions of H_2 and H_2O molecules with $N_2(A_3\Sigma u+)$

P 30. A.A. Sludnova[1,2], N.S. Mironov[1], P.A. Mikheyev[1,2] ([1]Samara National Research University, [2]P N Lebedev Physical Institute, Samara, Russia)
Study of a dielectric barrier discharge burner for plasma assisted combustion

P 31. A.A. Sultanova [1], V.M. Yanborisov [2] ([1]Academy of Sciences of the Republic of Bashkortostan, [2]Ufa State Petroleum Technological University, Russia)
Mechanism of Methyl Methacrylate Polymerization in the presence of the initiating system "azobisisobutyronitrile-ferrocene"

P 32. V.E. Kozlov, N.S. Titova (Central Institute of Aviation Motors, Russia)
2D modeling of V-shaped turbulent methane-air flame

P 33. G. Tolstov[1], M. Zagidullin[1,2], N. Khvatov[2], A. Mebel[1,3], V. Azyazov[1,3] ([1]Samara University, [2]Lebedev Physical Institute, Samara, Russia, [3]Florida International University, USA)
Measurements of rate constants for $O_2(b^1\Sigma)$ quenching by CH_4, NO, N_2O at temperatures of 300−800 K

P 34. A.P. Torbin, A.A. Pershin, V.N. Azyazov (Samara University, Russia)
Ozone recovery in presence of CO

P 35. P.K. Tretyakov, A.V. Tupikin (Khristianovich Institute of Theoretical and Applied Mechanics SB RAS, Russia)
The impact of non-stationary electric field on hydrocarbon flames

P 36. V. Tyurenkova, N. Smirnov, M. Smirnova (Federal Science Center Scientific Research Institute for System Studies of RAS, Moscow M.V. Lomonosov State University, Russia)
Mathematical modeling of burning surface in parallel flow of oxidant

P 37. A.V.Emelianov, A.V. Eremin, P.I.Yatsenko (Joint Institute for High Temperatures, RAS, Russia)
Application of ARAS and MRAS methods to study the kinetics of CF_2 *radicals formation at pyrolysis* C_3F_7I

P 38. A.I. Klimov, S.E. Kurushina, N.E. Molevich, D.P. Porfiriev, I.P. Zavershinskii (Samara National Research University, Russia)
Plasma vortex reactor for production of heat energy and hydrogen

P 39. I.A.Zubrilin[1], S.G. Matveev [1], A. Marrone [2], D.M. Pastrone [2] ([1]Samara National Research University, Russia, [2]Politecnico of Turin, Italy)
Modeling of small gas turbine engine CO emissions based on reactor network

P 40. V.I. Bolobov (Saint-Petersburg Mining University, Russia)
Auto-ignition problem titanium of oxygen and possible ways of solving

26 July, Thursday

Session 3.1
Chair: Ralf Kaiser (University of Hawaii, USA)

9.00-9.40 Fei Qi (Shanghai Jiao Tong University, China) *Invited*
Recent progress in experiments and diagnostics for combustion chemistry

9.40-10.20 Akira Miyoshi (Hiroshima University, Japan) *Invited*
Kinetics of Autoignition

10.20-11.00 Feng Zhang,[a] C. Huang,[a,b] Sh. Li,[a,b] L. Xing,[a] B. Yang[b] ([a]University of Science and Technology of China, [b]Tsinghua University, China)
RRKM/master equation calculations for some typical combustion reactions and the uncertainty analysis

11.00-11.20 **Coffee Break**

Session 3.2
Chair: Oleg Korobeinichev (Institute of Chemical Kinetics and Combustion, Russia)

11.20-12.00 Alexander I. Boldyrev (Southern Federal University, Russia, Utah State University, USA)
Delocalized Bonding in Molecules, Clusters, Two-Dimensional Materials and Solids

12.00-12.20 Andrey G. Shmakov[1,2] K. Osipova[1,2], D. Knyazkov[1,2], I. Gerasimov[1], A. Dmitriev[1,2], T. Bolshova[1] O. Korobeinichev[1,2] ([1]Institute of Chemical Kinetics and Combustion, [2]Novosibirsk State University, Russia)
An Experimental and Numerical Study of Combustion Chemistry of Fatty Acids Esters

12.20-12.40 V.A. Strekalov, Ramil R. Shaimukhametov **(**Kazan Federal University, Russia)
The Acoustic Spectrums of the combustion Process in the IC-Engines

12.40-13.00 Pavel A.Maryandyshev, A. Kangash, V. Lyubov (Northern (Arctic) federal university named after M.V. Lomonosov, Russia)
Investigation of thermal degradation of hydrolysis lignin

13.00-14.30 LUNCH

Session 3.3
Chair: Feng Zhang (USTC, Hefei, China)

14.30-14.50 Anastasia Krikunova (MIPT, JIHT RAS, Russia)
The gravity impact on the V-shape flame instability

14.50-15.10 Artem V. Badernikov[1], S.A. Piralishvily[2], A.I. Guryanov[2] ([1]UEC-Saturn, [2]Rybinsk State Aviation Technical University, Russia)
Results of numerical modeling of combustion processes in a vortex chamber

15.10-15.30 L. Yanovskiy[1,2], N. Varlamova[1,2], A. Kazakov[2], V. Dubikhin[2], Alexander A. Molokanov[1,2], I. Popov[1], M. Stashkiv[1], C. Kasheeva[1], M. Ilina[1], V. Ezhov[1] ([1]Central Institute of Aviation Motors, [2]Institute of Problems of Chemical Physics of RAS)
Manometric Study of the Kinetics of Thermal Degradation of Alicyclic Hydrocarbons as Components of Advanced Aviation Fuels

15.30-15.50 Vadim G. Prokof'ev (Tomsk State University, Russia)
Spin Combustion of Gasless Systems with Melting Component: 3D Simulation

27 July, Friday

Session 4.1
Chair: Akira Miyoshi (Hiroshima University, Japan)

9.00-9.40 Vladimir V. Gubernov (P.N. Lebedev Physical Institute, RAS, Russia) *(Invited)*
Mechanisms performance for H_2/air burner-stabilized flames at various pressures

9.40-10.20 Oleg Korobeinichev[1], A. Shmakov[1], A. Karpov[2], A. Shaklein[2] ([1]Institute of Chemical Kinetics and Combustion Siberian Branch RAS, [2]Udmurt Federal Research Center, Russia) *(Invited)*
Physics and Chemistry of Combustion at Flame Spread over Solid Fuels

10.20-11.00 Nicolay N. Smirnov (Moscow M.V. Lomonosov State University, Russia)
Three-dimensional simulation of combustion, detonation and deflagration to detonation transition processes in cone and wedge induced focusing

11.00-11.20 Coffee Break

Session 4.2

Chair: Alexander Mebel (Florida International University, USA)

11.20-12.00 G. Galimova[1], A. Ghildina,[1] A. Oleinikov,[1] V. Azyazov,[1,2] A. Mebel[1,3] ([1]Samara university, [2]Lebedev Physical Institute, Samara, Russia, [3] Florida International University, USA) *(Invited)*
Oxidation of five-member rings in combustion

12.00-12.20 M. Tidswell, Siva Muppala, V. Rao (Kingston University, UK)
A numerical study of two turbulent flame speed models for H_2/CH_4/air premixed combustion

12.20-12.40 Alexander Drakon, A. Eremin **(**Joint Institute for High Temperatures RAS, Russia)
Inefficiency of suppression of methane-oxygen mixtures autoignition by halogenated hydrocarbons

12.40-13.00 Closing remarks

BOOK OF ABSTRACTS

INVITED TALKS

Probing Combustion Chemistry with molecular beams and synchrotron radiation

Musahid Ahmed

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, USA

Single photon ionization with vacuum ultraviolet (VUV) photons is an efficient (and "soft") method of ionizing fragile molecules, whereby the tunable radiation provides precise threshold ionization imparting little excess internal energy into the molecular ion.[1] Furthermore, tunable VUV ionization has been shown to be a selective, yet universal technique in elucidating molecule-specific information since it can resolve isomers via ionization energy (IE), absorption cross-sections follow rules which are quantifiable, and all molecules will ionize beyond its IE and hence can be detected in a mass spectrometer. In this talk I will describe two recent results showcasing how tunable synchrotron radiation allows for an understanding of molecular growth processes relevant to combustion.

We in collaboration with Ralf Kaiser (University of Hawaii, Manoa), and Alex Mebel (Florida International University) have performed systematic and extensive studies of two- and three-membered ring polycyclic aromatic hydrocarbons (PAHs)[2] utilizing a high temperature chemical reactor coupled to synchrotron based VUV photoionization mass spectrometry. Moving beyond these studies, the critical step in the understanding of the mass-growth processes from simple PAHs to soot particles is to unravel the synthesis of key building blocks as present in two- and three-dimensional precursors to soot: coronene and corannulene. In this talk I will describe our recent results on the formation of larger compounds (four ringed pyrene) generated from the reaction of the anthracenyl radical with acetylene.[3]

Working with Martin Head-Gordon (UC Berkeley, LBNL), we have formulated an understanding as to how non covalent interactions can drive chemical reactivity in small acetylene clusters upon photoionization. A dramatic dependence of product distribution on the ionization conditions is demonstrated experimentally and understood from simulations. The products change from reactive fragmentation products in a higher temperature, higher density gas regime towards a very cold collision-free cluster regime that is dominated by products whose empirical formula is $(C_2H_2)_n^+$, just like ionized acetylene clusters. Formation of the benzene cation is demonstrated in Ab-Initio Molecular Dynamics simulations of clusters of acetylene clusters with $n>3$, as well as other metastable $C_6H_6^+$ isomers.[4]

I will conclude by discussing how water affects the photoionization properties of PAH's and how these studies could shed light on processes relevant to energy science and astrochemistry.

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2. Yang, T.; Kaiser, R. I.; Troy, T. P.; Xu, B.; Kostko, O.; Ahmed, M.; Mebel, A. M.; Zagidullin, M. V.; Azyazov, V. N., HACA's Heritage: A Free-Radical Pathway to Phenanthrene in Circumstellar Envelopes of Asymptotic Giant Branch Stars. *Angew Chem Int Edit* **2017,** *56* (16), 4515-4519.

3. Zhao, L.; Kaiser, R. I.; Xu, B.; Ablikim, U.; Ahmed, M.; Joshi, D.; Veber, G.; Fischer, F. R.; Mebel, A. M., Pyrene synthesis in circumstellar envelopes and its role in the formation of 2D nanostructures. *Nature Astronomy* **2018**, doi:10.1038/s41550-018-0399-y.

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Carbon Oxidation Kinetics by Single Nanoparticle Mass Spectrometry

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This talk will describe use of single nanoparticle mass spectrometry (NPMS) to measure sublimation and oxidation kinetics of individual laser-heated carbon nanoparticles (NPs) trapped in the gas phase. The goal is to measure the effects of NP heterogeneity on kinetics, specifically the effects of NP-to-NP variations in size, shape, and nanostructure, and the effects of the distribution of surface sites on *individual NPs*, which evolve with time. In addition, we measure emission spectra for individual NPs over the 400 to 1650 nm range.

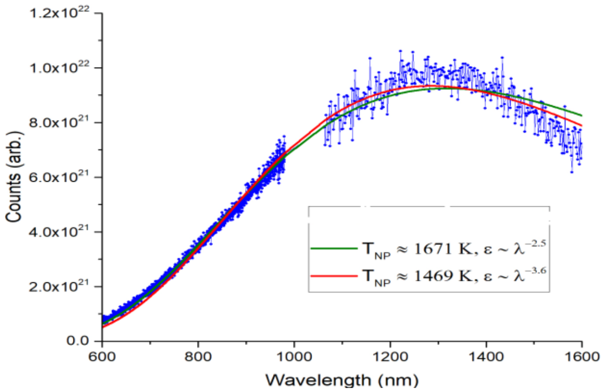

Fig. 1. Single NP emission spectrum

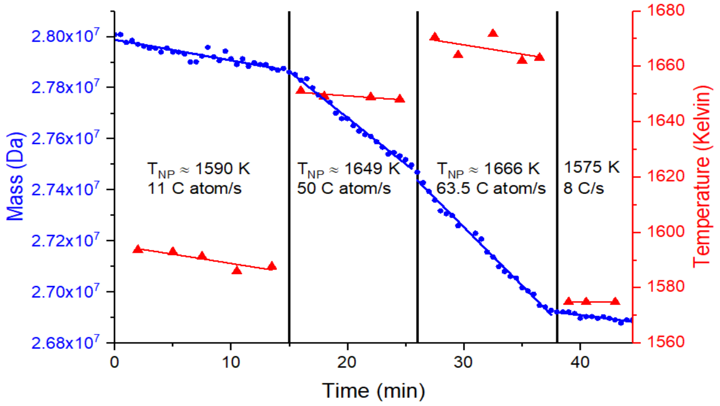

Fig. 2. Sublimation kinetics for a 28 MDa graphite NP

In NPMS, a single NP is trapped in an AC quadrupole trap, laser heated to incandescence, and its motion is detected optically. From the motional frequency, it is possible derive the mass M and charge Q of the NP, and since the measurement is non-destructive, kinetics for sublimation, addition reactions, and oxidation can be followed over ~5 orders of magnitude by tracking M vs. time. The temperature range is roughly 1400 K to 2500 K. In addition, the number of reactive sites on each individual NP can be measured using a site titration process, providing NP-by-NP correlations between the number of reactive sites and the kinetics. NP temperature (TNP) is determined simultaneously with kinetics, by measuring the emission spectrum using a pair of array spectrographs. Fig. 1 shows an example single NP emission spectrum acquired in 10 sec, along with fits assuming two simple models for the variation of emissivity with λ. Note that the spectrum shows significantly greater curvature in the IR that either model predicts. Fig. 2 shows an example of kinetics measured with simultaneous T_{NP} determination, in this case for sublimation of a graphite NP with initial mass of 28.007 MDa, heated with a CO_2 laser. During the initial period, T_{NP} drifted from ~1594 to ~1586 K, and the sublimation rate averaged 11 carbon atoms/sec, or ~4 ppm/sec. When T_{NP} was raised to ~1649 K, the rate increase to 50 atoms/sec, and raising the temperature to ~1666 K increased the rate to 63.5 atoms/sec, followed by a drop to 8 atoms/sec when T_{NP} was returned to 1575 K. When automation of the experiment is complete, the laser stability, frequency of T_{NP} determination, and range of rates that can be studied will increase substantially.

Reactions of oxygen atoms with aliphatic and aromatic hydrocarbons by crossed beam experiments

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Because of their relevance in combustion and other gaseous media, the rate coefficients for the reactions between ground state 3P oxygen atoms and unsaturated hydrocarbons have been determined in kinetics experiments as a function of temperature. Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). This piece of information is fundamental, however, because the products of one elementary reaction are the reactants of a subsequent one in the complex scheme of elementary reactions that account for the global combustion process [1]. For multichannel reactions like these, the primary products and their BR are not easy to predict because intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES) can occur, opening up other reaction channels not accessible on the triplet PES. The quantification of ISC as a function of temperature is a demanding task which requires an experimental or theoretical investigation.

For this reason, following the pioneering work of Y.T. Lee and coworkers [2], we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [3] with mass spectrometric detection empowered by soft electron impact ionization. Results on the reactions of atomic oxygen with alkynes [4], alkenes [5], dienes [6], and arenes (benzene and toluene) will be presented. Implications in combustion chemistry will be noted.

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Delocalized Bonding in Molecules, Clusters, Two-Dimensional Materials and Solids

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Canonical Molecular Orbitals (CMO) obtained by either the Hartree-Fock method or by the Density Functional Theory are completely delocalized over the whole chemical system. When systems are getting larger it is hard to interpret CMOs. Chemist on the other side prefer to use localized bonding based on Lewis model which operates with lone pairs and two-center two-electron (2c-2e) bonds. When Lewis model works, interpretation of chemical bonding is simple. However, more and more new chemical systems cannot be represented by Lewis model. The resonance description may be used in those cases, but it becomes very challenging for structurally complex chemical species. We recently introduced two new theoretical methods: Adaptive Natural Density Partitioning (AdNDP)[1] and Solid State Adaptive Natural Density Partitioning (SAdNDP)[2], which allow to express chemical bonding in terms of localized (1c-2e and 2c-2e) and delocalized (multi-center nc-2e) bonds. We initially search for all lone pairs, core electrons and 2c-2e bonds with good occupation numbers. In the ideal Lewis model occupation numbers correspond to 2 (an electron pair). After that we look for multicenter bonds still trying to use as small number of centers as possible, though in principle delocalized bonds can be delocalized over the whole chemical system. In my talk I will show how AdNDP and SSAdNDP methods allow us to use both localized and delocalized bonding elements for rationalization of chemical bonding in difficult cases of organic molecules, bare and embedded clusters, two-dimensional sheets and solids. I will discuss examples of delocalized bonding with 3c-2e bonds in supertetrahedral aluminum − a new allotropic ultralight crystalline form of aluminum, 4c-2e bonds in two-dimensional borane BH, 9c-2e and 10c-2e bonds in the transition metal centered boron wheel clusters, 8c-2e bonds in sodium vacancies in the high-pressure Na_2He compound, 6c-2e and 5c-2e bonds in oxygen vacancies in the bulk and on the surface of MgO crystal. AdNDP and SSAdNDP both provide a very efficient and visual approach to represent chemical bonding and could be used for research and for teaching chemistry.

Acknowledgements

This research was supported by the National Science Foundation (CHE-1664379) and by the Ministry of Education and Science of the Russian Federation (agreement no. 14.Y26.31.0016).

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Time-Resolved Kinetic Experiments Utilizing Photo-Ionization Mass-Spectrometers

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A pulsed laser initiation of a reaction combined with time-resolved photo-ionization mass-spectrometry detection of reactants and/or products is a versatile method to investigate combustion chemistry. Excimer laser photolysis is often used for radical production, either directly by breaking, for example, the -C-Br bond of a bromide precursor, or indirectly by producing Cl-atoms that subsequently react with a hydrocarbon. For mass-separation and detection of ionized species both quadrupole mass-spectrometer (QMS) and time-of-flight mass-spectrometer (ToF-MS) have their advantages; QMS is probably more sensitive which is important when no synchrotron radiation is available while a great advantage of ToF-MS is its ability to detect all masses of interest practically simultaneously. Combining ToF-MS with a tunable synchrotron radiation is brilliant method to investigate fuel-molecule oxidation under low-temperature-combustion conditions where multiple reaction channels are important. Scanning kinetic time, mass, and photon energy provides quantitative information on branching ratios of products, which can be directly compared with kinetic models of combustion. However, synchrotrons are very expensive facilities and not many have VUV-beamlines with energy range (~ 7 – 15 eV), resolution, and intensity (preferably an undulator beamline) suitable for time-resolved kinetic experiments, where efficient ionization of a sample beam taken from a reaction mixture is required. Due to these reasons, in experiments employing synchrotron radiation one needs to concentrate on the most important research topics, leaving much space for experiments which can be performed in a normal university laboratories. For this and also other reasons QMS with an intense ionization radiation provided by a gas-discharge (plasma) resonance radiation source is an attractive method for time-resolved kinetic experiments. In this presentation these methods are introduced and their capabilities and differences are discussed with example reactions.

Reactions which will be discussed range from alkyl-radical oxidation reactions central in autoignition of fuel – air mixture to reactions of resonantly-stabilized radicals with O_2 and NO_2. Alkyl radical R reactions with O_2, formation of RO_2 and bimolecular products, as well as formation of ketohydroperoxides in chain-branching reaction channel will be discussed. Very recently kinetics of these reactions have been measured for *n*-butane using the above instruments. Resonantly-stabilized radicals have low reactivity toward O_2 and high barrier for decomposition and, consequently, they play a central role in formation of aromatic ring-structures, which under favorable, fuel-rich conditions fuse together and initiate soot formation, for example in diesel engines. NO_x (= NO + NO_2) formation is also a significant problem in diesel engines and their reactions with resonantly-stabilized and other radicals is also discussed.

Modeling of Soot Oxidation

Michael Frenklach

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In this presentation I will review the state of knowledge in the area of soot oxidation, summarize recent advances in the underlying detailed reaction mechanisms, demonstrate the role of quantum-chemical calculations of key reaction rates, report results on developing a new model form for reduced modeling of soot oxidation, and suggest reactions that need further quantum-chemical studies.

Mechanisms performance for H_2/air burner-stabilized flames at various pressures

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The kinetic mechanism of hydrogen combustion is the most investigated combustion system. This is due to extreme importance of the mechanism for combustion processes, i.e. it is present as a submechanism in all mechanisms for hydrocarbon combustion systems. In spite of the progress made in understanding of the kinetics of hydrogen combustion there is a demand for further investigation of the detailed aspects of the flame-wall interaction under elevated pressure and under conditions of different wall and gas temperatures, local equivalence ratios etc.

The burner stabilized flame configuration can be efficiently used to study different aspects of chemical kinetics by varying the stand-off distance, pressure, temperature of the burner and mixture compositions. Moreover, the analysis of the unsteady dynamics of the burner stabilized flames can give a deep insight into transient processes in flames.

In the present work, a flat porous plug burner flame configuration is revisited. A hydrogen/air combustion system is considered with detailed molecular transport including thermo-diffusion and with 8 different chemical reaction mechanisms. Detailed numerical investigations are performed to single out the role of chemical kinetics on the loss of stability and on the dynamics of the flame oscillations. The results obtained for the burner stabilized flames are compared with the corresponding data for freely propagating deflagration waves. As a main outcome, it was found/demonstrated that the results of critical values, e.g. critical mass flow rate, weighted frequency of oscillations and blow-off velocity, with increasing the pressure scatter almost randomly. Thus, these parameters can be considered as independent and can be used to improve and to validate the mechanisms of chemical kinetics for the unsteady dynamics.

Data consistency of the burning velocity measurements

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Consistent datasets of experiments are highly important both for validation and optimization of kinetic mechanisms. Analysis of the data consistency of all available burning velocity measurements of hydrogen flames using the heat flux method at atmospheric pressure is performed in the present work. A comparison of many experiments performed in several laboratories with different types of dilution by various inerts was guided by kinetic modeling using two kinetic mechanisms. The Konnov (*Combust. Flame,* 162 (2015) 3753) and ELTE (*Int. J. Chem. Kinet*., 48 (2016) 407) models demonstrated uniform trend at all conditions tested: the second mechanism predicts lower burning velocities which are in better agreement with the heat flux measurements from different groups. Some experimental datasets, however, significantly disagree with one or both models; these conditions were revisited experimentally in the present work. The laminar burning velocity of $H_2 + O_2 + N_2$ mixtures with 7.7% O_2 in $O_2 + N_2$ oxidizer and of 85:15 ($H_2 + N_2$) and 25:75 ($H_2 + N_2$) fuel mixtures with 12.5:87.5 (O_2 + He) oxidizer have been measured. It was concluded that results of Hermanns et al. (*Energy Fuels,* 21 (2007) 1977) are somewhat higher than those of other studies at similar conditions and possible reason of this disagreement was suggested. Analysis of the measurements performed by Goswami et al. (*Proc. Combust. Inst.*, 35 (2015) 655) on high-pressure installation suggests equipment malfunction that led to the erroneous values of equivalence ratio for hydrogen and syngas flames. The ELTE mechanism developed using optimization approach shows very good performance in predicting laminar burning velocities of hydrogen flames measured using the heat flux method.

Physics and Chemistry of Combustion at Fame Spread over Solid Fuels

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A review of the recent experimental studies and numerical simulations made by the authors and their colleagues is presented, relating to the physics and chemistry of combustion at flame spread over solid fuels. As solid fuels, polymers polymethyl metacrylate (PMMA), polyethylene (PE), and polystyrene (PS) were used, with phosphorus-containing flame retardants (FR) and without them, as well as forest fuels. The thermal structure of the diffusion flames of solid fuels was investigated with the microthermocouple technique, while the chemical structure was studied by using probing mass spectrometry. Temperature and species concentration fields have been determined for flame spread in horizontal and vertical directions along polymer slabs, as well as heat fluxes from the flame to the solid fuel, the flame spread velocities and the impact of flame retardants on these parameters. The structure of counterflow flames of polymers has been investigated. OH radicals and H atoms were first identified in the polymer flame, and their concentrations were measured by molecular-beam mass spectrometry with soft ionization by electron impact. The influence of the additives of phosphorus-containing flame retardants on the concentration profiles of H and OH in polymer flame has been studied. The data obtained have been used for developing a model of flame spread over PMMA in supposition of a one-step global reaction in flame. Comparison of the experimental results and of numerical simulation relating to the flame spread velocity has shown them to be in satisfactory agreement. Certain divergence between the experimental data and modeling relating to the profiles of O2 and the fuel decomposition product, methyl metacrylate (MMA) can be attributed to the deficiencies of using the simple one-step mechanism of MMA oxidation in the model. The mechanism of the action of phosphorus-containing FR in reduction of polymers' flammability is discussed.

Acknowledgements

The study has been performed with partial support of the Russian Science Foundation (grant # 16-49-02017).

The authors express their gratitude to their colleagues who took part in the works: A.A. Paletsky, A.I.Karpov, M.B. Gonchikzhapov, I.E. Gerasimov, A.G. Tereshchenko, S.A. Trubachev, A.A. Shaklein, and R.K. Glaznev.

Oxidation of five-member rings in combustion

G.R. Galimova[1], A.R. Ghildina,[1] A.D. Oleinikov,[1] V.N. Azyazov,[1,2] and A.M. Mebel[1,3]

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Ab initio calculations of potential energy surfaces in conjunction with the RRKM-Master Equation theoretical approach have been employed to evaluate temperature- and pressure-dependent total and product specific rate constants and product branching ratios for unimolecular thermal decomposition of 2,4-cyclopentadienone C_5H_4O and for the C_5H_4O + H and C_5H_5 + O reactions. The formation of the cyclobutadiene + CO products via a ring contraction/CO elimination mechanism is shown to be the prevailing channel for the unimolecular decomposition of C_5H_4O. The unimolecular reaction is found to be relatively slow, but decomposition of cyclopentadienone can be greatly facilitated through bimolecular encounters with H atoms. The C_5H_4O + H reaction is predicted to be fast, with rate constants ranging from 4.6×10^{-12} to 1.8×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at $T = 500$-2500 K and finite pressures. Cyclic C_5H_5O intermediates formed after the initial H addition undergo ring openings by β-scissions and then decompose to either butadienyl C_4H_5 + CO or 1-oxoprop-2-enyl H_2CCHCO + C_2H_2, which are respectively predicted as the major and the minor reaction products. The calculations predict that thermal decomposition of the *ortho* and *meta* C_5H_5O radicals as well as pyranyl nearly exclusively forms the C_4H_5 + CO products, whereas decomposition of hydroxycyclopentadienyl C_5H_4OH predominantly produces cyclopentadienone + H. The C_5H_5 + O reaction is shown to proceed by barrierless oxygen addition to the ring followed by fast H migration, ring opening, and dissociation to C_4H_5 + CO. The C_5H_5 + O rate constant is calculated to be close to 1×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and to be pressure-independent and nearly independent of temperature. Modified Arrhenius expressions for rate constants for all considered reactions at the high-pressure limit and at finite pressures are generated for kinetic modeling.

Kinetics of Autoignition

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The gas-phase autoignition phenomenon of a hydrocarbon-air mixtures is one of the key issue in the technologies of reciprocating internal combustion engines, as it governs the ignition delays in Diesel combustion engines and the knocking in spark-ignition engines. The phenomenon is essentially driven by the branched chain reactions as well as the thermal feedback. In this study, it is shown that, despite the well-known complexity of the oxidation mechanisms of hydrocarbons, the autoignition phenomenon can be simply understood as a behavior of a linear system of ordinary differential equations (ODEs).

Firstly, the well-known chain reactions of H_2-O_2 system will be discussed. outside the second explosion limit, the chemistry in the autoignition induction period can be dominated by three reactions, and simply described by the largest positive eigenvalue of the coefficient matrix of the linear system of ODEs. Then it will be also shown that, even for the complex low-temperature oxidation mechanism, similar simple kinetic behavior can be observed in relatively low-temperature and high-pressure regime under which the autoignition in reciprocated internal combustion engines occurs. Some insight into, and, suggestion for, the technological problems will be also presented.

Recent progress in experiments and diagnostics for combustion chemistry

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Reliable and predictable chemical kinetic model can help us to understand the combustion process deeply, and potentially help us to design higher-performance engines, increase combustion efficiency and reduce harmful emissions. However, the development of chemical kinetic model is badly relied on the advances of experimental and diagnostic methods. In this talk, basic experimental and diagnostic methods will be introduced. And some recent results will be presented with the upgraded instruments located at Hefei Light Source (HLS) [1,2]. Benefiting from the new design with short distance between the sampling position and the ionization region, a lot of "new" reactive species can be unambiguously detected, i.e., H, O, OH, and hydroperoxides. Furthermore, the techniques can be applied in the detection of gas-phase products of heterogeneous reactions including catalysis reaction, biomass pyrolysis etc. Furthermore we will provide the high-frequency burst-laser based measurements for swirling flame and turbulent jet flame.

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Obtaining the Phenomenological Rate Coefficients from Direct Analysis of Experimental Data

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The increase in computer resources together with more sophisticated software makes the direct examination of experimental rate data using master equation methods practical. This approach avoids a number of difficulties and assumptions which are often encountered in analyzing reaction kinetic trace data. This methodology is particularly useful in cases where the decay of the observed species cannot be described by simple exponential or bi-exponential decay curves. A case study for the reaction of OH with ethylene is given and the modifications to the master equation formulation that are needed to do this analysis are discussed.

Three-dimensional simulation of combustion, detonation and deflagration to detonation transition processes in cone and wedge induced focusing

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Self-sustaining waves can propagate in meta-stable media; energy needed to support such waves is released by the wave itself. As a rule, two regimes of propagation exist, subsonic and supersonic; the difference is based on the different mechanisms of medium activation. Processes of transition between those regimes are less studied up to now, in comparison with pure subsonic or supersonic modes. Knowing mechanisms of controlling detonation initiation is important in order to work out effective preventive measures, such as suppressing deflagration to detonation transition in case of combustible mixture ignition, and mitigation of a detonation wave in case it is already developed. On the other hand, the advantages of burning fuel in a detonation regime in comparison with slow burning at constant pressure attract increasing attention to pulse detonation burning chambers and to their possible application to new generation engines.

Codes for simulation of deflagration, detonation and transition processes in homogeneous turbulized mixtures accounting for hybrid structure of supercomputer were developed.

A unique validation and verification basis, incorporating the data of laboratory experiments and exact solutions was developed. Comparison of numerical results with experimental data present in the validation basis was performed. The validation basis could be used for validating different codes including commercial ones for description of unsteady-state processes in chemically reacting mixtures in the domains of complex geometry.

The paper presents results of numerical and experimental investigation of mixture ignition and detonation onset in shock wave reflected from inside a wedge. Contrary to existing opinion of shock wave focusing being the mechanism for detonation onset in reflection from a wedge or cone, it was demonstrated that along with the main scenario there exists a transient one, under which focusing causes ignition and successive flame acceleration bringing to detonation onset far behind the reflected shock wave. Several different flow scenarios manifest in reflection of shock waves all being dependent on incident shock wave intensity: reflecting of shock wave with lagging behind combustion zone, formation of detonation wave in reflection and focusing, and intermediate transient regimes. Comparison of numerical and experimental results made it possible to validate the developed 3-D transient mathematical model of chemically reacting gas mixture flows incorporating hydrogen – air mixtures.

Russian Basic Research Foundation (Project 17-03-00607) is acknowledged for financial support.

Vector Correlations in Molecular Photodissociation: Femtosecond Stereodynamics

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As was realized many years ago, angular momentum correlations play a significant role in molecular photodissociation. Molecular interactions always occur through anisotropic

forces and give rise to anisotropic angular momentum distributions which may have relation to approach direction, scattering direction, photon polarization, etc [1].

The lecture reports the results of experimental and theoretical study of time-resolved vector correlations in the femtosecond photolysis of polyatomic molecules by predissociation and direct dissociation mechanisms [2]. Experimentally, the photolysis of methyl iodide (CH3I) via the B-band at 201.2 nm has been studied [3]. Time-dependent anisotropy parameters βi has been determined from fragment angular distributions using the pump-probe technique coupled with the velocity map imaging detection of the dissociation products CH3(v=0) and I*(2P1/2). The results obtained were theoretically interpreted with a quantum mechanical quasiclassical theory which took into account the alignment of CH3 photofragments orbital momentum, nonadiabatic interaction between the 3R1 and 3A1(E) excited states, excited state symmetries, the parent molecule rotation during dissociation, and the CH3 fragment rotation after the bond break. The time-dependent vector correlations were described by a set of the anisotropy transforming coefficients $\boldsymbol{c}_{K_d q}^{K}$ [4,5].

The results obtained demonstrate an important role of the molecular orbital angular momentum alignment and molecular rotation on the time-dependent photolysis. Comparison between the photolysis via the predissociative 3R1 and direct dissociative 3A1(E) excited states showed the profound role of the predissociation mechanism. The 3R1 and 3A1(E) excited state lifetimes, anisotropy transforming coefficients, parent molecule beam temperature, and molecular rotation angles were determined from the experimental data.

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RRKM/master equation calculations for some typical combustion reactions and the uncertainty analysis

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Rate constant parameters are important components of chemical kinetic mechanisms, which are required by numerical simulations of combustion. With the development of computational techniques including quantum chemistry methods and kinetic theories, rate constants from theoretical predictions, especially RRKM/master equation modeling, have been well accepted to build combustion kinetic models. Recently we have employed RRKM/master equation methods to compute the temperature and pressure-dependent rate coefficients with the high level potential energy surfaces for a series of C4 hydrocarbons including C_4H_7, C_4H_6 and C_4H_5, which will be reviewed here.

The uncertainties of rate constants are crucial to evaluate and minimize the uncertainty of modeling predictions. With the help of global uncertainty analysis, we are be able to explore the uncertainty of the rate constants predicted by RRKM/master equation calculations. Taking our computations on the C_4H_7 reaction system as a prototypical case, the uncertainty propagation behavior during the RRKM/master equation modeling will be discussed.

Combustion Chemistry for Alkenes: what have we learned from butene isomers?

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Alkenes are important intermediates formed in the combustion of larger hydrocarbons and alcohols. Moreover, liquefied petroleum gas (LPG) produced during oil refining contains a significant quantity of alkenes, particularly propene and butenes, with gasoline fuel containing butenes, pentenes, and hexenes in various amounts. Butene is the shortest alkene with structural isomers, isobutene, 1-butene, cis-2-butene, and trans-2-butene. 1-butene is the smallest unsaturated hydrocarbon having a secondary allylic carbon group and a primary carbon group which exhibit both alkane- and alkene-type chemistry. Moreover, understanding the combustion chemistry of the butene isomers is a prerequisite for a comprehensive description of the chemistry of C1–C4 hydrocarbon and oxygenated fuels. For the development and validation of combustion models, it is thus crucial to improve our knowledge of detailed C4 combustion chemistry. Building comprehensive kinetic model for butene isomers are also an extension of the work on propene.

Comprehensive chemical kinetic mechanisms have been developed to describe the combustion of butene isomers and are validated by comparison to the presently considered experimental measurements. Important reactions, highlighted via flux and sensitivity analyses, include: (a) hydrogen atom abstraction from butene isomers by hydroxyl and hydroperoxyl radicals, and molecular oxygen; (b) radical–radical recombination reactions, including 1- and 2-methylallyl radical self-recombination, the recombination of 1- and 2-methylallyl radicals with hydroperoxyl radicals; and the recombination of 1- and 2-methylallyl radicals with methyl radicals; (c) addition reactions, including hydrogen atom and hydroxyl radical addition to butene isomers ; and (d) 1- and 2-methylallyl radical decomposition reactions. The current mechanism accurately predicts the IDT and LFS measurements presented in this study, as well as the JSR and flow reactor speciation data already available in the literature.

The differences in low-temperature chemistry between alkanes and alkenes are also highlighted in this work. In normal alkanes, the fuel radical $\dot{R}$ adds to molecular oxygen forming alkylperoxyl ($R\dot{O}2$) radicals followed by isomerization and chain branching reactions which promote low-temperature fuel reactivity. However, in alkenes, because of the relatively shallow well (~20 kcal mol–1) for $R\dot{O}2$ formation compared to ~35 kcal mol–1 in alkanes, the $\dot{R} + O2 \rightleftharpoons R\dot{O}2$ equilibrium lies more to the left favoring $\dot{R} + O2$ rather than $R\dot{O}2$ radical stabilization. Based on this work, and related studies of allylic systems, it is apparent that reactivity for alkene components at very low temperatures (< 800 K) emanates from hydroxyl radical addition followed by addition of molecular oxygen to radical. At intermediate temperatures (800–1300 K), alkene reactivity is controlled by hydrogen abstraction by molecular oxygen and the reactions between resonantly stabilized radicals and hydroperoxyl radicals which results in chain branching. At higher temperatures (> 1300 K), the reactivity is mainly governed by the competition between hydrogen abstractions by molecular oxygen and $\dot{O}H$ radicals.

ORAL TALKS

Extinguish OIL Well's Fires

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This research paper concerns the oil and gas well's fires and the modern extinguishing process. We will introduce the fire thermal, chemical, and physical mechanisms on which our quenching mathematical model will be constructed based on the fire thermal parameters. The new technique involve the whole thermal sphere not only the fire visible core. Then the solution of the program was enhanced with the help of the international MATLAB program and was based on the available international fire data. Later the obtained solution shows very interesting results using the economic quenching matter and the process enhancement in optimum time. Practically we test the technique by building our own system and test it on three type of hydrocarbon fuels these are: 1- Kerosene, 2- Diesel, and 3- Benzene, the obtained results by adding clay to the sea water were very encouraging.

Key Wards: 1- Oil Specification, 2- Oil well, 3- Fire, 4- Model, 5- MATLAB program.

Developing novel PIMS apparatus to study oxidation kinetics at engine-relevant pressures

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Recent progress in development of new types of internal combustion engines and biofuels revived interest in studying reaction kinetics responsible for low temperature oxidation. Since many of the reactions in question showed significant pressure dependence and occurred at high pressures (>10 atm), it was necessary to develop a novel experimental technique to study kinetics at high pressure. This work presents recent development of a high pressure photoionization mass spectrometer (PIMS) apparatus.

The apparatus was completed and tested in 2016. The key features are high-pressure flow photolysis reactor capable of operation at <100 atm and <700 K simultaneously and enhanced detection efficiency to counter the reduction of sensitivity due to dilution of reaction media by buffer gas. The test results indicate that it can probe oxidation kinetics at the engine-relevant conditions in great detail.

Results of numerical modeling of combustion process in a vortex chamber

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Free opposite swirling jets interference researches confirm the presence of shear mixing layers that generate high-intensity turbulence, large-scale eddies and three-dimensional vortex structures. The observed effects are used to organize intensive mixing of fuel and air components, followed by firing augmentation of the prepared fuel-air mixture with high intensity in a limited volume. The mentioned concept has developed in the designs of various reverse-flow burner units, the basis of which is the modified design of the vortex tube [1].

The research of the combustion products velocity, the distribution of the temperature inside and at the outlet of the vortex chamber, was carried out in the paper [2]. The vortex chamber with a diameter Dk = 152.5 mm ($\overline{F}_c = 0.12$, $\overline{R}_d = 0.511$, $\overline{L}_k = 2$) is equipped with a quartz glass window for laser-optical measurements of the flow velocity and holes for platinum-rhodium thermocouples. The premixed mixture of air and natural gas was used as a fuel. Both ratio of the fuel components and their consumption are varied during the testing. Simplicity of configuration and a sufficiently large amount of experimental data of the paper [2] make it possible to use it as a model problem for adjusting the physical and mathematical model that correctly reflects the characteristic features inherent in the swirling flow in a vortex reverse-flow burner module, taking into account the combustion reactions.

The calculations of the combustion process in a vortex chamber [2] are given in this paper. The calculations were performed both on the original turbulence model RNG k-ε and with allowance for the curvature of streamlines [3]. For the calculations, the Eddy Dissipation Model (EDM) and the Burning Velocity Model (BVM) [4] were used, the chemical reaction kinetics was modeled by a 2-step scheme for the EDM model and a detailed kinetic mechanism containing 28 substances and 100 reactions for the BVM. The calculations were carried out both under the assumption of the vortex chamber adiabatic walls and in the formulation of the coupled heat exchange with the walls taking into account the emission. Calculations were carried out via ANSYS CFX software system. A block-structured hexahedral grid with a volume of 300,412 elements was constructed for calculations. The number of elements in the axial, radial, circumferential direction is 150x45x30, respectively.

Analysis of the calculation data indicated the following:

1) Measurement of the nonadiabaticity of the vortex chamber walls plays a significant role in the formation of the temperature field in the end part of the vortex chamber. 2) Applying the allowance for the curvature of streamlines makes it possible to predict the circumferential velocity component and the location of the flame front in the vortex chamber more accurately. 3) The calculation data on the combustion models EDM and BVM indicate close to each other results, which are in good agreement with the experiment. 4) Calculations have shown that, depending on the initial approximation, several possible stable solutions can be calculated.

The obtained results and adjustments of the physical and mathematical model will be used to calculate the vortex reverse-flow burner module.

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The concept of a low-emission combustion chamber, which uses a subcritical microwave discharge

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In the present work, the possibility of developing a low-emission combustion chamber with a reduced NO_x emission from natural or liquefied gas, as well as the possibility of burning extremely poor fuel mixtures with a subcritical microwave discharge, is considered.

A subcritical microwave discharge is created under conditions when the intensity of the initial field (E_0) is lower than the critical breakdown level (E_{cr}), and also when the air pressure exceeds the boundary pressure value and is a volume system of streamer channels.

Experiments on ignition of the fuel mixture subcritical microwave discharge were performed as part of this work. When the ignition is initiated by a subcritical discharge, a significant increase in the combustion efficiency is obtained. The possibility of ignition by a subcritical discharge of a particularly poor fuel-air mixture is demonstrated.

The experiments were performed on an installation, that generates electromagnetic oscillations with a frequency $f \approx 3.4 \cdot 10^9$ Hz, which corresponds to a wavelength $\lambda = 8.9$ cm, with a microwave pulse duration $T_{imp} = 40$ μs. The microwave beam power P_b can vary from 10^2 W to 10^6 W. As a fuel mixture, a stoichiometric, as well as depleted propane-air mixture was used with an oxidizer excess ratio higher than the ignition limit under normal conditions.

Experiments have shown that the use of a subcritical microwave discharge increases the combustion rate and the completeness of the combustion of the fuel mixture by about four times, and also allows burning a particularly poor fuel-air mixture. Combustion of super-poor mixtures allows to reduce NOx emissions, reduce specific fuel consumption, and also allows to maintain the necessary efficiency of the plant at a given temperature. A number of indirect signs indicate a virtually complete absence of nitrogen oxides in combustion products, which can be explained by the high burning rate and the absence of regions with a high temperature.

The work was supported by the Ministry of Education and Science of the Russian Federation (agreement No. 14.574.21.0151, unique identifier of the project RFMEFI57417X0151).

Double-arm three-dimensional ion imaging apparatus for the study of ion pair channels in resonance enhanced multiphoton ionization

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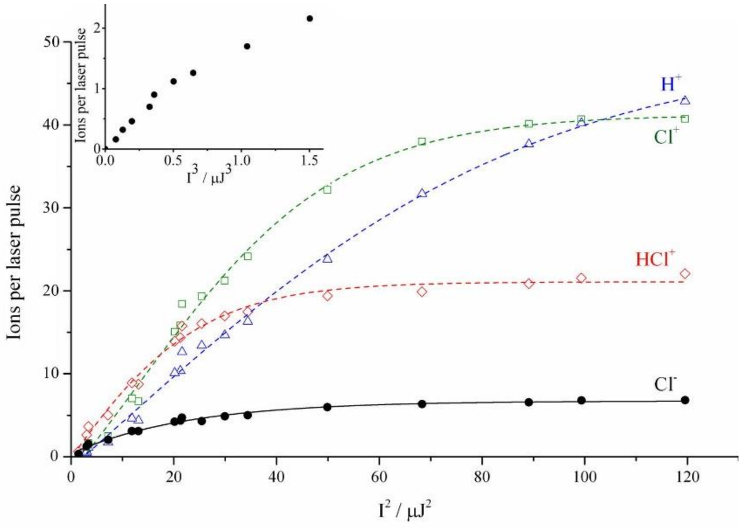
We present a novel experimental configuration for the full characterization of the multichannel resonance enhanced multiphoton ionization (REMPI) of small molecules in cases when the ion-pair dissociation channel is important. For this purpose, a double-arm time-of-flight mass spectrometer with three-dimensional (3D) ion imaging detectors at both arms is constructed. The REMPI of HCl molecules is used to examine the constructed setup.

The apparatus allows us to perform simultaneous measurements of the 3D velocity vector distributions of positive (H^+, HCl^+, and Cl^+) and negative (Cl^-) photoions. The characterization consists of the determination of “two-photon absorption cross sections” for the process $HCl(X) + 2h\nu \rightarrow HCl^*$, one-photon absorptioncross sections for subsequent processes $HCl^* + h\nu \rightarrow HCl^{**}$, and the probability of the subsequent non-adiabatic transition $HCl^{**} \rightarrow HCl(B) \rightarrow H^+ + Cl^-$, which leads to ionic pairs. All these data should be obtained from the analysis of the dependencies of the number of ions on the laser energy, see figure.



The full characterization of the laser beam and the knowledge of the ion detection probability are necessary parts of the analysis. Detailed knowledge of losses of produced ions in the mass spectrometer before detection requires understanding and characterization of such processes like electron emission from metallic grids under ion bombardment or charge transfer between positive ions and the metal surface of the grids, like $Cl^+ + (grid) \rightarrow Cl^-$. These important phenomena from surface science are rarely discussed in the imaging literature, and here, we try to compensate for this shortcoming.

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N_2 dissociation and kinetics of $N(^4S)$ atoms in nitrogen DC glow discharge

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N_2 dissociation in pure nitrogen plasma has a long history of research. It seems to be a complex process which comprises many reactions involving various electronic and vibrational nitrogen states whose contributions can vary depending on conditions. Here we studied N_2 dissociation in the stationary N_2 discharge both experimentally and theoretically. We used a DC glow discharge in quartz tube in pure N_2 at moderate pressures (5 – 50 Torr). Dissociation degree, the atomic nitrogen loss frequency and gas temperature were measured by applying optical emission spectroscopy (OES) and as a result an "effective" rate constant for nitrogen dissociation was obtained in the wide range of reduced field E/N. The analysis of N_2 dissociation was carried out using specially developed 1-D radial self-consistent model which takes into account the spatially inhomogeneities of species concentrations, E/N, EEDF, T_{gas}, *etc* together with fairly complete plasma-chemical kinetics and all the known up-to-date cross-sections for electron kinetics. The model was successfully validated through the obtained experimental results for electric field, gas temperature and N atom density. The comprehensive analysis of closely coupled processes in nitrogen plasmas - ionization, gas heating and N_2 dissociation, were carried out. Simulations reproduced well the experimental data on and allowed us to evaluate contributions of different dissociation channels considered. It was shown that nitrogen dissociation in the stationary N_2 discharge is mostly provided by direct electron impact via the excitation of the pre-dissociative states N_2* from the vibrationally excited nitrogen molecules $N_2(X,\upsilon)$.

Acknowledgements
This work was supported by RFBR Grant No 17-52-16001.

Inefficiency of suppression of methane-oxygen mixtures autoignition by halogenated hydrocarbons

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An influence of various halogenated hydrocarbons considered as fire suppressants, namely CCl_4, CF_3H, $C_2F_4Br_2$, CF_3I and C_3F_7I, on shock-induced ignition of diluted stoichiometric methane-oxygen mixtures at temperatures 1100-1900 K was experimentally investigated in a shock tube of a standard design. Ignition delays were measured by registration of the emission of OH radicals. Observed temperature dependencies of induction times indicate that all studied suppressants, while effectively suppressing hydrogen-oxygen mixture autoignition [1], do not show noticeable inhibiting activity at given conditions, but contrary reduce the ignition delay time in methane.

The ignition development in methane-oxygen mixtures was modeled using CHEMKIN software package by GRI-Mech 3.0 mechanism and suggested kinetic schemes of halogenated hydrocarbons pyrolysis and oxidation. Acceleration of ignition development was explained by the release of atomic halogens and active radical during pyrolysis and subsequent initiation of chain reactions of methane combustion. Performed analysis indicated that considered fire suppressants are incapable of inhibition of methane autoignition due to their instability at elevated temperatures and insufficient radical consuming rates. Provided estimations of necessary properties of effective inhibitor allowed concluding that chemical inhibition of methane autoignition by halogenated hydrocarbons is unlikely.

Obtained results should be taken into account during the development and testing of new explosion prevention methods.

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Formation of combustion wave in a hydrocarbon-air mixture in near high-voltage electrode of surface dielectric barrier discharge

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The study of nanosecond discharges for ignition purposes is presented in many works. The discharge influence in this case is reduced to the creation of chemically active particles by electron impact and fast gas heating. For example, in a number of works it is proposed to use SDBD – surface dielectric barrier discharge as a combustion initiator in the internal combustion engine. This type of discharge can create a diffuse plasma region at high pressures with a high reduced electric field in which chemically active particles are produced. It was noted that near a high-voltage electrode where the maximum energy is released, flame propagation in different directions may occur under certain discharge parameters.

In work [1] the ignition and propagation of the combustion wave in the stoichiometric mixture of air and C_2H_2, initiated by one nanosecond pulse were experimentally observed at P=1 bar, T_0=300 K. Also, based on the 2-D modelling of discharge and 0-D estimations of the ignition, the conclusion was made about possibility of ignition of the combustible mixture near high-voltage electrodes (including cathode layer) SDBD by one nanosecond pulse [1].

In given work, ignition conditions and the formation of a combustion wave in C_2H_2-air mixture near a high-voltage electrode of SDBD were investigated. A 1D numerical simulation based on the Navier-Stokes equations jointly with the equations of mass conservation for each component and the equations of chemical kinetics was carried out. Calculations show that only the heating of the gas in the cathode layer does not lead to ignition and further formation of the combustion wave. Since the discharge is a source of heating and O atoms, it is necessary to take into account the formation of O atoms as a result of dissociation. Only the corresponding combination of heating and O atoms concentration can lead to the formation of a combustion wave. As a result, a range of specific deposited energies and O atoms concentrations was found, at which a combustion wave was formed during $t<45$ μs - characteristic time of the formation of the combustion wave in [1]. It is shown that to simulate the initiation of a flame in discharge systems with high energy release it is important to take into account the gas-dynamic expansion of the hot area and its cooling by heat transfer on the surface of the metal electrode. Calculations in the 0-D approximation can lead to inaccurate results. During the discharge stage (40 ns), the fuel conversion is initiated, resulting in the formation of CO and H_2, which then burn, and CO_2 and H_2O are formed. The concentration of NO behind the front of the combustion wave was 0.1-0.2%.

This work was supported by LIA KaPPA-RFBR Grants No 17-52-16002 and 17-53-16003 (France- Russia).

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Detonation decay and flame propagation through a channel with porous walls

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We considered the problem of detonation suppression and weakening of the blast wave effects occurring during the combustion of hydrogen-air mixtures in the confined spaces.

Analyzing the combustion inside porous material could reveal the mechanism of flame quenching in porous materials, which is not fully understood. The main reasons for flame quenching seem to be the disappearance of transverse waves, heat losses into porous media, flame stretching, and increased curvature [1]. Metallic wool was used as an explosion-attenuating material since it has a big surface area per unit volume and high thermal conductivity [2]. The mixture composition and porous material thickness can also significantly change the flame propagation parameters [3,4]. Several works were dedicated to the normal shock wave impact on the porous cellular materials [5]. However the dynamics of the porous material under weak tangential shock waves was not studied.

The aim of this work was to study the dynamics of the detonation wave in the channel with porous walls, and to compare the detonation parameters in channels with solid walls and two types of porous materials: polyurethane foam (density of 0.03 g/cm^3, porosity of 95%, pore size of 0.8 mm) and steel wool (density of 0.15 g/cm^3, porosity of 99.8%, fiber size of 0.03 mm).

Detonation propagation was studied using pressure sensors PCB, photodiodes FD-256, high-speed camera “VideoSprint” and IAB-451 schlieren device. In both porous materials, the stationary detonation wave decoupled in the porous section of the channel into the shock wave and the flame front with velocity around the Chapman–Jouguet acoustic velocity. By the end of the porous section, the shock wave pressure reduction of 70% and 85% were achieved while using foam polyurethane and steel wool, respectively. The dependence of the flame velocity on the mixture composition (equivalence ratio) was determined. A non-monotonic influence of the porosity on the evolution of the detonation wave in the channel was observed.

The work was supported by the Russian Science Foundation, grant No. 14-50-00124.

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LES of Laser Initiation of Combustion of Gaseous Fuel-Air Mixture

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The laser initiation of combustible fuel-air mixture is tricky [1]. Strong laser pulse and hence a strong blast wave delay/inhibit the occurrence of a stable flame by removing the flammable mixture from the hot zone. A significant part of the absorbed energy by the fuel-air mixture or pure air from a strong laser pulse is lost via the blast wave which is generated shortly after cessation of the pulse. A very weak laser pulse is not able to create the air-breakdown. Perhaps, a moderately strong pulse is the right choice for the initiation of the combustion.

The location of the pulse with respect to the injector exit is also crucial. A Close proximity between the two along the spraying direction can sweep/convect the blast wave system (including the hot core) far downstream due to large velocity of the atomized spray at injector exit. In such case a favourable condition for flame establishment may not exist inside the combustion chamber. Too large a distance between the two may result in no ignition at all due to loss of heat from the hot core before the fuel-air vapour could arrive at it. A possible location could be just downstream of the fuel vapour formation zone. In the above it is assumed that the timing of the start of injection could be controlled electronically e.g. pulse jet injector.

The flow-field structure of the region behind the blast wave changes rapidly, starting from a simple radially outward velocity field to the region which contains a pair of counter rotating vortices initially and later the appearance of a third lobe surrounding the small hot core.

In order to understand the process of initiation of a stable flame from the hot core and fuel-air vapour mixture, LES is performed. The initial conditions for the LES are taken to be the flow field containing the counter rotating vortices and laser pulse induced turbulence within an ethyl alcohol-air mixture. The compressible Navier-Stokes equations along with species conservation equations are solved along with the basic Smagorinsky model for the eddy viscosity.

The numerical results would be complimented with in-house experimental observations of the Laser initiation of combustion. The facility consists of a vertical flow channel of hexagonal cross section, pulsed laser source of 50 mJ pulse energy, an electronically controllable air blast fuel atomizer, a co-flow air supply fitted with a honeycomb structure.

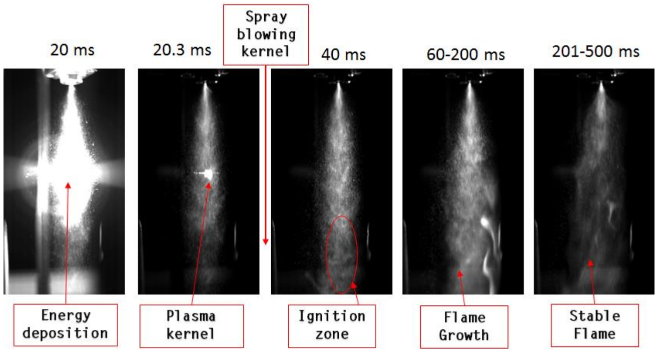

Figure 1; Experimental realization of laser initiation of combustion in ethyl alcohol-air mixture

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The experimental study of the enhancement of hydrogen-air mixture ignition promoted by the singlet oxygen molecules

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The influence of electronically excited oxygen molecules on the processes of ignition and combustion is under current investigations [1, 2] due to the possible prospects for the pollution decrease and combustion enhancement. Chemical activity and long lifetime of oxygen molecules in $a^1\Delta_g$ state encourages the production of these active particles in the electric discharge and their introduction to the burning mixture. There are few researches [3, 4] devoted to the experimental determination of the role of the electronically excited oxygen molecules in the ignition and combustion processes. Unfortunately, these experimental data does not cover the essential temperature range.

In this work, the induction zone length of the hydrogen/air mixture with different concentrations of oxygen molecules in the $a^1\Delta_g$ state was measured in the low-pressure flow reactor at 780-1000 K temperature range. Singlet oxygen molecules were produced in the glow discharge. Cowering of the discharge cell and supply duct by HgO [5] was performed in order to reduce the concentration of the atomic oxygen and ozone molecules in the discharge products. The special attention was paid to the diagnostics of discharge products. Spectroscopic techniques were applied for the measurements of the $O_2(a^1\Delta_g)$ and O_3 concentrations. Singlet oxygen deactivation on the walls was found to be significant along the reactor and must be taken into account in numerical simulation of the processes inside the reactor. It has been shown that the introduction of 3.5% $O_2(a^1\Delta_g)$ to the lean hydrogen/air mixture shortens the induction zone length by 10-50%, which is equivalent to the ~20 K heating.

The work was partially supported by the Russian Foundation for Basic Research (grants 17-08-01423-a, 18-38-00365)

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Burning of diesel fuel under vapor gasification conditions

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A new method of burning liquid fuel using water vapor was proposed in the Kutateladze Institute of Thermophysics SB RAS, in which gasification of carbon-containing particles of incomplete combustion of liquid hydrocarbons occurs [1]. Earlier, it was demonstrated on the example of burner-type evaporative-type devices [2, 3] that the supply of superheated water vapor to the burning zone of liquid hydrocarbons dramatically intensifies combustion. At the same time, stable ignition, high combustion completeness and low content of toxic components in combustion products are ensured. Such a method of combustion is promising for the environmentally safe disposal of low-quality liquid hydrocarbon fuels and combustible waste of production with the generation of thermal energy.

As continuation of previous studies, in this paper, using the example of diesel fuel the combustion of dispersed liquid hydrocarbon fuel in a burner with forced controlled steam supply is experimentally studied. Spraying of liquid fuel is provided as a result of interaction with high-speed jet of superheated water vapor. At using sub-standard liquid fuel this dispersion method has significant technical advantages, associated with preventing the coking of the injector and clogging the fuel supply channels, which improves the performance and reliability of the burner. To substantiate the regularities of the influence of the parameters of water vapor on the main characteristics of the combustion process of liquid hydrocarbons (the composition of the combustion products and the specific heat release power), it is necessary to obtain data in various combustion regimes. The investigations are carried out on a fire test bed equipped with a new burner (10 kW), an electric steam generator (average power consumption 1.5 kW), a plunger metering pump, an automated control system for a steam generator, a fuel supply system, electronic scales for controlling water and fuel consumption, and necessary instrumentation. The measurement of thermal power during the combustion of diesel fuel in the investigated regimes are carried out using a flow calorimeter [2,3]. To control the composition of the gaseous combustion products, the TESTO 350 gas analyzer are used. As a result of the study, regimes are found in which high completeness of combustion of the fuel is ensured, while a low content of harmful CO and NOx emissions in gaseous reaction products is ensured.

The research are carried out with the financial support of the state represented by the Ministry of Education and Science of the Russian Federation, RFMEFI60417X0185

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Shock tube study of plasma-assisted dimethyl ether ignition at temperatures near self-ignition threshold

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With growing concerns on environmental pollution and oil supplies, the global community is seeking non-petroleum based alternative fuels. Dimethyl ether (CH_3OCH_3 or DME) has remarkable self-ignition characteristics and is considered a promising alternative fuel. The purpose of this work is, using a shock tube with a discharge cell, to study DME ignition intensified by non-equilibrium discharge plasma for a wide range of gas temperatures including the values near self-ignition threshold.

Ignition delay time was measured behind a reflected shock wave after a high-voltage nanosecond discharge and in its absence. We studied stoichiometric DME:O_2 mixtures diluted with inert gases (Ar and He) for gas temperatures in the range 1000 – 1800 K and gas pressures in the range 0.3 – 1 atm. The experimental setup and methods used in this study are essentially the same as the ones used in our previous work [1]. Ignition delay time was measured using CH emission at 431 nm. Initiation of the discharge led to an order of magnitude decrease in the ignition time and to a decrease in the gas temperatures at which the same values of ignition time were observed. A numerical simulation of the processes in the discharge phase and the ignition phase were made to reveal the mechanisms of the plasma effect on DME ignition under the conditions studied. The densities of atoms, radicals, excited particles and charged particles produced in the discharge plasma were calculated and used as input parameters for ignition modeling.

Agreement was obtained between the calculated and measured self-ignition delay times in the mixtures under consideration. We reached reasonable agreement between measurements and calculations for plasma-assisted ignition only when considering plasma non-uniformity and the uncertainty in the cross section of electron-impact ionization of DME molecules, the process that is important during the discharge phase. These effects are more profound for gas temperatures near the self-ignition threshold. It was experimentally shown that the ignition delay time depends strongly on gas temperature for high temperatures and is independent of temperature near 1000 K. This seems to be associated with the so-called negative temperature coefficient behavior when an increase in temperature results in a decrease in reactivity. This behavior was previously observed for DME self-ignition at gas temperatures lower than 1000 K.

This work was supported by the Russian Science Foundation (project No 17-12-01051).

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Local Optical Diagnostics of High-Temperature Gas Media Using Laser-Induced Gratings

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Laser-induced gratings (LIGs) are spatially periodic modulations of the complex refractive index of a medium [1]. LIGs result from resonant or non-resonant interactions of gas molecules with the laser field in the form of the interference fringes created by a pair of focused pump beams from the same short-pulse laser. The beams are made to intersect at a very shallow angle in a small interaction volume. The fringe spacing is defined by the pump wavelength and the beams intersection angle. At resonant excitation a spatially-modulated variation of the population difference of the energy levels involved may produce a population grating. Subsequent collisional deactivation of the excited species is accompanied by the heat exchange with the medium that may result in formation of thermal gratings. In addition, a non-resonant electrostrictive contribution to LIGs is generated at any pump wavelength. The thermal and electrostrictive contributions reproduce a superposition of a standing acoustic wave and a stationary density modulation. LIGs are detected by diffracting a CW read-out laser beam, which intersects the planes of the fringes in the interaction (probe) volume at the appropriate Bragg angle, on the related spatial variations of the refractive index, and detecting the temporal evolution of the diffracted radiation power. The parameters of the LIG signal temporal profile provide information on local gas temperature and mixture composition [1, 2].

The application of the technique is exemplified by the results of the investigation of collisional deactivation of singlet $O_2(b\ ^1\Sigma^+{}_g)$ molecules resonantly excited by a 10-ns 762-nm laser pulse in high-pressure 4.3 vol % H_2/O_2 mixtures in the temperature range 291-850 K. The physical, rather than chemical, deactivation was shown to dominate in the collisions of H_2 with $O_2(b\ ^1\Sigma^+{}_g)$ and $O_2(a^1\Delta_g)$ up to temperatures of 780-790 K at time delays up to 10 μs after the excitation pulse.

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The gravity impact on the V-shape flame instability

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The burning of gaseous fuels is essential both in terms of fundamental knowledge and in terms of applicability. The influence of gravity on combustion processes, and especially on instability, is an important modern task. The instability of combustion from a practical point of view is related to stabilization problems. The main tasks of flame stabilization are the expansion of the range of velocity and concentration limits of ignition and stable combustion, and suppression of various types of instabilities leading to extinction. As is known, flame stabilization methods can be divided into active and passive. Active ones include methods that lead to a change in the composition of the fuel-oxidizer mixture and reagents, or in which a constant or periodic additional source of energy is introduced into the system. The most common active methods are stabilization by an ac/dc electric field, using of a pilot flame. Passive methods include methods that to some extent alter the geometry of the flow, basically it is aimed to create a recirculation zone for intensification of mixing and additional heating of the fuel in the vicinity of the reaction zone. For this, various stabilizing bodies are used, for example a cross, a disk, a cylinder, a ring, a wire or inclining blades, which swirl the flow as a whole. Also a combination of such methods is used, for example, burner rim, leads both to the appearance of a toroidal vortex, and to the fact that thin edges are warmed up and also serve as an additional source of heat for heating the burning mixture. The use of wire as a stabilizing body in the jet flame (similar to the use of stabilizing crosses in internal combustion engines) leads to the formation of a recirculation zone in the center of the flow. In this case, the conical flame turns into the inverted conical one (V-shape). Such a flame differs from a conical one. They generate different velocity gradients due to the buoyancy forces and because of the flame itself: the streamlines in the conical flame deviate from the axis as they pass through the flame front and the mixing layers move away from each other as they move away from the burner edge. Whereas in the V-shape it is vice versa, the streamlines deviate towards the center and the layers approach each other. Thus, the mixing layer, arising from the buoyancy forces in the conical flame, can affect the flame front flickering in the lower part of the flow, and in the inverted only in the upper part. The present work is devoted to the study of the gravity effect on the V-shape flame instability. Blow-off and flash-back limits were experimentally established, as well as flickering frequencies as a function of the direction of the gravitational vector with respect to the direction of the flame front propagation.

The project is supported by the Russian Foundation for Basic Research Grant No. 18-31-00462.

Features of oxygen metastable molecules kinetics in O2 plasma with increasing pressure

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As known, all excited electronic states in O_2 molecule below the dissociation limit are metastable because the O_2 ground state in contrast to most of molecules is triplet and of negative parity. So the lowest $a^1\Delta_g$ and $b^1\Sigma_g^+$ states have rather low rates both of radiative decay (radiative lifetimes are ~4000s and ~12s respectively) and of nonresonant collisional quenching. In case of neutrals only specific reactions going through the quasi-resonant energy exchange between singlet O_2 states and states of the neutrals are able to provide high loss rate. It opens opportunities for accumulating high percent of O_2 molecules in the singlet states (especially in $O_2(a^1\Delta_g)$) in order to use it further for application: such as lasing in COIL or initiating combustion. The electrical discharges provides effective excitation of O_2 electronic states and especially the lowest singlet states since the excitation energy of the last is below characteristic electron temperature for most of the discharges. And seemingly one can apply the discharges for effective and fast production of $O_2(a^1\Delta_g)$, but most of plasmas is found to be rather ineffective in it especially with increasing pressure and power despite that estimated quenching by neutrals is still low under those conditions.

This report is just devoted to detail consideration of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ kinetics in O_2 plasma at increased pressures where experimentally observed rather fast quenching of these molecules unexplained from the viewpoint of known kinetic schemes of reactions. The research was carried out with O_2 rf (81 MHz) in the pressure range of 10-100 Torr. It was transversal discharge with external electrodes in quarts tube to exclude fast heterogeneous quenching on metallic surface. Extremely fast $O_2(a^1\Delta_g)$ quenching was experimentally observed in discharge while quenching in afterglow was rather slow. It is shown that processes with secondary electrons and oxygen atoms are responsible for this fast quenching. Direct and secondary electron processes provide fast establishing balance between the populations of O_2 states while fast reactive quenching of $O_2(b^1\Sigma_g^+)$ by O atoms shift the balance to the ground state. This effect increases with pressure because of increasing O density and significantly grows with discharge power due to increasing gas temperature stimulating $O_2(b^1\Sigma_g^+)$ reaction with atomic oxygen.

Thus it provides quite clear limitation on discharge systems for effective pumping of singlet oxygen. This limitation concerns as oxygen pressure (including mixtures) and discharge schemes that should provide low power density at increased pressure for avoiding fast loss of metastable O_2 molecules.

Influence of internal molecular degrees of freedom on their electric and optical properties

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Electric properties of molecules, such as dipole moment and dipole polarizability, determine the variety of optical and electrical phenomena in molecular gases and play a dominant role in intermolecular and electron-molecular interactions [1].

It is known that excitation of internal degrees of freedom of molecules can significantly affect their electrical properties [2], which can lead to a change in the refractive index of a molecular gas, and affect the transport properties and the rates of chemical reactions.

The dependences of the electric dipole moment and static polarizability for a number of diatomic molecules important for combustion chemistry and the atmosphere (H2, N2, O2, NO, OH, CO, CH, HF, and HCl) were calculated for a wide range of internuclear distances on the base of quantum chemistry methods. The effective values of the dipole moment and the static polarizability of molecules in individual vibrational and rotational states were obtained up to the dissociation limit. It is shown that the excitation of the vibrational states of diatomic molecules can significantly (up to 1.5-3 times) affect the effective values of the dipole moment and the static polarizability averaged over the vibrations, while the effect of excitation of rotational states is weaker pronounced.

For a wide range of polyatomic molecules and atomic clusters (50 structures) that are of interest for a number of practical applications (materials science, combustion chemistry, atmospheric chemistry), the state-specific values of the dipole moment and polarizability were calculated. It is shown that the character of the influence of vibrational excitation on the electrical properties of polyatomic molecules is significantly different for individual vibrational modes.

For the molecules and clusters under consideration, an analysis of the effect of excitation of vibrational degrees of freedom on electric properties with respect to such properties as the refractive index and the diffusion coefficients was conducted.

Special attention was paid to the determination of the electrical properties of electronically excited molecular oxygen in the singlet a1Δg and b1Σg+ states owing to their importance in the atmospheric, combustion, and electric discharge chemistry.

This work was supported by the Russian Foundation for Basic Research (project No. 17-01-00810).

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Investigation of thermal degradation of hydrolysis lignin

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Recently more attention is being paid to wood biofuels, which are renewable energy sources and take the fourth position in the world energy balance after coal, natural gas and oil that are connected with some factors. One of these factors is development of wood biomass energy utilization technologies. Thus, there is a huge possibility of utilization of side product of wood treatment – lignin which is 40% of dry mass of wood.

In the technological cycle of hydrolysis industry lignin is being produced, which is a complex of components of different chemical structure. Hydrolysis lignin is composed of: mainly of changed lignin of vegetative cellulose (40-88% of dry mass); polysaccharides (13-45%); components of lingo humic complex (5-19%); non-washed monosaccharides after hydrolysis process; mineral and organic acids: mainly sulfur, formic and acetic, ashes and some other components.

Acid hydrolysis of wood and agricultural residues for the production of ethanol, fodder yeast, hexose and pentose sugars and their derivatives (i.e. furfural and xylitol) had industrial applications in Soviet Union and Bulgaria. It was based mainly on percolation hydrolysis using diluted H_2SO_4, which was developed in the former USSR and used from the 1930s to the 1990s, although some semi-industrial facilities for wood or agricultural residue hydrolysis using concentrated HCl were also used during this period. Wood hydrolysis facilities were built in both northern and southern European regions of Russia, as well as in Siberia and the Russian Far East. Other hydrolysis plant in the former USSR were located in Ukraine, Belarus, Uzbekistan, Kazahstan, Moldova and Lithuania. All or most of these facilities produced substantial amounts of excess lignin, so-called “hydrolysis lignin” (HL). In spite of the fact that there were energy utilizing boilers, they were not able to use all hydrolysis lignin for the energy production and main part of HL was stored in dumps.

Technology of energy utilization of HL, having a great potential is a production of granulated fuel. Perspective way is pelletization of HL. And combination of the preliminary torrefaction process of HL before its pelletization (isothermal heating at 250-300 °C without oxygen) of the initial HL will lead to receiving a new product with better heating values: energy yield and density. First experience of such plant in the Arkhangelsk region of the Russian Federations shows that pellets from HL has lower calorific value not lower than 21,34 MJ/kg (with W^r=6.27%; A^r=2.45%). However it is necessary to continue optimization of the granulation process to increase the mechanical strength of the final product, now it is *DU*=85.5-93.5% (mechanical strength DU characterizes the possibility of the sample to resist external mechanical influence, not being destroyed according to EN 152010-1).

Therefore a huge interest is being raised to the energy utilization of the hydrolysis lignin in the Russian Federation. For the effective energy utilization of the HL it is necessary to study deeply its characteristics, process of thermal decomposition and combustion, to analyze gas components and ashes during the process of thermal degradation, to carry out comparison with classical wood fuel (spruce, pine).

Furthermore definition of kinetic characteristic will lead to the optimization of the process of thermal degradation and combustion in heat generating equipment.

Design of a New Generation Molecular Beam Machine

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We present the design of a new molecular beam machine capable of elucidating the formation of carbonaceous molecules relevant to combustion chemistry and astrochemistry. The machine includes the following critical components:

1. **Main Chamber (MC)** is a 304 stainless steel box (120 cm × 120 cm × 70 cm; 778 L) and pumped by 2400 L/s magnetically suspended turbo molecular pumps (Osaka TG2400M) [1].
2. **Reflection Time-of-flight mass-spectrometer** (**RETOF**) produced by Jordan TOF Products, Inc. RETOF is connected to one turbo molecular pump (Osaka TG420M; 400 L/s). One scroll pump (Edwards XDS35iC; 10 L/s) backs the turbo pumps of the MC and RETOF.
3. **Source Chamber (SC)** is located inside the MC so that the reactant beam goes between a repeller plate and an extraction grid of the RETOF. SC is evacuated by a maglev pump (Osaka TG2400M) backed by a dry roots pump (Leybold WS505; 140 L/s) roughed by one scroll pump (Edwards XDS35iC).
4. **Pulse Valve.** The piezo-electric valve is designed for generation of short gas impulses (80 μs) at high repetition rates and high gas flow. Mounted in the SC in front of a skimmer (1 mm) on the XYZ translation stage.
5. **Pyrolytic source.** Consists of a resistively heated SiC tube of 22 mm length, 1 mm inner diameter; the achievable highest temperature of the tube was estimated to be around 1300–1400 K. The electrical heating and mounting of this tube occurs through two silicon carbide electrode sleeves and two molybdenum electrode blocks [2].
6. The frequency **tripling gas cell** (length 269 mm, diameter 35 mm), into which 355 nm pulsed, seeded Nd/YAG tripled laser radiation is focused, is used to generate the 118 nm (10.5 eV) radiation. The tripling cell contains a mixture of Xe and Ar gas (~1/10, 200 Torr) [3].

The new machine will allow us to measure product distributions for various unimolecular (pyrolytic) and bimolecular reactions under combustion-like conditions.

This work was supported by Ministry of Education and Science of the Russian Federation under the Grant No. 14.Y26.31.0020 to Samara University.

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Soot formation in pyrolysis of acetylene with hydrocarbon additions

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Soot formation is a topical problem in combustion science both in terms of reduction of harmful combustion emissions and synthesis of nanomaterials. One of insufficiently studied problem is acetylene combustion and pyrolysis kinetics with the following soot formation. Therefore the new experimental data obtained for the mixtures of acetylene with different hydrocarbons can clarify the kinetics features of these processes. This work is devoted to experimental study of methyl radical influence on soot formation during acetylene pyrolysis behind shock waves. The experiments were carried out in standard shock tube reactor. The laser light extinction was used for soot volume fraction and induction time of particle inception measurements and laser-induced incandescence was used for carbon nanoparticles sizing. Methane, dimethyl ether (DME) and diacetyl were used as additives to the acetylene. A fivefold increase in soot volume fraction with addition of 1% of methane to 2% of acetylene diluted in argon was observed. The less significant increase of soot volume fraction with addition of diacetyl was observed. And negligible increase of soot volume fraction with addition of DME was observed. Besides that, the additions of methane and DME caused the soot formation at lower temperatures comparing to pure acetylene mixtures. Qualitative kinetic analysis has shown that the reason of observed increase of soot volume fraction at low temperatures is the propargyl recombination leading to the acceleration of first aromatic ring formation. And the main channel of propargyl formation is recombination of methylene and methyl radicals, forming in the primary reactions of decomposition of used additives, with acetylene molecules.

Kinetics of thermodestruction of aliphatic cyclic hydrocarbons – perspective components of aviation fuels

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The increase in the range of flights of aircraft can be achieved by using energy-intensive components in the composition of aviation fuels. Aliphatic cyclic hydrocarbons possessing high density, volumetric heat of combustion and boiling point, which allow to consider them as promising components of aviation fuels.

Investigation of the kinetics of the thermal decomposition of the components was carried out using the manometric method for increasing the gas pressure under isochoric conditions at temperatures from 410 °C to 550 °C and pressures up to 50 atm [1]. Thermodestruction products were studied by IR spectroscopy on the SPECORD-M80 instrument.

According to the research was proposed and tested the kinetic schemes describing sequential decay of the components releasing gaseous products, and schemes containing reactions of initiating free radical chain. The rate constants of the chemical reactions of the thermal decomposition of hydrocarbons obtained during processing of the experimental results confirmed the proposed kinetic schemes. The obtained kinetic data calculated the activation energies and pre-exponential factors of Arrhenius equation, the dependences of rate constants of thermal decomposition on the temperature, and the thermal stability of the investigated components.

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A Theoretical Study of Pyrolysis of JP-10 (*exo*-Tetrahydrodicyclopentadiene) and its Primary and Secondary Unimolecular Decomposition Products

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Abstract. Theoretical calculations of the rate constants and product branching ratios in the pyrolysis of *exo*-tetrahydrodicyclopentadiene (JP-10) and its initial decomposition products at combustion-relevant pressures and temperatures have been performed and compared to experimental results from recently reported molecular beam photoionization mass spectrometry study of the pyrolysis of JP-10 (Zhao, L. et al. *Phys. Chem. Chem. Phys.* **2017**, *19*, 15780). The results allow us to quantitatively assess the decomposition mechanisms of JP-10 by a direct comparison with the nascent product distribution - including radicals and thermally labile closed-shell species - detected in the short-residence-time molecular beam photoionization mass spectrometry experiment. In accord with the experimental data, the major products predicted by the theoretical modeling include methyl radical (CH_3), acetylene (C_2H_2), vinyl radical (C_2H_3), ethyl radical (C_2H_5), ethylene (C_2H_4), allyl radical (C_3H_5), 1,3-butadiene (C_4H_6), cyclopentadienyl radical (C_5H_5), cyclopentadiene (C_5H_6), cyclopentenyl radical (C_5H_7), cyclopentene (C_5H_8), fulvene (C_6H_6), benzene (C_6H_6), toluene (C_7H_8), and 5-methylene-1,3-cyclohexadiene (C_7H_8). We found that ethylene, allyl radical, cyclopentadiene, and cyclopentenyl radical are significant products at all combustion-relevant conditions, whereas the relative yields of the other products depend on temperature. The most significant temperature trends predicted are increasing yields of the C2 and C4 species and decreasing yields of the C1, C6, and C7 groups with increasing temperature. The calculated pressure effect on the rate constant for the decomposition of JP-10 via initial C-H bond cleavages becomes significant at temperatures above 1,500 K. The initially produced radicals will react away to form closed-shell molecules, such as ethylene, propene, cyclopentadiene, cyclopentene, fulvene, and benzene, which were observed as the predominant fragments in the long-residence-time experiment. The calculated rate constants and product branching ratios should prove useful to improve the existing kinetic models for the JP-10 pyrolysis.

A numerical study of two turbulent flame speed models for H_2/CH_4/air premixed combustion

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A number of numerical studies have been carried out in order to validate the Zimont and Peter's turbulent flame speed models when applied to a low-swirl Methane/Air/Hydrogen flame. These models are contained as default options within the ANSYS Fluent Premixed reaction model. Two distinct tasks were completed as part of the study – non-reacting and reacting conditions – the latter of which was carried out with three different mixtures – 0, 40 and 60% hydrogen. The results show that the RANS approach provides a reasonable prediction of the cold flow conditions, whilst the reacting flow conditions, apart from the recirculation region, were well predicted up to 40% enrichment.

Experimental investigation of the gel fuel combustion process initial by the hot particle

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In recent years, the perspective of the space development influence to the development of the rocket and space industry in Russia, the United States, France, India, China and other countries [1]. One of the directions for implementing such programs is the development of new fuels, for example, gel fuels, and ways to initiate their combustion, which can be based on the conductive energy by group of small particles heated to high temperatures. Regularities and characteristics of physicochemical processes during the initiation of combustion of gel fuel essentially differ from the regularities and characteristics of the processes occurring when igniting the solid and liquid condensed matters [2, 3].

In this paper, we determined the ignition delay for a typical gel fuel by metal particles of various form. Determined the ignition delay times by varying the initial particle temperature. Determined the ignition delay times by varying the initial gel fuel temperature. The method of gel formation is presented [4].

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Mathematical modeling of the impact of forest fires on buildings and structures

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The protection of buildings and structures in a community from destruction by forest fires is a very important concern. This paper addresses the development of a mathematical model for fires in the wildland-urban intermix. The forest fire is a very complicated phenomenon. At present, fire services can forecast the danger rating of, or the specific weather elements relating to, forest fire. There is need to understand and predict forest fire initiation, behavior and impact of fire on the buildings and constructions. This paper's purposes are the improvement of knowledge on the fundamental physical mechanisms that control forest fire behavior. The mathematical modeling of forest fires actions on buildings and structures has been carried out to study the effects of fire intensity and wind speed on possibility of ignition of buildings. It is assumed that the forest during a forest fire can be modeled as 1) a multi-phase, multistoried, spatially heterogeneous medium; 2) in the fire zone the forest is a porous-dispersed, two-temperature, single-velocity, reactive medium; 3) the forest canopy is supposed to be non – deformed medium (trunks, large branches, small twigs and needles), which affects only the magnitude of the force of resistance in the equation of conservation of momentum in the gas phase, i.e., the medium is assumed to be quasi-solid (almost non-deformable during wind gusts); 4) let there be a so-called "ventilated" forest massif, in which the volume of fractions of condensed forest fuel phases, consisting of dry organic matter, water in liquid state, solid pyrolysis products, and ash, can be neglected compared to the volume fraction of gas phase (components of air and gaseous pyrolysis products); 5) the flow has a developed turbulent nature and molecular transfer is neglected; 6) gaseous phase density doesn't depend on the pressure because of the low velocities of the flow in comparison with the velocity of the sound. The modeling approach is based on the use of standard non-stationary three-dimensional conservation equations that are solved numerically under the input conditions specific for crown forest fires. It is considered the effect of forest fire front on the building which is situated near from the forest. The results of calculations can be used to evaluate the thermal effects on the building, located near from the forest fires. The model proposed there gives a detailed picture of the change in the velocity, temperature and component concentration fields with time. It allows to investigate the dynamics of the impact of forest fires on buildings under the influence of various external conditions: a) meteorology conditions (air temperature, wind velocity etc.), b) type (various kinds of forest combustible materials) and their state (load, moisture etc.). The calculations let to get the maximum distance from the fire to the building in which the object possible ignition. The paper was supported from RFBR (project code: № 16-41-700022 p_a) and within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.

Pyrolis of $C_{10}H_7Br$ in high temperature microreactor: experiment and modelling

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One of the key stages in combustion of compound hydrocarbon fuels is pyrolysis, or thermal decomposition, which initiate and drive the complex chemistry in the combustion. But this phase is quite poorly investigated. One of the promising tools of research that phenomena are high-temperature micro-reactors.

In present work, we investigate experimentally and theoretically the efficiency of bromonaphthalene pyrolysis in high-temperature ‘chemical reactor’ incorporated into a molecular beam machine equipped with Wiley-McLaren reflectron time-of-flight mass spectrometer. The principal part of the apparatus is a gas-flow tube made of SiC with an internal diameter of 1 mm, with a total length of 38 mm. The length of the section of the micro-reactor with the zone of ohmic heating up to 1300-1500 K is 13.2-33.2 mm from the entrance. The analysis of pyrolysis products was carried out with the help of PIMS. Theoretical calculation of the distribution of temperature, pressure, flow rate in the micro-reactor were carried out using the Comsol Multiphysics package [1]. The following processes were simultaneously modelled: the electric current and ohmic heating, the Navier-Stokes and heat transfer problems, the kinetics of the pyrolysis process. Reaction rates constants for the $C_{10}H_7Br$ dissociation were calculated using variable reaction coordinate transition state theory VRC-TST with help of ROTD [2] and MESS [3] software.

Calculations demonstrated high values of the temperature, pressure and velocity gradients in axial direction. Intensive pyrolysis took place in the 20-27 mm zone from the gas inlet of the SiC micro-reactor, in which the gas temperature was more than 1400 K, the gas velocity varied from 200 m/s to 400 m/s, the pressure dropped from 55 Torr to 30 Torr. The residence time of the gas in this zone was about 50 μs. Closer to the reactor outlet there was a sharp drop in pressure, temperature and acceleration of the gas flow, which practically led to the cessation of pyrolysis of bromonaphthalene. According to calculations, the efficiency of pyrolysis of bromonaphthalene was 16% at temperature of 1500K. The increase in temperature to 1600K led to an increase in pyrolysis efficiency to 56%. The result obtained is in satisfactory agreement with the experimental value of 40% pyrolysis efficiency at a micro reactor temperature of about 1500K.

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Spin Combustion of Gasless Systems with Melting Component: 3D Simulation

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Unstable three-dimensional combustion regimes of gasless systems are one of the most interesting problems in the combustion theory. Numerical studies revealed a large number of regimes characterized by a diverse propagation of high-temperature reactions and their interaction within the framework of a three-dimensional solid-phase model. The results have shown that the so-called spin combustion (propagation of reactions along a spiral trajectory) is one of the special cases of unstable combustion. It should be noted that unstable gasless combustion regimes were found and investigated in the systems which contained a low-melting component in porous samples in experiments.

The simulation of gasless combustion, considering the melting of one of the mixture components, found the new regimes of unstable combustion. The parameters of the phase transition were shown to influence on the stability of combustion. The study found the conditions for the formation of «strong spin waves», the regimes of which differed in the rate of reactions in the axial and tangential directions. The melt is assumed can be filtrated only at a temperature that is above the melting temperature. This study presents a 3D numerical solution for the gasless combustion of a cylindrical sample with allowance for the convective flow of a melt. The conducted computations showed the qualitative influence of convective heat transfer on the characteristics of combustion.

The Acoustic Spectrums of the combustion Process in the IC-Engines

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The burning of the fuel-air mixture inside the engine proceeds in special conditions of a closed volume. The flame is an effective generator of acoustic noise, so spectral analysis of the sound has much potential for yielding information about the dynamics of the combustion. In the present work, an experimental study of the acoustic spectrums of the burning in the internal combustion engines is performed.

The measurements were carried out on engines of various cars (Hyndai i40, 2.0 L, 150 hp; Hyundai Accent, 1.6 L., 105 hp; Chevrolet Cruze 1.6 L, 109 hp; Peugeot 4007, 2.4 L, 170 hp; Opel Astra 1.6 L, 115 hp). The acoustic signals were recorded using a voice recorder installed under the car's hood near the engine cylinders (in the frequency range 200-7000 Hz, signal-to-noise ratio 37 dB). The engine speed set to the fixed values from 900 to 3000 rpm. The raw data were collected at a sampling frequency of 16 kHz with 16-bits per sample. The frame length was 2048, each frame was 25% overlapped. Frames were windowed with Hamming window and 2048 points FFT was applied to each frame.

The energy spectrums have complex structure. The main energy of the acoustic noise is concentrated in the band 600 - 1600 Hz, the frequency of the maximum does not depend on the engine speed. The cylinder volume and the engine speed determine the width and structure of the spectrum.

Based on the flame propagation velocity in piston engines in the absence of detonation of 40-80 m/s, and the characteristic size of the combustion chamber 0.1 m (cylinder diameter), a lower frequency of combustion noise of 400-800 Hz can be estimated. The result is consistent with observations.

In the high-frequency part of the spectrum (above 4000 Hz), an increased level of energy is noticeable, which can be explained by the presence of detonation combustion waves.

Experimental records of engine acoustic noises contain a variety of information about the dynamics of the combustion. Determination of the dependence of the combustion parameters on the cylinder's geometric dimensions and fuel quality is of great practical importance for the development of internal combustion engines.

Reaction kinetics of H_2 with O_2 in highly excited electronic states

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The reactions of electronically excited oxygen in the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states (excitation energy values T_e are 0.98 and 1.63 eV, respectively) with molecular hydrogen are assumed to be the critical chain initiation channels under the conditions of laser-induced and plasma-assisted combustion of H_2-containing mixtures [1]. Reactions with higher (Herzberg) electronic states of O_2, such as $c^1\Sigma_u^-$ (T_e =4.05 eV) and $A'^3\Delta_u$ (T_e =4.20 eV), can also be potentially important in the latter case [1, 2]. However, the available kinetic data on these processes are rather scarce. In the past, relatively much attention was paid only to the kinetics of H_2+O_2($a^1\Delta_g$) reaction [3–6]. The rate constant for the H_2+O_2($b^1\Sigma_g^+$) process was estimated in the past, to our best knowledge, based on semiempirical schemes only [6], whereas the reactions of higher electronic states of O_2 with H_2 were considered neither theoretically nor experimentally until recently.

Comprehensive quantum chemical analysis with the usage of multireference state-averaged complete active space self-consistent field approach was carried out to study the reactions of H_2 with O_2 in $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, and $A'^3\Delta_u$ electronically excited states. The energetically favorable reaction pathways and possible intersystem crossings were revealed. The energy barriers were refined employing the extended multi-configuration quasi-degenerate second-order perturbation theory [7]. It was shown that the interaction of O_2($a^1\Delta_g$) and O_2($A'^3\Delta_u$) with H_2 occurs through the H-abstraction with relatively low activation barriers that resulted in the formation of the HO_2 molecule in A'' and A' electronic states, respectively. Meanwhile, O_2 in singlet sigma states ($b^1\Sigma_g^+$ and $c^1\Sigma_u^-$) was proved to be nonreactive with respect to H_2.

Appropriate rate constants for revealed reaction and quenching channels were estimated using variational transition-state theory including the corrections for tunneling, possible nonadiabatic transitions, and anharmonicity of vibrations for transition states and reactants. It was demonstrated that the calculated reaction rate constant for the H_2+O_2($a^1\Delta_g$) process is in reasonable agreement with known experimental data [3, 8].

This work was supported by the Russian Foundation for Basic Research (grants Nos. 17-08-01423 and 18-38-00365).

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A Geometric Approach to the Modeling of Critical Phenomena in Combustion Models

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The paper is devoted to the modeling of the critical phenomena in multiscale combustion models. Such models are usually described by singularly perturbed systems of differential equations to reflect the significant distinction in characteristic relaxation times of different physicochemical processes.

The paper proposes an approach for modeling of critical phenomena on the basis of the geometric asymptotic method of integral manifolds and the black swans and canards techniques [1-3]. The interest to critical phenomena is occasioned by not only of safety reason; in many cases namely the critical regime is the most effective in technological processes. The sense of criticality here is as follows. The critical regime corresponds to chemical reaction separating the domains of self-accelerating reactions and the domains of slow safe reactions.

Recall that a canard (or “French duck”) is a trajectory of a singularly perturbed system of differential equations if it move at first along a stable slow integral manifold and then for a while along an unstable slow integral manifold. The slow integral manifold is defined as an invariant surface of slow motions. In combustion models canards simulate the critical regimes when the temperature increases as high as possible but without explosion. A canard trajectory may be considered as the result of gluing stable (attractive) and unstable (repulsive) slow integral manifolds at one point of the breakdown surface, due to the availability of an additional scalar parameter in the differential system. However during a chemical process perturbations are possible. These perturbations can lead to the thermal explosion when the perturbed trajectory deviates from the canard. To solve this problem it is possible to glue the stable and unstable slow integral manifolds at all points of the breakdown surface simultaneously. For this goal an additional function of a vector variable parameterizing the breakdown surface is used. As a result we obtain the continuous stable/unstable integral surface or black swan. This guarantees the safety of chemical regimes, even with perturbations, during a chemical process.

This work was supported by the Ministry of Education and Science of the Russian Federation as part of a Program "Research and Development in Priority Areas of Advancement of the Russian Scientific and Technological Complex for 2014-2020" (RFMEFI58716X0033).

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An Experimental and Numerical Study of Combustion Chemistry of Fatty Acids Esters

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Depletion of petroleum sources makes search for alternative fuels quite relevant. Biodiesel based on methyl and ethyl esters is one of the most promising types of oxygenated fuels. CFD methods are used to optimize the construction and increase the efficiency of engines. Knowledge of the kinetic mechanisms for combustion of biodiesel fuels is necessary to use this method. One of the most informative techniques for studying combustion chemistry is probing molecular-beam mass spectrometry (MBMS), which in combination with numerical simulation makes it possible to develop and validate the combustion mechanisms for biodiesel combustion.

The aim of this work includes obtaining new experimental and modeling data on the structure of flame of model biodiesel fuels, among them methyl acetate (EA), ethyl butanoate (EB), ethyl pentanoate (EP), methyl propanoate (MP), methyl hexanoate (MH) as well as blends of MH or EP with n-heptane/toluene mixtures.

The flames of blends of the above listed fuels with oxygen and argon were stabilized on a flat burner at atmospheric and subatmospheric pressures. Microthermocouples and MBMS with soft ionization by electron impact and VUV photoionization were used for measuring the temperature and mole fraction profiles of reagents, the main combustion products and intermediate species, including unsaturated hydrocarbons, which are known as potential soot precursors. In total more than 30 intermediate species were identified in the studied flames and their mole fraction profiles, including atoms and radicals, were measured quantitatively. The experimentally measured mole fraction profiles of species were compared with the modeling results, obtained using mechanisms developed earlier. It was established that the used mechanisms quantitatively predict the mole fraction profiles of the main initial reagents and final combustion products, but for most intermediate species the agreement between the results of modeling and measurements is basically of a qualitative nature. These discrepancies indicate the need for further improvement of the tested kinetic mechanisms. The analysis of the primary reaction pathways for isomeric esters (EA – MP, EB – MP, EP – MH) showed that for ethyl esters reactions of monomolecular decomposition produce ethylene and the corresponding fatty acids while for methyl esters the key transformations occur via interactions with H, OH and O. It is established that the contribution of monomolecular decomposition reactions of ethyl esters is noticeably increased with increasing fuel-air equivalence ratio.

CARS and Fluorescent Study of Ignition of H_2-O_2 Mixtures upon Photo-Dissociation of O_2 Molecules

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The methods of resonant and nonresonant laser radiation impact of the working mixture leading to ignition as a result of gas heating, optical breakdown, photoionization or photodissociation are considered.

An experimental setup is described that allows to investigate the ignition process of various gaseous fuels with oxygen, whose reactivity is instantly (within 20 nsec) activated in relation to chain reactions by oxygen atoms, obtained as a result of dissociation of O2 molecules. It is important to note that the ignition volume of mixture does not contain impurities of the recombining plasma characteristic of methods of optical or electrical breakdown.

When the values of temperature, pressure, composition and energy of the laser for O_2/H_2 mixtures ignition vary, the interrelated threshold values of the listed parameters were determined above which the ignition of the combustible mixture is observed.

Based on the study of spatiotemporal distributions of OH radicals in the field of laser ignition of O_2/H_2 mixtures heated below the self-ignition temperature, data on ignition delays after exposure to laser radiation are obtained and the propagation velocity of the flame front in the space filled with a combustible mixture is measured. The induction times were measured, which was defined as the interval of time from pulse initiation to the "start of combustion", where the "start of combustion" accepted "moment" of emergence of the observed zone of the chemiluminescence of OH radicals with size tending to zero.

Temperature measurements by means of a CARS spectroscopy made it possible to experimentally observe the presence of a high temperature ≥ 1000 K at delay times of 30 μs and to establish that starting from this time there is ignition with transition to steady burning.

The work was supported by the Russian Foundation for Basic Research (project no.17-08-01423-a, project no.18-38-00365).

Relativistic and quasirelativistic electronic structure calculations on the alkali metal - rare gas molecules

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The accurate estimates of spectroscopic, kinetic and thermodynamic properties of the weakly bound diatomic pairs formed in interactions of alkali metal vapors and inert buffer gas are indispensably required to construct and operate high-power optically pumped lasers [1]. The state-of-art quantum chemistry machinery provides both interatomic adiabatic potential energy curves (PECs) and transition dipole moments (TDMs) which reproduce the observed spectroscopic and radiative properties of many diatomic molecules with accuracy close or comparable to experimental one.

At the present work we have performed, in the framework of high level ab initio electronic structure calculations, a comparative study of the full relativistic and quasirelativistic affects on energies and electronic transitions probabilities between the ground and low-lying excited states of the exciplex RbAr and CsAr molecules. The different sets of small core relativistic pseudopotentials were used to account for both scalar and spin-dependent (spin-orbit) relativistic effects. The core-valence correlation was included in the quasirelativistic treatment by means of a large-scale multi-reference configuration interaction (MR-CI) method. The alternative full relativistic calculations employed the Fock-space coupled clusters (FS-CC) method. The finite-field (FF) method was applied for evaluating the corresponding TDM functions within the FS-CC theory [2].

Peculiarities in a shape of the resulting PECs and TDM functions revealed at intermediate and large interatomic distance were discussed. The reliability of the derived PECs and TDM functions were accessed through a comparison with previous theoretical and experimental results. The present *ab initio* data have been used to simulate the absorption spectra for RbAr and CsAr pairs as well as radiative lifetimes of the excited states in the framework of semiclassical approximation.

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Reaction Dynamics of Radical Intermediates formed during Hydrocarbon Combustion

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The crossed molecular beams technique was utilized to explore the formation of C_5H_3 radicals via the bimolecular reactions of singlet/triplet dicarbon [$C_2(X^1\Sigma_g^+/a^3\Pi_u)$], produced via photolysis of tetrachloroethylene [$C_2Cl_4(X^1A_g)$], with 1-butyne [$C_2H_5CCH(X^1A')$] at a collision energy of 26 kJ mol^{-1}. The elusive methyl-loss pathway was detected with the resulting C_5H_3 translational energy and angular flux distributions characteristic of indirect reaction dynamics via chemically activated C_6H_6 intermediate(s) that underwent exoergic (-92 ± 16 kJ mol^{-1}) dissociation by methyl emission. This channel forms the resonantly stabilized penta-1-yn-3,4-dienyl-1 [$H_2CCCHCC(X^2A)$] radical along with the methyl radical [$CH_3(X^2A_2'')$] and is open exclusively on the triplet potential energy surface with a computed reaction energy of -86 ± 10 kJ mol^{-1}. The preferred reaction pathways proceed by barrierless addition of triplet dicarbon to the π-electronic system of 1-butyne to form methyl-bearing triplet C_6H_6 intermediates that ultimately decompose to $C_5H_3 + CH_3$ via a tight exit transition state. The successful unraveling of this methyl-loss channel underscores the viability of the photolytically generated dicarbon beam as an unprecedented tool to access reaction dynamics underlying the formation of resonantly stabilized free radicals that are vital to molecular mass growth processes that ultimately lead to polycyclic aromatic hydrocarbons in combustion systems.

Numerical study of H_2S-H_2O-air mixture conversion to hydrogen via activation of air by an electric discharge

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Hydrogen sulfide, which is a part of associated petroleum and so-called acid natural gases and which forms from the sulfur-containing fuels in petroleum refining industries, can serve as a source of hydrogen that is considered lately as an energy efficient and environmentally safe fuel. The direct conversion of H_2S to H_2 occurs only at rather high temperature, and such a process requires a fairly large amount of heat to be supplied to the system. For the implementation of low-temperature conversion of H_2S, an approach based on the partial oxidation of H_2S upon activation of the oxidizer (air) by an electric discharge is considered in this work.

Numerical study is carried out in an adiabatic flow reactor with the length of L=1 m at pressure P=1 atm and inlet gas velocity U_0=1 m/s, which corresponds to the gas residence time in the reactor of τ_r~1 s. Air, activated in an electrical discharge, and H_2S-H_2O mixture are supplied to the flow reactor inlet separately, where they mix and the homogeneous mixture moves in the reactor. Both flows are preliminarily heated up to the temperature T_0=500 K, the reduced electric field E/N in the discharge varies in the range of 1–150 Td (1 Td=10^{-17} V·cm^2), the specific energy put into the discharge is E_s=0.3–0.5 J/ncm^3, fuel-to-oxidizer equivalence ration was chosen to be ϕ=2, basing on the preliminary thermodynamic analysis, according to which, for such ϕ value, a maximum or close to the maximum yield of H_2 in H_2S-air mixture is realized.

Calculations have shown that a significant amount of H_2 is formed only after the H_2S-H_2O-air mixture ignites. At E_s=0.5 J/ncm^3, the mixture with a fraction of water vapor $\varepsilon = n^0_{H_2O} / n^0_{H_2S}$ =0–1 ($n^0_{H_2O}$ and $n^0_{H_2S}$ are the molar flow rates of H_2O and H_2S at the reactor inlet) ignites inside the reactor for any E/N value. But the shortest ignition length is realized for the discharge, producing maximum amount of $O_2(a^1\Delta_g)$ molecules. The values E/N~4–10 and 120–150 Td are most favorable. At E_s=0.3 J/ncm^3, the mixture ignites only at ε=0–0.2 and only at the E/N values, when the molar fraction of $O_2(a^1\Delta_g)$ molecules is maximal. If the mixture ignites inside the reactor, H_2 yield does not depend on E/N. With an increase of the amount of H_2O in the mixture and a reduction of the energy E_s, supplied into the discharge, the range of E/N values, at which H_2S conversion occurs, narrows. On the other hand, the addition of water vapor leads to an increase of the relative yield of hydrogen $\delta = n_{H_2} / n^0_{H_2S}$ (n_{H_2} is the molar flow rate of H_2 at reactor exit) from 0.25 to 0.3 when ε varies from 0 to 1.

The work was supported by the Russian Science Foundation (project no.16-19-00111) and by the Russian Foundation for Basic Research (project no.17-01-00810-a) in the part of analysis of mechanism of H_2 production during low-temperature plasma-assisted partial oxidation of H_2S.

The numerical study of hydrogen-air mixture ignition under laser photo-dissociation of O_2 molecules

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Numerical modeling and investigation of the peculiarities of the hydrogen-air mixture ignition under the impact of a focused resonance laser radiation pulse with a wavelength of 193 nm, leading to photodissociation of O_2 molecules, are carried out. Initial distribution of atomic oxygen in the initiation zone of ignition was obtained on the basis of a detailed one-dimensional calculation of the absorption of laser radiation in the Schumann-Runge bands taking part the spatial temperature distribution in the region under consideration.

Modeling the ignition and combustion of H_2-O_2 mixture in a closed reactor was carried out in a two-dimensional axisymmetric formulation using the quasilaminar combustion model and the detailed kinetic mechanism of hydrogen oxidation [1] extended by the block of reactions responsible for the formation of electronically excited $OH(A^2\Sigma^+)$ molecules [2]. The initial distribution of the O atoms in the region of the impact of the laser radiation was borrowed from the data obtained at the first calculation stage.

The results of the calculation of the induction time τ_{in} and velocity of combustion wave propagation U_f are in a good agreement with experimentally measured values. The effect of fuel equivalence ratio φ and mixture pressure on τ_{in} and U_f values is analyzed. During modeling, the features of distribution of OH и $OH(A^2\Sigma^+)$ radical concentrations behind the combustion front depending on φ were revealed.

The work was partially supported by the Russian Foundation for Basic Research (grants 17-08-01423-a, 18-38-00365)

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Stabilization of combustion front in supersonic flow using streamer's discharge

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Thermodynamic analysis shows that for flight with velocity exceeding Mach 6, it is required to burn fuel not in a subsonic but in a supersonic flow. In this paper, one of the possible methods to create a stationary combustion front in a supersonic flow is studied. This method is based on ignition of the mixture by an attached microwave discharge. Discharges are created on the resonator by means of a pulsed source of quasi-optical microwave radiation. Completed in the past 20 years in the Moscow Radiotechnical Institute of the Russian Academy of Sciences, detailed studies of such discharges have shown that the above-mentioned method exceeds by one or two orders from the point of view of energy costs other methods, including corona discharge and spark ignition. At the same time, the electric field strength required to create a discharge is much less than the critical field of air breakdown, i.e. discharges are subcritical.

In the current work, a semiempirical and numerical simulation of the development of a subcritical streamer discharge attached to the surface of a dielectric and a deep subcritical diffusion discharge is performed. Calculations have shown that the speed of propagtion of streamers is several km / s, so they are not blown off by a supersonic flow. Similar calculations for the diffuse discharge demonstrate that the discharge is not blown away by the flow, at least up to a speed of 1 km / s. Experiments have been conducted to ignite the flow of a mixture of propane with air by various discharges at speeds up to twice the speed of sound. In all cases, the experiments confirmed a steady burning of the fuel, which was monitored by measuring the temperature and the braking pressure. Baltic State Technical University "Voenmeh"

The work was supported by the Ministry of Education and Science of the Russian Federation (agreement No. 14.577.21.0277, unique identifier of the project RFMEFI57717X0277).

Actinometry of O atoms with Kr at elevated pressures (10 - 100 Torr) in pure O_2 discharge

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This work is crucial part of fundamental research focused on plasma-chemistry of medium-pressure pure oxygen plasmas, where atomic oxygen plays important role. Kinetics of ground state oxygen atoms $O(^3P)$ is studied in rf (81 MHz) CCP discharge in quarts tube at pressures 10-100 Torr by means of actinometry: 5% of Kr was added to the discharge for determination of both relative $[O(^3P)]/N$ (N is total gas density) and absolute concentrations of atomic oxygen in stationary as well as in modulated discharge regimes. Spatial profiles of $[O(^3P)]/N$ were measured to determine atom loss rate on the wall. N was determined using the gas temperature found from the measurements of spectra of $O_2(b^1\Sigma_g^+,v=0)\rightarrow O_2(X^3\Sigma_g^-,v=0)$ molecular band. Thus, combination of spatially-resolved actinometry in stationary conditions together with time-resolved actinometry in pulsed regimes allowed studying kinetics of $O(^3P)$ atoms and making direct estimations of O atom loss frequency ν_{loss}^{O} and production rate k_{diss}^{O2} in the different plasma conditions.

Actinometry technique is optical emission spectroscopy (OES) method that is used to determine concentrations of atoms and molecules in plasmas relatively to known concentration of an actinometer – chemically stable (e.g., noble) gas, which is added in small quantities to the studied plasma so that its properties remain almost unchanged. Comparison of the light intensity produced by excited states of studied species and that of actinometer allows to determine the amount of the studied species relatively to amount of the actinometer, i.e., in our case, $[O(^3P)]/[Kr]$ can be found from the measurements of the emission line ratio I_O/I_{Kr}. However, this requires the detailed account for the balance of excitation and de-excitation of both O and Kr atoms, which, in turn, requires the knowledge of the corresponding reaction rates and electron energy distribution function (EEDF). The first problem of actinometry application in O_2 plasmas at elevated pressures lies in the predominance of collisional quenching of excited atoms while the corresponding rate constants are often unknown. Secondly, an accurate experimental obtaining of EEDF in such conditions is impossible. Therefore, the actinometer should be chosen in such a way that the actinometry becomes as weakly dependent on EEDF variations as possible. These questions of the actinometry applicability are discussed.

This research is supported by Russian Foundation for Basic Research (RFBR) Grant No. 18-32-00932\18 and No. 16-52-16024.

POSTERS

The maturation of the workflow of combustion chamber with toroidal recirculation mixing zone

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The construction of a serial airborne auxiliary power was used as a prototype during the design of new engine. A scheme solution of the air inlet duct and the radial-flow compressor was saved in new project. The inward flow turbine was meant to be an axial turbine. This required a change in the design of the combustion chamber (CC). After the consideration of a number of possible schemes, it was decided to choose a straight-flow annular CC with toroidal recirculation-mixing zone which has significant reserves of minimization in size with relative simplicity of technological execution. A feature of a particular combustion chamber is its diagonal arrangement relative to the axis of the engine. The working process of the CC has a number of problems, which arise due to the lack of experimental and calculated data.

The aim of the study is the maturation of the design of the CC with toroidal recirculation-mixing for the workflow optimization.

The first step of maturation involved the organization of swirl structure at primary zone by means of changing the diameters and number of dilution-closing holes and by means of adding a “springboard” on the inner shell of the flame tube. On the second step there were conducted the maturation of the flame shape in primary combustion zone. The nozzle was replaced with an ink jet and blade vortexers were added to the channel between the deflector and the wall of the flame tube. The third step was devoted to the formation of the necessary temperature field at the exit from the combustion chamber. To this end, work has been done to refine the necessary penetration depth of the jets, the number and location of the mixing holes.

As a result of the maturation, an acceptable design of the combustion chamber of the engine was obtained, in which it was possible to achieve flame stabilization in the primary combustion zone, distribution of the temperature field inside the chamber, eliminating its burnout and reducing the unevenness of the temperature field at the outlet.

This work was supported by the Ministry of education and science of the Russian Federation in the framework of the implementation of the Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020" (RFMEFI58716X0033).

Active oxygen species in combustion

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Active oxygen species (AOS – ozone O_3, molecular singlet oxygen O_2(a) (0.98 eV) and O_2(b) (1.63 eV), atomic oxygen O(^{3}P) and O(^{1}D) (1.97 eV)) play an important role in the combustion, especially when it is initiated by plasma [1, 2]. In recent years, a wide interest to them is because the processes involving AOS can be used to expand the limits of combustion and ignition. In order to reduce harmful emissions, primarily nitrogen oxides NO_x, requires reduction of the maximum gas temperature in the combustion chamber. For this purpose, the use of lean air-fuel mixture is preferable, as this also leads to a reduction in fuel consumption. Expanding the limits of combustion and ignition with the increase in the ratio "air/fuel" is one of the most pressing problems in the theory of combustion. These limits can be extended by external impact: plasma, chemical or the light (laser).

Creation of non-equilibrium plasma with high levels of reduced electric field, E/N, and a significant level of energy load may provide a high yield of oxygen atoms at O_2 plasma dissociation. The oxygen atoms enter into rapid chemical reactions with hydrocarbons and cause initiation of the combustion process. The possibility of using an electric discharge has been experimentally demonstrated in terms of thermal engines, such as in [1, 3]. Selective excitation of internal degrees of freedom of ozone and oxygen molecules by laser radiation can also increase the limits of the ratio "air/fuel".

With an excess of O_2 (the atmosphere, the air-fuel mixture, oxygen-containing plasma), oxygen atoms are effectively removed in the three-body recombination process

$$O + O_2 + M \rightarrow O_3(v) + M.$$

This forms a highly reactive O_3(v) molecule which, together with the atomic oxygen may play an important role in the initiation of combustion, recovery of ozone in the atmosphere, etc. These processes were not previously included in the kinetic scheme of planetary atmospheres, combustion and oxygen-containing plasma. The vibrational excitation of ozone greatly accelerates the rate of reactions with O and O_2(a) [4]. To determine the role of the reaction pathways to the dynamics of ozone in the atmosphere, in the combustion and in oxygen-containing plasma, new kinetic data are required that are not currently available in the literature and databases.

Plasma–chemical processes in air–fuel mixtures result in the formation of O_2(b) molecules that may activate chain reactions in the combustion zone. Analysis of the reaction kinetics involving O_2(b) is difficult due to the fact that there is little published data concerning the deactivation kinetics at temperatures above 350 K. In this report a new kinetic data related to O_3(v) and O_2(b) are presented.

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Products distribution in the reaction of atomic carbon with pyridine: theory and experiment

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We investigated the reaction of atomic carbon (C; ^3P_j) with pyridine (C_5H_5N; X^1A_1) at a collision energy of 34 ± 4 kJ mol^{-1} utilizing the crossed molecular beams technique. Forward-convolution fitting of the data was combined with high-level electronic structure calculations and statistical (RRKM) calculations on the triplet C_6H_5N potential energy surface (PES). These investigations reveal that the reaction dynamics are indirect and dominated by large range reactive impact parameters leading via barrier-less addition to the nitrogen atom and to two chemically non-equivalent 'aromatic' carbon-carbon bonds forming three distinct collision complexes. At least two reaction pathways through atomic hydrogen loss were identified on the triplet surface. These channels involve multiple isomerization steps of the initial collision complexes via *ring-opening* and *ring expansion* forming an acyclic 1-ethynyl-3-isocyanoallyl radical (**P1;** $^2A''$) and a hitherto unreported seven-membered 1-aza-2-dehydrocyclohepta-2,4,6-trien-4-yl radical isomer (**P3;** ^2A), respectively. Based on the computations, the molecular fragmentation channel eliminating acetylene (C_2H_2) plus 3-cyano-2-propen-1-ylidene (**P6**; $^3A''$) plays also an important role the reaction of atomic carbon with pyridine proposing a probable destruction pathway of interstellar pyridine. These results are also discussed in light of the isoelectronic carbon – benzene (C_6H_6; X^1A_1) system with important implications to the rapid degradation of nitrogen-bearing polycyclic aromatic hydrocarbons (NPAHs) in the interstellar medium compared to mass growth processes of PAH counterparts through ring expansion.

Increase of the energy plant efficiency in special conditions of its operation

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Development of the arrangements for decrease of the internal combustion engines (ICE) power plant exploitation for consumer in conditions of market relationships in Russian economics is actual task. This fact forces ICE manufacturers to decrease cost of available products during its realization and production for expansion of the manufacturing and selling area.

To solve this problem, modernized system of air supply (MSAS) is suggested. This system considers steam injection in turbo-compressor which provides increase of its power and also increase air supply in ICE cylinders. Turbo-compressor power is increased by working fluid flow rate increase in the form of steam-gas mixture. Temperature of the steam-gas mixture is decreased because steam has lower temperature than exhaust gas. Further, increase of the air flow rate through ICE causes decrease of the specific fuel consumption and temperature of the exhaust gases which in turn increases durability of entire power plant.

Another way to increase the power plant efficiency is high-temperature refrigeration (HTR). Application of HTR during ICE exploitation gives certain positive effect which is decrease of the mass-dimensional characteristics to 8-20%, which is important for power plants of transport vehicles and for their placement as a drive for different equipment.

HTR system equipment is not complicated but this regime promotes increase temperature of the sleeve assembly elements. This fact can slow down application of HTR because every degree increment of the refrigeration liquid temperature causes the increase of the sleeve assembly temperature on 0.8 degree. That’s why application of arrangement which provide decrease of the sleeve assembly in HTR regime is important task.

This article deals with calculation algorithm which purpose is determination of the amount of steam which can be received from the system of exhaust gases and charge it to flow area of gas turbine of the turbo-compressor as well as determination of ICE parameters changed as a result of MSAS implementation.

Calculation result of ICE parameters during its operation with modernized system of air supply shows that its economic efficiency on given level of power output is increased which causes increase of the exploitation economic efficiency of power plant and simultaneously decrease of hazard working fluids exhaust together with exhaust gases from not burned fuel. Decrease of the steam-gas mixture and increase of the air flow rate through ICE promotes decrease of the temperature of sleeve assembly elements which promotes increase of the durability of power plant in special conditions

Thermometry in a sealed discharge cell with noble gas

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Noble gas radiation is useful for calibration of optical spectral instruments, since it consists of a set of intensive well-resolved spectral lines. Sealed low-pressure cells with a suitable noble gas are usually used as sources of calibration light radiation. At the same time, the simplest low-power RF generators are used to excite gas, which are manufactured directly in the laboratory. With the operation of such devices, variations in the RF power supplied to the excitation electrodes are observed, which is accompanied by changes in the temperature and pressure of the gas in the cell. In turn, changes in the gas state parameters cause shifts and broadening of the reference spectral lines, which leads to errors in the calibration of optical wavelengths. To estimate the possible errors, it is necessary to determine the changes in the temperature and pressure of the noble gas in the sealed discharge cell when the power of the exciting RF generator is varied.

The gas temperature and pressure can be determined from the spectral line profile. In general, the line has a Voigt profile, which is a convolution of the Doppler and Lorentz contours. The temperature of the gas under investigation can be determined from the Doppler broadening and the gas pressure can be determined from the amount of the Lorentz broadening. In [1] the technique of "reference" points is presented, which makes it possible to separate the Doppler and Lorentz components of the Voigt profile broadening of a single spectral line. However, the results of the verification of the calculated procedure given in [1] do not look quite complete, since experimental data were used from the literature sources and only for the temperature.

In this paper, we compare the calculated data obtained by the "reference" points method from the absorption line profile with the results of direct measurements performed by the pressure sensor. The diode laser spectroscopy and a discharge cell with an established gas flow were used for these measurements. The discharge cell with the gas flow allowed us to change the pressure inside it in a controlled way. Then, the tested technique of "reference" points was applied to the evaluation of variations in temperature and pressure in the sealed argon cell of a optical wavelength calibrator [2].

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Photodissociation dynamics of SCl_2: resonance enhanced multi-photon ionization/time-of -flight mass spectroscopy study

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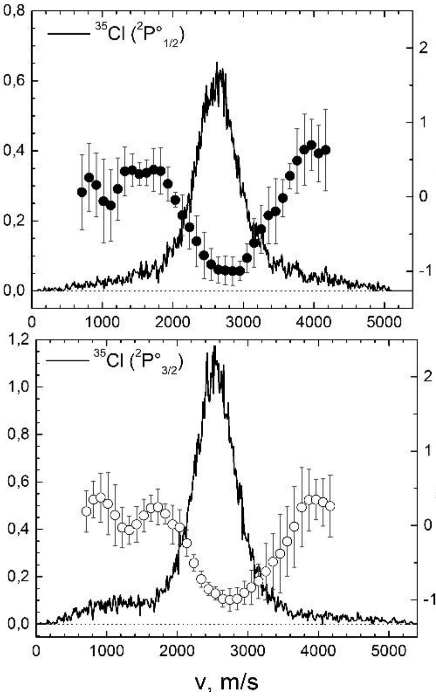
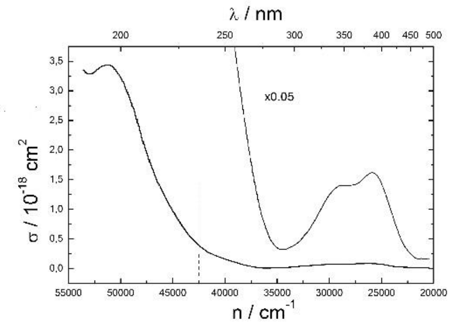
The dynamics of photodissociation of SCl_2 at 235 nm has been studied by monitoring of ground state $Cl(^2P_{3/2})$ and spin-orbitally excited $Cl^*(^2P_{1/2})$ atoms. Time-of-flight mass-spectroscopy and resonance enhanced multi-photon ionization (REMPI) combined with a position sensitive detector (delay-line anode) were employed. The three-dimensional (3D) momentum vector of a single reaction product was directly determined by this ion imaging technique. Also, the S^+ photoions have been produced and monitored by non-resonant multiphoton ionisation.



The speed distributions and speed-dependent anisotropy parameters β for all these three particles have been determined. The speed distributions of $Cl(^2P_{3/2})$ and $Cl^*(^2P_{1/2})$ atoms both have a single main peak, see first figure. This strong peak comes from direct abstraction of Cl atom from the parent molecule, the weak peaks are assigned to secondary processes, mainly to photodissociation of SCl and S_2Cl_2.

The anisotropy parameters β for chlorine atoms are close to -1, indicating that the one-photon photodissociation of SCl_2 at 235 nm is due to the perpendicular transition $^1A_1 \rightarrow {}^1B_2$ in the point symmetry group C_{2v}. The dipole transition moment of this transition is perpendicular to the plane of molecule. In the absorption spectrum of SCl_2 (see second figure) there is another transition $^1A_1 \rightarrow {}^1A_1$, which is much stronger, it has maximum near 190 nm, which is not far from 235 nm. Our β parameter indicates, that this strong transition have very small contribution to the photodissociation of SCl_2 at 235 nm.



The relative yields of excited $Cl^*(^2P_{1/2})$ atoms is found to be 0.38±0.04.

Simulation of plasma initiation of ignition of methane-air mixtures under atmospheric pressure

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The idea of using plasma methods of ignition of fuel-air mixtures is based on nonequilibrium production of chemically active particles in an electric discharge to accelerate combustion. Detailed reviews of the current state of this problem are presented in [1-3]. Theoretical and experimental aspects of the plasma initiation of combustion in hypersonic ramjet air-jet engines are discussed in [4-5]. In [6] studies were carried out to improve stability of combustion by electric discharge in gas turbines operating on a lean mixture with natural gas. An experimental study of plasma initiation of combustion of methane and ethylene air mixtures in a gas stream at a pressure of about a hundred Torr was performed in [7-8].

In this paper the results of calculations of the plasma initiation of ignition in the flow of a stoichiometric methane-air mixture at atmospheric pressure at various initial temperatures (300, 500 and 700 K) and various excitation powers of 20-100 kW/g are presented. To verify the model, a comparison was made with the data on plasma initiation of ignition given in [7-8], where a subsonic flow of methane and ethylene-air mixtures passed through a barrier discharge excited by nanosecond pulses with a repetition rate of 10-50 kHz is used. The lengths (times) of ignition and the specific energies of the discharge necessary to ignite the methane-air mixture were found. The energy values depended on the initial temperature of the gas and were in the range 170-380 J/g. The results of calculations of temporal evolution of the number densities of various plasma components are presented: in particular, for different electron-excited states – $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma^+{}_g)$ and $N_2(A^3\Sigma^+{}_u)$.

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Formation mechanisms of phenanthrene and anthracene from naphthalene radicals

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Polycyclic aromatic hydrocarbons (PAH) and soot, which generated in combustion processes, are harmful by-products. Therefore studying formation mechanisms of PAH from elementary chemical reactions initiating and propagating growth PAH at the molecular level, to successive nucleation of soot particles, particle coagulation and their surface growth, is very important research goal. The main task for understanding the molecular evolution of PAH is unraveling the elementary step of PAH expansion by one extra ring, which could be an additional six-member or five-member ring.

Formation mechanisms of indene and naphthalene from benzene were detailed studied in work [1]. Therefore, the question about expansion PAH from 1 to 2 rings can be considered solved. It seems interesting to investigate expansion PAH from 2 to 3 rings. Process of formation anthracene and phenanthrene from naphthalene radicals can be seen like a prototype of that elementary step evolution of PAH.

Main and additional reaction channels of interaction naphthalene radicals with vinilacetylene were defined in this work. Transition states and local minimums (wells) were optimized. G3 energy were calculated for them. Based on this data potential energy diagram was plotted (Fig. 1 shows the very small part of this diagram) and rate constants and relative yields of reaction were calculated.

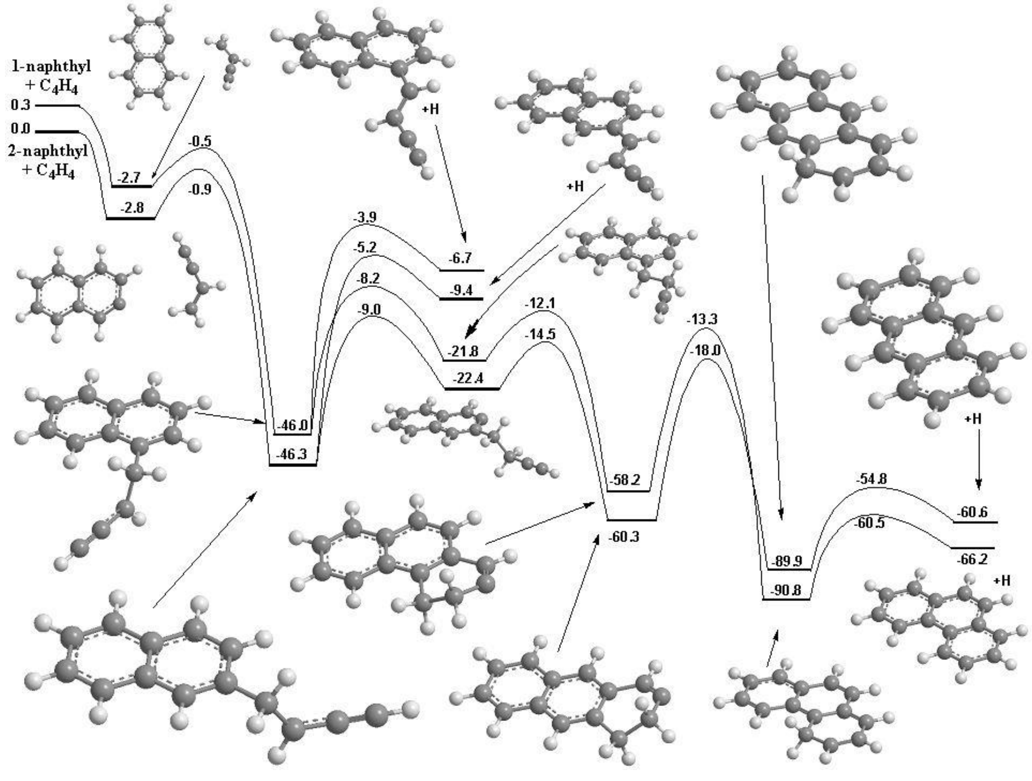

Fig.1 – The part of potential energy diagram with some main reaction channels

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Study of pyrotechnic delay composition using reinforced composite material with carbon nanotubes

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At present, the efforts of scientists are mainly aimed at the development of reinforced composite materials with carbon nanotubes. The unique properties of carbon nanotubes make it possible to use them in various branches of science and technology. With the introduction of the carbon nanotubes, the properties of materials and products from them change substantially.

Also in recent years there has been growing interest in the use of reinforced composite materials with carbon nanotubes as a fuel agent in pyrotechnic delay compositions

Pyrotechnic delay compositions are widely used in civil industrial systems and delay devices for various purposes, which serve to create time delays that provide the necessary duration.

In this work, to improve the macrokinetic characteristics, the reliability and the stability of delay composition, the reinforced composite material with carbon nanotubes were added. Ti and 4% CNT were mixed by the planetary ball mill AGO-2 with water cooling, which is the most energy-intensive of all devices of this type. Milling time was varied from 1 to 11 min. Particle size analysis showed that particle size exponential declined with increase in milling time. SEM results showed that after 2 min of milling on the surface of titanium particles there are no carbon nanotubes, which indicates their dispersion into titanium powder, then with an increase milling time mechanocomposites of various sizes of irregular shape are formed. Then Ti/CNTs were applied to fuel agent of delay composition. We studied the burning rate, burning time and physical and chemical characteristics of $BaCrO_4$/CNTs/Ti delay composition.

Thus, the addition of certain amount of CNTs to the delay composition allows improve the physicochemical characteristics and increase the ignition reliability of delay compositions.

Reaction mechanism for the oxidation of $C_{15}H_9$ with hydroxyl

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The $C_{15}H_9$ molecule is invoked as a soot surface site bearing five-member ring for modeling of the oxidation of soot[1]. Here we report the potential energy surfaces for the oxidation reaction of $C_{15}H_9$ by OH calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory. Fig. 1 exhibits the calculated most likely configurations resulting from the interaction of $C_{15}H_9$ with OH.

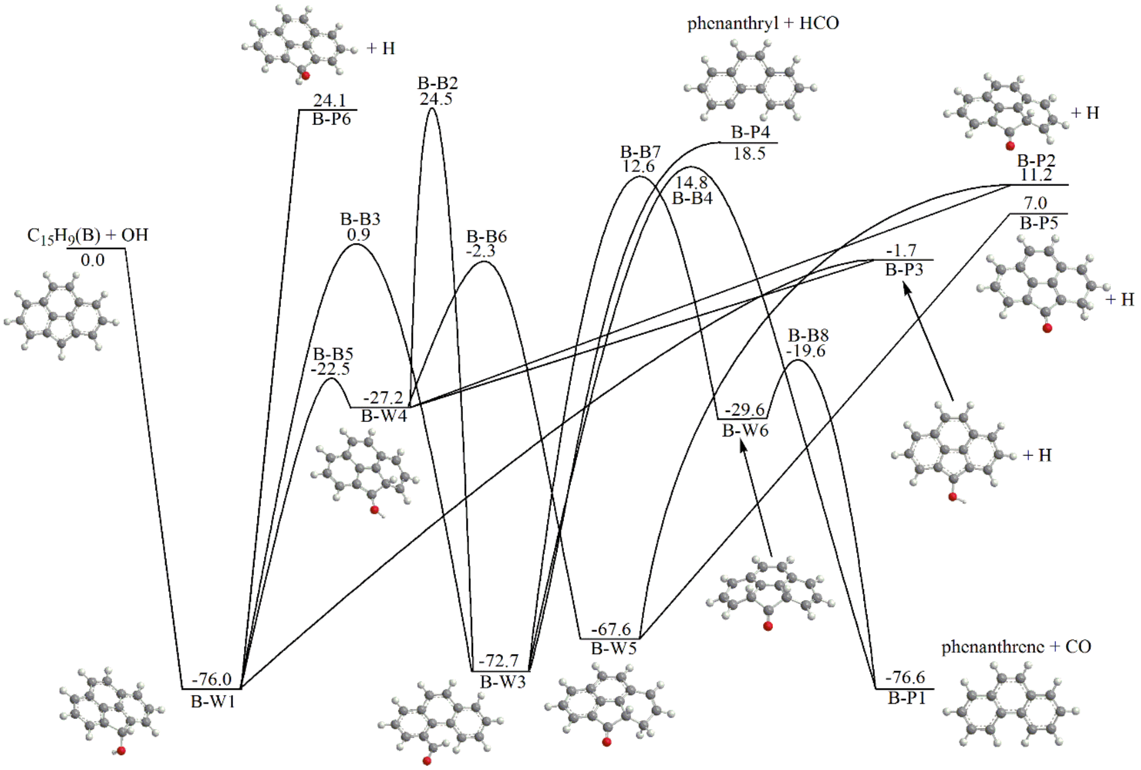

Fig. 1 Possible pathways for the $C_{15}H_9$ + OH reaction. The relative energies of stable species, intermediates, and transition states are depicted with italic numbers (in kcal/mole).

The $C_{15}H_9$(B) + OH reaction is found to predominantly proceed by the stabilization/dissociation channel forming $C_{15}H_{10}O$ (B-W1), which the further dissociates to $C_{15}H_8OH$ + H (B-P3) or back to the $C_{15}H_9$(B) + OH reactants, whereas the pathway producing B-P6 directly is only minor. Removal of CO is unlikely; because the degree of embedding of a five-membered ring is deep (the five-membered ring has three common edges with the surrounding six-member rings).

The presentation will also address the reaction of $C_{15}H_9$(A) where the embedded five-member ring has two common edges with the surrounding six-member rings, as well as oxidation reactions of $C_{15}H_9$(A) and $C_{15}H_9$(B) with atomic oxygen.

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The rate constants calculations and the potential energy surface for indenyl C_9H_7 +O_2 reaction by ab initio methods

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Polycyclic aromatic hydrocarbons, which are considered among the most abundant pollutants and as soot precursors, exert a great impact on environment and health. The C_9H_7 + O_2 reaction may play a significant role in combustion processes. Ab initio calculations were employed to calculate the energies of various reaction pathways and final products; geometries of the reactants, various intermediates, transition states, and products on the C_9H_7 + O_2 PESs were optimized at the density functional B3LYP/6-311G(d,p) level of theory and single-point energies were refined at the G3(MP2,CC) level (Figure 1).

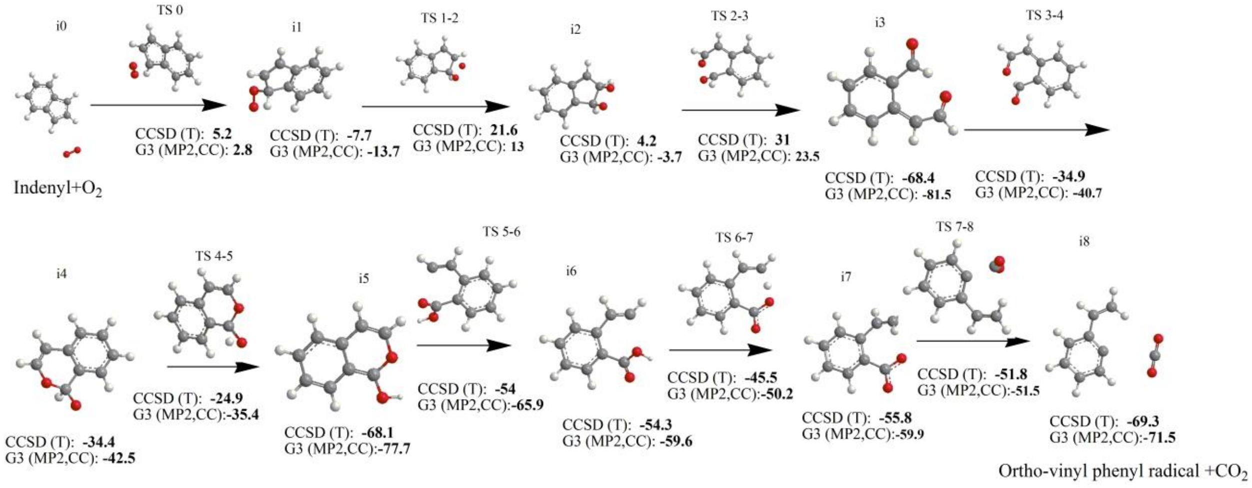

Fig. 1 The C_9H_7 + O_2 reaction pathway leading to the ortho-vinylphenyl radical C_8H_7 formation: the energies are indicated for both CCSD(T) and G3(MP2,CC) levels of theory.

The reaction can proceed by two possible pathways; both of them involve O_2 insertion into the 5-membered ring eventually leading to CO_2 elimination with formation of ortho-vinylphenyl radical (Fig. 2) and styrenyl as main reaction products. Rate constants and product branching ratio calculations have been performed for all reaction pathways.

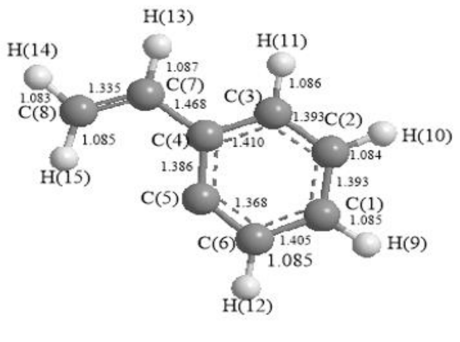

Fig. 2 Optimized geometry of the ortho-vinyl phenyl radical; the numbers show bond lengths in Å.

Combustion characteristics of model composite propellants with aluminum diboride

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Key words: composite propellant, boron, aluminum, aluminum diboride, burning rate, sampling technique, condensed combustion products, particle size distribution, microscopy, SEM, EDS, cerimetric chemical analysis, combustion completeness, efficiency of energy release.

The work continues comparative investigations of highly loaded model propellant formulations with ca. 40 % of different boron containing fuels. This work is focused on aluminum diboride and mechano-activation effects.

A research objects – three model propellants based on ammonium perchlorate, energetic binder and combined fuel. First fuel, MA1, – “raw” material – is mechanically-activated (MA) mixture of aluminum and boron powders taken in the same mass ratio as in aluminum diboride. Second fuel, MA2, is aluminum diboride made of this “raw” material. Third fuel, MA3, is MA2 subjected again to mechanical activation. Thus, we compared three fuels of AlB_2-type obtained with different MA-actions.

The data on the burning rate at pressures of 1.2 MPa and 2.5 MPa and on the condensed combustion products (CCP) parameters are reported in present work. For the particles extinguished near the burning surface the oxidation of fuel *on* and *above* the surface is actually investigated. Sampled particles are so called *primary* CCP. The particles mass size distributions in the range from 0.5 microns to millimeters are delivered; the CCP particles morphologies (obtained via optical microscopy, SEM, EDS) are described. The millimeter-sized products are the skeleton-layer or *carcass* remaining in a glass after propellant specimen burned out. The data on the combustion completeness of fuel was obtained via cerimetric method.

The approaches to compare fuels in mass parameters of the combustion products and in efficiency of energy release are developed.

For the analysis of data on combustion completeness the complex parameter E is proposed named “efficiency of the energy release”. This parameter integrates the incompleteness of fuel combustion, the mass fractions of Al and B in the combined fuel, the reducing number and the specific heat of combined fuel, as well as the mass of carcass residue in a glass.

In general, the efficiency of the energy release E essentially depends on the burning rate value and on the agglomeration process features as well as on the propellant formulation and the combined fuel parameters.

The propellant with fuel MA3 was most energy release efficient among three formulation under study.

Acknowledgment. The reported research was partially funded by Russian Foundation for Basic Research, grant № 15-03-04321.

Simulation of ozone formation in an electric discharge in mixtures of methane with air

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We took a model of the discharge at an atmospheric pressure in air, described in detail in [1] as a basis for our discharge model. We implemented it to describe the characteristics of quasistationary [1], pulsed [2] and corona [3] discharges, as well as the transition from corona discharge to a glow [4] discharge in air at atmospheric pressure at room temperature. The processes involving the methane molecule and its derivatives were taken from [5].

The calculations were performed for atmospheric pressure and room temperature for air and its mixtures with methane. A pulsed-periodic electric discharge and its afterglow in a gas flow were investigated by the homogeneous model. The maximum specific energy input in the discharge was 50 J/g. In the case of air, the dependence of the ozone number density in the afterglow zone on the specific energy input is close to linear. The addition of methane leads to a several times decrease in the ozone number density. The dependence of the ozone number density on the specific energy input differs markedly from linear.

It is known that atomic oxygen is formed as a result of dissociation of oxygen molecules by plasma electrons and collisions of molecular oxygen with electronically excited nitrogen molecules. Analysis of simulation results showed that the main mechanisms leading to a decrease in ozone concentration are competition of quenching of electronic levels of molecular nitrogen by oxygen and methane molecules [6-7]. The process of dissociation of methane in the discharge leads to the formation of hydrogen atoms, which also leads to a decrease in the concentration of oxygen and ozone atoms as a result of chemical reactions.

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Justification of the expediency of using the combustion chamber with a toroidal recirculation zone in the small GTE

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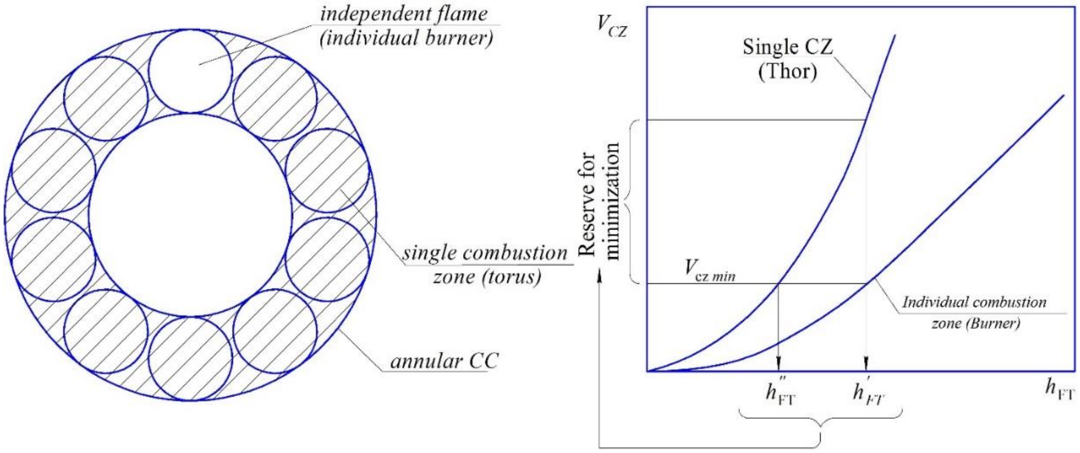
At present, the use of small-size gas turbine engines (SGTE) in various sectors of the national economy and in the interests of the Ministry of Defense is constantly increasing. Accordingly, the number of requirements put forward for these engines is increasing: mass-dimensional, ecological, resource, etc. The fulfillment of most of these requirements is related to the design and the combustion chamber (CC) of the engine implemented in its framework.

One of the main requirements, associated with the provision of specified dimensions and engine mass, is directly determined by the dimensions of the compressor.

However, the reduction in the size of the combustion chamber in each particular case has its limits, determined by the type of diffuser, the design of the front-line device, the space necessary for organizing the combustion and burnout of the fuel. In many combustion chambers SGTE, for the organization of the working process, variants are used for front-end devices with spatula swirlers, evaporative fuel tubes, rotating nozzles and other technically difficult to implement elements. Many of these methods of preparing the fuel-air mixture and the formation of the combustion zone have a significant disadvantage - a volume is formed between the injectors, which is not used for combustion. In turn, combining the combustion zone would reduce the dimensions of the CC (Figure 1).



a) b)

Figure 1 - Comparison of the volume of combustion zones

In this paper, the theoretical foundations of the organization of the working process using the toroidal recirculation zone with the help of which the combustion chamber of the SGTE was designed, which was then made in the form of a real sample using prototyping technology, is considered.

The results of numerical simulation on a computer using a proven method showed the operability of this combustion chamber while respecting and meeting the basic requirements of the Technical Task. At present, the experimental debugging of this combustion chamber is taking place.

This work was supported by the Ministry of education and science of the Russian Federation in the framework of the implementation of the Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020" (RFMEFI58716X0033).

Formation mechanisms of triphenylene and 4- vinylacephenanthrylene in the interaction of 9-phenanthryl and vinilacetylene

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Polycyclic aromatic hydrocarbons (PAH) and soot, which generated in combustion processes, are harmful by-products. Therefore studying formation mechanisms of PAH from elementary chemical reactions initiating and propagating growth PAH at the molecular level, to successive nucleation of soot particles, particle coagulation and their surface growth, is very important research goal. The main task for understanding the molecular evolution of PAH is unraveling the elementary step of PAH expansion by one extra ring, which could be an additional six-member or five-member ring.

Formation mechanisms of indene and naphthalene from benzene were detailed studied in work [1]. Therefore, the question about expansion PAH from 1 to 2 rings can be considered solved. Some information about generation anthracene and phenanthrene in reaction naphthalene radicals with vinylacetylene is also available. Therefore, it seems interesting to investigate expansion PAH from 3 to 4 rings. Process of formation triphenylene and 4-vinylacephenanthrylene from 9-phenanthryl can be seen like a prototype of that elementary step evolution of PAH.

Main and some additional reaction channels of interaction 9-phenanthryl with vinylacetylene were defined in this work. Transition states and local minimums (wells) were optimized. G3 energy were calculated for them. Based on this data potential energy diagram was plotted (Fig. 1 shows some part of this diagram) and rate constants and relative yields of reaction were calculated.

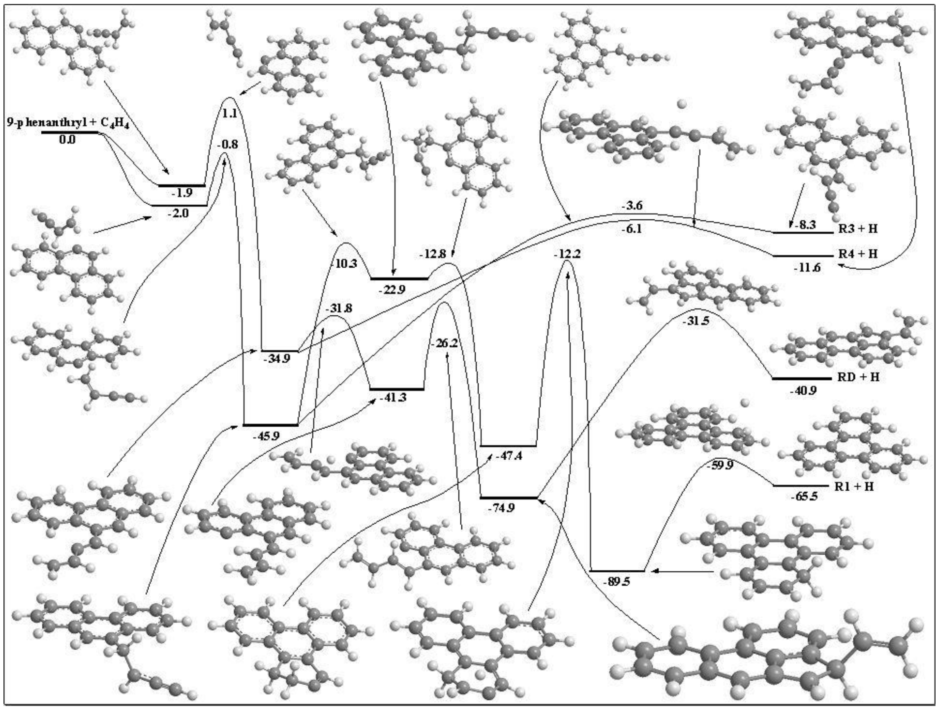

Fig.1 – The part of potential energy diagram with some main reaction channels

References:

1. Mebel, A.M.; Landera, A.; Kaiser, R.I.; Formation Mechanisms of Naphthalene and Indene From the Interstellar Medium to Combustion Flames. J. Phys. Chem. A. 2017, 121(5), 901-926

Methane-air flame thermometry using Planar Laser-Induced Fluorescence (PLIF)

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Planar laser-induced fluorescence (PLIF) method of diagnostics [1-3] employs laser radiation to selectively excite electronic energy levels of probe molecules and radicals (OH in our case). The excitation laser beam is configured to the planar geometry to achieve two-dimensional spatially-uniform irradiation of the area of interest. The target molecule emission occurs both from the laser-excited level and from other levels populated by molecular collisions. After spectral suppression of the scattered radiation at the excitation wavelength, the fluorescence light from the laser beam plane is imaged onto a two-dimensional optical detector.

The ratio R of the PLIF signals obtained after resonant laser excitation of the probe molecules at two different wavelengths λ_1 and λ_2, contains information about local gas temperature T and for each pixel of the images may be described by the expression:

$$R = C\times(I_{\lambda1}/I_{\lambda2})\times\exp[-(E_i - E_k)/kT],$$

where $I_{\lambda1}/I_{\lambda2}$ is the ratio of the incident laser light intensities, k is the Boltzmann constant, $(E_i - E_k)$ is the difference of the energies of the initial levels, while the coefficient C takes into account Einstein coefficients and Franck-Condon factors for the corresponding transitions, as well as collisional deactivation rates for the upper levels. Determination of the coefficient C in one pixel of the image allows deriving spatial temperature distribution from the PLIF signals.

In this work, spatially-resolved PLIF temperature measurements were performed in a partially premixed flame of a laboratory methane-air burner, previously characterized using coherent anti-Stokes Raman scattering (CARS) [4]. PLIF of OH radicals was excited by frequency-doubled radiation of a narrow-band dye laser at two different lines of the (1-0) band of the $X^2\Pi - A^2\Sigma^+$ electronic transition. For this purpose, the image processing algorithms were developed, and the temperature calibration procedure was realized.

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Laminar burning velocities of n-decane with ethanol additions

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Aviation kerosene or jet fuel is a complex mixture of different classes of hydrocarbons with the major contributors being normal alkanes, branched chain paraffins (iso-alkanes), aromatic molecules and cyclic paraffins, cycloalkanes. Biofuel additions to jet fuel increase the burning velocity and improve combustion process. Laminar burning velocity of iso-octane, n-heptane with ethanol additions has been determined in Lund before. n-Decane is a representative of the class of alkanes and many previous studies proposed n-decane as a component of surrogate blends for aviation or engine fuels. Measurements of the adiabatic laminar burning velocities of *n*-decane with ethanol additions are reported. Non-stretched flames were stabilized on a perforated plate burner at 1 atm. The Heat Flux method was used to determine burning velocities under conditions when the net heat loss from the flame to the burner is zero. Initial temperatures of the gas mixtures with air were 338, 358 and 400K. The measurements were performed on two experimental setups at Lund University and Samara *National Research* University. Our results obtained at the same initial temperatures are in good agreement. The high-temperature detailed (ver. 1412) kinetic mechanism for kerosene developed at Politecnico di Milano was used to simulate the results. Uncertainties of the measurements were analyzed and assessed experimentally. The overall accuracy of the burning velocities was estimated to be better than ±1 cm/s.

This work was supported by the Ministry of education and science of the Russian Federation in the framework of the Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020" (RFMEFI58716X0033). The authors would also like to acknowledge the financial support from the Centre for Combustion Science and Technology (CECOST), Sweden.

Research materials and structures of space vehicles by multifrequency measuring system on the basis of eddy current transducers

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Strengthening of parts and units of machines, increased reliability and longer service life is an important task of modern aerospace industry. The aim of research was to apply boride coatings on surface of steel parts. Timeliness is subject to necessity to harden surface of steel used in high-load conditions. Samples of coatings on 65 G grade steel, applied by HFC-heating, were obtained. Research of samples with different coatings by means of metallurgical microscope was carried out. Data on samples with different coatings research by means of an eddy current measuring system was obtained and conclusion on electrical conductivity distribution along the sample surface depending on flux quantitative content during boriding was made.

Formation mechanisms of benzo(c)phenanthrene and 4-vinylpyrene in the interaction of 4-phenanthryl and vinylacetylene

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Polycyclic aromatic hydrocarbons (PAH) and soot, which generated in combustion processes, are harmful by-products. Therefore studying formation mechanisms of PAH from elementary chemical reactions initiating and propagating growth PAH at the molecular level, to successive nucleation of soot particles, particle coagulation and their surface growth, is very important research goal. The main task for understanding the molecular evolution of PAH is unraveling the elementary step of PAH expansion by one extra ring, which could be an additional six-member or five-member ring.

Formation mechanisms of indene and naphthalene from benzene were detailed studied in work [1]. Therefore, the question about expansion PAH from 1 to 2 rings can be considered solved. Some information about generation anthracene and phenanthrene in reaction naphthalene radicals with vinylacetylene is also available. Therefore, it seems interesting to investigate expansion PAH from 3 to 4 rings. Process of formation benzo(c)phenanthrene and 4-vinylpyrene from 4-phenanthryl can be seen like a prototype of that elementary step evolution of PAH.

Main reaction channels of interaction 4-phenanthryl with vinylacetylene were defined in this work. Transition states and local minimums (wells) were optimized. G3 energy were calculated for them. Based on this data potential energy diagram was plotted (Fig. 1 shows some part of this diagram) and rate constants and relative yields of reaction were calculated.

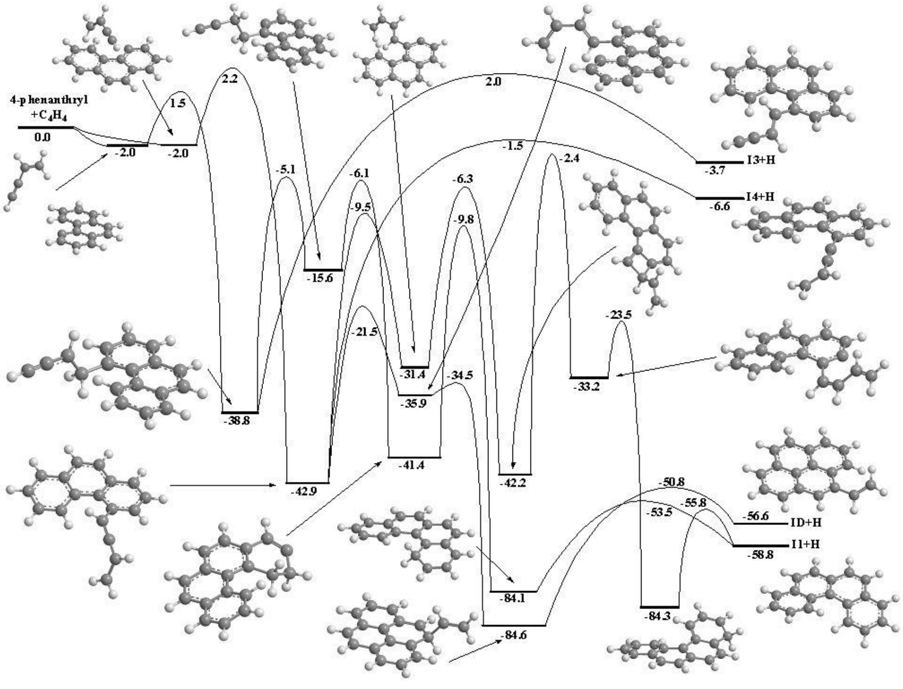

Fig.1 – The part of potential energy diagram with some main reaction channels

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Experimental study of chemiluminescence in UV and VIS range at hydrogen-oxygen mixtures ignition

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Nonequilibrium radicals are important intermediates in hydrogen-oxygen kinetics. Controlling the level of electronic and vibrational nonequilibrium can become the key for the changing the limits of hydrogen ignition, which has great practical importance. The purpose of this paper is an experimental study of the emission spectrum in the UV and VIS region of electronically nonequilibrium radicals and molecules, analysis of their impact on the ignition of hydrogen and the search for inhibitors and promoters to control the process of ignition. The stoichiometric hydrogen-oxygen mixtures ignition with additions of halogenated inhibitors of combustion ($C_2F_4Br_2$,CCl_4 etc) was studied behind the reflected shock wave in temperature range of 950-1200 K and pressure range of 2.5-6.5 bar. The concentration of the combustible mixture was 10% ($2H_2+O_2$) diluted with argon. Nonequilibrium radiation was detected in the UV at 220-310 nm and in visible range at 400-500 nm presumably corresponding to electronic excited radicals and molecules OH^*, HO_2^* and $H_2O_2^*$. The temperature dependences of the ignition delay, measured by the appearance of radiation, were in agreement with other experimental data and numerical simulations. The temperature dependences of maximum radiation intensity have shown that the investigated additives results in a significant increase of emission. The possible kinetic reasons are discussed.

Environmental advantages of composite fuels based on industrial wastes and different ranks of coal

Nyashina Galina

National Research Tomsk Polytechnic University

Thermal power plants and boiler units generate most of the anthropogenic emissions around the world. This is especially true for the industrialized and industrializing economies (China, India, the USA, the European Union, and Russia). Solid fuels are regarded as the most hazardous of all the primary energy sources (coal, gas, fuel oil, and petroleum) in terms of anthropogenic emissions. Countries with advanced coal-based heat and power industries are the ones contributing the most to the problem of global warming. A promising solution to many problems that heat and power industry is facing today would be switching from conventional coal dust combustion to composite liquid fuels (CLF). These are also known as coal-water slurries containing petrochemicals (CWSP). Here, we perform an experimental study of the most hazardous anthropogenic emissions (sulfur and nitrogen oxides) from the combustion of high-potential CWSP. We identify the main benefits and potential drawbacks of using CWSP in heat and power industry. A set of components and additives to CWSP are explored that significantly affect the environmental and energy performance of fuels. The anthropogenic emissions from the combustion of CWSP made of widespread coal and oil processing wastes are no higher than those from coal dust combustion. Using specialized additives to CWSP, we can change the concentrations of NO_x and SO_x several times. The most appealing additives to CWSP are sawdust, straw, charcoal, limestone, and glycerol. They provide better environmental, economic, and energy performance and improve the rheological properties of CWSP. Used oils and oil sludge added to CWSP may impair the environmental performance but boost the cost and energy efficiency. Using coal-water slurries containing petrochemicals as a fuel at heat and power plants is an environmentally friendly as well as cost- and energy-efficient way to recover industrial wastes. It generates energy and mitigates the negative impact of coal-based heat and power industry on the environment.

The reaction of 2-naphthyl with 1,3-butadiene: a theoretical study

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Recently obtained experimental and theoretical results of the investigation of the reaction of 1-naphthyl plus 1,3-butadiene defy the thesis that PAH growth is predominantly a high temperature phenomenon[1]. This work is devoted to theoretical investigation of 2-naphthyl + 1,3-butadiene reaction to complete the understanding of formation mechanisms of dihydrophenanthrene and dihydroanthracene in the reactions of n-naphthyl (n = 1, 2) with 1,3-butadiene. All intermediates and transition states, their vibrational frequencies and zero-point vibrational energies were calculated at G3(MP2,CC)//B3LYP/6-311G** theoretical level to generate the corresponding potential energy surface. Figure 1 represents the possible reaction pathways and scaled B3LYP potential energy surface. The results clearly indicate the possibility of the formation of both dihydrophenanthrene and dihydroanthracene in the title reaction.

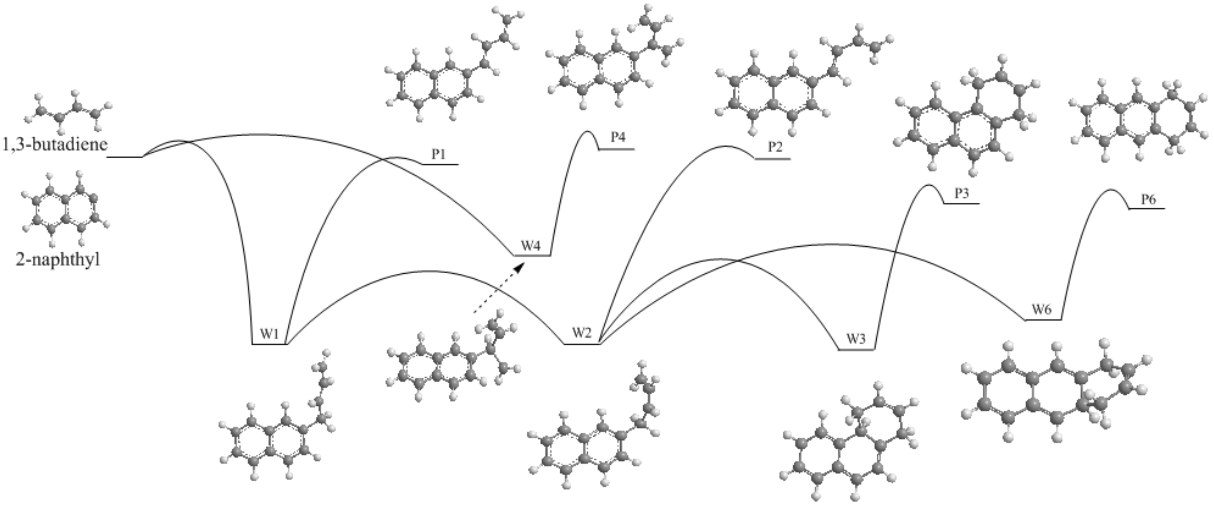

Figure 1. The pathway for the reaction of 2-naphthyl plus 1,3-butadiene depicting hydrogen-loss channels from various $C_{14}H_{13}$ adducts.

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Ozone recovery in the presence of nitrous oxides

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The temporal profiles of ozone number densities after pulsed UV laser photolysis in a gas mixture O_2-O_3-N_2-N_2O obtained by time-resolved absorption spectroscopy was presented. The experimental results demonstrated the dominance of the stabilization channel over the reactive one for the reaction of O_3 (υ) with N_2O and NO. The rate constants for the processes $O_3(\upsilon) + N_2O \rightarrow O_3 + N_2O$ and $O_3(\upsilon) + NO \rightarrow O_2 + NO_2$ was obtained to be $(1.5\pm0.2) \times 10^{-13}$ cm^3/s and $(2.0\pm0.2) \times 10^{-11}$ cm^3/s, respectively, using kinetics modeling of experimental data.

Vibrationally excited ozone can react with compounds of fuel-air mixtures in fire zones of power-producing units, also with nitrious oxides in high temperature zones.

Reaction of vibrationally excited ozone with nitrogen oxide $O_3(\upsilon) + NO \rightarrow NO_2 + O_2$ (1) has more probability then reaction with thermalized ozone $O_3 + NO \rightarrow NO_2 + O_2$ with rate constant 1.8×10^{-14} см^3/с [1-4]. Also, kinetic data for relaxation process $O_3(\upsilon) + N_2O \rightarrow O_3 + N_2O$ (2) are missed in literature. In this work rate constants for processes (1-2) was found by temporal profiles of ozone number densities in different conditions of gas mixture O_2-O_3-N_2-N_2O after UV laser photolysis [5]. The rate constants for the processes (1) and (2) was obtained to be $(2.0\pm0.2) \times 10^{-11}$ cm^3/s and $(1.5\pm0.2) \times 10^{-13}$ cm^3/s, respectively.

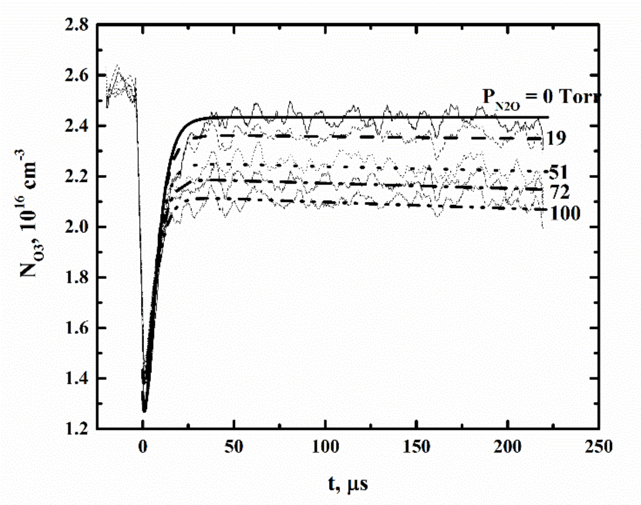

Figure 1 – Temporal profiles for concentration of O_3 for E=70 mJ/cm^2, P_{tot}=807 Torr, P_{O2} =600 Torr, T=300 K and different pressures of N_2O.

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Modeling of the formation of ultrafine particles as coals burning

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The presence of highly dispersed particles in the atmosphere is ecologically hazardous. One of the sources of the aforementioned type of atmospheric pollution is the emission of submicron particles upon combustion of coals. The bulk condensation of vapors of substances produced from the mineral moiety of coals during combustion is a probable formation mechanism of submicron particles in this case. For efficient trapping of the above-mentioned particles, it is necessary to know the parameters of condensation aerosols that result from combustion, such as their number concentration and size distribution, which can be used for numerical simulation of the bulk condensation process. As applied to the combustion products of coals, which are multicomponent reactive systems, it is reasonable to use a comprehensive thermodynamic and kinetic approach. Thermodynamic analysis of the composition of combustion products have been performed for 15 types of coals with and without allowance for potassium and sodium aluminosilicates. Based on the results obtained, a closed model has been proposed for the formation of submicron particles in the combustion products of the coals. The bulk condensation of potassium sulfate vapor in the flow of the combustion products and upon their cooling along a technological path has been numerically simulated by means of computer assisted realization of the proposed model. The concentration and size distribution of the formed particles have been determined. The calculated and experimental data on the fractional composition of the particles are compared. Agreement with experimental data has been reached at a reasonable value of a free parameter of the model.

Kinetics of the 1-acenaphthyl + O_2 Reaction: A Theoretical Study

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Since about 80% of the energy consumed in the world is produced by various power units using hydrocarbon fuels, polycyclic aromatic hydrocarbons (PAHs) growth and soot formation is one of the major challenges for environmental conservation. One of the key processes of that phenomena is oxidation of soot particles and precursors, which counteracts expansion of those structures. But widely employed reaction models suffer from lack of reliable values for corresponding rate constants and use those for small molecules.

In proposed research, we investigate a reaction between molecular oxygen and 1-acenaphthyl as a model system for oxidation of 5-membered ring embedded in “zigzag”-type edge of soot macromolecule by molecular oxygen. Single-point energies for potential energy surface has been calculated using composite scheme [1] with ab initio calculations at the CCSD(T)/6-311G(d,p) and G3(MP2,CC)//B3LYP/6-311G(d,p) levels of theory. The MESS program package [2] was then used to compute temperature- and pressure-dependent rate constants solving the one-dimensional master equation. Due to different stoichiometry of consecutive steps, we constructed a kinetic scheme of the reaction and a corresponding system of differential equations. This system was solved by the standard means for variety of 1-acenaphthyl and O_2 concentrations and temperatures of interest.

The most preferable path of the reaction leads eventually to formation of 1-naphthyl and consists of two subsequent CO-eliminations. The second one is much faster than the first, which turns out to be rate determining. The ultimate quest of calculation of the total rate constant for reaction 1-acenaphthyl + O_2 → 1 - naphthyl + 2 CO fails because of strong dependency on initial reagents concentrations. Thus, the reaction, in general, should be considered in steps: initial addition 1-acenaphthyl + O_2 → 1 - acenaphthyl peroxy radical and monomolecular dissociation 1 - acenaphthyl peroxy radical → 1 - naphthyl + 2 CO.

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Percolation model of combustion

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We consider how combustion processes in inhomogeneous media gain inhomogeneity because of exponential dependencies in equations. Amplification of local fluctuations takes place during the starting stage of combustion cycle in ICE after fuel injection.

In ideal conditions reaction rate depends on molecular concentration and some factor k as $-da_1/dt = -da_2/dt = ka_1a_2$. Here k depends on temperature as $k = k_0 \exp(-ER^{-1}T^{-1})$ and apparently this coefficient has a remarkable variation range. Let consider typical activation energy E be equal to $40 kal \cdot mol^{-1}$ and the universal gas constant R be equal to $1.99 \cdot 10^{-3} kcal \cdot mol^{-1} \cdot K^{-1}$. Then here we observe $k(500K^o) = 10^{-17.4}$ and $k(1000K^o) = 10^{-8.7}$· So if temperature T increases 2 times the coefficient $k(T)$ will increase billion times! [1]

Molecular concentrations a_1, a_2, T and other magnitudes are statistically distributed in real life. Also T has feedback coupling with local energy output. Therefore, values form random fields in a combustion gap. Stochastical behavior leads to dramatic intensification of combustion processes in some rare but meaningful areas. And one can investigate intermittent random fields using statistical moments using follow rule: if M_k increases as k increases this will point out irrelevancy of averaging approaches. For instance, a fuel spray notably clear demonstrates intermittent properties because it definitely encapsulates pure fuel droplets and areas of irregularly saturated vapor. There exists a set of small areas giving a boost to local burning process. These areas configure clusters with very irregular structure and could be described by fractal dimension D. So in some cases inflaming frontier should pass a very long path in between different areas with very different properties.

Computer simulation shows that flame propagation time from one point to another one depends on the shortest path length between two points. We show that this length significantly increases at the percolation threshold. So lengths of paths could explain an ignition timeout and its statistical properties. Also in some cases path does not exist between two points. This means that some areas are inaccessible by the flame. So completeness of combustion is attributable to a balance of accessible and inaccessible areas in a percolation system. We performed 3D computer simulation and theoretical researches in order to find out other properties and features of clusters and surfaces important for combustion theory.

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Ab initio study of magnesium surface oxidation

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We have performed ab initio study of magnesium surface oxidation based on density functional theory methods [1] in general gradient approximation (GGA) level with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [2]. Numerical calculations have been done with CRYSTAL14 program package [3] exploring modified Gaussian-type DZVP basis sets for magnesium and oxygen atoms from article [4]. Using super-cell approach we found magnesium surface energies to be in the range of 39 – 64 meV/ Å^2 for different crystallographic planes with Miller's indices (001), (100) and (110). The electron work functions found to be in the range 2.40-2.75 eV that is a little smaller of experimental value for (001) plane – 3.84 eV [5]. As we hope, the difference should be vanished after inclusion of ghost atom layer in the modeling super-cell. We have obtained good agreement with experimental data for calculated inter-layer distances for first three layers near the surface. Obtained values of oxygen adsorption energies per oxygen atom are in a good agreement with previous study with VASP program package [6], 4.9-5.1 eV. It was shown that energy profile of oxygen atom along the line perpendicular magnesium surface (001) has series of peaks which values are 0.5-1.0 eV. We have found that energy shifts of 2p electron in magnesium atoms near the surface are in the range 0.1-1.0 eV depending on oxygen density.

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Rate constants calculations of the CH_2 + CH_2CO reactions in triplet and singlet states by ab initio methods

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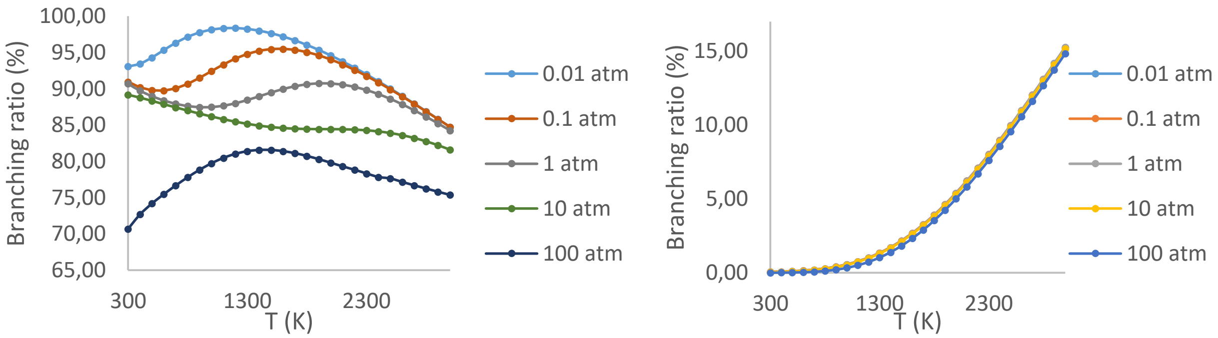
A variety of oxygen-containing compounds, such as alcohols, aldehydes, ketones, and others, are often formed in combustion flames. One of the simplest and yet important species produced in burning of hydrocarbon fuels is ketene. Mechanism and rate constants of reactions of ketene with methylene radical in triplet and singlet states were characterized through ab initio calculations of the PES combined with RRKM-ME calculations. The reactions have been shown to proceed through four main channels for triplet methylene and three channels for singlet methylene. The most important channels of reaction of ketene with triplet methylene lead to formation HCCO + CH_3 and C_2H_4 + CO products. The alternative reaction pathways, in particular, the formation of allene + O and the production of acetylene and formaldehyde are shown to be insignificant even at the highest temperatures considered. The predominant products of the reaction of ketene with singlet methylene are C_2H_4 + CO. The formation of these products proceeds through a collisionally stabilized intermediate CH_3CHCO. The calculated rate constants at different pressures were fitted by the modified Arrhenius expressions, which are proposed for kinetic modeling of ketene reactions in combustion. The results show that the rate constants to produce C_2H_4 + CO exhibit significant pressure dependence, whereas those to form HCCO + CH_3 are independent of pressure.



a *b*

Fig 1. Branching ratios of different reaction channels calculated at different pressure: CO+$^1C_2H_4$ (*a*); H_2CC+^1H_2CO (*b*).

Quantum chemical study of the reactions of H_2 and H_2O molecules with $N_2(A^3\Sigma_u^+)$

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Molecular nitrogen excited to the lowest triplet electronic state $A^3\Sigma_u^+$ is quite interesting species for the following reasons: (*i*) it has rather high radiative lifetime (≈ 2 s) and (*ii*) its electronic excitation energy (T_e=6.22 eV) exceeds the energy barriers for many endoergic chemical reactions that indicates a potentially high reactivity [1]. Elementary reactions with $N_2(A^3\Sigma_u^+)$ molecules participate in the nitrogen and nitrogen-oxygen discharge plasma chemistry, play an important role in the atmospheres of different planets and in high-enthalpy flows [2-4]. The reactions of $N_2(A^3\Sigma_u^+)$ that can be easily produced in a specially arranged electric discharge with small H_nO_m species are also of special interest because of their possible crucial role for plasma-assisted combustion and plasma-chemical fuel reforming [5].

Comprehensive quantum chemical analysis with the usage of the second-order perturbation multireference XMCQDPT2 [6] approach was carried out to study the kinetic processes in the $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ systems. The energetically favorable reaction pathways were revealed based on the exploration of potential energy surfaces. It was shown that the reactions $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ occur with small activation barriers and, primarily, lead to the formation of N_2H + H and N_2H + OH products, respectively. Further, the interaction of these species could give rise the ground state $N_2(X\,^1\Sigma_g^+)$ and H_2 (or H_2O) products, however, the estimations, based on RRKM theory and dynamic reaction coordinate calculations, exhibited that the $N_2(A^3\Sigma_u^+)+H_2$ and $N_2(A^3\Sigma_u^+)+H_2O$ reactions lead to the $N_2(A^3\Sigma_u^+)$ dissociative quenching predominately. Appropriate rate constants for revealed reaction channels were estimated by using a canonical variational theory taking into account the tunneling and the effects of vibrational anharmonicity of transitions states and reactants. It was demonstrated that these rate constants are in reasonable agreement with known experimental data (see [7]). Besides, the obtained thermally equilibrium rate constants were partitioned into the state-specific rate coefficients to compare with measurements available in the literature [7, 8].

This work was supported by the Russian Foundation for Basic Research (grants Nos. 18-38-00365 and 18-31-00140).

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Study of a dielectric barrier discharge burner for plasma assisted combustion

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Low temperature nonequilibrium plasma is an efficient tool for speeding up chemical processes relative to combustion, and extensive studies of plasma ignition and plasma-assisted combustion are under way at present [1,2]. Dielectric barrier discharge (DBD) is of special interest in this field, because of its design simplicity and ability to be easily integrated in different flow configurations.

The aim of this work was to obtain experimental data to verify numerical modeling of the DBD for initiation of combustion.

In the course of this work a diffuse dielectric barrier discharge was obtained in a coaxial burner. The burner was made out of a glass tube 16 mm inner diameter and 1.5 mm wall thickness. There was a 1 mm gap between the inner anodized aluminum electrode and the tube wall. An outer electrode was a fine steel mesh 5 mm long along the tube wall, providing a homogeneous discharge in air [3] and CH4:Air mixtures. The discharge power was on the order of 10 W. Due to the small discharge gap ignition did not occur.

Experiments were carried out for lean and stoichiometric CH4:Air mixtures. Ozone number densities, produced in the discharge were measured, and in dry air they were on the order of 1016 cm^{-3}, exhibiting a twofold decrease in CH4:Air mixtures.

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Mechanism of Methyl Methacrylate Polymerization in the presence of the initiating system "azobisisobutyronitrile-ferrocene"

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In order to suppress the gel effect in the radical polymerization of methyl methacrylate (MMA), experimental studies on the use of metallocenes (MC) are being intensively carried out. However, the mechanism of the polymerization reactions in the presence of an initiator and a real MC is not set, as well as the kinetic parameters of these reactions. A scheme of radical coordination polymerization (RCP) [1] is proposed, and the process proceeds by the reactions of Organometallic Mediated Radical Polymerization (OMRP) [2]. In [3], an algorithm for simulating the process of radical polymerization of MMA in the presence of real initiators by the Monte Carlo method was developed and programmed.

The purpose of this work was to determine the mechanism of polymerization of MMA in the presence of azobisisobutyronitrile (AIBN) and ferrocene (FC).

The results of modeling the polymerization of MMA in the presence of the initiator of AIBN and FC according to the schemes of RCP and RCP-OMRP coincided, it was impossible to select with certainty the type of MMA polymerization mechanism. Therefore, in order to identify the mechanism of the process, experimental data on the polymerization of MMA in the presence of a macroinitiator were additionally used [4]. In this case, when solving the inverse problem, it was possible to adequately describe the conversion of the monomer in the simulation of the process according to the RCP-OMRP scheme.

Thus, by simulation by the Monte Carlo method, it has been shown that in the polymerization of MMA in the presence of the initiating system of AIBN-FC, both RCP and OMRP reactions occur.

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2D modeling of V-shaped turbulent methane-air flame

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A methodology for simulating of turbulent combustion in a two-dimensional formulation is presented in the work. A distinctive feature of this methodology, based on the URANS approach, is the assignment of the non-stationary profiles of velocity components at the input to the computational domain. These profiles are determined wiyh the use of the algorithm of artificial turbulence [1] that specifies the necessary values of both the intensity of pulsations and the integral scale of turbulence in the incoming flow. In technical terms, the User Defined Function (UDF), provided in the Fluent program, is used for this purpose. Quasilaminar combustion model, k-ε realizable turbulence model and the kinetic mechanism DRM-19, describing combustion of methane in air and including 84 reactions for 21 species, are used for calculations. The results of modeling has shown that this methodology describes with good accuracy the angle of inclination of the V-shaped flame front observed in the experiment [2] and its broadening depending on the distance from the flame stabilization point.

Based on the developed methodology, the influence of various parameters of the incoming flow on the characteristics of the V-shaped flame was analyzed.

— With an increase in the intensity of the velocity pulsations, the turbulent burning velocity and the angle of inclination of the flame front increase (with an increase in the intensity of the velocity pulsations from 6.25 to 14%, the turbulent combustion rate increases by 36% and the angle of the flame front grows by 30%).

— The integral scale of turbulence significantly affects the change in the angle of flame front broadening and weakly affects the turbulent burning rate (with an increase in the integral scale of turbulence by 2.5 times, the angle of front broadening increases by a factor of 1.8 and the turbulent burning rate decreases no more than than by 2%).

— The completeness of mixing of methane with air (the intensity of pulsations of the fuel mole fraction in the range 0–6% and the integral scale of pulsations of the fuel mole fraction in the range 0–5 mm) has small effect on the characteristics of turbulent combustion.

— The introduction into the flow of a separating plate oriented along the incoming stream leads to a decrease in both the turbulent burning rate (by 12%) and the angle of front broadening (by a factor of 3).

The work was supported by the Russian Foundation for Basic Research (projects no.17-08-01423).

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Measurements of rate constants for $O_2(b^1\Sigma)$ quenching by CH_4, NO, N_2O at temperatures of 300−800 K

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Electronically excited oxygen has an important place in the kinetic schemes of the processes taking place in the atmosphere, in the active medium of an oxygen-iodine laser, and in plasma-assisted combustion. Over the past decades, a large amount of data on the rate constants of quenching $O_2(b)$ on a large number of collision partners (http://iupac.pole-ether.fr/) has been accumulated. However, they mostly refer to the results of measurements at room temperature. The temperature dependences of the rate constants for the relaxation of $O_2(b)$ are very meager.

In this paper, rate constants for the quenching of $O_2(b^1\Sigma_g^+)$ by collisions with N_2O, NO and CH_4 have been determined in the temperature range from 297 to 800 K, by the laser-induced fluorescence method. $O_2(b^1\Sigma_g^+)$ was excited by pulses from a tunable dye laser, and the deactivation kinetics were followed via observing the temporal behavior of the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ fluorescence. From the analysis of experimental results, the following temperature dependencies of the quenching rate constants by these gases were obtained, and could be represented by the expressions: $k_{CH4}=(3.54\pm0.4)\times10^{-18}\times T^{1.5}\times exp\left(\frac{-220\pm24}{T}\right)$, $k_{N2O}=(2.63\pm0.14)\times10^{-18}\times T^{1.5}\times exp\left(\frac{590\pm26}{T}\right)$, and $k_{NO}=exp(-56.8\pm0.05)\times T^{3.8}\times exp\left(\frac{1250\pm28}{T}\right)$ cm^3 $molecule^{-1}$ s^{-1}. All of the rate constants measured at room temperature were found to be in good agreement with previously reported values.

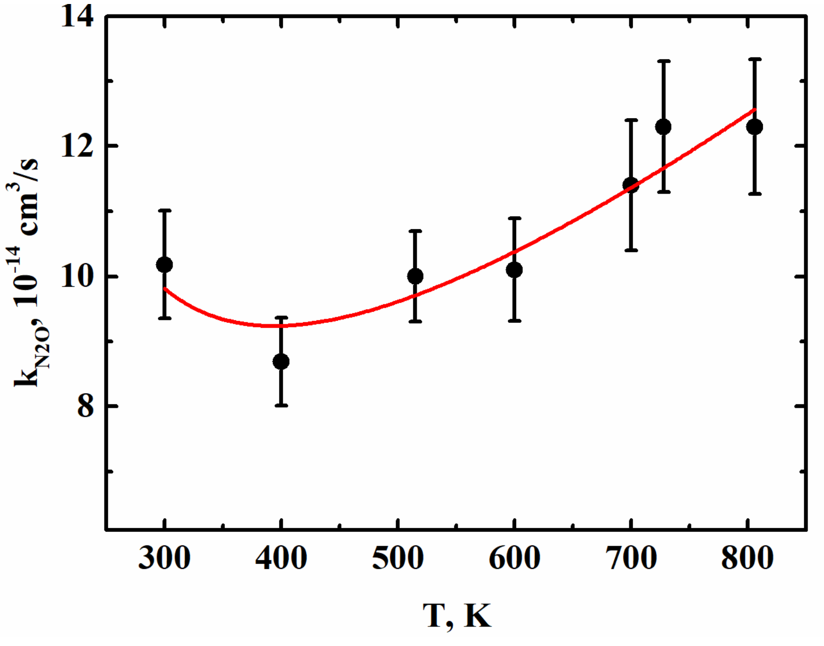

Figure 1. Temperature dependence of quenching rates of O_2 by N_2O.

Ozone recovery in the presence of CO

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The temporal profiles of ozone number densities after pulsed UV laser photolysis in a gas mixture O_2-O_3-Ar-CO obtained by time-resolved absorption spectroscopy was presented. The experimental results demonstrated the dominance of the stabilization channel over the reactive one for the reaction of O_3 (υ) with CO. The rate constants for the processes $O_3(\upsilon) + CO \rightarrow O_3 + CO$ was obtained to be $(1.5\pm0.2) \times 10^{-13}$ cm^3/s using kinetics modeling of experimental data.

There are some experimental data showing the high reactive activity of vibrationally excited ozone $O_3(\upsilon)$ [1–4] which, in the presence of O atoms and O_2 molecule excess (fuel–air mixtures, upper atmosphere layers, oxygen-containing plasma, and others), are efficiently generated in the recombination process $O + O_2 + M \leftrightarrow O_3(\upsilon) + M$, (1), where M is the third body.

The reaction of vibrationally excited ozone with carbon monoxide at moderate temperatures can proceed in two possible channels: reaction channel $O_3(\upsilon) + CO \rightarrow CO_2 + O_2$, (2),

stabilization channel $O_3(\upsilon) + CO \rightarrow O_3 + CO$. (3)

In this work, we present the time dependences of the ozone concentration in the region after photolysis as a function of the carbon monoxide content in the O_2-O_3-Ar-CO initial mixture, measured using pulsed laser equipment and time-resolved emission spectroscopy.

Figure 2 shows the typical time dependences of the ozone concentration after laser photolysis of mixture O_2-O_3-Ar-CO at a wavelength of 266 nm for specific pulse energy E = 70 mJ/cm^2, total gas pressure P_{tot} = 720 Torr, oxygen pressure P_{O2} = 180 Torr, gas mixture temperature T = 300 K, and initial ozone pressure P_{O3} = 0.85 Torr.

Kinetic modeling of processes in the photolysis cell during experiments was performed. The best agreement with experimental data was achieved at the process (3) rate constant of $(1.5 \pm 0.2)\ 10^{-13}$ cm^3/s.

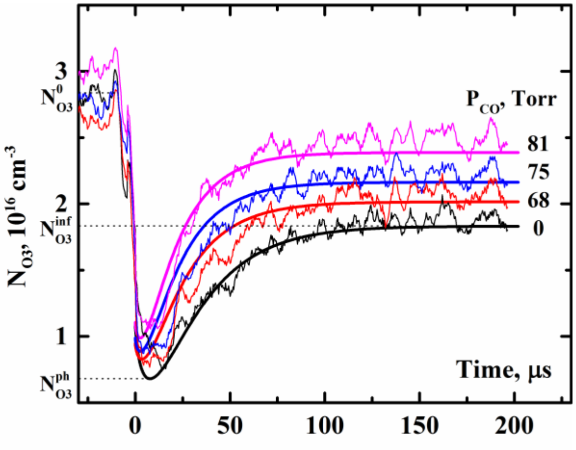

Figure 1 – Time profiles of the O_3 concentration at E = 70 mJ/cm^2, P_{tot} = 720 Torr, P_{O2} = 180 Torr, T = 300 K, and various CO pressures. Smooth curves are time profiles calculated by kinetic modeling.

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The impact of non-stationary electric field on homogeneous hydrocarbon flames

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It is known that hydrocarbon flames are sensitive to external electric field. This is due to reactions of chemiionization when burning [1], and in the zone of reaction is the high concentration of charges (10^{12} sm^{-3}). The carrier of negative charge are electrons, the carrier of positive charge are positive ions (for example, H_3O^+). The large difference in mobility of charges leads to hydrodynamic imbalance when applying an electric field to the flame. From the literature [2,3] it follows that can be implemented three different mechanism of field effect on the combustion: ohmic heating, the change in the kinetics of the reactions and electrohydrodynamically impact. For weak electric fields ($E < 10^3$ V/sm^2) the first two mechanisms do not play a significant role.

The paper presents data showing, then for pre-mixed hydrocarbon-air mixtures the influence of external electric field on the combustion front is localized in the area of chemical reactions and leads to a change in the degree of stretching of the flame. Experimental results are consistent with calculations performed by M. Scobina for homogeneous propan-air flame, in an electric field of axial symmetry.

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Mathematical modeling of burning surface in parallel flow of oxidant

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The condensed fuel burning in an oxidant gas flow occur in investigations of various processes, for example: burning of fuel in hybrid engines; interaction of hypersonic flying vehicles with the atmosphere; exo- and endothermic reactions in chemical engineering; spreading of flame over the fuel surface, the origination of explosions and the propagation of detonation in unmixed two-phase systems of the gas-film type.

For all of the above processes it is necessary to calculate the heat and mass transfer between a chemically reacting gas layer and a reacting, melting, subliming, or otherwise destructing, surface. The methods of investigations in this field are very complicated, because the motion of a gas is governed not only by force and temperature fields but also by chemical processes depending in turn on velocity and temperature fields. This requires a conjugate solution of dynamic, thermal and diffusional problems with allowance for the equations of chemical kinetics, multi-component diffusion and variability of thermophysical properties of a medium with distributed parameters. The process incorporates the thermochemical destruction of the surface when vapours of fuel substances, comprising the surface material, diffuse into a boundary layer and react chemically with the external flow.

Of special interest is the flame propagation in microgravity. The air flows in the atmosphere of the space station and the heat flows in the inner coating materials exert primary control over this process. An investigation of material flammability is especially important to space flight safety, but this topic is not completely understood. To study of the combustion process in microgravity NASA with the European Space Agency and the group of experts, which includes scientists from Russia, conducted a series of experiments under the name «Saffire». The experimental setup for modeling the ignition and flame propagation over the material sample was created and placed in a specialized block «Cygnus». After that Cygnus was mounted in the rocket. In space Cygnus separated from the main part, and the experiment started. The experimental data were transferred to the NASA center, and the block «Cygnus» burned in the Earth atmosphere.

The present work investigates the burning of the flat surface of fuel in an oxidant flow.

Application of ARAS and MRAS methods to study the kinetics of CF_2 radical formation in pyrolysis of C_3F_7I

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A variety of halogenated hydrocarbons are widely used in various industries. The effectiveness of suppressing combustion by these substances is primarily determined by the processes of chemical inhibition of chain reactions of combustion by the products of their pyrolysis. At the moment, bromine-containing freons [13B1 (CF3Br), 114B2 (C2F4Br2), and 12B1 (CF2ClBr)] remain the most common fire-extinguishing substances. However, awareness of the need to protect the ozone layer in the Earth’s atmosphere and the decisions taken by the world community to stop the production of ozone-depleting substances stimulated the search for new, efficient, and environmentally pure fire extinguishing agents. Among the most promising additives, another group of halocarbons, iodine-containing freons, such as CF3I and C3F7I, have become of interest. These halocarbons are characterized by suitable physical properties, as well as being completely ozone-friendly. However, for industrial applications, it is necessary to study the inhibitory and toxic properties of these compounds. Moreover, it is necessary to study the kinetics of dissociation of both the primary substance and its secondary components.

In this work the C3F7I + Ar reaction was studied by sequential application of atomic and molecular resonance absorption spectroscopy (ARAS and MRAS) using resonance line of iodine atom I at 183.04 nm and CF2 radical band at 251.9 nm behind reflected shock waves. As a source of resonance radiation of iodine atoms and CF2 radical, a microwave discharge lamp representing a flowing quartz tube was used, through which a pre-prepared mixtures of 0.4% CF3I in He or 1%CF3H+He were pumped. The experiments were performed at the temperatures from 800 to 1500 K and pressures of 0.6 to 8.3 bar. The initial concentration of C3F7I in Ar was varied from 1 to 1000 ppm.

As a result of the experiments the time profiles of CF_2 and I concentration, forming at C3F7I dissociation were obtained. From these experimental data the temperature dependences of the rate constants of CF_2 and I formation and their activation energy were determined. Moreover, it was found that at a temperature at least below 1500K and a pressure above 0.6 bar, the resulting rate constant C3F7I + Ar = C3F7 + I + Ar is in the high-pressure range. These new data allow presenting in detail the kinetic mechanism of C3F7I decomposition in a wide range of temperatures and pressures.

Plasma vortex reactor for production of heat energy and hydrogen

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The problem of creating efficient energy sources, including alternative ones, has become increasingly noticeable. One of the most promising technologies is the use of plasma vortex reactor (PVR), which can be both heat and hydrogen generator. The efficiency of hydrogen and heat production obviously increases in the vortex flows, which carried their downstream. At the same time, the structure of the flow is strongly influenced by a number of factors: the organization of the input and output of the mixture components, the shape and arrangement of the discharge electrodes, swirl number, the mass flow of components. Here, a numerical simulation of the structure of the gasdynamic and thermal fields formed in a 3D unsteady viscous turbulent vortex flow of pure argon in a PVR duct under experimental conditions is carried out for different configurations of electrodes system and source localization. The spatial distributions of the source power, duct geometry and electrodes configuration were chosen phenomenologically.

The no-slip velocity and fixed temperature conditions were imposed along the tube and electrode surfaces. At the duct inlet and outlet, fixed mass flux conditions were used. At the outlet, we imposed the boundary conditions with the static pressure equal to the atmosphere pressure. To closing of the Navier-Stockes system the Spalart-Allmaras model with option of curvature correction was used. Pressure-velocity coupling schemes were tested and gave equal results. For spatial discretization of density, momentum, energy and turbulent quantities, a second-order upwind scheme is applied. The program package solves governing equations using the finite volumes method. The computational grids consisted of about 4·106 hexahedral cells. Three different types of electrodes are considered in the simulation: a thick electrode, a thin electrode, and a pipe-like electrode.

Largely, the structure of the flow is determined by the paraxial counterflow zone, typical for strongly swirled flows [1,2]. Between the electrodes, a stagnation zone is formed. Eventually, it leads to the zone overheating. At the combination of thick anode and pipe-like cathode the pressure gradient along the symmetry axis draws out the hot gas from the interelectrode area. The counterflow zone weakens, but overheating is also quite significant, which lead to rising of radiative loss through the side walls. Optimum is the combination of a thin anode and a hollow cathode located at the output of the PVR. In this case, heat is effectively carried away upstream, so that the overheating zone is not formed. A qualitative agreement between the simulation and the experimental data for pure argon has been obtained.

The study was supported in part by the Ministry of education and science of Russia by State assignment to educational and research institutions under project 3.1158.2017/4.6, 14.Y26.31.0020 and by RFBR under grant 16-41-630591.

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Modelling of small gas turbine engine CO emissions based on reactor network

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Thanks to the development of the computational power and sources it was possible, across the years, to simulate in greater detail the combustion process that occurs in reality by the using and the combination of different models for the chemical-kinetic and turbulence phenomena. The main point of focus is the prediction of the pollutant emissions of these combustors, like NOx and CO, and also the concentration of other species, like UHC, responsible of particulate emissions.

The combustor chamber of the small-scale turbojet SR-30 engine (Turbine Technologies) is here analyzed. The experimental values of pollutant emissions measured at different regimes of rotational speed are compared with numerical results obtained using different CFD methods.

The interaction between turbulence and chemistry for the air/fuel mixture is the partially-premixed combustion, where the species are not perfectly mixed before combustion. A first approach here used is the Flamelet Generated Manifold (FGM), that is a chemistry reduction technique based on the analysis of the flame front and the resolution of the structure of flame stretch. The FGM, combined with the Probability Density Function (PDF) method, responsible of the stochastic description of the turbulence-chemistry interaction, that totally replaces the deterministic one, allows to evaluate NOx emissions, described by the thermal mechanism of Zeldovich. In the present study several parameters (i.e. the mesh size, the approaches used to evaluate the concentration of O and OH, and the dimension of the mean diameter of the fuel particles distributions at the injector) are changed to perform the simulations. When a proper mesh size is selected, the fuel particles size appears to be the parameter that more affects the values of NOx and allows to have a good match of numerical values and experimental data.

A different approach, i.e. the Reactor Network method (RN), instead is used to evaluate CO emissions. This method is based on a subdivision of the combustor volume into a given number of reactors: in this work all the reactors are perfectly stirred ones. Each reactor is characterized by a specific fuel fraction and a proper residence time. Typically, increasing the number of reactors allows to describe much better the experimental results.

The flow field during these simulations is defined by the RANS equations that describe the mean flow field, avoiding the so high computational cost of Direct Numerical Simulations (DNS). Finally Large Eddy Simulation (LES) is considered as a further method to obtain more accurate results, to be compared to the ones previously obtained.

This work was supported by the Ministry of education and science of the Russian Federation in the framework of the implementation of the Program "Research and development on priority directions of scientific-technological complex of Russia for 2014-2020" (RFMEFI58716X0033).

Auto-ignition problem titanium of oxygen and possible ways of solving

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Noting the negative feature of titanium alloys spontaneous combustion in an oxygen environment, which prevents their widespread use in autoclave equipment operating with oxygen. The basic tenets of the theory of metals in fire destruction with an explanation of the anomalous ability of titanium to spontaneous combustion in oxygen. Concluded that the exclusion of self-ignition of titanium alloys in an oxygen environment autoclaves can be achieved developing technical measures to prevent the heating of the potential sites of friction titanium structures to auto-ignition temperature T * alloys at these partial pressures of gaseous reactants.

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Scientific and Practical Edition

International Conference
on Combustion Physics and Chemistry

(Samara, Russian Federation, July 24-28, 2018)

Technical program and Book of abstracts

Edited by A.M. Mebel & V.N. Azyazov

Подписано в печать 10.07.2018
Формат 60 x 84/8. Бумага ксероксная. Печать оперативная.
Объем – 14,5 усл. печ. л. Тираж 120 экз. Заказ № 138

Отпечатано в типографии издательства «Инсома-пресс»
443080, г. Самара, ул. Санфировой, 110А, оф. 22А,
Тел. 222-92-40, E-mail: insoma@bk.ru