ComPhysChem

2d International Conference on Physics and Chemistry of Combustion and Processes in Extreme Environments

TECHNICAL PROGRAM
and
BOOK OF ABSTRACTS

Samara, Russian Federation,
July 12-16, 2022

International Conference on Physics and Chemistry
of Combustion and Processes in Extreme Environments
(Samara, Russian Federation, July 12-16, 2022)

TECHNICAL PROGRAM
AND
BOOK OF ABSTRACTS

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А35

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

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This collection presents the program and abstracts of presentations at the International Conference on Physics and Chemistry of Combustion and Processes in Extreme Environments (ComPhysChem’22) held at Samara on Jul. 12-16, 2022. The presentations covered a broad range of fundamental and applied areas in physics and chemistry of combustion and processes in extreme environments including fundamental physical-chemical processes, reaction kinetics and dynamics in extreme environments including astrochemistry and astrobiology, quantum chemical studies of potential energy surfaces of chemical reactions in flames and in interstellar media, 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 Ministry of Education and Science of the Russian Federation under Grant No. 075-15-2021-597.

Intended for graduate students in the areas of physical chemistry, chemical physics, combustion science and technology, astrochemistry, 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 Physics and Chemistry of Combustion and Processes in Extreme Environments** (**ComPhysChem'22**). 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, a Laboratory on Physics and Chemistry of Combustion was established at Samara National Research University within a megagrant from the Ministry of Science and Higher Education of the Russian Federation 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 laboratory 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 including active forms of oxygen, 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 high-temperature microreactor has been developed with universal photoionization mass spectrometric (PIMS) detection of products of chemical reactions and with distinction of different isomers based on their photoionization cross sections. Another major research organization behind the ComPhysChem'22 is the Center for Laboratory Astrophysics (CLA) established at the Samara Branch of Lebedev Physical Institute of Russian Academy of Sciences in collaboration with University of Hawaii, Manoa. CLA is a new multidisciplinary research organization aimed at understanding of evolution of complex organic molecules in the interstellar medium. The center is funded by a megagrant No. 075-15-2021-597 "The origin and evolution of organic molecules in our Galaxy".

We have organized this **ComPhysChem'22** 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'22** include

- Fundamental physical-chemical processes in combustion.
- Reaction kinetics and dynamics in extreme environments including astrochemistry and astrobiology
- 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.
- 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.

With our very best wishes,
Valery N. Azyazov, on behalf of the Organizing Committee

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Conference Venue: ComPhysChem'22 is held in the "Univer Studia" of the Samara University. Address: 151, Molodogvardeyskaya str., Samara, 443001, Russia.

TECHNICAL PROGRAM

Samara time UTC +4	12 July Tuesday	13 July Wednesday	14 July Thursday	15 July Friday	Samara time UTC+4	16 July
09.30-10.00	**Registration**	**Feldman** (invited)	**Shmakov** (invited)	**Bykov** (online) (invited)	09.30-10.10	DEPARTURE
10.00-10.20	**Opening remarks**					
		Vasyunin (invited)	**Kolobov** (invited)	**Antonov I** (online)	10.10-10.30	
10.20-11.00	**Smirnov** (invited)					
				Zasimov (online)	10.30-10.50	
		Wiebe (invited)	Coffe break	**Volkova** (online)	10.50-11.10	
11.00-11.20	**Knyazkov** (invited)					
		Coffe break	**Kasymov**	**Perminov** (online)	11.10-11.30	
11.20-11.40	Coffe break					
		Medvedkov	**Ponomarev**	Coffe break	11.30-11.50	
11.40-12.00	**Kobtsev**					
		Murga	**Bolshova**	**Osipova**	11.50-12.10	
12.00-12.20	**Dmitriev**					
		Labutin	**Antonov D**	**Gorn**	12.10-12.30	
12.20-12.40	**Kislov**					
		Zakuskin	**Lebedev**	**Glushkov**	12.30-12.50	
12.40-13.00	**Krikunova A.**					
		Krasnoukhov	**Lunch**	**Lunch**	12.50-14.30	
13.00-13.20	**Kostritsa**					
		Lunch				
13.20-14.50	**Lunch**					
				Vershinina	14.30-14.50	
14.50-15.10	**Porfiriev** (invited)	**Gubernov** (invited)	**15.30-19.30** **Ferry trip along the Volga River (4 hours)** **Boarding 15.00**	**Yanovsky**	14.50-15.10	
15.10-15.30	**Mikhalchenko**	**Mislavskii**		**Nikolayev**	15.10-15.30	
15.30-15.50	**Nikitin**	**Salgansky**		**Closing remarks**	15.30 15.45	
15.50-16.10	**Zambalov**	**Karandashev**		**Excursion with a visit to the Bunker (3 hours)**	16.00-19.00	
16.10-16.30	**Kiselev**	**Semenikhin**				
16.30-16.50	Coffe break	Coffe break				
16.50-17.10	**Yakovlev**	**Poster** 17.00 -19.00				
17.10-17.30	**Minekhanova**					
17.30-17.50	**Gaidukova**					
17.50-18.10	**Belova**					
18.30-20.30	Welcome Party					
20.00-23.30			**Conference Dinner** (is not included in the conference fee)			

Address: 151, Molodogvardeyskaya str., Samara, 443001, Russia, “Univer Studia” of the Samara University.

12 July, Tuesday (Samara time UTC +4)

10.00-10.20 **Opening and Welcome Remarks**

Session 1.1
Chair: Vladimir V. Gubernov (P.N. Lebedev Physical Institute of RAS, Moscow)

10.20-11.00 Nickolay N.Smirnov (Moscow M.V.Lomonosov State University, FSC “Scientific Research Institute for System Analysis of Russian Academy of Sciences”, Moscow) *(Invited)*
Ignition, combustion and detonation onset in non-uniform dispersed fuel-air mixtures

11.00-11.20 Denis A. Knyazkov, A.V. Cherepanov, I.E. Gerasimov, T.A. Bolshova, V.G. Kiselev, A.G. Shmakov (Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia) *(Invited)*
Positive ion chemistry in flames: mass-spectrometric and kinetic modeling study

11.20-11.40 **Coffee Break**

Session 1.2
Chair: Andrey G. Shmakov (Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novoibirsk)

11.40-12.00 Vitaly D. Kobtsev[1], D.N. Kozlov[1,2], S.A. Kostritsa[1], S.N. Orlov[1,2], V.V. Smirnov[1,2], S.Yu. Volkov[1,2] ([1] Central Institute of Aviation Motors, [2] Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia)
Simultaneous determination of time and length scales of local temperature fluctuations in a turbulent flame by using coherent anti-Stokes Raman spectroscopy

12.00-12.20 Artëm Dmitriev[1,2], K. Osipova[1,2], I. Gerasimov[2], D. Knyazkov[1,2], A. Shmakov[1,2] ([1] Voevodsky Institute of Chemical Kinetics and Combustion, [2]Novosibirsk State University, Novosibirsk, Russia)
Molecular beam mass spectrometric study of the laminar flame structure of ethyl levulinate

12.20-12.40 Vladimir Kislov, Yu. Tsvetkova, A. Zaichenko, M. Tsvetkov, E. Salgansky, E. Pilipenko, M. Salganskaya, D. Podlesniy (Institute of Problems of Chemical Physics, Chernogolovka, Russia)
The effect of the addition of solid calcium-based sorbents on the absorption of sulfur during the thermal disposal of car tires

12.40-13.00 Anastasiia Krikunova, D. Lunin (Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia)
Stability of premixed methane-air swirled flame

13.00-13.20 K.O. Aiyyzhya, E.V. Barmina, V.D. Kobtsev, D.N. Kozlov, Sergey A. Kostritsa, S.N. Orlov, S.Yu. Volkov, A.M. Saveliev, V.V. Smirnov, G.A. Shafeev (Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia)
CARS and chemiluminescence diagnostics of a diffusion flame of boron nanoparticles in isopropanol with oxygen

13.20-14.50 LUNCH

Session 1.3
Chair: Andrey V. Kolobov (P.N. Lebedev Physical Institute of RAS, Moscow)

14.50-15.10 Denis P. Porfiriev[1,2], A.M. Mebel[3], V.N. Azyazov[1] ([1] Lebedev Physical Institute, Samara Branch, [2]Samara National Research University, Samara, Russia, [3]Florida International University, Miami, Florida, USA) *(invited)*
Decomposition of 1-propenol: theoretical investigation

15.10-15.30 Elena Mikhalchenko, V. Nikitin, (Federal Science Center “Scientific Research Institute for System Analysis of Russian Academy of Sciences”, Moscow)
Numerical simulation of a rotating detonation wave engine for various concentrations of combustible mixture

15.30-15.50 Valeriy Nikitin, E. Mikhalchenko (Federal Science Center “Scientific Research Institute for System Analysis of Russian Academy of Sciences”, Moscow)
Using an unsaturated hydrocarbon as mitigator of developed detonation in hydrogen/syngas/air

15.50-16.10 Sergey Zambalov (Tomsk Scientific Center SB RAS)
Numerical simulation of syngas combustion in rotary engine

16.10-16.30 Vitaly G. Kiselev,[1,2,3] K.A. Monogarov,[3] N.V. Muravyev,[3] A.N. Pivkina[1,2] ([1] Institute of Chemical Kinetics and Combustion SB RAS, [2] Novosibirsk State University, Novosibirsk, Russia, [3]Semenov Federal Research Center for Chemical Physics RAS, Moscow, Russia)
Modern Predictive Quantum Chemical Calculations for Thermochemistry and Decomposition Kinetics of Energetic Materials

16.30-16.50 Coffee Break

Session 1.4
Chair: Denis P. Porfiriev (Samara National Research University, Lebedev Physical Institute of RAS, Samara Branch, Samara)

16.50-17.10 Igor Yakovlev (Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia)
Pore-scale numerical simulation of flame stabilization in two-layer porous burner

17.10-17.30 Y. Titova, Alsy Minekhanova, A. Amosov, D. Maidan, G. Belova (Samara State Technical University, Samara, Russia)
Preparation of highly dispersed ceramic nitride-carbide composition Si_3N_4–TiC by SHS method using halide salt and sodium azide

17.30-17.50 Olga Gaidukova[1], S. Misyura[2], P. Strizhak[1] ([1] National Research Tomsk Polytechnic University, Tomsk, Russia, [2] Kutateladze Institute of Thermophysics, Novosibirsk, Russia)
Study of the gas hydrate combustion initiation initial stage

17.50-18.10 Galina S. Belova, Yu.V. Titova, A.P. Amosov, D.A. Maidan, I.A. Uvarova (Samara State Technical University, Samara, Russia)
Exploring the possibility of synthesis of Si_3N_4-SiC highly dispersed ceramic nitride-carbide composition during combustion in Si–NaN_3–$(NH_4)_2SiF_6$–C system

13 July, Wednesday (Samara time UTC +4)

Session 2.1
Chair: Valery N. Azyazov (Lebedev Physical Institute of RAS, Samara Branch, Samara)

9.30-10.10 Vladimir I. Feldman (Lomonosov Moscow State University, Moscow, Russia)
Modeling of cold astrochemical processes through matrix isolation: extremely hot chemistry at extremely low temperatures

10.10-10.50 Anton I. Vasyunin[1], A. Punanova[1], M. Murga[2], G. Fedoseev[1], V. Krushinsky[1], M. Kiskin[1], N. Satonkin[1], V. Sokolova[1], ([1]Ural Feferal Institute, Chelyabinsk, [2]Institute of Astronomy of the RAS, Moscow, Russia)
Mechanisms of the formation of organic matter in protostellar objects

10.50-11.10 Dmitri Z. Wiebe (Institute of Astronomy of the RAS, Moscow, Russia)
Carbon dust life cycle in the Universe

11.10-11.30 Coffee Break

Session 2.2.
Chair: Vladimir I. Feldman (Lomonosov Moscow State University, Moscow)

11.30-11.50 Iakov A. Medvedkov[1,2], G.I. Tolstov[2], O.V. Kuznetsov[1], M.M. Evseev[1], V.N. Azyazov[1,2], ([1]Lebedev Physical Institute, Samara, Russia, [2]Samara university, Samara, Russia)
Launch of a new molecular beam machine

11.50-12.10 Maria Murga[1,2], D. Wiebe[1] ([1] Institute of astronomy of Russian academy of sciences, [2]Lomonosov State University, Moscow, Russia)
Relationship between polycyclic aromatic hydrocarbons, graphenes and fullerenes in the interstellar medium

12.10-12.30 Timur A. Labutin[1], A.S. Zakuskin[1], S.M. Zaytsev[1], A.A. Berezhnoy[2], A.M. Popov[1], E.A. Bormotova[1], A.V. Stolyarov[1] ([1]Department of Chemistry, Lomonosov Moscow State University, [2]Sternberg Astronomical Institute, Lomonosov Moscow State University, Moscow, Russia)
In search of equilibrium in laser-produced cloud: role of pressure, chemical quenching, and plasma expansion

12.30-12.50 Aleksandr Zakuskin, B. Beglaryan, A.M. Popov, T.A. Labutin (Lomonosov Moscow State University, Moscow, Russia)
Formation of CaO in laser plasma studied by emission and fluorescence spectroscopy

12.50-13.10 Vlad Krasnoukhov[1,2], M. Zagidullin[1], I. Zavershinskii[2] ([1]Lebedev Physical Institute, Samara Branch, [2] Samara National Research University, Samara, Russia)
Formation of two-ring PAHs in circumstellar envelopes of asymptotic giant-branch stars

13.10-14.50 LUNCH

Session 2.3
Chair: Dmitri Z. Wiebe (Institute of Astronomy of the RAS, Moscow)

14.50-15.10 A. Moroshkina[1], V. Mislavskii[1], Vladimir Gubernov[1], V. Bykov[2], U. Maas[2] ([1]P.N. Lebedev Physical Institute of Russian Academy of Sciences, Moscow, Russia, [2]Karlsruhe Institute of Technology, Karlsruhe, Germany) *Invited*
Investigation of diffusive-thermal oscillations of the burner stabilized CH_4-H_2*-air flames*

15.10-15.30 Vladimir Mislavskii, Vladimir Gubernov (P.N. Lebedev Physical Institute of Russian Academy of Sciences, Moscow, Russia)
Quenching rate constants of the nitrogen molecule

15.30-15.50 Eugene Salgansky[1], K. Borovik[1,2], S. Fetsov[1,2], N. Lutsenko[1,3], L. Yanovskiy[1,4] ([1]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, [2]Far Eastern Federal University, [3]Institute of Automation and Control Processes, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, [4] Moscow Aviation Institute, Moscow, Russia)
Modeling of gasification of complex solid porous polymer in low-temperature gas generator for high-speed flying vehicle

15.50-16.10 Iakov M. Karandashev, M.Yu. Malsagov, E.V. Mikhalchenko, V.F. Nikitin (Federal Science Center «Scientific Research Institute for System Analysis of Russian Academy of Sciences», Moscow, Russia)
Modeling the dynamics of hydrogen combustion using the neural network UNET

16.10-16.30 Aleksandr S. Semenikhin, A.S. Savchenkova, D.V. Idrisov, V.M. Anisimov, O.V. Kolomzarov, S.S. Matveev, I.V. Chechet, S.G. Matveev (Samara National Research University, Samara, Russia)
Hydrogen abstraction from o-xylene: A theoretical study

16.30-16.50 Coffee Break

17.00-19. 00 Poster Session

P1. Anastasia Moroshkina, V. Gubernov, V. Mislavskii (P.N. Lebedev Physical Institute of Russian Academy of Sciences, Moscow, Russia)
Measurement of activation energy of combustion of methane-air mixture using the thin-fiber pyrometry method

P2. N. Bystrov, A. Emelianov, A. Eremin, Pavel Yatsenko (Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia)
ARAS-study of the interaction of pentanol isomers with oxygen behind shock waves

P3. A. Drakon, A. Eremin, Mayya Korshunova, E. Mikheyeva (Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia)
Soot formation during ethylene pyrolysis with biofuels

P4. A.V. Drakon[1], A.V. Eremin[1], E.V. Gurentsov[1], E.S. Khodyko[1,2] and Roman N. Kolotushkin[1] ([1]Joint Institute for High Temperatures of the Russian Academy of Sciences, [2] Bauman Moscow State Technical University, Moscow, Russia)
Optical properties of soot formed under different conditions. Application to the effects of soot on climate

P5. Vladimir M. Kislov, Yu.Yu. Tsvetkova, A. Yu. Zaichenko, M.V. Tsvetkov, M.V. Salganskaya, D.N. Podlesniy, E.A. Salgansky (Institute of Problems of Chemical Physics of Russian Academy of Sciences, Chernogolovka, Russia)
Thermodynamic assessment of the absorption of acid gases by calcium-based sorbents during the gasification of solid fuels

P6. Vladimir Kislov, A. Zaichenko, M. Tsvetkov, M. Salganskaya, Y. Tsvetkova, E. Pilipenko (Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia)
The influence of the particle size of the gasified material on the absorption of sulfur during filtration combustion sulfur coal with marble

P7. Alexey Chichinin (Institute of Chemical Kinetics and Combustion, Siberian Branch RAS, Novosibirsk, Russia)
Potentials and energies of atoms and molecules inside C60 cage

P8. N. Smirnov[1], Valery Nikitin[1], E. Mikhalchenko[1], S. Park[2] ([1] Federal Science Center "Scientific Research Institute for System Analysis of Russian Academy of Sciences", Moscow, Russia [2]Korea Aerospace University, Goyang, Republic of Korea)
Investigation of a detonation chamber for possible use in perspective aerospace propulsion systems

P9. Lyuben Stamov, V. Tyurenkova, E. Mikhalchenko (Federal Science Center Scientific Research Institute for System Analysis of Russian Academy of Sciences, Moscow, Russia)
Numerical simulation of combustion processes in combustion chamber of hybrid solid fuel engine

P10. V.F. Nikitin[1,2], V.V. Tyurenkova [1,2], Maria N. Smirnova [1,2] ([1]Federal Science Center Scientific Research Institute for System Analysis of Russian Academy of Sciences, [2]Moscow M.V. Lomonosov State University Moscow, Russia)
Burning of two-phase fuel droplets in weightlessness

P11. Anna 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)
Tri phenyl phosphate decomposition through the reaction with H, CH_3*, OH radicals*

P12. Anna S. Savchenkova[1], A.S. Semenikhin[1], I.V. Chechet[1], V.Y. Abrashkin[1], M.Y. Anisimov[1], S.G. Matveev[1], A.A. Konnov[2], A.M. Mebel[3] ([1] Samara National Research University, Samara, Russia, [2] Lund University, Lund, Sweden,[3] Florida International University, USA)
C_3H_2 *oxidation by molecular oxygen: a theoretical study*

P13. Vlad Krasnoukhov[1,2], M. Zagidullin[2], A. Mebel[3] ([1] Lebedev Physical Institute, Samara Branch, [2] Samara National Research University, Samara, Russia, [3]Florida International University, Miami, Florida, USA)
Indenyl radical self-reaction study

P14. Aleksandr S. Semenikhin, K.D. Tsapenkov, S.S. Novichkova, A.D. Popov, M.M. Hernandez, D.V. Idrisov, I.A. Zubrilin, S.S. Matveev, I.V. Chechet, S.G. Matveev (Samara National Research University, Samara, Russia)
Choice of a kerosene surrogate for prediction of the emission of carcinogenic polycyclic aromatic hydrocarbons

P15. N. Bystrov, A. Emelianov, A. Eremin, Pavel Yatsenko (Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russia)
Experimental study and quantum-chemical calculation of C_3H_7I *initial dissociation kinetics and its thermodynamic properties in a wide temperature range*

P16. Aleksei Torbin[1,2], A. Chernyshov[1], P. Mikheyev[1] ([1]Lebedev Physical Institute, Samara Branch, [2] Samara National Research University, Samara, Russia)
NO_2 *production in a dielectric barrier discharge in air-*CH_4 *mixtures*

P 17. N. Khvatov[1], Aleksei Torbin[1,2], I. Medvedkov[1,2] ([1]Lebedev Physical Institute, Samara Branch, [2] Samara National Research University, Samara, Russia)
Threshold intensities for laser spark in pure O_2, N_2 *and* CH_4

P 18. Galina Nyashina, Pavel Strizhak (Heat and Mass Transfer Laboratory, National Research Tomsk Polytechnic University, Tomsk, Russia)
Pyrolysis of mixed and slurry fuels

P19. Kristina K. Paushkina, D.O. Glushkov, A.G. Nigay, A.O. Pleshko (National Research Tomsk Polytechnic University, Tomsk, Russia)
Micro-explosive dispersion of gel fuel composition ignited in a high-temperature air medium

P 20. Vitaly D. Kobtsev[1,2], D.N. Kozlov[2,1], S.A. Kostritsa[1,2], V.V. Smirnov[2,1], S.A. Torokhov[1], S.Yu. Volkov[2,1] ([1] Central Institute of Aviation Motors, [2] Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia)
Ignition dynamics of H2/CO/air mixture after photodissociation of O2 molecules by a UV laser pulse

P 21. Vladislav A. Novikov[1], A.P. Amosov[1], E.M. Kachkin[1], N.A. Kryukov[1], A.A. Titov[1] (Samara State Technical University, Samara, Russia)
Combustion modes during the synthesis of ZnO from aqueous solutions of zinc nitrate with various fuels

P 22. A.D. Rybakov, Alfia R. Luts, A.P. Amosov (Samara State Technical University, Samara, Russia)
Influence of carbon forms on the synthesis of highly dispersed titanium carbide by combustion in aluminum melt

P 23. Evgeny I. Latukhin, A.P. Amosov, E.R. Umerov, V.A. Novikov (Samara State Technical University, Samara, Russia)
Combustion of Ti-Si-C powder system with infiltration by molten copper

P 24. Emil R. Umerov, A.P. Amosov, E.I. Latukhin (Samara State Technical University, Samara, Russia)
Combustion synthesis of Ti_3SiC_2 *skeleton with infiltration by tin melt*

P 25. Vladislav Knestyapin, Igor Zavershinsky (Samara National Research University)
Numerical simulation of a swirling flow of water vapor with aluminum micro- and nanoparticles and a heating source

P 26. Pavel Pivovarov[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)
Fluorene formation in the reaction of phenyl and benzyl radicals theoretical study

P 27. Vladislav M. Anisimov[1], M.Y. Anisimov[1], N.I. Gurakov[1], O.V. Kolomzarov[1], A.S. Semenikhin[1], D.V. Radin[1], N.I. Fokin[2], D.S. Tarasov[2], A.A. Ivanovskii[2], N.O. Simin[2] ([1] Samara National Research University, Samara, Russia, [2] JSC Power Machines, St. Petersburg, Russia)
The Influence of Hydrogen Addition on the Combustor Thermal State

P 28. Nikita I. Gurakov, O.V. Kolomzarov, I.A. Zubrilin, D.V. Idrisov, A.S. Semenikhin, V.M. Anisimov, V.Y. Abrashkin, S.S. Matveev, S.G. Matveev (Samara National Research University, Samara, Russia)
Simulation of CO emission in the small-sized combustion chamber with liquid fuel injected by pressure swirl atomizer

P 29. Nikita I. Gurakov, S.S. Novichkova, V.M. Anisimov, A.S. Semenikhin, A.S. Savchenkova, S.S. Matveev, S.G. Matveev, N.O. Simin, A.A. Ivanovsky, D.S. Tarasov ([1] Samara National Research University, Samara, Russia, [2] JSC Power Machines, St. Petersburg, Russia)
Experimental-numerical investigation of hydrogen-methane combustion in model power plant combustion chamber

P 30. Danila V. Radin[1], S.S. Matveev[1], A.D. Popov[1], D.S. Tarasov[2], N.O. Simin[2], G.M. Makaryants[1], A.I. Safin[1], M.Yu. Anisimov[1] ([1] Samara National Research University, Samara, Russia, [2] JSC Power Machines, St. Petersburg, Russia)
Experimental study of the effect of hydrogen addition to fuel on combustion instability

P 31. Sergey S. Matveev[1], N.I. Gurakov[1], D.V. Idrisov[1], S.S. Novichkova[1], A.S. Savchenkova[1], D.S. Tarasov[2], N.I. Fokin[2], A.A. Ivanovskii[2] ([1] Samara National Research University, Samara, Russia, [2] JSC Power Machines, St. Petersburg, Russia)
Review of advances in the field of methane-hydrogen mixtures application in industrial gas turbines

P 32. Oleg V. Kolomzarov[1], V.Y. Abrashkin[1], N.I. Gurakov[1], D.V. Idrisov[1], A.S. Semenikhin[1], A.S. Savchenkova[1], D.V. Radin[1], I.V. Chechet[1], N.I. Fokin[2], N.O. Simin[2] ([1] Samara National Research University, Samara, [2] JSC Power Machines, St. Petersburg, Russia)
Experience in carrying out experimental studies for a dual-circuit burner using methane-hydrogen mixtures

P 33. Dmitry V. Idrisov[1], N.I. Gurakov[1], O.V. Kolomzarov[1], I.V. Chechet[1], V.M. Anisimov[1], S.S. Matveev[1], S.G. Matveev[1], N.I. Fokin[2], D.S. Tarasov[2], A.A. Ivanovskii[2], N.O. Simin[2] ([1] Samara National Research University, Samara, [2] JSC Power Machines, St. Petersburg, Russia)
Experimental and numerical study of lean flame blow-out during methane-hydrogen mixture combustion with a different hydrogen addition

P 34. Andrey V. Cherepanov[1,2], D.A. Knyazkov[1,2], V.G. Kiselev[1,2], I.E. Gerasimov[1], A.G. Shmakov[1,2] ([1]Voevodsky Institute of Chemical Kinetics and Combustion, [2]Novosibirsk State University, Novosibirsk, Russia)
Study of cation chemistry in ethylene flames

P 35. Lubov I. Krikunova[1,2], A.A. Nikolayev[1,2], D.P. Porfirev[1,2], A.M. Mebel[3] ([1] Lebedev Physical Institute, Samara, [2] Samara National Research University, Samara, Russia; [3]Florida International University, USA)
Potential energy surfaces for the Reaction of the Methylidyne Radical (CH $X^2\Pi$) with the Propionitrile C_2H_5CN ($X^1\Sigma^+$) Molecule

P 36. Mikhail Evseev, V. Azyazov (Lebedev Physical Institute, Samara, Russia)
Gas phase synthesis of [5]-helicene

P37. Oleg Kuznetsov, Valeriy Azyazov (Lebedev Physical Institute, Samara, Russia)
Formation mechanism of 1- and 2-propanols in reaction CO and C_2H_5

P 38. Kh.R Karimov, I.A. Saidov (Samarkand State University, Samarkand, Uzbekistan)
Thermodynamics of swelling of polymeric sorbents in aqueous solutions

P 39. A.V. Mokshin (Kazan Federal University, Kazan, Russia)
Alkai Plasmas: from equation of state to thermodynamics characteristics

14 July, Thursday (Samara time UTC +4)

Session 3.1
Chair: Nicolay N. Smirnov (Lomonosov State University, FSC “Scientific Research Institute for System Analysis of Russian Academy of Sciences”, Moscow)

9.30-10.10 Andrey Shmakov[1], A.Mebel[2], O.Korobeinichev[1], D.Porfiriev[3], K. Osipova[1], I. Gerasimov[1], D. Knyazkov[1], B. Yang[4] ([1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia, [2]Florida International University, Florida, USA, [3] Samara National Research University, Samara, Russia, [4] Tsinghua University, Beijing, China)
Invited
Experimental and theoretical study of the kinetics and mechanism of thermal decomposition of triphenyl phosphate in inert media

10.10-10.50 M. Kuznetsov V. Gubernov, Andrey Kolobov, (P.N. Lebedev Physical Institute of Russian Academy of Sciences, Moscow, Russian Federation) *Invited*
Influence of heat loss on the stability of oscillatory modes in combustion wave propagation

10.50-11.10 **Coffee Break**

Session 3.2
Chair: Denis A. Knyazkov (Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk)

11.10-11.30 Denis Kasymov[1,2], M. Agafontsev[1,2], V. Perminov[1], V. Reyno[2], K. Orlov[1], E. Golubnichii[1], P. Martynov[1,2] ([1] National Research Tomsk State University, [2] Zuev Institute of Atmospheric Optics SB RAS, Tomsk, Russia)
Experimental study of the combustion process on the surface of wood construction materials

11.30-11.50 Andrey Ponomarev, Dmitriy Sharaborin (Institute of Thermophysics SB RAS, Novosibirsk, Russia)
Experimental and numerical study of monodisperse ethanol mist combustion

11.50-12.10 Tatyana A. Bolshova, A.G. Shmakov, I.E. Gerasimov, O.P. Korobeinichev, (Voevodsky Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia)
Combustion of a polymethyl methacrylate sphere in air

12.10-12.30 G. Nyashina, Dmitrii Antonov, P. Strizhak (Heat and Mass Transfer Laboratory, National Research Tomsk Polytechnic University, Tomsk, Russia)
Micro-explosive droplet fragmentation of promising biofuels

12.30-12.50 M.E. Shiryaev [1], A.V. Sysa [2], R.M. Ryazanov [2], D.G. Gromov [1], Egor A. Lebedev [1,2] ([1]National Research University of Electronic Technology – MIET, [2] Scientific-Manufacturing Complex "Technological Centre"Zelenograd, Moscow Russia)
Adjustment of the combustion mode in CuO/Al multilayer thermite materials

12.50-14.40 LUNCH

15 July, Friday (Samara time UTC +4)

Session 4.1 (online)
Chair: Marsel V. Zagidullin (Lebedev Physical Institute of RAS, Samara Branch, Samara)

9.30-10.10 Viatcheslav V. Bykov[1], Andrey Koksharov[2] ([1] Karlsruhe Institute of Technology, Institute of Technical Thermodynamics, Karlsruhe, Germany, [2] German Aerospace Center (DLR), Stuttgart, Germany) *(Invited)* ***online***
Efficient quasi-spectral numerical method to integrate chemical master equation

10.10-10.30 Ivan Antonov[1,2], S.Venkataramanababu[2], B. Odom[2], H. Guo[3], A. Li[4] ([1]Lebedev Physical Institute, Samara Branch, [2]Northwestern University, USA, [3]University of New-Mexico, USA, [4]Northwest University, China) ***online***
Dynamic rotational effect in reaction of SiO+ super rotors with H2

10.30-10.50 Pavel V. Zasimov, E.V. Sanochkina, V.I. Feldman (Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia) ***online***
Radiation-induced transformations of acetaldehyde molecules at cryogenic temperatures: a matrix isolation study

10.50-11.10 Nina Volkova[1], A. Kazakov[1], A. Nabatova[1], A. Zholudev[1], M. Kislov[1], I. Averkov[1], D. Dashko[2], D. Lempert[1], L. Yanovsky[1,3] ([1]Institute of Problems of Chemical Physics of RAS, Chernogolovka, Moscow Region, Russia, [2]Special Design and Technological Bureau SDCB “Technolog”, Saint Petersburg, Russia, [3]Moscow Aviation Institute, Moscow, Russia) ***online***
Physico-chemical characteristics of energy condensed compositions based on polynitrogen heterocyclic compounds, poly-2-methyl-5-vinyltetrazole and SKI-3 rubber

11.10-11.30 Valeriy Perminov, K. Sysolov (Tomsk Polytechnic University, Tomsk, Russia) ***online***
Mathematical modeling of surface fire initiation and spread

11.30-11.50 **Coffee Break**

Session 4.2

Chair: Anna S. Savchenkova (Samara National Research University, Samara)

11.50-12.10 Ksenia Osipova [1,2], A. Dmitriev[1,2], O. Korobeinichev[1], A. Shmakov[1,2] ([1]Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, [2] Novosibirsk State University, Novosibirsk, Russia)
The flame structure of ammonia/ hydrogen/ oxygen/ argon blends at 4 and 6 atm

12.10-12.30 Margarita Gorn[1,2], K. Monogarov[3], I. Dalinger[4], N. Muravyev[3], V. Kiselev,[1,2] ([1]Novosibirsk State University, [2]Voevodsky Institute of Chemical Kinetics and Combustion Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia, [3]Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, [4]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia)
Thermal Decomposition of Dinitropyrazoles: New Insights from Predictive Electronic Structure Theory and Thermal Analysis

12.30-12.50 Dmitriy O. Glushkov, A.G. Nigay, K.K. Paushkina, A.O. Pleshko (National Research Tomsk Polytechnic University, Tomsk, Russia)
Influence of gel fuels composition on ignition and combustion characteristics under radiant heating

12.50-14.30 LUNCH

Session 4.3

Chair: Valery N. Azyazov (Lebedev Physical Institute, Samara Branch)

14.30-14.50 Ksenia Vershinina, D. Romanov, V. Dorokhov, P. Strizhak **(**National Research Tomsk Polytechnic University, Tomsk, Russia)
Characteristics of ignition and combustion of fuel blends based on coal slime

14.50-15.10 A. Moloknov[1,2], Leonid Yanovsky[1,2], N. Varlamova[1], G. Tarasov[1,2], A. Kazakov[1], N. Plishkin[1], T. Bakalchuk[3] ([1] Institute of Problems of Chemical Physics of RAS, Academician Semenov, Chernogolovka, Moscow region, Russia, [2] National Research University "Moscow Power Engineering Institute", [3] SBEI of Moscow "School No. 1533 "LIT", Moscow, Russia)
Assessment of coke deposits during heating of hydrocarbon fuel under dynamic and static conditions

15. 10-15.30 Anatoliy Nikolayev[1,2], V. Azyazov[1,2], A. Mebel[1,3] ([1] Lebedev Physical Institute, Samara Branch, [2] Samara National Research University, Samara, Russia,[3] Florida International University, Miami, Florida, USA)
Transformation of acetone into 1-propen-2-ol in the ice phase

15.30-15.40 **Closing remarks**

BOOK OF ABSTRACTS

INVITED TALKS

Efficient quasi-spectral numerical method to integrate chemical master equation

Viatcheslav Bykov[1], Andrey Koksharov[2]

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Chemical Master Equation (CME) approach is typically used to estimate the rate coefficients of elementary chemical reactions on the level of molecular dynamics [1]. At present, existing conventional methods to treat this problem especially for multi-well systems are semi-empirical and remain rather computationally demanding [2]. The conventional method leads to a linear but highly dimensional systems of equations, which are employed to evaluate estimations for elementary reaction rates [2, 3]. In our study a quasi-spectral method to integrate single-, multi-well CMEs systems is presented [4]. For a given reaction system, CMEs are integrated such that the evolution over the energy range of entire populations of the species involved in the mechanism can be determined. Afterwards the detailed solution can be used to define the rates of elementary reactions in a systematic manner. For this a method to estimate reaction rate constants of a phenomenological model is proposed as a generic solution of an inverse problem for these rates.

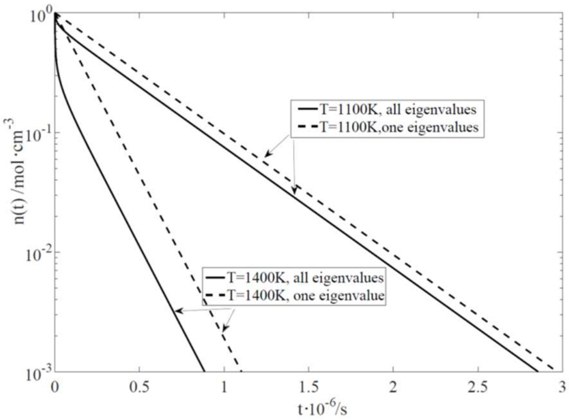

Fig.1. Concentration evolution of the allene, dashed lines show the phenomenological model based on the standard estimation approach, while actual concentration evolution is shown by solid lines for different initial temperature and normal pressure.

The suggested approach is implemented and illustrated by the problem of the allene isomerization into propyne through cylcopropene [3, 5]. The comparison of the allene concentration evolution given by conventional method and the proposed method is presented in Fig. 1. The figure shows transparently possible over estimations of the concentration produced by conventional method.

Authors would like to thank the DFG for the financial support within the DFG-TRR 150 project, project number: 237267381.

References

1. Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*, Blackwell: Oxford, UK, **1990**.
2. J.A. Miller, S.J. Klippenstein, *J Phys Chem A* **2006**, 110, 10528.
3. J.H. Kiefer, S. S. Kumaran und P. S. Mudipalli, *Chemical physics letters* **1994**, 224(1-2), 51.
4. A. Koksharov, C. Yu, V. Bykov, U. Maas, M. Pfeifle, M. Olzmann, *Int. J. Chem. Kin.* **2018**, 50(5), 357.
5. Mebel, A. M., W. M. Jackson, A. H. H. Chang und S. H. Lin, *Journal of the American Chemical Society* **1998**, 120(23), 5751.

Modeling of cold astrochemical processes through matrix isolation: extremely hot chemistry at extremely low temperatures

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The chemical evolution of molecules in space is induced by solar and galactic radiation, which make it possible to initiate the reactions in cold astrochemical media, including diffuse interstellar molecular clouds, cometary and planetary ices. Matrix isolation is a useful tool to simulate possible reaction channels for the key relevant molecules and to elucidate the mechanism of molecular assembling occurring under the conditions of completely frozen diffusion mobility. This lecture gives an overview of recent results of the matrix isolation studies on the radiation-induced transformations of astrochemically important molecules and their complexes obtained in our laboratory.

The experimental approach was based on X-ray irradiation of deposited solid-noble gas films doped with small amounts of target compounds at 6 K followed by monitoring of product formation by a combination of FTIR and EPR spectroscopy [1]. In this way we have extensively characterized the mechanism of radiation-induced decomposition of a number of key astrochemical molecules, such as HCOOH [2], CH_3OH [3], CH_3CN [4], CH_3CHO [5] and simple aromatics [6]. An important finding is that physical properties of inert matrix have strong effect on the degradation efficiency and pathways because of primary significance of the excess energy relaxation. To a certain extent, the observed chemistry may look quite “hot” in conventional terms, even though the medium temperature is quite low. In addition, the data obtained in model studies make a challenge for astronomical search of some intermediate species, not yet reported in space [7].

Another direction is concerned with the radiation chemistry of isolated intermolecular complexes. In fact, this approach implies a concept of “building blocks”, which may provide an important insight into the mechanism of cold astrochemical synthesis. In this way, we have directly observed elementary steps of the low-temperature reactions, which may be responsible for formation of intermediates and molecules detected in interstellar media, including both prebiotic species and polycyclic aromatic hydrocarbons (PAHs) [8 - 11]. Also, the photoinduced and tunneling dynamics of intermediates was explored [12]. Some new intriguing results and implications are discussed.

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References

1. V.I. Feldman et al., *Rad. Phys. Chem.* **2016**, 124, 7.
2. S.V. Ryazantsev, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2015**, 17, 30648.
3. E.V. Saenko, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2016**, 18, 32503.
4. S.V. Kameneva, A.D. Volosatova, V.I. Feldman, *Rad. Phys. Chem.* **2017**, 141, 363.
5. P.V. Zasimov, E.V. Sanochkina, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2022**, 24, 419.
6. M.A. Lukianova, E.V. Sanochkina, V.I. Feldman, *J. Phys. Chem. A* **2019**, 123, 5199.
7. A.D. Volosatova, S.V. Kameneva, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2019**, 21, 13014.
8. P.V.Zasimov, S.V. Ryazantsev, D.A. Tyurin, V.I. Feldman, *MNRAS* **2021**, 506, 3499.
9. P.V.Zasimov, S.V. Ryazantsev, D.A. Tyurin, V.I. Feldman, *J. Am. Chem. Soc.* **2022**, accepted
10. A.D. Volosatova, M.A. Lukianova, P.V. Zasimov, V.I. Feldman, *Phys. Chem. Chem. Phys.*, **2021**, 23, 18449
11. M.A. Lukianova, V.I. Feldman, *Rad. Phys. Chem.* **2022**, 191, 109847.
12. S.V. Ryazantsev, V.I. Feldman, L. Khriachtchev, *J. Am. Chem. Soc.* **2017**, 139, 9551

Investigation of diffusive-thermal oscillations of the burner stabilized CH_4-H_2-air flames

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In this talk we present our recent results on the investigation of the onset and dynamics of the diffusive-themal instabilities of laminar flames of the binary fuel mixtures stabilized over a flat porous burner. The mixture of methane and hydrogen (hythane) is used as a fuel, which is considered today as a promising intermediate step in the transition to the hydrogen energy.

The experimental and numerical methodology is described in detail in our previous work [1,2]. In experiments, the flame is stabilized on the flat cylindrical porous burner with liquid cooling and nitrogen co-flow. The emergence and characteristics of the flame oscillations are analysed via the observation of the chemiluminescence signal emitted by OH* radicals. The structure of the combustion wave is also investigated by using the Laser induced fluorescence method allowing us to determine the time and space resolved profiles of OH* radicals. The experimental results are also compared to the data of numerical calculations obtained within the models with detailed reaction mechanisms. Several well known mechanisms are used such as GRI, San-Diego and Warnatz.

The employment of the nitrogen co-flow configuration to isolate the flame from the surrounding air allows us to obtain the experimental data of high fidelity such that the difference between the numerical data calculated with different reaction mechanisms is greater than the experimental uncertainty, demonstrating that the proposed technique can be used to verify the reaction mechanisms. The sensitivity analysis is carried out and allows us to find the most important reactions involved in both steady and pulsating regimes of combustion. Two critical events are found: the blow-off and the onset of pulsations. The critical parameter values for them are determined. It is shown that the addition of hydrogen to the fuel mixture extends the regions of the existence of flat combustion fronts and the onset of flame pulsations in the parameter space.

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References

1. S. Nechipurenko, T. Miroshnichenko, N. Pestovskii, S. Tskhai, B. Kichatov, V. Gubernov, V. Bykov,U. Maas, *Combust. Flame* **2020**, 213, 202–210.
2. V. Mislavskii, N. Pestovskii, S. Tskhai, B. Kichatov, V. Gubernov, V. Bykov, U. Maas, *Combust.Flame* **2021**, 234, 111638.

Positive ion chemistry in flames: mass-spectrometric and kinetic modeling study

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Charged species occurring in flames have been extensively studied for several decades. In the last 10 years, the ion chemistry in flames has again become of considerable interest. This is related to the increased demand for new approaches to monitoring of combustion processes, particularly, with application of electric field and various forms of gas discharge. Recently, the interest in ionic flame chemistry has especially increased in connection with the opportunities offered by the ion sensitive technologies for controlling the operation of engines.

Although the concentration of naturally occurring charged species in flames is low (~10^8-10^{11} cm^{-3}), they can be detected by molecular beam mass spectrometry (MBMS). Since the ion-molecular reactions are rather fast, they are easily equilibrated. Therefore, the concentrations of some neutral species can potentially be derived from the signals of flame-sampled cations if the equilibrium constants of the major pathways of the ions formation and consumption are known. This opens new opportunities for determination of concentrations of those neutral species that are hard to detect by conventional flame-sampling MBMS, such as, for example, polycyclic aromatic hydrocarbons, which play a key role in soot formation as precursors and pose the health hazards in combustion emissions. Thus, understanding the kinetics of cation formation in flames provides the basis for the development of new diagnostic methods.

The kinetic models for ion chemistry in flames presented in the literature are imperfect due to the lack of reliable experimental data for their validation. In this work, the recent data from the laboratory of combustion kinetics ICKC SB RAS of MBMS measurements of spatial distributions cations in premixed burner-stabilized flames of different fuels (methane, ethylene, dimethyl ether, ethanol) are reported. The effect of sampling probe on the measured distributions of cations is discussed. The ion chemistry mechanisms proposed earlier in the literature were validated against the novel experimental data on the spatial distributions of the major cations presenting in all flames, like hydronium (H_3O^+), HCO^+, protonated ketene, protonated methanol, $C_3H_3^+$. An improved kinetic mechanism for the charged species was developed and its performances as compared to that published recently by Chen et al. [Combust. Flame 202 (2019) 208] are demonstrated. To this end, the highly accurate W2-F12 quantum chemical calculations were used to obtain the reliable formation enthalpies of all cations considered in the mechanism. The mechanism is extended with the reactions involving $C_3H_5^+$ cation, which was detected in ethylene flames, and the reaction pathways involving $C_3H_3^+$ are revised. The key directions for the further refinement of the mechanism are considered based on the insights derived from the experimental observations.

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Influence of heat loss on the stability of oscillatory modes in combustion wave propagation

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The propagation of planar combustion waves in non-adiabatic model with two-step chain-branching reaction mechanism is investigated. The travelling combustion wave becomes unstable with respect to pulsating instabilities as the critical parameter values for the Hopf bifurcation are crossed in the parameter space. The Hopf bifurcation is demonstrated to be of a supercritical nature and it gives rise to periodic pulsating combustion waves as the neutral stability boundary is crossed. Further increase of the bifurcation parameter leads to the period-doubling bifurcation cascade and a chaotic regime of combustion wave propagation. In the absence of heat losses in the chaotic region, regular windows of period 5, 6, and 7 are observed. The period 3 window is not reached due to flame extinction. The heat losses are shown to modify the location of critical parameter values for the Hopf and period doubling bifurcations in the parameter space. However, the most important impact of the heat losses is that the region of chaotic dynamics is significantly shortened and extinction of combustion wave is promoted.

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Decomposition of 1-propenol: theoretical investigation

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Research into unimolecular decomposition can provide valuable insights about complex chemical dynamics of combustion systems. Moreover, it also suggests paths by which large molecules can be formed for example in astrochemistry.

In present work we studied thermal decomposition of 1-propenol theoretically using quantum chemistry tools which allow one to achieve errors of relative energies less than 1 kcal mol^{-1} according to the assessment by Zhang and Valeev [1]. The C_3H_6O-PES was compiled using geometry optimization of local minima (reactants, intermediates, and products) and transition states at the density functional B3LYP/6-311G(d,p) level of theory [2,3]. Energies of structures were refined by singlepoint calculations that employed the explicitly-correlated coupled clusters CCSD(T)-F12 [4,5] method with Dunning's correlation-consistent cc-pVTZ (E_{TZ}) and cc-pVQZ (E_{QZ}) basis sets [6]. Then final values (E_{CBS}) were calculated for the complete basis set limit $E_{CBS} = E_{QZ} + 0.69377\cdot(E_{QZ} - E_{TZ})$.

The constructed PES profile suggests that the decomposition of cis- and trans-1-propenol will be carried out mainly by two mechanisms - this is the direct detachment of a hydrogen molecule with the formation of acrolein and, through an intermediate transition to propanal, decomposition into 3 molecules: ethylene, carbon monoxide and hydrogen. For reverse fusion, the $CCH_2 \rightarrow 2-$propenol → acetone →propanal → cis-/transpropenol mechanism seems to be the most promising taking into account only energy requirements. The second variant, although it has a higher barrier, stems from more stable acrolein and hydrogen molecules which recombination immediately leads to propenol. The reactions of ethynol with methane and propyne with water, another possible routes to initial reagent, are characterized by higher (by approximately 20 kcal/mol) barriers. The barrier for the three-molecular mechanism $C_2H_4+CO+H_2 \rightarrow$ cis-/transpropenol is approximately 10 kcal/mol lower than for the previous two pathways, but such collisions are much more rare.

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References

1. J. Zhang and E. F. Valeev, J. Chem. Theory Comput., 2012, 8, 3175–3186.
2. A. D. Becke, J. Chem. Phys., 1993, 98, 5648–5652.
3. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys., 1988, 37, 785–789.
4. T. B. Adler, G. Knizia and H.-J. Werner, J. Chem. Phys., 2007,127, 221106.
5. G. Knizia, T. B. Adler and H.-J. Werner, J. Chem. Phys., 2009,130, 054104.
6. T. H. Dunning, J. Chem. Phys., 1989, 90, 1007–1023.

Experimental and theoretical study of the kinetics and mechanism of thermal decomposition of triphenyl phosphate in inert media

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The increasing use of synthetic polymer materials has in many cases been held back by their high fire hazard. The reducing the flammability of polymers is one of the most important problems. The main method for reducing the combustibility of polymeric materials is the introduction of flame retardants into them. One of the well-established classes of flame retardants are organophosphorus compounds. However, until now, scientists still do not know how processes involving phosphorus-containing flame retardants occur in real objects. The main scientific issue is the site of action of flame retardants, since they can both slow down the thermal decomposition of polymers and reduce the rate of release of combustible gases from them, as well as suppress the combustion of these combustible gases when mixed with ambient air. It is also important to understand how the chemical structure of flame retardant molecules affects the above two processes, since such information can help to purposefully synthesize flame retardant molecules with the desired structure. Thus, the purpose of this work was to experimentally and theoretically study the conversion of triphenyl phosphate (TPP) during its thermal decomposition in an inert medium, i.e. under conditions that are characteristic of the flame zone near the surface of the polymer.

The high-temperature pyrolysis of TPP vapor in argon was studied by using thermal flow reactor at a pressure of 1 atm. Mass spectra of products of thermal decomposition of TPP vapors were measured by probe molecular beam mass spectrometry in the temperature range of 300-1000°C. Using the G3(MP2,CC) model chemistry along with the B3LYP method in the framework of density functional theory (DFT) with the 6-311G(d,p) basis set, calculations were performed to optimize the geometry of all structures on the considered potential energy surfaces of TPP and products of primary and secondary decomposition of TPP. The kinetic rate constants of the thermal decomposition reaction of TPP were also calculated using the Rice-Ramsberger-Kassel-Marcus theory and the method of the main kinetic equation (RRKM-ME) implemented in the MESS program code, thermochemical parameters for TPP and products of primary and secondary decomposition of TPP in temperature range 200-6000K were obtained. Based on the results of calculations, as well as the mechanisms of transformation of the phenyl and phenoxyl radicals from the literature, a combined detailed chemical-kinetic mechanism was created that describes the pyrolysis of TPP in inert medium.

Comparison of the results of numerical calculations of the composition of TPP pyrolysis products in the reactor showed that the developed mechanism quantitatively predicts the dependence of the TPP concentration on the reactor temperature distribution, and for intermediate compounds this mechanism well describes the experimentally observed trends in the conversion of phosphorus-containing substances on the reactor temperature.

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Ignition, combustion and detonation onset in non-uniform dispersed fuel-air mixtures

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The paper presents the review of results of theoretical, numerical and experimental investigations of combustion and detonation initiation in heterogeneous polydispersed mixtures. The problems of fuel droplets atomization, evaporation and combustion and the non-equilibrium effects in droplets atomization and phase transitions were taken into account. The effects of droplets size non-uniformity and spatial distribution non-uniformity on mixture ignition and flame acceleration were investigated for strong and mild initiation of detonation: by a shock wave and spark ignition followed by deflagration to detonation transition (DDT). Peculiarities of jet injection and ignition in reaction chamber are studied.

In ignition of turbulized organic particles mixture with air turbulence brings to an increase of flame propagation velocity, but inhibits ignition due to rapid dispersion of ignition energy from the ignition point. (Fig. 1)

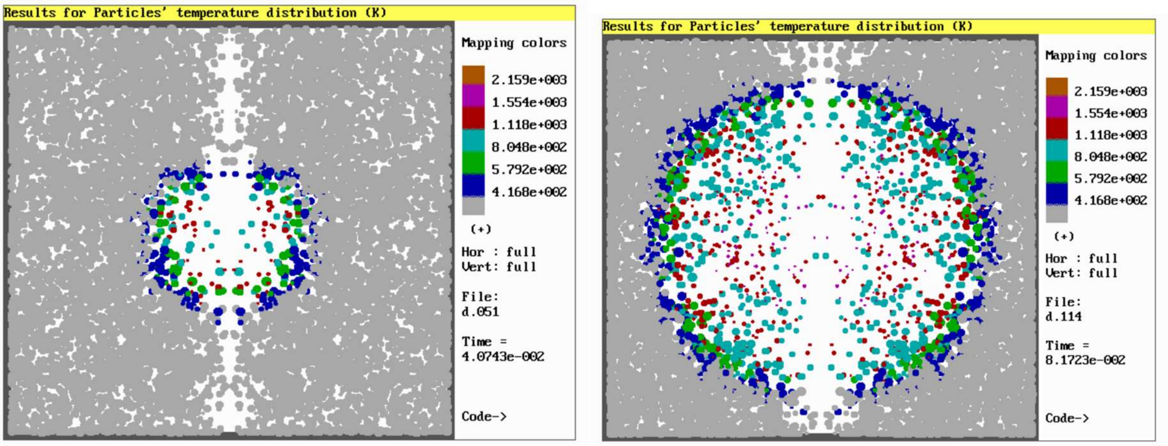

Fig.1.

Investigating droplet cloud strong ignition by a shock wave showed that droplets atomization and heating takes place behind the shock wave. Gradual heating and evaporation of droplets gives birth to ignition of mixture. Fig. 2 shows one stage of shock wave entering the dispersed mixture: *droplets size and temperature.*

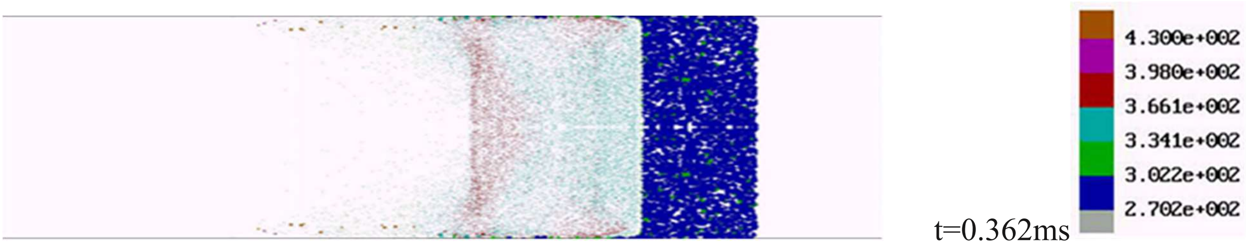

Fig. 2

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Mechanisms of the formation of organic matter in protostellar objects

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The origin of life in the universe remains one of the most fundamental and interdisciplinary questions in modern science. In recent years, astrophysical studies aimed at studying the molecular composition of the interstellar medium have made a significant contribution in solving these questions. Next-generation ground-based instruments, as well as space missions, make it possible to discover an ever-widening variety of molecules in space.

Despite significant progress in observations, experiments and theoretical research, the picture of the evolution of organic matter in the Galaxy, as well as an understanding of the mechanisms and factors that influence the evolution of organic molecules in space, is still far from complete. Formation of complex organic molecules in several important astrophysical environments, including earliest stages of low-mass star formation and photodissociation regions (PDRs) is yet to be fully understood. Laboratory experiments on low-temperature reactivity on the analog of interstellar grains carried out recently challenge several long-standing concepts in astrochemistry, including important reaction schemes, e.g., formation of methanol, and even the entire diffusive chemistry paradigm.

Recent promising developments in astrochemical research include scenarios for the formation of cold complex molecules via gas-grain chemistry facilitated by reactive desorption, non-diffusive chemistry in the ice, understanding the role of cosmic rays in the processing of interstellar ice, observational constraints on the efficiency of reactive desorption and steps toward understanding the “top-down” chemistry in PDRs. It was shown that “top-down” chemistry can significantly affect abundances of species observed in PDRs, while gas-phase reactions between reactants formed on grains and ejected to the gas via reactive desorption, and non-diffusive chemical processes in interstellar ices may lead to the production of large amounts of complex organic molecules in prestellar cores. Research with recently launched James Webb Space Telescope (JWST) is expected to give a further boost to astrochemical research, especially to our understanding of the formation and evolution of complex organic molecules in the ices. New experimental facilities such as Monitor for Astrochemical Reactions on Surfaces (MARS) as well as microscopic and macroscopic models of the evolution of interstellar ices and astrophysical environments in general (e.g., MONACO) are already either under development or available for the community.

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References

1. A.I. Vasyunin et al., *Astrophys. J.* **2017**, 842, 33V.
2. A.F. Punanova et al., *Astrophys. J.* **2022**, 927-2, 213.
3. M.S. Murga et al., *MNRAS*, **2020**, 497-2, 2327-2339.
4. G.S. Fedoseev et al., *VAK-2021 proceedings*, **2021**, p. 55

Carbon Dust Life Cycle in the Universe

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It is now well established that a significant fraction of the interstellar dust is represented by carbon-bearing particles having different sizes and structures [1]. This suggestion has been confirmed back in 1960s by both considerations on the possible origin of such particles [2] and by direct observational evidence [3]. However, the exact nature of carbon-bearing grains is still far from being firmly established. They may contain graphite, amorphous carbon, certain kind of aromatic compounds (vaguely referred to as polycyclic aromatic hydrocarbons, PAH [4]) as well as some more exotic components, like diamonds, fullerenes, and nanotubes. It is widely believed that evolved stars are a major source of carbon-bearing grains (see e.g. [5]). After having been expelled from a parent star, a carbon grain makes it into the interstellar medium, where it is subject to numerous processes that either destroy it [6–8] or alter its structure [9–10]. Eventual destruction of carbon grains by ultraviolet radiation of hot massive stars may increase abundances of small hydrocarbons in the interstellar gas [11]. Obviously, to follow all these transformations, one needs to construct an evolutionary model. which would account for various changes in the dust size distribution, charge state, bond structure, etc. [12].

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References

1. A.P. Jones et al., *Astron. and Astrophys.* **2013**, 558, A62.
2. F. Hoyle, N. C. Wickramasinghe, *MNRAS* **1962**, 124, 417.
3. F.C. Gillett, F.J. Low, W.A. Stein, *Astrophys. J.* **1968**, 154, 677.
4. A.G.G.M. Tielens, *ARA&A* **2008**, 46, 289.
5. I. Cherchneff, J.R. Barker, A.G.G.M. Tielens, *Astrophys. J.* **1992**, 401, 269.
6. E. R. Micelotta, A. P. Jones, A. G. G. M. Tielens, *Astron. and Astrophys.* **2010**, 510, A36.
7. E. R. Micelotta, A. P. Jones, A. G. G. M. Tielens, *Astron. and Astrophys.* **2010**, 510, A37.
8. E. R. Micelotta, A. P. Jones, A. G. G. M. Tielens, *Astron. and Astrophys.* **2010**, 526, A52.
9. M. S. Murga, S. A. Khoperskov, D. S. Wiebe, *Astronomy Reports* **2016**, 60, 233.
10. M. S. Murga, S. A. Khoperskov, D. S. Wiebe, *Astronomy Reports* **2016**, 60, 669.
11. J. Pety et al., *Astron. and Astrophys.* **2005**, 435, 885.
12. M. S. Murga et al., *MNRAS* **2019**, 488, 965.

ORAL TALKS

Micro-explosive droplet fragmentation of promising biofuels

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Rapeseed oil is a promising biofuel and it significantly improves the environmental indicators of working engines and power facilities. It is possible to increase the efficiency of combustion of slurry based on rapeseed oil by implementing micro-explosive breakup of fuel droplets. To identify the outcome of the micro-explosion, it is necessary to modify the composition through an increase in the proportion of the liquid combustible component [1].

In this study, at the first stage, the optimal concentrations of slurry components to provide the micro-explosive breakup were determined. The initial composition was as follows: 55 wt% coal slime, 35 wt% water, 10 wt% rapeseed oil. Then we varied the concentration of the slurry components. According to the experimental results, the composition with 9 wt% coal slime, 10wt% water, 81 wt% rapeseed oil provided the sufficient conditions for the sustainable explosive breakup and atomization (at above 900°C). We used this slurry for all further studies. The key regimes of droplet behavior under intense heating were evaporation, puffing, and micro-explosion. A droplet of slurry is found to evaporate steadily at the heating medium temperatures below 900°C. The minimum puffing temperature is 900°C. The occurrence of micro-explosion requires the minimum temperature of 1050 °C. Fig. 1 shows the liquid surface area ratios before and after the slurry droplet breakup with varying air temperature in the muffle furnace.

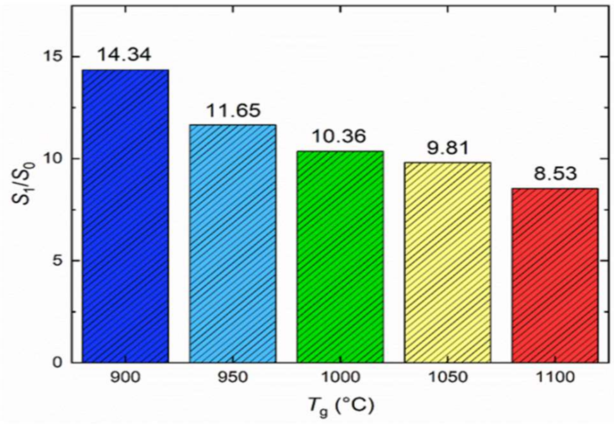

Fig. 1. Liquid surface area ratios before and after the breakup of a slurry droplet (9 wt% coal slime, 10wt% water, 81 wt% rapeseed oil, D_0≈2.35 mm) with varying air temperature in the muffle furnace.

An analysis of the experiments showed that the micro-dispersion of heterogeneous droplets may provide a more than 10-fold increase in the evaporation surface area. An increase in the air temperature from 900 to 1100°C leads to the enlargement of child droplets and hence to the reduction of the evaporation area ratio before and after the breakup. This effect stems from the agglomeration of solid particles in the near-surface layer of the droplet at high temperatures as well as the fast evaporation of smaller droplets in the gas phase [2].

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References

1. K. Meng, W. Fu, F. Li, Y. Lei, Q. Lin, G. Wang, *J Energy Inst.* **2020**, 93, 1, 152-164.
2. D.V. Antonov, G.S. Nyashina, P.A. Strizhak, D.S. Romanov. *Fuel*. **2021**, 283, 118949.

Dynamic rotational effect in reaction of SiO^+ super rotors with H_2

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Super rotors are molecules rotating at very high speed, whose rotational energy may approach or exceed electronic bonding energy. Steady-state silicon monoxide cation (SiO^+) super rotors with rotational quantum numbers N up to 170 were prepared in a linear quadrupole trap by means of optical pumping. Our measurements showed that the rate of reaction of SiO^+ super rotors with molecular hydrogen increased by a factor of 3 compared to thermal SiO^+ molecules. Quasiclassical trajectory (QCT) calculations explained the observed rate increase by a dynamic effect via coupling of SiO^+ rotational motion to a reaction coordinate of the intermediate reaction complex.

Exploring the possibility of synthesis of Si_3N_4-SiC highly dispersed ceramic nitride-carbide composition during combustion in Si–NaN_3–$(NH_4)_2SiF_6$–C system

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Ceramic single-phase materials silicon nitride (Si_3N_4) and silicon carbide (SiC) have good chemical stability and strength at high temperatures. Their Si_3N_4-SiC composites have such enhanced properties as high hardness, high-temperature strength and fracture toughness [1]. It is well known that the structure of these composite materials (particle size and shape) has an important influence on their properties. Traditional methods of manufacturing Si_3N_4-SiC composites have disadvantages such as complexity, high cost and low productivity, which complicates the production and use of these composites.

In this paper, the possibility of obtaining Si_3N_4-SiC composites using a simple energy–saving method of azide self–propagating high–temperature synthesis (SHS) in the combustion mode of a mixture of Si-NaN_3-$(NH_4)_2SiF_6$-C powders was investigated [2]. Experimental studies were carried out in a 4.5-liter SHS laboratory reactor in a nitrogen atmosphere at a relatively low pressure of 4 MPa and at a bulk density of mixtures of initial powders. The "xSi-6NaN_3–$(NH_4)_2SiF_6$–yC" system was used to synthesize the Si_3N_4–SiC composition with a molar ratio of the target phases from 1:4 to 4:1. It was found that the combustion products of the charge "3Si+6NaN_3+$(NH_4)_2SiF_6$+C" consist mainly of ultrafine particles of equiaxed and fibrous forms with a particle size of 100-300 nm and a fiber diameter of 50-500 nm with a length of up to 3 μm. The XRD results show the formation of four phases: the main phase of silicon nitride of two modifications (α-Si_3N_4 and β-Si_3N_4) with a significantly higher content of α-modification, silicon carbide (SiC), as well as a small amount of free silicon (Si) and carbon (C), (hereinafter indicated in wt.%): α-Si_3N_4 - 57.6%, β-Si_3N_4 - 22.1%, SiC - 17.0%, Si - 1.3%, C - 2.0%. With a fourfold increase in the carbon content and a twofold increase in silicon in the charge "6Si+6NaN_3+$(NH_4)_2SiF_6$+4C", the combustion products are mainly fibrous particles with a fiber diameter of 50-250 nm with a length of up to 3 μm. The XRD results show the formation of the same phases, but with a slight decrease in silicon nitride and an increase in the content of silicon carbide: α-Si_3N_4 - 33.3%, β-Si_3N_4 - 27.1%, SiC - 29.2%, Si - 5.3%, C - 5.1%.

Thus, the technology of azide SHS made it possible to produce in one stage a promising ceramic nitride-carbide ultrafine powder composition Si_3N_4-SiC, moreover, with a different ratio of the target phases Si_3N_4-SiC.

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References

1. T. Hirano, K. Niihara, Microstructure and mechanical properties of Si_3N_4/SiC composites. *Mater. Letters*, **1995**, 22, 249.
2. G.V. Bichurov. Halides in SHS azide technology of nitrides obtaining. In: Nitride Ceramics: Combustion synthesis, properties, and applications. Eds. A.A. Gromov, L.N. Chukhlomina. Weinheim: Wiley, **2015**. P. 229-263.

Combustion of a polymethyl methacrylate sphere in air

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Polymethyl methacrylate (PMMA) – is a synthetic polymer of methyl methacrylate (MMA, $C_5H_8O_2$), thermoplastic transparent plastic, widely used in industry, construction and everyday life. Due to its useful properties (transparency, resistance to moisture and microorganisms, electrical insulating properties) it is used as a structural, optical and decorative material. The main disadvantage of PMMA is its low heat resistance. At temperatures above 200oC, PMMA depolymerizes to form a monomer - methyl methacrylate. Thus, the study of flame propagation over surface of such polymers is very important task for fire safety investigations. CFD (Computational fluid dynamics) – is a modern and accurate simulation method available to conduct such studies.

The aim of this work is to study the propagation of flame over the curved surface of PMMA under normal conditions. For this purpose, CFD simulation of the combustion process, based on experimental data, was carried out with the inclusion of a detailed kinetic model of the PMMA oxidation. The object of research was a sphere made of cast PMMA with a diameter of 40 mm burned in still air. Temperature, mass loss rate, concentration profiles of the main products and reactants near the combustion surface were obtained experimentally. The gas dynamic flow and combustion were calculated using the ANSYS Fluent software package [1] with the full set of Navier-Stokes equations. The PMMA conversion mechanism includes a surface reaction describing polymer pyrolysis and MMA oxidation chemistry in the gas phase. To speed up the calculations the reduced gas-phase kinetic mechanism, including only 29 components and 44 reactions, was used [2]. This mechanism was obtained with the mechanism reduction procedure implemented in the Mechanism Workbench software package (Kintech Lab) [3]. The rate constant of PMMA pyrolysis was taken from the previous studies [4].

As a result of calculations, the fields of temperatures, gas flow velocity and mole fractions of substances in the flame were obtained. A comparison of the simulation results and experimental data showed that the proposed model satisfactorily describes the combustion of a PMMA sphere and can be used to describe the combustion of other objects, in particular, the combustion of PMMA plates.

References

1. Academic Research, Release 19.5.0 for ANSYS 2019 R3, http://www.ansys.com/
2. T.A. Bolshova, A.A. Chernov, A.G. Shmakov, *Comb., Expl. and Shock Waves* **2021**, 57 (2), 159.
3. MechWork software (Kintech Lab) http://www.kintechlab.com/products/ mechanism– workbench/
4. S.A. Trubachev et al., *Proc.Comb.Inst*. **2021**, 38, 4635.

Molecular beam mass spectrometric study of the laminar flame structure of ethyl levulinate

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4-oxopentanoic acid ethyl ester or just ethyl levulinate (EL) is considered as one of perspective fuels from cellulosic biomass. It could be easily derived from inexpensive woody biomass with a high yields [1] making this biofuel especially attractive. In different works EL is considered either as a diesel additive [1,2] or as an octane booster [3,4]. Such ambiguity stems mainly from the lack of kinetic studies of EL. Although levulinic fuels have become popular in the last five years, only a few kinetic studies on EL reactivity are presented in literature. Therefore this study aims to broaden the experimental database on this fuel along with validation of existing kinetic conceptions.

Fuel-rich ($\varphi=1.4$) laminar premixed flame of EL/O_2/Ar mixture was chosen as the main object. The flame was stabilized over a flat flame burner at atmospheric pressure. Chemical speciation in the flame front was measured via the molecular-beam mass-spectrometric technic. The reactants, stable and intermediate products including the main flame radicals were detected.

Since EL has both ester and ketone functionalities, the measurements were focused on the specific intermediates such as levulinic acid and methyl vinyl ketone to track the corresponding reaction pathways. The work of Ghosh et al.[4] was used as the basic kinetic scheme for the analysis. The results obtained have shown the peculiarities of the competition between the esteric and ketone pathways.

References

1. J. F. Leal Silva, R. Grekin, A. P. Mariano and R. Maciel Filho, *Energy Technology*, **2018**, 6, 613–639.
2. T. Lei, Z. Wang, Y. Li, Z. Li, X. He and J. Zhu, *BioResources*, **2013**, 8, 2696–2707.
3. M. Tian, R. L. McCormick, J. Luecke, E. de Jong, J. C. van der Waal, G. P. M. van Klink and M. D. Boot, *Fuel*, **2017**, 202, 414–425.
4. M. K. Ghosh, M. S. Howard, Y. Zhang, K. Djebbi, G. Capriolo, A. Farooq, H. J. Curran and S. Dooley, *Combustion and Flame*, **2018**, 193, 157–169.

Study of the gas hydrate combustion initiation initial stage

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Gas hydrates are distributed throughout the world, have a high energy density and are an environmentally friendly energy source with great potential. Today, experimental and theoretical studies of gas hydrates are associated with four important areas: gas hydrate formation and dissociation [1], extraction and transportation technologies [2], and combustion behavior [3]. An important direction is related to the stability of the composition and structure of gas hydrates.

To study the characteristics of the combustion of gas hydrates, various methods of initiating the process are used. The purpose of this work was a theoretical study of the gas hydrate combustion initiation initial stage under convective heating conditions.

Under conditions of convective heating (at 973-1273 K), the gas hydrates ignition delay time decreases by 90-93% with a change in the heat transfer coefficient (α) in the ranges of 0–200 W/m^2·K (Fig. 1), which corresponds to the air flow velocity of up to 6 m/s. The minimum decrease in the ignition delay time, i.e., from 0.1001 s to 0.0255 s (by 75%), corresponds to a heating temperature of 1073 K. The maximum decrease is at a temperature of 1273 K, where by ignition delay time changes from 0.1001 s to 0.0083 s (by 92%), the value of α varies between 0 and 200 W/(m^2·K).

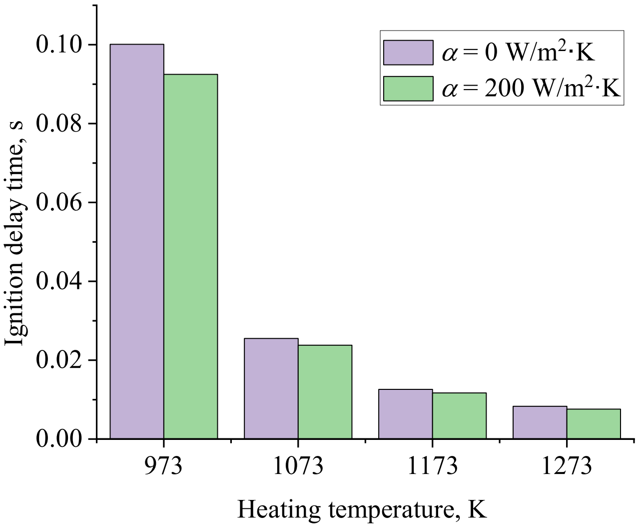

Figure 1 – Theoretical dependency ignition delay time on heating temperature under convective heating conditions.

In this paper, a model for initiating the combustion of gas hydrate during heating with the dominance of convective heat transfer has been developed. The dependence of the ignition delay time on the heating temperature by varying the heat transfer coefficient has been established.

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References

1. X.-Y. Li, J.-C. Feng, X.-S. Li, Y. Wang, H.-Q. Hu, *Appl. Energy* **2022**, 305, 117852.
2. H.P. Veluswamy, A. Kumar, Y. Seo, J.D. Lee, P. Linga, *Appl. Energy* **2018**, 216, 262-285.
3. G. Cui, Z. Dong, K. Xie, S. Wang, T. Guo, J. Liu, X. Xing, Z. Li, *Fuel* **2021**, 300, 120926.

Influence of gel fuels composition on ignition and combustion characteristics under radiant heating

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One of the ways to improve the energy characteristics of fuels is to add fine particles into composition [1]. The presence of such particles in the gel fuel composition can affect microexplosive dispersion characteristics during gel fuel ignition and combustion processes [2]. In addition, gel fuels are characterized by higher energy characteristics, lower negative impact on the environment, and lower cost of the component base in comparison with widely known solid and liquid fuels. [3]. Thus, the purpose of the research is to experimentally study and establish the characteristics of the processes occurring during the ignition and combustion of gel fuel particles, including those with the addition of fine metallic and non-metallic particles, in a high-temperature motionless air medium.

Oil-filled cryogels (gel fuels) are prepared on the basis of a 10 wt% aqueous solution of polyvinyl alcohol with the addition of 30 wt% finely dispersed solid components: coal particles, inert particles, aluminum. The preparation of gel fuels was carried out according to the well-known method [4].

The characteristics of the micro-explosive dispersion of single gel fuel particles during ignition were explored using a well-tested experimental technique and setup [5], consisting of a tubular muffle furnace, a high-speed video camera and a minirobotic arm with a holder for introducing fuel particles into a high-temperature oxidizer medium.

The ignition delay times (t_d) of fuel particles and the average speed values of fine fragments (V_p), formed throughout the droplet dispersion of the fuel melt were recorded during experiments. The effect of microexplosive dispersion was observed during ignition of all gel fuel compositions. Unlike it is with liquid single-component fuels, combustion is initiated not in the immediate vicinity of the droplet but in a rather large area. This positively affects the development of subsequent combustion of the fuel and enhances the burnout of components.

By varying the heated air temperature in the range of 600–1000 °C the ignition delay times change from 1 to 10 s, and the fine particles velocities after the micro-explosive dispersion of fuel melt droplet change from 0.3 to 1.4 m/s. The most intense ignition of the composition with the addition of fine coal particles in the entire range of heating source temperature variation. Gel fuel with Al particles exhibits the worst ignition and combustion characteristics (highest value of t_d, lowest value of V_p). At temperatures above 900 °C, the composition of the fuel does not significantly affect the ignition delay times.

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References

1. M.B. Padwal, B. Natan, D.P. Mishra, *Progress in Energy and Combustion Science.* **2021**, 83, 100885.
2. D. Sundaram, V. Yang, R.A. Yetter, *Progress in Energy and Combustion Science.* **2017**, 61, 293.
3. D.O. Glushkov, A.G. Nigay, V.A. Yanovsky, O.S. Yashutina, *Energy and Fuels*. **2019**, 33, 11812.
4. D.O. Glushkov, G.V. Kuznetsov, A.G. Nigay, V.A. Yanovsky, O.S. Yashutina. *Powder Technology.* **2020**, 360, 65.
5. D.O. Glushkov, A.O. Pleshko, O.S. Yashutina, *International Journal of Heat and Mass Transfer*. **2020**, 156, 119895.

Thermal Decomposition of Dinitropyrazoles: New Insights from Predictive Electronic Structure Theory and Thermal Analysis

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Nitrogen-rich heterocycles and their derivatives are promising environmental-friendly energetic compounds. In present work, we studied most important safety concerns, thermal decomposition, of 3,5-dinitropyrazole (3,5-DNP), and 5-amino-3,4-dinitropyrazole (5-ADP) using a complementary combination of thermal analysis and quantum chemical calculations. Differential scanning calorimetry (DSC) measurements were performed at atmospheric and elevated pressures (up to 5 MPa) under different heating rates (0.5 - 20 K/min). The increase of the external pressure renders the decomposition kinetics to be dominant rather than vaporization process. The experimental data were processed using isoconversional and formal kinetic approaches to derive the kinetic models. The experiment was complemented by the highly accurate CCSD(T)-F12 and DLPNO-CCSD(T) quantum chemical calculations to justify the use of particular reaction models and to compare the kinetic parameters for the dominating primary thermolysis reactions. Among the reaction pathways, conventional reactions, namely, radical reaction of C-NO_2 bond scission, the intramolecular oxidation, hydrogen transfer, and nitro-nitrite rearrangement were considered. The most energetically favorable channels for 35-DNP we identified new decomposition channel that commences from sigmatropic [1,5] H-shift followed by the pyrazole ring opening yielding a molecular nitrogen and a nitro radical as simple primary products. The limiting stage is the first hydrogen transfer with the effective activation energy Ea = 60.7 kcal/mol. For 5-ADP the decomposition starts with a [1,2] sigmatrophic hydrogen shift, followed by another [2,3] hydrogen shift leading to 5-amino-3,4-dinitro-3H-pyrazole, which can then decompose via several pathways. The limiting stage of the process is the second hydrogen transfer with an effective activation energy is 52 kcal/mol. To understand the autocatalytic nature of 5ADP decomposition, we also considered the secondary thermolysis reactions. Among those reactions we identified the one that can be responsible for the autocatalytic nature of 5ADP decomposition: viz., the primary radical product can be easily accessed from the reactants and then NO_2 is promptly eliminated.

M.G. and V.K. are indebted to Russian Foundation for Basic Research for a financial support of this work (project 20-33-90176); support by the Supercomputer Center of Novosibirsk State University and Irkutsk Supercomputer Center of SBRAS is also acknowledged.

Modeling the dynamics of hydrogen combustion using the neural network UNET

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The paper investigates the possibility of solving problems of chemical kinetics using artificial neural networks. A model of combustion of hydrogen with oxygen in air was chosen for the study. In the reaction at high temperatures (500-4000 K) hydrogen H2, oxygen O2, their derivatives (H, O, OH, H2O, HO2, H2O2), as well as neutral elements argon Ar and nitrogen N2 are interact. The whole process is described by 28 chemical reactions [1-2]. Mathematically, the problem is reduced to a system of differential equations:

$$\frac{\partial X_k}{\partial t} = \sum_{r=1}^{N_R} \nu_{rk} \omega_r \left(T, X_1, \ldots, X_{N_C} \right).$$

The main problem in solving such problems by numerical methods is that their complexity increases sharply with an increase in the number of parameters (more variables, more equations). Neural networks allow you to save computational costs when changing the number of input and output parameters.

For modeling, a neural network architecture was chosen, in which there is a skip connection from input to output - such as the UNET architecture [3], only with fully connected layers. Thus, the neural network only needs to learn the change in the concentration of substances over time, which allows the parameters of the neural network to learn more quickly (usually 50-100 training epochs are enough).

n_{steps}	$\langle MSE \rangle$	σ_{MSE}	$MSE_{\max}$
1	0.00114	0.00254	0.0228
2	0.000728	0.00215	0.0268
5	0.000492	0.00113	0.0139
10	0.000217	0.000526	0.00480
20	8.97E-05	0.000189	0.00172
30	8.77E-05	0.000211	0.00170
40	0.000134	0.000541	0.00755
50	8.86E-05	0.000204	0.00221

Table 1. Error for different number of prediction steps during training

In order to reduce the error incursion and improve the quality of prediction, it was proposed to include in the loss function the results of predicting the neural network several steps ahead in the recurrent mode. As a result of such training, the quality of prediction has improved significantly (Table 1), and the graphs of neural network prediction and real numerical calculation almost coincide.

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References

1. N. N. Smirnov, V. B. Betelin, V. F. Nikitin, L. I. Stamov, and D. I. Altoukhov. Accumulation of errors in numerical simulations of chemically reacting gas dynamics. Acta Astronautica, 117:338–355, 2015.
2. GRI-Mech Version 3.0 7/30/99 CHEMKINII format, at http://www. me. berke-ley.edu/gri_mech/.
3. Ronneberger, Olaf, Philipp Fischer, and Thomas Brox. "U-net: Convolutional networks for biomedical image segmentation." In International Conference on Medical image computing and computer-assisted intervention, pp. 234-241. Springer, Cham, 2015.

Experimental study of the combustion process on the surface of wood construction materials

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Infrared thermography (IRT) is becoming a commonly used technique to nondestructively inspect and evaluate wood structures [1]. Based on the radiation emitted by all objects, this technique enables the remote visualization of the surface temperature without making contact using a thermographic device [2, 3].

A number of laboratory experiments on estimation of fire-hazardous properties of various types of wood construction materials (plywood, chipboard, and oriented strand board) were carried out using a scientific infrared (IR) camera JADE J530SB. Use of noncontact method in estimation of the fire-hazardous properties of wood construction materials allowed one to obtain a temperature field distribution on the sample surface after seat of fire exposure [4-5].

Experimental investigations included simulated cases of firebrands, on the one hand, formed during a wildfire and gathered on a roof and corners of buildings, near fences or got inside the premises causing the ignition, on the other hand, burning front from the ground fire effects on objects made of wood construction materials treated with various fire retardants. Furthermore, a method for the fast analysis of fire-hazardous properties for fire retardants, depending on consumption, the species of wood and the source of fire (a layer of plant fuels, firebrands of pine bark and pine branches) were developed.

In the Large Aerosol Chamber of of the Center for Collective Use (CCU) "Atmosphere", preliminary experiments were carried out on a “Firebrand Shower” model exposure, which is naturally occurring firebrands with some types of construction materials (chipboards). The exposure of the samples to flow of firebrands was provided using a firebrand generator of own original design. The database of the main fire-hazardous characteristics for construction materials would become a key factor in the prediction of fire hazard during wildland-urban interface fires. Moreover, the results would be used in creation of building regulations and refinement available one for residential and industrial facilities.

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References

1. Z. Gossorg, Mir, Moscow, **1988**.
2. N. Ludwig, V. Redaelli, E. Rosina, F. Augelli, *Infrared Phys. Technol.* **2004**, 46(1):161-166.
3. G. López, L.A. Basterra, L. Acuña, *Infrared Phys. Technol,* 2018. 89(1): 242-246.
4. D.P. Kasymov, M.V. Agafontsev, V.V. Perminov, V.V. Reyno, P.S. Martynov, *Vestn. Tomsk. Gos. Univ. Mat. i Mekhanika*. **2019**, 65–78.
5. Kasymov D, Agafontsev M, Perminov V, Martynov P, Reyno V, Loboda E. *Fire.* 2020; 3(4):61. https://doi.org/10.3390/fire3040061.

Modern Predictive Quantum Chemical Calculations for Thermochemistry and Decomposition Kinetics of Energetic Materials

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Highly accurate theoretical values of bond energies and activation barriers of primary decomposition reactions are crucial for reliable predictions of thermal decomposition and detonation-related phenomena of energetic materials (EM). However, due to the prohibitive computational cost, high-level ab initio calculations had been impractical for a large number of important EMs of medium size, including, e.g., CL-20. The widely used DFT calculations very often could not provide the uniform “chemical accuracy” (~1 kcal/mol) and, ultimately, the convincing mechanistic evidence on the decomposition pathways of important EMs.

Here we report on the advantages in the theoretical thermochemistry and kinetics of EM achieved with the use novel local modifications of the coupled cluster (DLPNO-CCSD(T)). These render feasible high-accuracy calculations on caged polynitroamino and polynitro EMs, e.g., CL-20 and octanitrocubane (ONC). For all important species studied, the obtained values of bond energies are at least 10 kcal/mol more accurate than those reported in the literature so far. We also studied in detail the gas-phase thermochemistry of novel high-energy polynitro derivatives of 5/6/5 heterocyclic frameworks comprised of fused tetrazine and two triazole or pyrazole rings. To this end, we proposed and benchmarked a “bottom-up” approach. First, highly accurate multi-level procedures W2-F12 and/or W1-F12 in conjunction with the atomization energy approach were utilized for smaller species. In turn, for medium-sized species (up to 24 non-H atoms), these values were complemented with the enthalpies of isodesmic reactions calculated using DLPNO-CCSD(T)/aVQZ. We obtained a set of accurate and mutually consistent gas-phase formation enthalpies for 12 energetic heterocyclic species. As a rule, DLPNO-CCSD(T) allows for routine QZ-quality coupled cluster calculations with reasonable turnaround computational times for the energetic species comprised of ~30-40 non-H atoms. In a more general sense, this offers a new level of predictive computational thermochemistry and kinetics for important EMs. The reliable DLPNO-CCSD(T) key thermochemical values comprise a viable step beyond the commonly used DFT procedures.

We also proposed a new approach for the determination of standard (solid) state enthalpy of formationof EM based on complementary high-level quantum chemical calculations (W1-F12 and W2-F12) of the gas-phase values and advanced thermal analysis techniques yielding sublimation enthalpies. We performed a massive benchmarking of the proposed procedure on a large set of EMs.

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The effect of the addition of solid calcium-based sorbents on the absorption of sulfur during the thermal disposal of car tires

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Sulfur is found in many solid fuels and man-made combustible waste. One of these fuels is energy brown coals. When burned, the sulfur contained in them in the form of acid gases enters the atmosphere and harms the environment. The purpose of this work was to study the distribution of sulfur compounds during the combustion of sulfurous brown coals in the filtration mode and to study the possibility of sulfur neutralization by adding calcium-based sorbents.

The experiments were carried out on a laboratory quartz reactor with a diameter of 46 mm (fig. 1). The air gasification of mixtures of particles of energy sulphurous brown coal of a coal Moscow basin (5-10 mm) and a solid coolant is investigated. In one series of experiments, the heat carrier was porcelain Raschig rings (5-10 mm), and in another - a marble crumb (3-5 mm) capable of chemically binding sulfur compounds. The composition of the resulting ash residue, gaseous products, combustion temperature and rate, as well as the yield and composition of resins were determined.

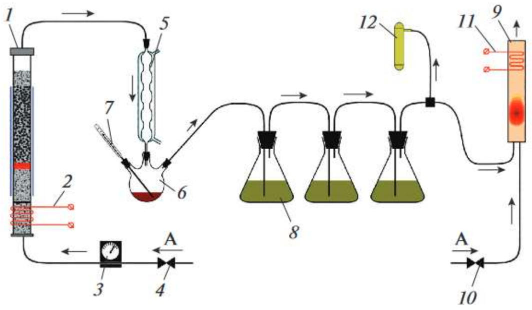

Fig. 1. Schematic diagram of the experimental setup: 1. reactor; 2. electric coil; 3. rotameter; 4, air supply valve to the reactor; 5. water cooler; 6. resin collecting flask; 7. thermometer; 8. bubbling flasks; 9. combustible gas afterburner; 10. air supply valve to the afterburner; 11. electric coil of the afterburner; 12. sampling of gaseous products.

Experiments have shown that when Raschig rings are used as a coolant, with an increase in the mass fraction of rings in the mixture to 50%, the heat of combustion of gaseous products decreases from about 3.60 to 2.75 MJ/m^3, and the proportion of sulfur passing into ash decreases from 12 ± 1% to 1 ± 1%. The addition of up to 50% marble leads to a decrease in the heat of combustion of gaseous products from about 3.60 to 2.55 MJ/m^3. The proportion of sulfur passing into solid combustion products with 50% marble addition increases linearly from 12 ± 1% to 36± 2% compared to the gasification of the initial coal. The resin yield in both series of experiments was approximately 8 ± 1.5% of the fuel mass, the elemental composition of the resins was: C = 74.5-75.5%, H = 6.8-8.4%, O = 10.7-13.3%, N = 0.8-1.2%, S = 2.9-4.6%.

The measurements of the elemental composition of the materials used and the combustion products were carried out in the Analytical center for collaborative using of the IPCP RAS.

The study was carried out with the financial support of State Task No. 0089-2019-0018 State registration No. AAAA19-119022690098-3.

Simultaneous determination of time and length scales of local temperature fluctuations in a turbulent flame by using coherent anti-Stokes Raman spectroscopy

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Determination of time and length scales of local gas temperature fluctuations in a turbulent flame by using coherent anti-Stokes Raman scattering (CARS) spectroscopy has been demonstrated for the first time. Two CARS-spectrometers [1] with synchronized 10 ns pulse duration 10 Hz repetition rate lasers were employed to perform two-point "instantaneous" temperature measurements by recording series of single-shot CARS spectra of N_2 molecules at a variable temporal delay between two sequential laser shots following each other in pairs. The spectra were obtained from two small probe volumes ($0.03\times0.03\times2$ mm^3) separated from each other by a variable distance in an open partially-premixed methane-air flame. From the spectra, series of temperatures at certain delays [2] and/or distances were derived. The obtained values enabled calculation of the time, space and space-time correlation coefficients of temperature fluctuations *vs* the delays and distances and thus evaluation of characteristic time and length scales of these fluctuations.

The results are presented for the series of 500 single-shot coupled measurements of temperatures at the delays in the range 0.1 μs-10 ms and the distances from 0.2 to 2.5 mm in a few spatial points of the flame with the average temperatures between 1200 and 1800 K and different visually distinguishable stability of combustion. The measurements, performed at various mixture flow rates and equivalence ratios, provided correlation times in the interval 100-400 μs and correlation lengths, across or along the flame axis, about 1-2 mm. The results show that, based on temperature correlation coefficients, mean axial flow velocity can be evaluated, and fuel and oxidizer mixing quality can be characterized.

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References

1. V.V. Smirnov, S.A. Kostritsa, V.D. Kobtsev, N.S. Titova, A.M. Starik, *Combust. Flame* **2015**, 162, 3554.
2. V.D. Kobtsev, D.N. Kozlov, S.A. Kostritsa, S.N. Orlov, V.V. Smirnov, S.Yu. Volkov, *Journ. Phys.: Conf. Series* **2021**, 2127 , 012012.

CARS and chemiluminescence diagnostics of a diffusion flame of boron nanoparticles in isopropanol with oxygen

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The analysis of diffusion combustion of a composite fuel (formed by addition of boron nanoparticles, NPs, to isopropanol in the amount of 0.5 wt %) with oxygen was performed. For these purposes an experimental stand was developed and built, consisting of a special burner equipped with the diagnostic system to detect CARS and chemiluminescence radiations for the measurements of temperature distributions in the diffusion flame, the ignition delay time, and the velocity of a flame front propagation.

The morphology of the boron powder particles was studied using a transmission electron microscope, the diffraction patterns were measured on an X-ray diffractometer, and the size distribution of the NPs was determined using a disk centrifuge. The diffractogram showed that the boron NPs were amorphous with the presence of a crystalline phase of boron hydroxide B(OH)3. The mass distribution of the particles was bimodal, and most of the boron mass (99%) was concentrated in large particles with diameters on the order of 750 nm. At the same time, most of the particles were less than 50 nm in size. The number of large particles was small (<0.1%) [1].

The flame temperature distributions were derived from CARS spectra of N2 molecules along the direction, perpendicular to the axis of the flame propagation, at a few distances from the nozzle exit of the burner. The experimental results showed that during combustion of the composite fuel temperature in the flame front region increased by approximately 150°C compared with that in the flame of pure isopropanol [1].

The ignition delay time and the velocity of the flame front propagation were measured upon the photo dissociation of O2 molecules by the resonance 193-nm laser radiation. The experiments on recording the chemiluminescence of OH(A2+) radicals indicate that it is possible to ignite a composite fuel with oxygen at rather low temperatures <600 K, which are below the auto ignition temperature, under the action of the focused laser radiation with the pulse energy of ~25mJ. The induction time was rather small and varied in the range of 200–400 ns depending on mixture parameters and the pulse energy.

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References

1. E.V. Barmina, M.I. Zhilnikova, K.O. Aiyyzhy, V.D. Kobtsev, D.N. Kozlov, S.A. Kostritsa, S.N. Orlov, A.M. Saveliev, V.V. Smirnov, N.S. Titova and G.A. Doklady Physics, **2022**, Vol. 67, No. 2, p. 39

Formation of two-ring PAHs in circumstellar envelopes of asymptotic giant-branch stars

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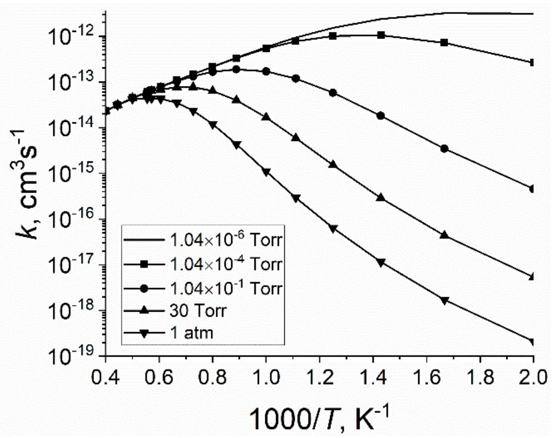
It is known, that PAHs can form from the growth of small aromatic molecules such as benzene and toluene in the shells of carbon-rich AGB stars and planetary nebulae. Methyl-substituted and, more generally, alkylated PAHs, the prototype molecule of which is toluene, can play a special role in the growth of PAHs. In high-temperature environments, for example, in circumstellar envelopes or during combustion, they can be formed as a result of methylation/alkylation processes, that is, as a result of CH_3/alkyl radical-to-H exchange reactions, which require significant barriers. The benzyl radical is formed from toluene by abstraction of an H atom from the methyl group. The present study revisited the mechanism and kinetics of the $C_7H_7 + C_3H_3$ reaction using advanced methods of transition state theory to evaluate critical rate constants of barrierless entrance and exit reaction channels. The calculations uphold the reaction mechanism proposed in the earlier work by Matsugi and Miyoshi[1], but provide new quantitative details. The final energy refinement was based on a modified combined scheme: E[G3] = E[CCSD(T)/6-311G**] + E[MP2/G3Large] - E[MP2/6-311G**] + E(ZPE), where CCSD(T) is the coupled cluster method with the 6-311G** basis, and MP2 is the Möller-Plesset second-order perturbation theory method with the 6-311G** and G3Large basis sets. The reaction mechanism includes several biradical compounds (singlets with open shells), for which geometry optimization and vibration frequency calculations were performed using the unrestricted UB3LYP/6-311G** approach, and the total energies were refined using the composite triplet-singlet-gap method[2]: $E^S = E^T$ [G3(MP2,CC)] + $\Delta E^{S\text{-}T}$(CASPT2(10,10)/cc-pVTZ) + ZPE^S, where E^T[G3(MP2,CC)] is the G3(MP2,CC) energy of the triplet state without ZPE with an optimized open-shell geometry, $\Delta E^{S\text{-}T}$(CASPT2(10,10)/cc-pVTZ) is the difference between the singlet and triplet states calculated using the second-order multiconfiguration perturbation theory method CASPT2 with an active space consisting of 10 electrons distributed over 10 orbitals and with the basis cc-PVTZ. It is shown that at high temperatures about 2500 K, the constant rates of formation methyleneindanyl radicals for the measured pressure values in the AGB stars are at the level of about 2.31×10^{-14} cm^3 s^{-1}. However, with a decrease in temperature and the rate of formation (p9+p10) + H increase by orders of magnitude, which interrupts the apparent weakening of the appearance of the initial complexes and an increase in the yield of bicyclic reaction products.



Picture 1 – Constant rates of the reaction $C_7H_7 + C_3H_3 \rightarrow (p9 + p10) + H$ expected at various pressures

References

1. A. Matsugi, A. Miyoshi, Int. J. Chem. Kin. **44**, 206 (2011).
2. J. A. Miller, S. J. Klippenstein, Y. Georgievskii, L. B. Harding, W. D. Allen, A. C. Simmonett, J. Phys. Chem. A **114**, 4881 (2010).

Stability of premixed methane-air swirled flame

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The structure of non-reacting swirling jets is known to be largely dependent on the degree of swirling and the way of swirling. [1]. Helical instability modes are amplified, the vortex core breaks up, and a recirculation zone appears when the mixing layer swirls sufficiently. Thermal expansion effects are superimposed on top of all the other effects in reacting swirling flows. As a result, flow swirling is commonly used as a method for forming large-scale vortex structures. The presence of stagnant recirculation zones in such structures allows for an increase in the reaction products' contact time with the fresh fuel-air mixture. The fuel-air mixture is heated during contact, which facilitates ignition, in turn the vortex core's precession significantly increases the intensity of heat and mass transfer. All of this improves combustion stability, especially in lean combustible mixtures. This highlights the importance of studying the nature of the stability of reactive flows with large-scale vortex structures. Gravity, through the buoyancy, is known to play a significant role in the dynamics and stabilization of the flame, as well as other characteristics. Because there is a competition between the buoyancy forces and the flow energy in this case, the lower the flow velocity, the greater the influence. When swirling, the recirculation zone is just an area with a reduced velocity, which means that it is subjected to a noticeable effect from gravitational forces. This shows the expediency of analyzing the influence of gravitational forces on swirling reacting flows.

The limits of stable combustion of a swirling methane-air flame under normal and reverse gravity are investigated in the present study. The burner is a Vitoshinsky nozzle with a contraction length of 28 mm and an inlet diameter of 30 mm and an outlet diameter of 15 mm. A bladed swirler was placed inside the nozzle to swirl the flow. In the work, the swirl coefficient ranged from 0.4 to 1.2. A constant temperature hot-wire anemometer was used to assess the dynamic characteristics of a swirling isothermal flow (measuring the mean value and standard deviation of the velocity). The stability of the flame under various gravitational conditions was estimated based on the stability diagram. In the coordinates of flow rate versus fuel equivalence ratio, the parameters of dettaching, re-attaching and blow off were determined for conditions of normal and reverse gravity. Under normal and reverse gravity conditions, the results are compared for a flow without a swirler and for a flow with a swirler. It can be seen that the boundaries of a complete blow-off are in conditions of significantly higher velocities in reverse gravity compared to normal gravitational conditions. At the same time, such a swirler does not affect the blow-off conditions for +1g conditions, and the effect becomes noticeable under reverse gravity conditions, and grows with an increase in the excess of fuel in the mixture. In this case, the swirl allows you to get a detached and re-attached flame.

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References

1. H. Liang, T. Maxworthy, *J. Fluid Mech.* **2005**, 525, 115.

In search of equilibrium in laser-produced cloud: role of pressure, chemical quenching, and plasma expansion

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The properties of laser plasma vary significantly depending on the pressure and composition of the environment, that makes it a promising emission source to imitate the radiation from various objects in atmosphere (meteor wake, airglow) and in outer space. We aimed to register spectra of FeO and CaO bands in laser plasma and vary conditions to make spectra profiles as close as possible to the ones observed during the Benešov bolide event. It allows to reconstruct the composition and behavior of meteor wake.

We fit synthetic CaO infrared system spectra by varying temperatures in the range from 1000 to 8000 K to the spectra measured in laser-induced plasma. It was found that the excitation (atomic species), vibrational and rotational temperatures of the experimental spectra indicate the absence of local thermodynamic equilibrium (LTE) and do not match each other. The atomic excitation temperature is close to 10000 K, vibrational temperature varies in the range of 3500–5000 K, while the rotational temperature is noticeably lower than ~2000–3000 K. Moreover, the specific values of rotational temperatures vary greatly from band to band. We also found the significant deviation of lines' wavelengths and transition probabilities between experimental spectra and model spectra based on EXOMOL data.

Calculation of the chemical composition of laser-produced clouds formed by laser heating of Fe and CaCO3 targets were performed. Timescales of main reactions with participation of Fe- and Ca-containing species were calculated using rate constants of the reactions. The results of calculations of equilibrium composition of laser-produced and impact-produced clouds are presented. Quenching conditions of chemical reactions in laser-produced and impact-produced clouds are found.

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Adjustment of the combustion mode in CuO/Al multilayer thermite materials

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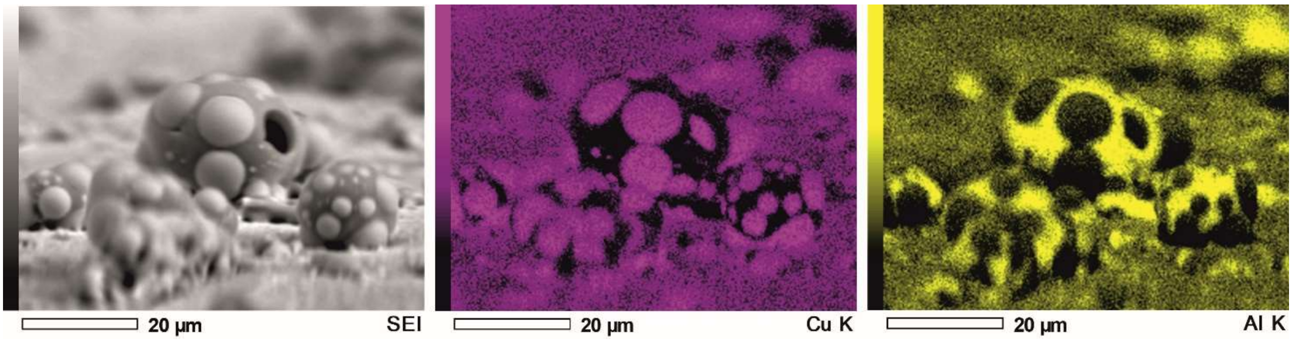
Multilayer thermite materials are a type of energy materials in which the fuel and the oxidizing agent are made in the form of alternating thin layers with a thickness from units to hundreds of nanometers. Such materials can be fabricated by traditional microelectronics methods - magnetron sputtering, electron beam, ion-plasma sputtering, etc. The formed laminated thermite materials can act as local heat sources and be used to bond surfaces, including heat sensitive components.

The most studied thermite materials are «aluminum–iron oxide» and «aluminum–copper oxide» pairs, which are characterized by large thermal effects and high adiabatic reaction temperatures of 4.1 kJ and 2843 K and 3.7 kJ and 3135 K respectively.

In the framework of this work, multilayer CuO/Al structures were studied, which were formed on the surface of various substrates (glass-ceramic or monocrystalline silicon) by magnetron sputtering. Sputtering of copper and aluminum oxide targets was carried out in an argon atmosphere. The samples differed in the ratio of component layer thicknesses and in the total thickness of the multilayer structure. Combustion was initiated using a spark from piezoelectric current source. The features of the combustion process were studied using high-speed video recording. The composition and geometric characteristics of multilayer structures were controlled using elemental analysis and electron microscopy (figure below).



SEM image of combustion products of a CuO/Al multilayer thermite structure

The possibility of adjustment the combustion mode of multilayer structures by changing the ratio of the thicknesses of the components was experimentally demonstrated - to change the intensity of gas evolution, to control the aggregate state of the reaction products after the reaction - solid, liquid or gaseous. An increase in the aluminum content in multilayer structures led to a significant decrease in gas evolution and an increase in the speed of propagation of the combustion front.

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Launch of a New Molecular Beam Machine

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We present a new molecular beam machine (fig .1) 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). Minimum pressure 10^{-11} Torr.
2. **Reflection Time-of-flight mass-spectrometer** (**RETOF**) with a max mass resolution $m/\Delta m=200$. A preamplifier Ortec 93061, a discriminator F-100T (ARI Corp), and a multi-scaler (MCS8A-2-T8 Fast Comtec) are used for data acquisition.
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.
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.
5. **Pyrolytic source.** Consists of a resistively heated tube of 22 mm length, 1 mm inner diameter; the achievable highest temperature of the tube was estimated to be around 1300-1400 K.
6. The frequency **tripling gas cell**, into which 355 nm pulsed, seeded Nd:YAG tripled laser radiation is focused, is used to generate soft VUV (118 nm, 10.5 eV). The tripling cell contains a mixture of Xe and Ar gas (~1/10, 200 Torr).

The fragmentation-free spectrums of the different hydrocarbons were obtained. The new machine will allow us to measure product distributions for various unimolecular (pyrolytic) and bimolecular reactions under combustion-like conditions.

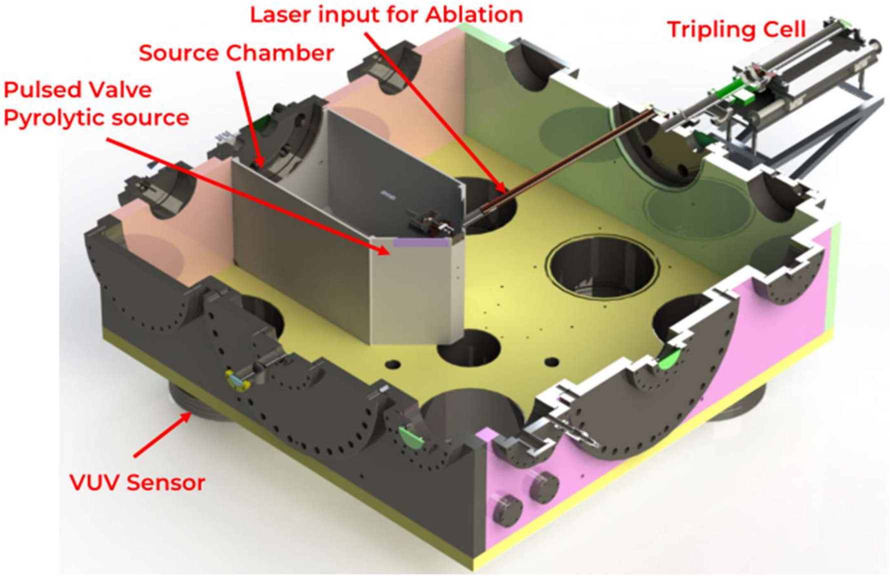

Fig. 1. Section view of the machine.

Numerical simulation of a rotating detonation wave engine for various concentrations of combustible mixture

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For a long time, the higher effectiveness of detonation regime of combustion against a common deflagration is well known [1], together with the possibility of its implementation in new engines. There are two main types of a detonation engine, pulse detonation engine [2], and an engine with a contiguous rotating detonation wave [3]. Recently, the second type of engines is of a great interest; its main advantages are: increased work cycle frequency, and a possibility of sub-sonic inflow of combustible mixture. There are three main geometries of a rotating detonation engine (RDE): annual RDE, hollow RDE, and disk RDE [4]. Among annual RDE’s, an elliptic-shaped combustion chamber racetrack RDE is featured, e.g. such a chamber was considered in [5], and it was shown that curvatures influence processes in the chamber, and conditions for a stable detonation are stricter than for an ordinary annual RDE. A disk RDE configuration is regarded in works by Bykowski [6], and in the paper [7].

The current work presents the results of computational modeling of processes in the combustion chamber of a detonation engine. A 3D numerical simulation of the combustion chamber of an engine with a rotating detonation wave of a cylindrical type with an internal body was carried out. The mathematical model was based on a multicomponent gas dynamics model which considered chemical transformations and a RANS turbulent model. To describe the combustion of acetylene, a short kinetic scheme was used, involving the following components in the reaction: C_2H_2, CO, CO_2, H_2, O_2, H_2O, OH, O, H, N_2. The mechanism was tuned against full kinetic mechanisms using a self-ignition delay time. The calculations were carried out using the geometry of an engine prototype. Comparison with experimental data was made.

This work was supported by the subsidy of the Ministry of Science and Education of Russian Federation on the topic: “Investigation and development of detonation combustion chambers being used in perspective aerospace propulsion systems” (No. 075-15-2021-1385). We would like to express our gratitude to the Center for Collective Use of the Joint Supercomputer Center of the Russian Academy of Sciences for the provided computing resources.

References

1. P. Wolański, Detonative propulsion, *P COMBUST INST* 34 ,**2013**, 125–158
2. K. Matsuoka, H. Taki, A. Kawasaki, J. Kasahara, T. Endo, *Combustion and Flame* 205, **2019**, 434-440
3. F. A. Bykovskii, S. A. Zhdan, E. F. Vedernikov, *Explosion and Shock Waves* 41(4), **2005**, 449–459
4. V. Anand, E. Gutmark, *Progress in Energy and Combustion Science* 73, **2019**, 182-234
5. H. Wen, Q. Xie, B. Wang, *Combustion and Flame* 210, **2019**, 389–398
6. F. A. Bykovskii, S. A. Zhdan, E. F. Vedernikov, A. N. Samsonov, A. S. Zintsova, *Combust Explos Shock Waves*; 52 (4), **2016**, 446–456.
7. R. Huff, M. D. Polanka, M. J. McClearn, F. R. Schauer, M. Fotia, J. L. Hoke, *2018 AIAA Aerospace sciences meeting Kissimmee*, Florida; **2018**

Preparation of highly dispersed ceramic nitride-carbide composition Si_3N_4–TiC by SHS method using halide salt and sodium azide

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Currently, Si_3N_4 is the main ceramic material for the production of products operating under high loads, for example, it is used for processing Ni-based superalloys [1]. However, the use of modern cutting tools based on pure Si_3N_4 for processing iron-containing alloys is limited due to the strong chemical interaction between Si and Fe [2]. It should also be taken into account that ceramics made of pure Si_3N_4 are very hard and difficult to machine even with a diamond tool, which significantly increases the cost of finished parts made of it. A simpler and cheaper method of electroerosion treatment turns out to be inapplicable here due to the very low electrical conductivity of Si_3N_4 ceramics, therefore much attention is paid to obtaining electrically conductive composite ceramics based on Si_3N_4, primarily Si_3N_4-TiC ceramics [3]. The best conductivity is observed in samples with a TiC content of more than 30% and is $2.3*10^{-2}$ S/cm [4].

In this paper, the possibility of obtaining a Si_3N_4-SiC composition by the azide self–propagating high–temperature synthesis (SHS-Az) method using NaN_3 as a nitriding reagent, as well as the halide salt $(NH_4)_2TiF_6$ is investigated [5]. The compositions of mixtures for obtaining single-phase Si_3N_4 and TiC powders by this method are known, from the analysis of which the equation was used to synthesize the Si3N4-TiC composition:

$15Si+6NaN_3+(NH_4)_2TiF_6+xC+(x–1)Ti=5Si_3N_4+xTiC+6NaF+4H_2$, $x = 1, 2, 4, 6, 8, 10$ mole.

Experimental studies of the possibility of obtaining the Si_3N_4-SiC composition were carried out in a laboratory SHS reactor in a nitrogen atmosphere at a relatively low pressure of 4 MPa and at a bulk density of mixtures of initial powders. The results of microstructure studies, energy dispersion and X-ray phase analyses have shown that combustion products of all initial mixtures consist of α- and β-Si_3N_4 fibers with a diameter of 70-150 nm and equiaxed TiN and TiC particles with a size of 100 to 500 nm. Note that combustion products also contain free Si at $x < 4$ mole. At $x \geq 4$ mole, free Si is replaced by SiC.

Thus, the use of the initial mixtures "$15Si+6NaN_3+(NH_4)_2TiF_6+xC+(x-1)Ti$" provides the preparation of compositions of ceramic highly dispersed Si_3N_4-TiN-TiC and Si_3N_4-SiC-TiN-TiC powders by the SHS-Az method, which differ significantly in the content or absence of free Si and the absolute absence of free Ti of compositions previously obtained by the SHS method [6]. It is planned to conduct further research in this direction in order to obtain a Si_3N_4-TiC nanopowder composition.

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References

1. M. Nalbant, A. Altın, H. Gökkaya, *Materials and Design*. **2007**, 28, 4.
2. G. Zheng, J. Zhao, Y. Zhou, Z. Gao, *Advanced Materials Research*. **2011**, 152.
3. C.Tian, N. Liu, M. Lu. *International Journal of Refractory Metals & Hard Materials*. **2008**, 26.
4. Y. Jiang, L. Wu, W. Sun, *AIP Conference Proceedings*. **2013**, 1542, 125.
5. Yu.V. Titova, A.P. Amosov, D.A. Maidan, G.S. Belova, *AIP Conf. Proceedings*. **2020**, 2304, 020008.
6. L.A. Kondratieva, I.A. Kerson, et al., *IOP Conf. Series: Mater. Sci. Eng*. **2016**, 156, 012032.

Quenching rate constants of the nitrogen molecule

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The emission spectroscopy methods are used to measure the lifetime of the excited states of nitrogen molecules and ions corresponding to the second positive and first negative systems of its radiation. The measurements are carried out in mixtures of molecular nitrogen with hydrocarbons in the afterglow of a repetitive high-voltage nanosecond discharge. As a result of processing the data obtained by varying the composition of gas mixtures and their pressure, the rate constants for quenching of the excited states of nitrogen in collisions with hydrocarbon molecules are determined.

The method used was verified by measuring the lifetime of the excited states of nitrogen molecules and ions in pure nitrogen and in a mixture with oxygen. After processing the data and obtaining the values of the quenching rate constants, the results were compared with those obtained by other authors [1, 2].

In this work, the time of the exponential fall of the radiation intensity is measured at various pressures of the studied gas mixtures with a known proportion of the incoming components, which makes it possible to vary the values of [N_2]. We find the quenching constants and the radiative lifetime of the vibrational levels $N_2(C^3\Pi_u,\ v' = 0,\ 1,\ 2,\ 3 \rightarrow B^3\Pi_g,\ v)$ and $N_2^+(B^2\Sigma_u^+,\ v' = 0 \rightarrow X_2\Sigma_g^+,\ v)$ corresponding to the second positive and first negative vibrational–rotational nitrogen systems.

The quenching constants of excited states of nitrogen molecules in mixtures containing hydrocarbons, in particular ethane and propane, have been measured. The second positive $N_2(C^3\Pi_u,\ v' = 0,1,2,3 \rightarrow B^3\Pi_g,\ v)$ and the first negative $N_2^+(B^2\Sigma_u^+,\ v' = 0 \rightarrow X_2\Sigma_g^+,\ v)$ nitrogen emission systems were studied.

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References

1. Pancheshnyi S. V., Starikovskaia S. M., Starikovskii A. Y. Collisional deactivation of N2 (C 3Πu, v= 0, 1, 2, 3) states by N2, O2, H2 and H2O molecules //Chemical Physics. – 2000. – T. 262. – №. 2-3. – C. 349-357.
2. Valk F. et al. Measurement of collisional quenching rate of nitrogen states N2 (C 3Πu, v= 0) and //Journal of Physics D: Applied Physics. – 2010. – T. 43. – №. 38. – C. 385202..

Relationship between polycyclic aromatic hydrocarbons, graphenes and fullerenes in the interstellar medium

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The interstellar medium is abundant of aromatic molecules which is revealed by observations. It is believed that mostly large carbonaceous molecules such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes are formed in carbon-rich asymptotic branch stars. However, some observations indicate that evolution goes on further in the interstellar medium due to influence of different factors (ultraviolet irradiation, erosion, etc.). Thus, abundance of PAHs and fullerenes changes in the ISM and within an individual object. This evolution has not been described in details so far.

This work is devoted to the study of the evolution of PAHs, graphenes, and fullerenes in the interstellar medium. Based on a number of recent experimental and theoretical investigations we developed the model in which PAHs evolve undergoing processes of photodesorption (carbon and hydrogen loss) and hydrogenation. Dehydrogenated PAHs, graphenes, may isomerise or fold into the closed structures - fullerenes. Fullerenes, in its turn, may also be hydrogenated and become fulleranes, can be photoprocessed, i.e. they lose their carbon and hydrogen atoms. The carbon loss leads to the shrinking of the fullerenes to smaller ones.

We calculate the abundance of all three carbonaceous compounds and ratios between each other depending on outer conditions: the gas temperature, intensity of radiation field, number density of atomic hydrogen and carbon, electrons. In addition, we calculate synthetic infrared spectra and ratios between fluxes of the bands specific to PAHs, fullerenes and graphenes. Relied on the calculations we highlight the conditions which are favourable for the mechanism of fullerene formation from PAHs. We applied our model to the photodissociation region Orion Bar with the enhanced radiation field intensity. Fullerenes were detected in this object by specific infrared bands at 17.4 and 18.9 mkm. We compare our estimations of the fullerene abundance in this object with the observations and conclude that our model gives satisfactory results.

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Using an unsaturated hydrocarbon as mitigator of developed detonation in hydrogen/syngas/air

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Detonation is a complex phenomenon due to a three-dimensional wave structure with an inhomogeneous dynamic wavefront [1-4]. The inhomogeneous front contains pressure triple points moving along it. If the triple points move in the vicinity of a soot-covered detonation tube surface, shear forces from them mark a fishnet-like pattern on the inner walls of the tube. This pattern is known as a detonation cell. As the leading shock front propagates downstream, the triple points alternate. Simultaneously, the transverse waves oscillate perpendicular to the direction of propagation [5]. Sizes of these detonation cells have been found to be one of the most important parameters in detonation research. The paper considers the influence of a hydrocarbon inhibitor on the developed detonation in a hydrogen-air or syngas-air mixture, on the destruction of the detonation front and subsequent decay of detonation cells.

The chemical reaction of hydrogen with air is a classic example of a branching chain reaction. In chain reactions, radicals play an important role as intermediate products of elementary stages. Without the mediation of radicals, the final product is not formed. The most mobile and active radical is atomic hydrogen H which plays an important role in nearly all combustion mechanisms involving hydrogen or its compounds. If its activity is reduced with a help of some chemical additive, the reaction will slow down. A slowdown in the reaction does not diminish its energy: the additive could be flammable itself. A decrease in the hydrogen atom activity can be achieved in many ways, one of which is using an unsaturated hydrocarbon; its reaction with H eliminates the double bond between the carbon atoms. The resulting alkane radical is much less active than atomic hydrogen. The amount of inhibitor could be several per cents by volume.

In the work, propylene C_3H_6 acts as an inhibitor; addition of atomic hydrogen to it gives the propyl radical C_3H_7. The self-sustaining properties of detonation are largely determined by the heat release delay time, which is determined by the development time of the chain process. Partial removal of atomic hydrogen from the chain process slows down the reaction and leads to the transition of the initially developed overdriven detonation into the combustion mode.

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References

1. V.N. Gamezo, A.A. Vasil'ev, A.M. Khokhlov, E.S. Oran *Proceedings of the Combustion Institute* **2000** Vol. 28(1), p. 611-617.
2. J.Lee, R. Knystautas, A. Freiman, *Combustion and Flame*, **1984** Vol. 56.
3. K. Kuo., Principles of Combustion, McGraw-Hill, Boston**, 2005.**
4. V.A. Levin, I.S. Manuylovich, V.V. Markov. T *Papers of the Academy of Sciences*, **2015**, 460 (1): 35–38.
5. A. Gavrikov, A. Efimenko, S. Dorofeev, *Combustion and Flame*, 2000, Vol. 120, p. 19-33. (in Russian)

Transformation of acetone into 1-propen-2-ol in the ice phase

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There are some theories of the origin of life on the Earth. One says that the very first important precursors of biomolecules were formed near hot springs, whereas another states that these molecules were created after lightning strikes due to a lot of releasing energy at this moment. However, aromatic compounds have been found in meteorites delivered to the Earth. Therefore, we can not rule out that building blocks for biomolecules are ubiquitous in outer space. This was confirmed by observations via radio telescopes. The thing is that due to the high rarefaction of the interstellar medium, atoms and molecules in the gas phase rarely collide. Organic precursor compounds are formed just during molecular collisions. On the other hand, we know that there are molecular dust clouds in space, from which, in fact, solar systems are formed. The density of the substance in dust grains is high, and the reaction rates are much higher than in a gas. This may explain the evolution of complex compounds in the low-temperature conditions of space [1, 2].

The purpose of the work is about revealing the mechanisms of the chemical conversion of acetone into prop-1-en-2-ol in the ice-phase reaction. The relevance is that the quantum chemical study of the mechanisms of miscellaneous ice-phase chemical reactions is of great importance in astrochemistry and astrobiology since it is one of the ways to find out how complex organic molecular species vital for the origin of life on the Earth were formed in the Universe.

Geometry optimization of different species related to searching for the ice-phase transition state between acetone and prop-1-en-2-ol was carried out at the long-range corrected hybrid density functional ωB97X-D level of theory with the 6-311G(d,p) basis set in Gaussian 09. At the first stage, the integrated water environment surrounding the molecules related to the transition state and imitating ice-phase conditions was not used. Moreover, there is the second stage where these ice-phase conditions were created by applying the SCRF=(PCM, solvent=water) approach in Gaussian that allows calculations to be performed in the presence of a solvent by placing the solute in a cavity within the solvent reaction field. Nevertheless, there are several obtained transition states at the first stage where water molecules helping an atomic hydrogen atom to migrate from carbon to oxygen without using SCRF=(PCM, solvent=water) approach was gradually added. The transition states of the first stage of optimization further were refined by performing a single-point calculation ωB97X-D/6-311G(d,p)+SCRF=(PCM, solvent=water) in Gaussian to check how the energies could change compared to the both approaches of geometry optimization. The final stage will be to refine energies of the second stage of optimization using the explicitly correlated couple clusters technique with single and double excitations, as well as perturbative treatment of triple excitations CCSD(T)-F12 along with Dunning's correlation-consistent cc-pVTZ-f12 basis set in Molpro 2010.

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References

1. S.A. Sandford, M. Nuevo, P.P. Bera, T.J. Lee, *Chem. Rev.* **2020**, 120, 11.
2. G. Molpeceres, *J.* Kästner, G. Fedoseev, H. Linnartz, T. Lamberts, *J. Phys. Chem. Lett.* **2021**, 12, 44.

The flame structure of ammonia/hydrogen/oxygen/argon blends at 4 and 6 atm

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One of the key problem of the modern energy systems is the transition to zero-carbon fuels. Hydrogen is the most perspective one. However, the application of pure hydrogen due to its specific properties inevitably encounters the problems of fire and explosion safety. The use of hydrogen carriers, in particular, ammonia, enables to solve these problems. Ammonia has well established infrastructure of its storage, transportation and distribution. Nevertheless, ammonia has high ignition energy and ammonia/air flames have very low burning velocity. The addition of hydrogen could improve ammonia combustion properties. Moreover, hydrogen can be produced via ammonia decomposition.

The aim of the present work is to obtain new experimental data on the flame structure of ammonia/hydrogen/oxygen/argon blends with different stoichiometry (φ=0.8, 1.0 and 1.2) at the pressure of 4 and 6 atm and to compare experimental results with numerical data obtained with four published chemical kinetic mechanisms (Models).

The experiments on the flame structure at elevated pressures were performed using molecular beam mass-spectrometric setup with soft electron impact ionization. Flames were stabilized on the flat burner. The burner temperature was 368K throughout the experiment. The burner was placed at high-pressure chamber. Nitrogen was used to maintain the pressure value. Temperature profiles were measured with thin S-type thermocouples made from the wire with a diameter of 0.03mm.

Numerical simulations were performed using PREMIX code from CHEMKIN package. The comparison of experimental and numerical data showed that the Model 4 recently developed in the work [1] showed the best predictive capability.

One of the key problems of the potential application of ammonia is fuel-nitrogen, which enhances NOx formation. The experimental data showed that the main nitrogen-containing species, which are present in the post-flame zone are N_2 and NO whereas concentration of N_2O and NO_2 is negligible. The analysis showed that the transition to rich fuel blends is more effective in terms of reduction of NO concentration in the post-flame zone as well as peak-concentration of NO, N_2O and NO_2. The pressure increase also results into the decrease of NO concentration in the post-flame zone as well as the decrease of NO, N_2O and NO_2 peak mole fractions.

The obtained data showed that mole fraction profile of NO is described well with the Model 4. However, there are larger discrepancies for N_2O and NO_2 peak mole fraction is significantly overpredicted. Numerical analysis revealed that N_2O and NO_2 form from ammonia molecule via NO. Thus, to improve the agreement of experimental and numerical data for N_2O and NO_2 it is necessary to refine rate constants of reactions involving NO.

This work is supported by the Ministry of Science and Higher Education of the Russian Federation (Project No: 075-15-2020-806)

References

1. X. Zhang, S.P. Moosakutty, R.P. Rajan, M. Younes, S.M. Sarathy, Combust Flame. **2021**, 234, 11653.

Mathematical modeling of surface fire initiation and spread

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The problems of wildfire initiation and spread was carried out in this paper. A mathematical model has been developed that describes the processes of heat and mass transfer in the surface layer of the atmosphere and in the forest zone, taking into account their mutual influence. Within the limits of the earlier applied models overterrestrial layer of atmosphere and the combustion front are considered as separate components or otherwise approximate relationships are used for description of their interaction [1]. It doesn't allow to describe nonstationary phenomena proceeding in the environment in a concrete way. The surface layer of forest is considered as a homogeneous two temperature, reacting, non - deformed medium. Temperatures of condensed (solid) and gaseous phases are separated out. The first includes a dry organic substance, moisture (water in the liquid-drop state), condensed pyrolysis and combustion products (coke, ash), mineral part of forest fuels components. In the gaseous phase we separate out only the components necessary to describe reactions of combustion (oxygen, combustible products of pyrolysis of forest fuels and the rest inert components). The solid phase constituting forest fuels has no intrinsic velocity, and its volumetric fractions, as compared to the gaseous phase, can be neglected in appropriate equations. It is considered that 1) the flow has a developed turbulent nature, molecular transfer being neglected, 2) 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, 3) forest canopy is supposed to be non-deformed porous medium. To describe the transfer of energy by radiation we use a diffusion approximation, while to describe convective transfer controlled by the wind and gravity, we use Reynolds equations for turbulent flow. The research is done by means of mathematical modeling of physical processes. It is based on numerical solution of three - dimensional Reynolds equations for chemical components and equations of energy conservation for gaseous and condensed (for canopy) phases. The boundary-value problem is solved numerically using the method of splitting according to physical processes. In the first stage, the hydrodynamic pattern of flow and distribution of scalar functions are calculated. The system of ordinary differential equations of chemical kinetics obtained as a result of splitting are then integrated. A discrete analog for equations is obtained by means of the finite volume method using the SIMPLE algorithm. As a result of mathematical modeling the fields of temperatures, mass concentrations of components of gaseous phase, volume fractions of components of solid phase, as well as vectoral fields of velocity at different instants of time with taking into account mutual influence of the overterrestrial layer of atmosphere and a crown fire on each other will be obtained. It allows to investigate dynamics of surface fire initiation and spread under influence of various external conditions: a) meteorology conditions (air temperature, wind velocity etc.), b) terrain, c) type(various kinds of forest combustible materials) and their state(load, moisture etc.). A great deal of final and intermediate gaseous and dispersed combustion products of forest fuels is known to be exhausted into the atmosphere during fires: carbon monoxide, carbon dioxide, nitrogen oxide, soot, smoke, methane, other hydrocarbons and etc.

References

1. A.M. Grishin, Mathematical Modeling Forest Fire and New Methods Fighting Them. Publishing House of Tomsk University, Tomsk (Russia). **1997**.

Experimental and numerical study of monodisperse ethanol mist combustion

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Ethanol is a promissing alternative to fossil fuels, which can be obtained by fermentation of biomass products. While ethanol was subjected to wide research, ethanol spray combustion with a controlled dispersion composition is not yet comprehensively studied. In the current work, we present a combined experimental and numerical study of monodisperse ethanol mist combustion.

The experimental setup consisted of a nozzle with Vitoshinsky profile, a jet of an air-ethanol mixture, and fine mist with different concentrations created by an ultrasonic mist generator. The combined Particle image velocimetry (PIV) and Planar laser-induced fluorescence (PLIF) study was performed to determine the laminar flame speed.

The numerical simulation was performed using the “sprayFoam” solver from OpenFoam (www.openfoam.com) open-source CFD package. The solver utilized a mixed Eulerian-Lagrangian approach, where the droplets are simulated as Lagrangian parcels and the gas phase is resolved on a fixed (Eulerian) grid. For the gas phase, a reduced chemistry model was used with resolving of 66 chemical reactions for 31 species. For spatial and temporal discretization, a second order implicit scheme was used (central differencing for space and Crank-Nicolson for time derivatives, respectively).

The simulation was performed in 3D for Reynolds number of 1000, approximately 10^7 grid nodes and solitary Lagrangian parcels. The inlet diameter of the droplets was chosen to be 14 10^{-6} m which is consistent with the experimental data.

We compare numerical and experimental data. For the droplets phase, the advection, collision (coalescence), and evaporation processes were considered. The temperature profiles and flame height were compared between those obtained with simulation and experiment.

The study was supported by the Russian Science Foundation, grant No. 22-19-00803. The experiment is carried out as part of the implementation of the state task in the IT SB RAS.

Modeling of gasification of complex solid porous polymer in low-temperature gas generator for high-speed flying vehicle

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Currently, research is underway to create a high-speed flying vehicle equipped with a solid fuel engine. At high flight speeds, the stagnation temperature of the incoming air flow reaches high values which do not allow air to be used as a coolant in the cooling system. In this case, hydrocarbon fuel placed on board the flying vehicle can be used to cool the engine. To implement such flying vehicle, it is necessary to use low-temperature gas generators of combined charges, consisting of propellant and evaporated solid energy-condensed fuel. This will allow the engine to be cooled by the convective flow of the gasification products of the evaporated fuel. In [1-2], a mathematical model and a numerical method were proposed for calculating the gasification of solid porous fuel, and this process was numerically investigated for the case when the gas pressure at the inlet of porous fuel was fixed, but inlet gas velocity was unknown and non-constant. The present work is devoted to the theoretical study of the regularities and mechanisms of gasification of solid porous fuel when solid porous fuel consists of different materials.

The influence of the characteristics of solid fuel on the operating conditions of the gas generator has been investigated for polymethyl methacrylate (PMMA) and polyethylene (PE). Four variants of the fuel composition are considered: 1) the fuel consists of PMMA, 2) the fuel consists of PE, 3) the fuel consists of PMMA:PE=50:50, 4) the fuel consists of PE:PMMA=50:50. It is shown that the composition of the fuel is a control parameter that determines the operating time of the gas generator.

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References

1. E. A. Salgansky, N. A. Lutsenko, V. A. Levin et al., *Aerosp. Sci. Technol.* **2019**, 84, 31.
2. E. A. Salgansky, N. A. Lutsenko, *Aerosp. Sci. Technol.* **2021**, 109, 106420.

Characteristics of ignition and combustion of fuel blends based on coal slime

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The purpose of this research was to study the main characteristics of the ignition and combustion of fuel compositions based on coal flotation waste (coal slime). Wood waste, waste turbine oil, and rapeseed oil were the additional components (5% wt.). Fuel mixtures were burned in a laboratory furnace in the form of slurry droplets, pellets, and a loose layer.

The temperature of stable heterogeneous ignition of all the studied fuels varied in the range of 480–550 °C. In the temperature range of 400–500°C, the volume fraction of CO in flue gases varied in the range of 1.3–4%, the fraction of CO_2 was 1.8–6%. In this temperature range, there is still no intense visible combustion of the coke residue, but oxidation occurs, which is well recorded using a gas analyzer. At higher temperatures (550–900 °C), the amount of carbon monoxide significantly decreased for all fuels, while the amount of carbon dioxide increased. In this temperature range, the generalized range of changes in the CO concentration was 0.5–3.1%, CO_2 was 1–9%.

The completeness of burnout improved with increasing temperature in the furnace. The main trend was that the mixtures of coal slime with additives burned out better than without additives. For example, the mass of the unburned residue of a coal slime pellet burned at 500 °C averaged about 40% of the initial mass of the sample. At a similar temperature, this value decreased to 27% if 5% sawdust was added to the pellet composition. In general, all additives increased burnout with similar efficiency (4–7% difference). During the combustion of water-containing slurry droplets at 700°C, the mass of the unburned residue was no more than 20% of the initial mass of the sample. Such values were not achieved even at 900 °C if the mixtures were burned in the form of a pellet or a loose layer. It can be concluded that there are quite good reasons to develop the technology of combustion of atomized fuel slurries, including due to the possibility of reducing losses that occur due to incomplete combustion.

The experiments confirmed that the diffusion of oxygen and combustion products outside the fuel and inside (in cracks and pores) can play a decisive role in the endo- and exothermic stages, especially at furnace temperatures below 800 °C. A more intense burnout is characteristic of slurry droplets. For fuel pellets, in general, the oxidation was weak due to the complicated supply of oxygen to the inner surfaces of the sample.

The composition of the fuel mixture largely determines the development of the combustion reaction. The decrease of the gas-phase ignition time by at least 2 times occurred when additives (turbine oil, sawdust, and rapeseed oil) were added to the coal slime. The decrease in the duration of the endothermic stage was maximum (3–6 times) when the coal slime was mixed with turbine oil, which, however, did not always lead to faster heterogeneous ignition.

The results obtained can be useful for optimizing technological processes at thermal power plants and boiler houses designed to burn fuel compositions based on combustible low-grade components and waste.

The study was supported by a grant from the Ministry of Science and Higher Education of Russia, Agreement No 075-15-2020-806 (Contract No 13.1902.21.0014).

Physico-chemical characteristics of energy condensed compositions based on polynitrogen heterocyclic compounds, poly-2-methyl-5-vinyltetrazole and SKI-3 rubber

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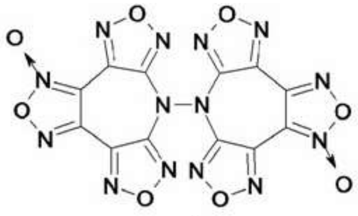
As an energetic condensed material (**ECM**), it was proposed to use a composition of high-enthalpy polynitrogen compound 1,1'-dioxide-7,7'-bis(tris([1,2,5]oxadiazolo)[3,4-b: 3', 4'-d: 3",4"-f] azepine) (**$Az_2(O)_2$**), isoprene rubber **SKI-3** and poly-2-methyl-5-vinyltetrazole (**PMVT**) as an active binder. The latter can serve as a useful additive to hydrocarbon binder to increase the temperature of the adiabatic transformation of solid fuel and to improve the characteristics of its combustion.



$Az_2(O)_2$

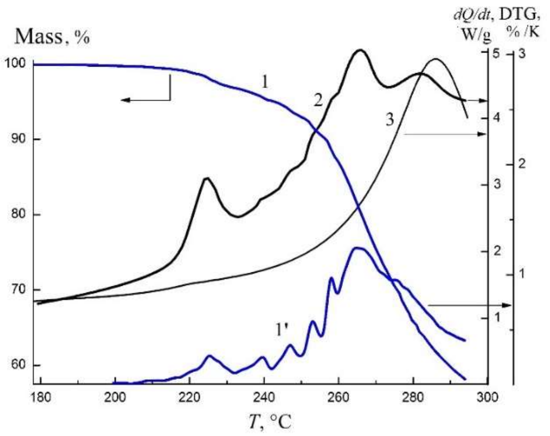


Figure 1. TGA (1) and differential TGA (1') of the **$Az_2(O)_2$ + PMVT** mixure; DSC in the decomposition of **$Az_2(O)_2$+PMVT** (2) and **PMVT** (3). Temperature rise rate 20 K/min.

The kinetic regularities of thermal decomposition and ballistic characteristics of a number of compositions based on **$Az_2(O)_2$** have been determined. It has been established that the burning rate of binary compositions **$Az_2(O)_2$ - PMVT** increases, and the thermal stability decreases compared to the corresponding characteristics of the initial components. It is shown that under nonisothermal conditions of decomposition of the mixture of 50 wt % **$Az_2(O)_2$** + 50 wt % **PMVT**, the DSC curves exhibit several maxima of the heat release rates, which are symbatic with the inflection points of the TGA curves. Thus, when creating formulations for energy condensed materials, it is necessary to take into account the possibility of their thermal decomposition processes occurring through a number of macroscopic stages, which, under certain conditions, can go into an oscillatory mode. The compositions were optimized on the basis of the above three components in terms of such characteristics as burning rate, thermal stability and relative flight range.

The work was done on the topic of the State tasks with State number registration №AAAA-A19-119101690058-9 and №AAAA-A19-119100800130-0.

Pore-scale numerical simulation of flame stabilization in two-layer porous burner

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Porous media burners are one of the most prospective devices in the energy industry due to its unique advantages following from heat recuperation mechanism. Such energy feedback from the combustion product to the fresh mixture leads to enhanced flammability limits, large effective flame speed, and low pollutant emission as well. In porous media burners, the flame can be stabilized at the external radiating surface, using cooling tubes, in the divergent flow. Different stabilization technique has been proposed by Trimis and Durst [1] based on the idea to close the flame between two different upstream and downstream porous sections with sub- and supercritical Péclet number respectively.

In the previous pore-scale simulations [2] it was shown that the flame stabilization mechanism is a complex interplay of heat recuperation, stretching effect, and flow hydrodynamics. In this work, the model two-dimensional two-layer porous burner was studied numerically within the framework of the pore-scale approach, principles and mathematical formulation are presented in the paper above.

Figure 1 shows the flame structure with the superficial flow velocity of 1.7 m/s when the front is stable and located at the interface between upstream and downstream layers. It can be noticed that the front is highly curved and stretched by the flow. During that, it anchors the particles and locates at the separating layer behind them. Similar flame behavior has been observed in many studies, devoted to flames near bluff bodies [3]. In spite of the difference in shapes and circular particles section, the stabilization mechanism is similar, considering solid-to-solid heat transfer via radiation.

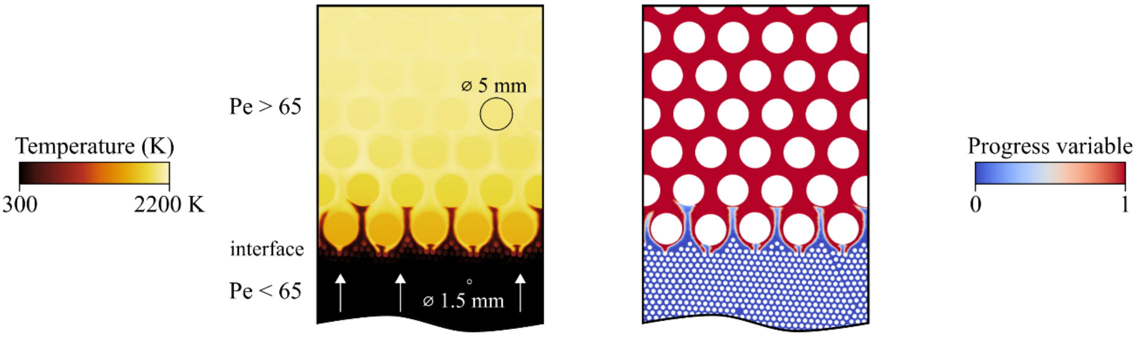

Fig. 1. Flame structure in two-layer porous burner

The pore-scale approach in some manner allows us to consider different effects on the local flame behavior. It can be seen, that physics of the flame stabilization at pore scale is more complicated than heat or velocity balance, but includes flame front deformation by non-uniform flow field and local configuration of particles packing.

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References

1. D. Trimis, F. Durst, *Combust. Sci. Technol.* **1996**, 121, 153–168.
2. I. Yakovlev, A. Maznoy, S. Zambalov, *Combust. Flame.* **2021**, 231, 111468.
3. K.S. Kedia, A.F. Ghoniem, *Combust. Flame*. **2015**, 162, 1304–1315.

Assessment of coke deposits during heating of hydrocarbon fuel under dynamic and static conditions

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A comprehensive assessment of coke deposits during heating of hydrocarbon fuels was carried out. Samples of RT and T-6 jet fuels developed at JSC TANECO were considered as objects of research.

Coke deposits in aggregates of fuel systems of aircraft at temperatures of 150-350 ºC are formed mainly due to the processes of interaction with oxygen. At temperatures of 350-500 ºC, the contribution of thermal decomposition becomes significant. Therefore, the key parameter determined in the experiments was the propensity of the fuel to form deposits in the processes of its thermal oxidation and thermal decomposition.

A dynamic method with a flow-heated reactor was used to study the thermo-oxidative stability of the samples. The main parameter to be determined was the rate of change in the hydraulic resistance of the test reactor (due to the formation of deposits) over time at a constant final temperature of the fuel flowing through it.

To study the process of thermal decomposition of samples, a static method was used, implemented on a manometric installation. In the course of the work, the kinetics of the thermal decomposition process, the final gas release (mol/kg) and the mass of the formed coke (% mass) were determined.

It was found that under the conditions of the absence of an increase in the hydraulic resistance of the test reactor, under dynamic conditions with an operating time of 50 hours, the maximum temperature of the RT fuel application is 200 ºC. For T-6 fuel, this temperature is 330 °C. Thus, in terms of thermal-oxidative stability, expressed in terms of the maximum application temperature, T-6 fuel exceeds RT fuel at the operating time specified in the experiment.

According to the results of studies of the kinetics of thermal decomposition of samples under static conditions at temperatures of 390-460 ºC, it has been experimentally shown that the thermal decomposition of T-6 and RT fuels obeys the first-order reaction equation. The activation energies of the thermal decomposition processes of the considered fuels are close and amount to ~ 256 kJ/mol. The rate constant of thermal decomposition of T-6 fuel under the same experimental conditions is on average 15% lower. This indicates its greater thermal stability in comparison with RT fuel. When the T-6 fuel sample is completely decomposed under experimental conditions, 2.8 times less coke is formed than when the RT fuel sample is decomposed. This indicates a large contribution of condensation processes with the formation of pyrolysis carbon (coke) during thermal degradation of RT fuel compared to T-6 fuel.

The data obtained is planned to be used to optimize the operation of fuel systems of power plants.

Formation of CaO in laser plasma studied by emission and fluorescence spectroscopy

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Laser-induced plasma is a universal plasma source for spectral diagnostics of processes under extreme conditions. Due to possibility to freely vary laser energy, ambient pressure, compositions of the ablation target and surrounding environment plasma parameters can also be varied within a wide range. Typical temperatures (0.2-4 eV) and electron number densities (10^{15}-10^{19} cm^{-3}) along the plasma evolution allow observation of both atomic emission and emission of small, predominantly diatomic, molecules. In spite of spatial inhomogeneity of laser plasma (which also can be considered as a benefit for laboratory modeling), its certain symmetry opens up space for spatially resolved studies. Laser-induced fluorescence in plasma appears to be one of the most promising tools for spatially resolved plasma diagnostics. All these unique properties of laser plasma, combined with research interest in combustion processes during the meteor events in the Earth's atmosphere, led us to the study of Ca and CaO distribution in laser plasma under low ambient pressure.

We measured emission spectra of atomic calcium and calcium monoxide varying delay after laser pulse and ambient pressure from 0.16 Torr to atmospheric. Plasma temperature and electron number density were calculated where possible. By comparison of experimental spectra and spectra of Benešov bolide at different heights we showed that the emitting bolide wake is formed under 7-10 times higher pressure than the one at the corresponding altitude. The obtained data lead us to suggestion that the formation of CaO in plasma occurs primarily using oxygen from atmosphere. Therefore, abundance of CaO should have a strong dependency on the pressure of the surrounding media.

Also, we performed plasma elemental imaging (resolution of 200μm along each of 2 axes) by the means of Ca and CaO fluorescence in laser plasma. Ca atomic lines Ca I 428.30 nm and Ca I 430.52 nm and bands of CaO red system were used for this purpose. The estimated spatial distribution of Ca atoms and CaO molecules in laser plasma proves our suggestion that CaO is formed both in laser plasma and in the meteor wake primarily using oxygen from ambient air on the periphery of the cloud and this process almost does not involve oxygen from the ablated material ($CaCO_3$).

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Numerical simulation of syngas combustion in rotary engine

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The synthesis gas can be considered as a key intermediate in energy conversion from fossil fuel to decarbonized and low-carbon technologies [1]. The synthesis gas (abbreviation – syngas) is a mixture mainly comprised of hydrogen and carbon monoxide. Usually it can include other gases: methane, carbon dioxide and nitrogen depending on the oxidation agent. Syngas can be produced from various carbonaceous feedstock (natural gas, naphtha, coal, biomass, etc.) with a limited gasifying agent (air, oxygen, steam), thus providing ample opportunities for fuel flexibility [2].

The internal combustion engines represent well-established technology of syngas utilization for power generation in remote areas [3]. However, there is a lack of knowledge related to syngas utilization in alternative engine types with different design such as the Wankel rotary engine. It is interesting to analyze the possibilities of the rotary engine fueled by syngas, produced on a large scale from various feedstocks by mature technologies. The biomass, coal and natural gas are considered as representative sources for syngas generation. The operation of the rotary engine fueled by natural gas is considered as a reference case.

It was shown that the main performance characteristics of the rotary engine are affected by the chemical composition of the fuel used. The high hydrogen concentration with minimum inert content of CO_2 of syngas produced from natural gas via steam methane reforming results in maximum power, heat release rate and thermal efficiency for stoichiometric and lean conditions. The natural gas and syngas produced by coal gasification provide comparable characteristics of indicated thermal efficiency under stoichiometric conditions. However, the presence of hydrogen in syngas produced by coal gasification allowed the enhancement of combustion characteristics at lean conditions in comparison with natural gas due to the increased reactivity of the mixture. Nitrogen addition and lower H_2 concentration in syngas produced from natural gas by non-catalytic partial oxidation and syngas produced by biomass gasification have an inhibiting effect on efficiency with a drastic decrease at lean conditions.

A great advantage in terms of emission is not always achieved by syngases fueling of the rotary engine. 71% of hydrogen in syngas produced from natural gas via steam methane reforming results in maximum NO_x emission due to high flame temperatures. the opposite trend can be observed between NO_x and CO emission pathways.

The use of syngas in a rotary engine can be considered as a valid method of electricity, power and heat production. The choice of appropriate production technology depends on the local availability of resources without excessive transportation costs. Syngas power generation system can provide environmental sustainability to the industry and reduce the external demand of energy carriers.

The reported study was funded by Russian Science Foundation according to the research project №21-79-00170, https://rscf.ru/en/project/21-79-00170/.

References

1. M. Fiore, Internal combustion engines powered by syngas: A review, *Appl. Energy* **2020**, 276, 115415.
2. N.N. Mustafi. Spark-ignition engine performance with “Powergas” fuel (mixture of CO/H_2): A comparison with gasoline and natural gas, *Fuel*, **2006**, 85, 1605–1612.
3. A.L. Boehman, O.L. Corre. Combustion of syngas in internal combustion engines, *Combust. Sci. and Tech.*, **2008**, 180, 1193–1206.

Radiation-induced transformations of acetaldehyde molecules at cryogenic temperatures: a matrix isolation study

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Acetaldehyde is one of the key small organic molecules involved in astrochemical and atmospheric processes occurring under the action of ionizing and UV radiation [1]. While the UV photochemistry of acetaldehyde is well studied [2], little is known about the mechanism of processes induced by high-energy radiation. In this study, we performed the first systematic study on the chemical transformations of CH_3CHO molecules resulting from X-ray irradiation under the conditions of matrix isolation in different solid noble gases (Ne, Ar, Kr, and Xe) at 5 K.

Matrix samples were obtained by deposition of gaseous mixtures (CH_3CHO/Ng or CD_3CDO/Ng 1/1000; Ng = Ne, Ar, Kr, or Xe) onto a cold KBr substrate mounted in a closed-cycle helium cryostat. The deposition temperatures were typically about 8, 18, 25 and 33 K for Ne, Ar, Kr and Xe matrices, respectively. The deposited matrices were irradiated with X-rays (45 kV_p, anode current 80 mA, effective energy ca. 20 keV) to different doses (up to 111 kGy) at 5 K. Photolysis of the irradiated samples was performed using appropriate ARPL-STAR-3W LEDs (λ_D = 620 nm and λ_D = 520 nm). The radiation-induced products and intermediates were characterized by FTIR spectroscopy.

The results of this study [3] demonstrate that CO, CH_4, H_2CCO, $H_2CCO–H_2$, $C_2H_2\cdots H_2O$, CH_2CHOH, $CH_3CO^\bullet$, $CH_3^\bullet$, $HCCO^\bullet$, and CCO are the main acetaldehyde radiolysis products. It was found that the dominant pathway of acetaldehyde degradation involves C–C bond cleavage leading to the formation of carbon monoxide and methane. The second important channel is dehydrogenation resulting in the formation of ketene, a potentially highly reactive species. The significant effect of the matrix media both on the decomposition efficiency and distribution of the reaction channels was observed. Based on these observations, it was suggested that the formation of the methyl radical as well as vinyl alcohol and the $C_2H_2\cdots H_2O$ complex presumably included a significant contribution of ionic pathways. The decomposition of acetyl radicals under photolysis with visible light leading to the $CH_3^\bullet$–CO radical-molecule pair was detected in all matrices, while the recovery of $CH_3CO^\bullet$ in the dark at 5 K was found only in Xe. This finding represents a prominent example of matrix-dependent chemical dynamics, which may involve the tunnelling mechanism. Probable mechanisms of acetaldehyde radiolysis and their implications for astrochemistry, atmospheric chemistry and low-temperature chemistry are discussed.

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References

1. C.J. Bennett, C.S. Jamieson, Y. Osamura, R.I. Kaiser, *ApJ* **2005**, 624, 1097.
2. A. W. Harrison et al., *Phys. Chem. Chem. Phys.* **2019**, 21, 14284 and references therein.
3. P.V. Zasimov, E.V. Sanochkina, V.I. Feldman, *Phys. Chem. Chem. Phys.* **2022**, 24, 419.

POSTER TALKS

The Influence of Hydrogen Addition on the Combustor Thermal State

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One way to reduce combustion chamber emissions is to use hydrogen additives to hydrocarbon fuels, such as using a methane-hydrogen mixture. However, hydrogen has a high flame speed, a high combustion specific heat and, as a result, a high thermal load on the combustion chamber components. Therefore, the use of hydrogen additives leads to a revision of the setting of operating parameters in order to comply with technical requirements.

The aim of this study is to determine the effect of hydrogen additives in the fuel on the thermal state of the combustor.

The study was carried out on a model combustion chamber by experimental and computational methods. The combustion chamber includes two fuel supply circuits: main and pilot. There is also an air supply circuit that goes to cool the flame tube with the ability to adjust the flow rate. Seven thermocouples were installed along combustor length on the outer surface of the flame tube in order to experimentally determine the thermal state.

Conjugate thermal simulation was carried out using the Ansys Fluent software package in a steady state. A three-dimensional geometric model of the combustion chamber was built, a finite element mesh was generated with a conformal interface between the fluid and solid.

The calculation and experiment were carried out under standard atmospheric conditions with a pressure drop of 3%, an air/fuel ratio of 1.5, and various additions of hydrogen to methane.

As a result of the study, a comparison of the temperature along the length of the combustor wall, obtained by calculation and experimental methods, was obtained. The influence of the proportion of hydrogen addition on the thermal state of the combustor was obtained.

ARAS-study of the interaction of pentanol isomers with oxygen behind shock waves

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Pentanol isomers (n-$C_5H_{11}OH$, i-$C_5H_{11}OH$) are promising applicants for the complete replacement of gasoline fuel. Several scientific groups are conducting research on the development of the chemical-kinetic mechanism of combustion of this biofuel, but it still needs significant improvements. The main goal of this work is the experimental study the interaction of pentanol isomers with oxygen at the high temperatures 1800-3000 K and pressures 2-3 bar. The kinetics of reaction of pentanol molecules with oxygen atoms formed at N_2O dissociation in mixture 10 ppm N_2O + 10 ppm n-$C_5H_{11}OH$ or i-$C_5H_{11}OH$ in argon behind reflected shock waves is studied. The quantitative measurements of the time profiles of the concentration of oxygen atoms in the ground electronic state $O(^3P)$ were carried out by the precise method of atomic resonance absorption spectroscopy (ARAS) on the resonant vacuum-UV line of an oxygen atom at 130.5 nm. Along with the experimental measurements, a detailed kinetic analysis was carried out using the OpenSMOKE++ code, with a simulation of oxidation processes using current kinetic mechanisms and a corresponding sensitivity analysis of considered reactions. The data obtained during a comprehensive study provide new valuable information on the features of the interaction of pentanol isomers with oxygen at high temperatures, which will help both in verifying existing mechanisms and in creating new reliable kinetic schemes in a wide range of temperatures and pressures.

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Study of cation chemistry in ethylene flames

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The flame is a weakly ionized plasma. Understanding the ion chemistry in a flame is crucial for the development of new diagnostic methods, as well as for the development of ion-sensitive technologies for controlling combustion processes. In this work, the spatial distribution of positive ions (cationic structure) in premixed ethylene/oxygen/argon flames stabilized on a flat-flame burner at atmospheric pressure was measured by molecular beam mass spectrometry in a wide range of equivalence ratios $\phi = 0.4\div1.5$. Numerical calculations of the cationic structure of these flames as well as profiles of the rate of production of the main flame ions have been carried out using the Cantera software (V.2.5.1) [1]. For the calculations, a detailed ion chemistry mechanism was used. The mechanism was developed on the basis of ion chemistry models available in the literature [2] and augmented with reactions for the $C_3H_5^+$ cation. A comparison of the experimental and simulation data has shown that the mechanism correctly describes the relative content of the most abundant oxygen-containing cations (CH_5O^+, $C_2H_3O^+$) in flames, as well as of the $C_3H_5^+$ cation found experimentally in a rich flame (ϕ=1.5). However, the mechanism significantly underestimates the relative mole fraction of the $C_3H_3^+$, a key cation in fuel-rich flames. Several aromatic and cyclic cations with the general formula C_xH_y were also detected in the fuel-rich flame (ϕ=1.5). The obtained data will serve as a basis for further improvement of the ion chemistry mechanism in fuel-rich hydrocarbon flames.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Project No: 075-15-2020-806).

References

1. David G. Goodwin, Raymond L. Speth, Harry K. Moffat, and Bryan W. Weber. Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes.
2. Knyazkov D. A. et al. Cationic structure of premixed near-stoichiometric CH4/O2/Ar flames at atmospheric pressure: New insights from mass spectrometry, quantum chemistry, and kinetic modeling //Combustion and Flame. – 2022. – T. 241. – C. 112106.

Potentials and energies of atoms and molecules inside C_{60} cage

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Much of this work was stimulated by the discussion on the quantized rotation and ortho–para conversion of single water molecules permanently entrapped inside closed fullerene C_{60} cages, see experimental and theoretical studies [1-4] and references therein. Of particular interest is, first, the observed splitting of the ground state of ortho-H_2O, raising the three-fold degeneracy into two states with degeneracy 2 and 1 [1] and, second, the enrichment of para water at low temperatures due to conversion of fullerene-encapsulated para water to ortho water [2]. In the present study we try to attribute both effects to interaction between water "vibrational" and rotational motions. Hereafter we denote the movement inside the cage as "vibrational", but it possess rotational momentum.

Ab initio calculations of He, Ne, Ar, HF, and H_2O molecules entrapped inside C_{60} cage are reported. We choose not only the water molecule, but molecules with different masses and rotational degrees of freedom. Program Orca was used on the B3LYP D3BJ TZV def2/J level of theory, where B3LYP is DFT functional, D3BJ is the Becke–Johnson damping version, TZV is valence triple-zeta basis set, and def2/J is universal auxiliary basis sets of Weigend.

The "vibrational" energies of three noble atoms inside C60 are represented in the table below, they are characterised by quantum numbers *n* and *L*, as in a hydrogen atom. The energies are given in cm^{-1}, they are calculated by using both WKB (Wentzel–Kramers–Brillouin) approximation and direct solution of the radial part of Schrēdinger equation.

	$He+C_{60}$			$Ne+C_{60}$			$Ar+C_{60}$		
n	*L*=0	*L*=1	*L*=2	*L*=0	*L*=1	*L*=2	*L*=0	*L*=1	*L*=2
1	204.0			130.9			257.5		
2	461.2	588.3		304.8	440.5		599.6	770.1	
3	715.6	846.8	981.3	478.9	615.2	741.4	940.3	1110.0	1279.3
4	982.6	1122.8	1267.0	654.3	792.0	919.8	1279.8	1448.8	1617.3

The $Ne+C_{60}$ system has almost the same reduced mass as H_2O+C_{60}, hence their "vibrational" energies should be similar. As it follows from the table, the "vibrational" transitions $n,L \rightarrow n',L'$ lies rather far from low-temperature rotational transitions in H_2O and from vibrational transitions in H_2O. Note that the "vibrational" transitions obey usual selection rule $\Delta L=\pm1$.

The movement of HF and H_2O molecules inside C_{60} was analysed similarly. In the model of "quick rotation" the movement in the case of HF changes from two-dimensional vibrational oscillator when F atom is close to the wall of the cage to the free rotation when F atom is close to the centre of gravity. More realistic model, in which H atom rotates with a speed comparable with the speed of F atom, permit rather small range of spherical θ angles for the rotation of H atom. Hence it was found that the fullerene cage shifts the rotation levels of the two molecules, in moderate agreement with experiment.

References

1. K. S. K. Goh et al., *PCCP*, **2014,** 16, 21330
2. B. Meier et al., *Phys. Rev. Lett.*, **2018**, 120, 266001
3. S. Mamone et al., *J. Chem. Phys.*, **2014**, 140, 194306
4. C. Beduz et al., *Proc. Natl. Acad. Sci. USA*, **2012**, 109(32), 12894

Gas phase synthesis of [5]-helicene

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During the last decades, helicenes — ortho-fused polycyclic aromatic hydrocarbons (PAHs), in which benzene building blocks are annulated at an angle of 60° to form helically-shaped molecules — have received considerable attention from the organic and physical chemistry and material science communities due to their unique features in optics (chiroptical activity, nonlinear optics and circular polarization) and chiral sensing (chemical sensors) along with exceptional properties in organocatalysis and distinctive molecular structures. Considering the molecular structure of helicenes, the backbone twists in opposite directions due to the steric hindrance between the terminal rings. Helicenes are distinguished for their chirality despite missing asymmetric carbon atoms with the chirality developing from the handedness of the helix. Clockwise and counterclockwise helices are non-superimposable as the result of their axial chirality with a left- and right-handed helices being defined by minus (M) and plus (P).

Here, we reveal a versatile route to form helicenes via a directed, vinylacetylene mediated gas phase chemistry. In contrast to the traditional routes following solution chemistry and often ionic reaction intermediates, the innovative gas phase synthesis encompasses low-barrier reactions through targeted, stepwise ring expansion mechanisms involving free radical reaction intermediates. We reveal the gas phase chemistry synthesizing [5]-helicene along with atomic hydrogen via the bimolecular reaction of the [4]-helicenyl radical with vinylacetylene. The energies and molecular parameters of the local minima and transition states involved in the reaction were computed at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory with a chemical accuracy of 3–6 kJ/mol for the relative energies and 0.01–0.02 Å for bond lengths as well as 1–2° for bond angles.

The facile route to synthesize [5]-helicene through the reaction of the [4]-helicenyl radical with vinylacetylene represents a versatile pathway that could in principle be extended to higher helicenes. Our mechanistic studies reveal that the key step of the reaction is a low-barrier benzannulation through a resonance-stabilized free radical intermediate that leads to the helicene. In circumstellar environments, starting from [4]-helicene, propagation via hydrogen loss by photodissociation followed by reaction with vinylacetylene provides an exceptional route to [5]-helicene and eventually to [6]-helicene thus supplying a directed, stepwise synthesis of racemic, helically-shaped three-dimensional nanostructures via elementary neutral-neutral reactions.

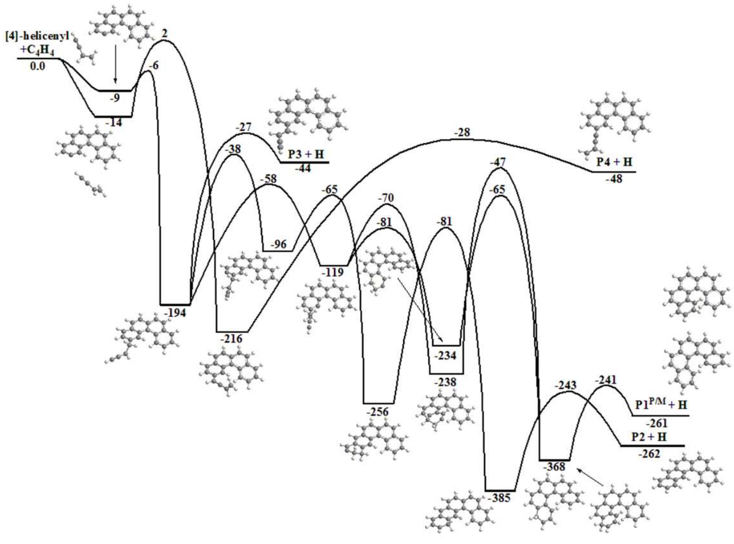

Fig.1 Potential energy surface (PES) for the [4]-helicenyl reaction with vinylacetylene. This PES was calculated at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory for the channels leading to [5]-helicene P1 and benzo[a]tetraphene P2.
The relative energies are given in kJ/mol.

Tri phenyl phosphate decomposition through the reaction with H, CH_3, OH radicals

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Tri phenyl phosphate $C_{18}H_{15}O_4P$ (TPP) is widely used as flame retardant during polymer combustion processes. From 10% to 20% of TPP addition results in reduction of the flame spread rate, the mass burning rate and conductive heat flux from the flame to the polymer surface. Hence, the study of TPP interaction with widespread radicals like H, CH_3, OH in the combustion conditions and subsequently decomposition of TPP are essentials for the further reducing of polymer flammability.

The geometries and vibrational frequencies of tri phenyl phosphate and its decomposition products are calculated using the methods of density functional theory, using the functional ωB97XD[1,2].

The proposed ways of TPP decomposition are as follows – 1) addition of H atom in TPP structure leads either to H2 migration from one of C_6H_5O moiety or to addition of H atom on C1 atom of C_6H_5O, which both then lead to C-O cleavage and $C_{12}H_{10}O_4P$ compound. 2) addition of OH and subsequent decomposition on $C_{12}H_{10}O_4P$ and C_6H_5OH and as well 3) addition of CH_3, which will finally form $C_{12}H_{10}O_4P$ and C_7H_8. Then, $C_{12}H_{10}O_4P$ will undergo the series of C-O and P-O cleavages and be decomposed.

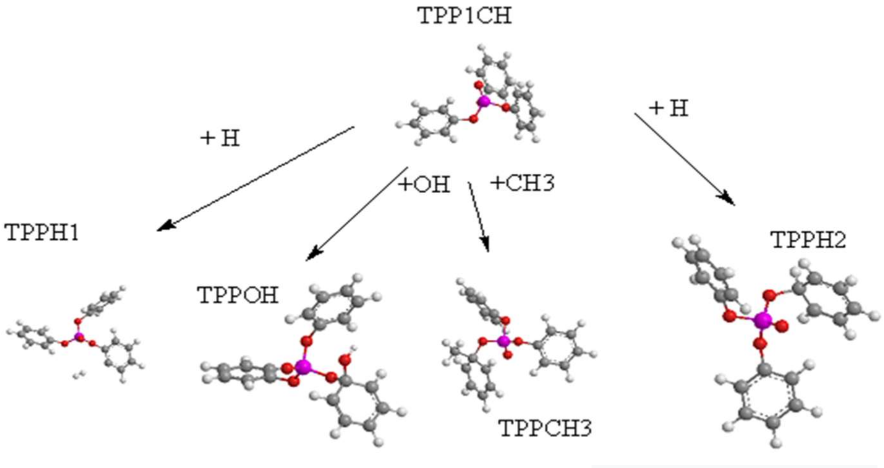

Fig.1 – The proposed initial pathways steps for $C_{18}H_{15}O_4P$ + H/OH/CH_3

In the work the probable pathways have been predicted and as well the potential energy surface (PES) has been presented. PESs were optimized at the density functional ωB97XD/6-31G* level of theory. This reaction is explored by the means of DFT theory and couple-cluster technique combination, realized with Gaussian 09 and MOLPRO 2020 software. Electronic structure/Rice-Ramsperger-Kassel-Marcus Master Equation calculations were applied to unravel the mechanism and kinetics of the $C_{18}H_{15}O_4P$ + H/OH/CH_3. All the gained values of reaction compounds energies and frequencies have been used to calculate pressure and temperature dependent reaction rate constants and product branching ratios.

References

1. J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, 128, 084106.
2. J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, 10, 6615 (2008).

Simulation of CO emission in the small-sized combustion chamber with liquid fuel injected by pressure swirl atomizer

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The preparation process of the air-fuel mixture is one of the most important in organizing the working process in the combustion chamber since it affects such characteristics as the combustion efficiency, the stability of the combustion process, and the emission of harmful substances. The most common type of atomizer used for combustion chambers of small size gas turbine engines is the pressure-swirl atomizer.

In this paper, a method for calculating the characteristics of liquid fuel injection by pressure swirl atomizers to set the boundary conditions for injection into the combustion chamber is proposed. In addition, the paper presents the results of CO emission simulation in a model combustion chamber with two variants for setting the boundary conditions for liquid fuel injection. A method for setting the boundary conditions for liquid fuel injection using a discrete phase model (DPM) is proposed, for which the parameters characterizing the fuel atomization are obtained as a result of two-phase flow simulation by the volume of fluid (VOF) method. For comparison, the parameters characterizing the atomization for setting the boundary conditions for fuel injection were also calculated using the pressure swirl atomizers calculation method proposed by H. Lefebvre. By comparison of two boundary conditions setting methods, it was found that the proposed method for determination of the boundary conditions for injection allows to increase the accuracy of CO emissions prediction several times compared to the classical semi-empirical pressure swirl atomizers calculation method.

As a result of determining the characteristics of liquid fuel atomization by pressure swirl atomizer, for using it as boundary conditions for fuel injection into the combustion chamber, the following results were obtained:

1. An operation scheme of a hybrid method designed to determine the parameters of the primary fuel atomization by pressure swirl atomizers that are necessary to set the boundary conditions for fuel injection into the combustion chamber for combustion processes simulation has been formed;
2. It can be seen from a comparison of two variants of the boundary conditions that the droplet tracks, the characteristics of which are determined by the semi-empirical method of A. Lefebvre, extend up to the outlet section of the combustion chamber, which can lead to overestimated values of incomplete combustion products when simulating pollutant emissions;
3. Comparing the calculated and experimental values of CO emission in the model combustion chamber, it was found that the standard deviation between the values obtained using the injection parameters determined using the developed calculation method does not exceed 15%, which is an acceptable result;

Therefore, it can be concluded that when setting the injection parameters obtained using the developed method of calculation of pressure swirl atomizers atomization characteristics, it is possible to increase the accuracy of determining CO emission by 1.5–2 times compared to the classical semi-empirical pressure swirl atomizers calculation method.

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Experimental-numerical investigation of hydrogen-methane combustion in model power plant combustion chamber

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Recently hydrogen and methane-hydrogen mixtures combustion technologies are finding larger application in the design and retrofitting of gas turbine power plants with lean premixed combustion. At the same time, the issue of the combustion processes of hydrocarbon fuels with hydrogen additives simulation is of great relevance. One of the problems of the methane-hydrogen fuel combustion simulation is the choice and verification of the kinetic combustion mechanism, as well as the combustion processes results validation with experimental data. Therefore, the purpose of this paper is to verify the proposed combustion model with the chosen kinetic combustion mechanism.

In the work, a computational and experimental determination of the combustion products concentrations and the pollutant emission during methane-hydrogen mixture combustion under various operating conditions was carried out. A model power plant combustion chamber with the setup of a premixed air-fuel combustion was chosen as the object of research.

As a result of the computational and experimental research, it was found that the implemented mathematical combustion model for methane-hydrogen mixtures shows good qualitative and quantitative agreement between the calculated and experimental data on the main combustion products, as well as a qualitative agreement between the data on the pollutant emissions. In the following, this combustion model in conjunction with the selected kinetic combustion mechanism can be used to analyze the emission characteristics of the developed power plant combustion chambers designed to operate on hydrogen-containing mixtures.

Experimental and numerical study of lean flame blow-out during methane-hydrogen mixture combustion with a different hydrogen addition

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In the last decade, a method for increasing the stability of "ultra-lean" (heater air excess factor $\alpha > 2.3$) low-emission combustion based on the use of alternative fuels or on the use of initiating additives to conventional fuels has been actively studying in Russia.

Research of combustion processes and pollutant emissions in the combustion products of hydrocarbon fuels, carried out abroad and in Russia, show an improvement in combustion characteristics when using hydrogen as a fuel, and as an additive to hydrocarbon conventional fuels. Even a relatively small addition of hydrogen, which has a high burning velocity, makes it possible, on the one hand, to reduce the emission of a number of pollutants, and, on the other hand, by operating on “lean” mixtures, to ensure the efficiency and stability of the fuel combustion process.

At the same time, as is known, when using hydrogen additives in fuel, a number of problems arise, namely:

- increased heat load on the elements of the combustor of the engine;
- high probability of flashback upstream, which can lead to partial or complete destruction of the flame tube head;
- high probability of occurrence of high-amplitude pressure pulsations, which can lead to the destruction of the combustion chamber elements;
- change in the combustion chamber stable operation range along the border of lean blow-out, considering the change in the laminar flame propagation velocity.

Therefore, when developing new combustion devices, it is necessary to determine the combustion chamber stable operation range, namely, lean blow-out and the probability of flashback upstream. At the stage of combustion devices development it is advisable to use verified calculation methods in a three-dimensional formulation, using the methods of computational fluid dynamics and combustion to solve these problems.

Thus, the objective of the study in this paper is the development and verification of a methodology for determining the limits of stable combustion in the methane-hydrogen mixture combustion.

As a result of research performed, computational and experimental research were carried out to determine the lean blow-out and flashback upstream on a model combustion chamber in combustion of a methane-hydrogen mixture with a hydrogen fraction of 0..60% by volume.

Thermodynamics of swelling of polymeric sorbents in aqueous solutions

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It is known that for real systems, the Gibbs free energy of swelling of polymeric sorbents [1] in water or in aqueous solutions changes according to the following formula:

$$\Delta G_{\bar{n}} = RTln\bar{a}_w \qquad (1)$$

where: $\Delta G_{\bar{n}}$ - change in Gibbs free energy of swelling, R-gas universal constant, T-temperature, $\bar{a}_w$ - activity of sorbed water in the polymer sorbent phase.

If the standard state of water in polymer sorbents and solutions are the same, then the activity of water in both phases will be the same $\bar{a}_w = a_W$, and the change in the Gibbs free energy of swelling in this case is described by the following formula [2]:

$$\Delta G_{\bar{n}} = RTlna_w = RT\varphi lnN_w = RT\varphi \ln(1 - N_{AX}) == RT\varphi \ln\left(1 - \frac{vm}{\left(\frac{1000}{M_w}\right) + vm}\right) \approx RT\varphi \ln\left(1 - \frac{vmM_w}{1000}\right) \qquad (2)$$

where: m is the molal concentration of the solution, φ is the molal osmotic coefficient of the solute, M_w is the molecular weight of the solvent, v is the number of ions in the molecule of the solute.

In this paper, experimental results show the dependence of the change in the Gibbs differential free energy of swelling of polymeric sorbents in water or in aqueous solutions on the amount of water sorbed by the polymer, on the nature of the functional groups of polymers, on the ionic form, on the amount of divinylbenzene, and on the activity of water in the external solution.

The dependences of the change in the Gibbs differential free energy of swelling on the counterions of polymer sorbents, on the concentration of the equilibrium solution, and on the coions of the solution were studied using the KB-4 cation exchanger from different solutions of sodium, potassium, ammonium and calcium salts, as well as hydrochloric acid with different concentrations.

Experiments to study the dependence of the change in the Gibbs differential free energy of swelling on the number of cross-links of polymeric sorbents and on the activity of water in an equilibrium solution were carried out on the nitrate form of the APA anion exchange resin containing 4, 12 and 20% cross-links from NH_4NO_3 solutions of various concentrations.

From the experimental data, it was revealed that the change in the Gibbs differential free energy of swelling is directly proportional to the counterions of polymeric sorbents and to the concentration of the equilibrium solution and does not depend on the coions of the equilibrium solution. In addition, it was shown that the amount of water sorbed by the ARA anion exchanger and the change in the Gibbs free energy of swelling are directly proportional to the amount of cross-links of the polymer sorbent.

References:

1. Ivanov V.A., KarpyukE.A, Gavlina O.T, Kargov S.I. Superheated solutionsin dual-temperature ion exchange separations: //Reac.Func.Pol. 2018. V.122. P.107-115.
2. Иванов В. А., Карпюк Е. А. //Термодинамика ионного обмена. Москва 2016. 134 с

The influence of the particle size of the gasified material on the absorption of sulfur during filtration combustion sulfur coal with marble

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The presence of sulfur in coals significantly constrains their use in the chemical industry and energy, therefore, the search for environmentally friendly ways of processing coals becomes a very urgent task. Our experiments on gasification of mixtures of sulfur dioxide and marble particles have shown that the addition of up to 50% marble to the gasified material allows to absorb up to 37% of the sulfur contained in the coal. The aim of this work was to find ways to increase the proportion of absorbed sulfur during the gasification of high-sulfur brown coals in the filtration combustion mode. The subject of the study was to study the effect of the particle size of coal and marble on the proportion of absorbed sulfur.

Experiments on gasification of mixtures of coal and marble particles were carried out in a quartz reactor with a diameter of 45 mm, the size of the coal and marble particles used was 1.5, 2.5, 5.0 and 7.5 mm. The object of the study was the sulphurous brown coal of the Moscow basin. The coal content in the gasified mixture was 50%.

Experiments have shown that temperature of combustion practically does not change with decreasing particle size, the rate of combustion increases linearly, and the content of carbon monoxide in gaseous products increases significantly. The heat of combustion of gaseous products of gasification increases from 2.0 to 3.0 MJ/m^3. The proportion of absorbed sulfur with a change in particle size from 7.5 to 2.5 mm changed little, increasing from about 37 to 43%, and with the gasification of a mixture with a particle size of 1.5 mm increased to about 60%.

Thus, with a decrease in the particle size, the proportion of absorbed sulfur increases, but in order to significantly increase the amount of absorbed sulfur, the particle size must be reduced by five or more times.

The measurements of the elemental composition of the materials used and the combustion products were carried out in the Analytical center for collaborative using of the IPCP RAS.

The study was carried out with the financial support of State Task No. 0089-2019-0018 State registration No. AAAA19-119022690098-3.

Thermodynamic assessment of the absorption of acid gases by calcium-based sorbents during the gasification of solid fuels

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The combustion of fossil fuels and municipal solid wastes are the two main potential sources of environmental pollution, caused by HCl and SO_2. Among the widely used methods for reducing acid gas emissions, the addition of calcium-based sorbents is effective and easy to implement.

To assess of the absorption of acid gases by calcium-based sorbents at filtration combustion of real systems in reactors, thermodynamic calculations were carried out using the Terra program. The case of a stationary wave in a continuous gasifier is considered, in which the porous solid fuel moves countercurrent to gas flow containing water vapor.

The regularities of HCl release from calcium chloride and SO_2 from calcium sulfate during steam-air gasification of solid fuel in the filtration combustion mode were studied. The limiting amounts of HCl and SO_2 released into the gas phase under real conditions of a shaft kiln gasifier were estimated. It was shown that the most important factors responsible for the stability of $CaCl_2$ are the humidity of an oxidant gas and the process temperature, while only the temperature affects the stability of $CaSO_4$. The decomposition of calcium chloride starts at about 800°C, and the decomposition of calcium sulfate - at about 1200°C. The amount of hydrogen chloride and sulphur dioxide released into a gas phase on the passage of a high-temperature combustion wave does not increase with the mass fraction of chloride or sulfur in the solid phase. Thermodynamic calculations were compared with experimental results on the absorption of acid gases during coal gasification in the filtration combustion mode.

The investigation was financially supported by State Assignment No. 0089-2019-0018, State Registration No. AAAA19-119022690098-3.

Numerical simulation of a swirling flow of water vapor with aluminum micro- and nanoparticles and a heating source

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Currently, significant interest is being shown in research on the creation of environmentally friendly energy sources, in particular, autonomous installations for the production of hydrogen and thermal energy.

A relatively complete kinetic scheme of plasma-chemical reactions in a discharge in water vapor in the presence of metal micro- and nanoparticles includes a significant number of reactions. Therefore, simplified kinetic schemes are usually developed that make it possible to calculate the parameters of discharges and flows.

The work took into account the heterogeneity of the working mixture of water vapor/aluminum powder. An analysis of experimental work showed that the ignition temperature of particles ~1 µm in size is about 1500 K. In turn, the simplified kinetic scheme of chemical reactions takes into account that aluminum oxide Al_2O_3 does not exist in the gas phase and very quickly decomposes into sub-oxides.

The rate constants are obtained from a number of works and the US National Institute of Standards and Technology database. The thermodynamic parameters of the substances involved in the reactions were calculated using NASA seven-coefficient polynomials.

Based on the solution of the system of Reynolds-averaged Navier-Stokes equations, a three-dimensional multicomponent flow in the PVR was studied, accompanied by the combustion of aluminum supplied in the form of powder. The turbulence model SST k-ω was used to close the system. At the inlets of the swirler, a constant mass flow rate of the mixture, the mass fraction of the metal, and its temperature were set.

The calculations were carried out with varying power of the heat source, which simulated the heating of the mixture in the discharge region, and the mass fraction of supplied aluminum. Within the framework of the scheme used, an increase in the maximum concentration of both atomic and molecular hydrogen was demonstrated with increasing heating and increasing the concentration of the supplied metal, Fig. 1

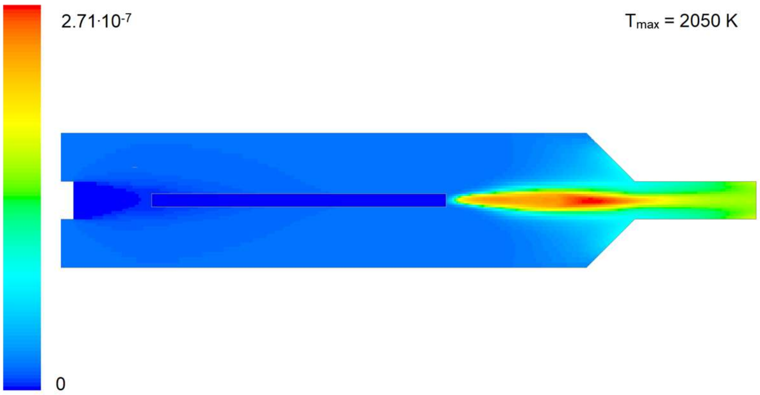

Fig.1. Distribution of the molar concentration of atomic hydrogen (H) at the maximum temperature T_{max} = 2050 K, mol/cm^3

The study was supported by the Ministry of education and science of Russia by State assignment under project FSSS-2020-0014.

Ignition dynamics of H_2/CO/air mixture after photodissociation of O_2 molecules by a UV laser pulse

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Ignition process and early stage of combustion of the H_2/air and the syngas (H_2/CO – 1:1)/air mixtures after the photodissociation of oxygen molecules were investigated using the approach described in [1]. The analysis of the consecutive series of OH* radical chemiluminescence images registered from the focusing area of ArF excimer laser radiation employed for the photodissociation was performed to obtain ignition delay times and combustion front propagation speeds for the considered mixtures.

The laser radiation at 193 nm wavelength (110 mJ per 10 ns pulse) was focused to the center of a pulsed burner to generate oxygen atoms which caused the ignition of the mixtures at fuel-air equivalence ratios 0.8–1.6, pressure of 1 atm and temperature of 578 K. Images of the 80 mm^2 ignition region were registered at short exposure times in the spectral range 260-390 nm using a CCD-camera. The time delay between the photodissociating laser pulse and the camera shutter was being varied from 10 to 400 µs. Ignition delay times for H_2/air and syngas/air mixtures under the experimental conditions equal 46 and 78 µs, respectively, were determined. Combustion front of the H_2/air mixture showed twice-higher propagation speed with respect to that of the syngas/air mixture.

A numerical simulation of the ignition process was performed based on a two-dimensional approach employing the detailed kinetic mechanism and the results of laser radiation absorption modeling. Results of the calculation showed a good agreement with the experimental data.

The realized approach proved to be a productive way to investigate the ignition process of gaseous mixtures under controlled nonequilibrium conditions created by laser radiation.

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References

1. V.D. Kobtsev, S.A. Kostritsa, A.V. Pelevkin, V.V. Smirnov, A.M. Starik, N.S. Titova, S.A. Torokhov, K.A. Vereshchagin, S.Yu. Volkov. *Combustion and Flame*, 2019, 200, 32-43.

Experience in carrying out experimental studies for a dual-circuit burner using methane-hydrogen mixtures

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An experiment is a procedure performed to support, disprove, or confirm a hypothesis or theory. The study of processes in the burner device can be attributed to diffuse systems, that is, systems in which it is impossible to clearly distinguish individual phenomena. Therefore, experimental systems must combine and ensure accuracy, safety, repeatability of results, fixing or maintaining the specified parameters during the experiment in a narrow range in order to obtain high-quality results.

Experiments are carried out at the premises of the SEC FDR, which, among other things, are used to validate and verify computational mathematical models designed to describe combustion processes in both individual elements and the whole combustion chamber.

This paper presents the features of carrying out experimental studies using hydrogen-containing fuel, since the carrying out of experiments and the preparation of an experimental base when using hydrogen requires stand retrofitting and can make adjustments to the characteristics determination methods.

The article provides a detailed description of the air supply system, fuel supply system and measuring equipment arrangement, which is used during tests. A natural gas/hydrogen mixing system is shown. The measures that have been taken to ensure safe operation with hydrogen-containing fuels are listed.

Changes and additions that were made to the experimental procedures are also mentioned. The aspects of the choice and combination of experimental equipment for carrying out research of the burner are described.

As a test object, a burner device with a two-circuit fuel supply system for the pilot zone (diffusion combustion) and the main zone (premixed) was considered. Combustion takes place inside a quartz tube, which makes it possible to exclude air mixing and to make photo and video recording of the combustion process.

In conclusion, the results of photofixation and the characteristic of lean blowout obtained on the actual experimental setup with various hydrogen fractions are presented.

Optical properties of soot formed under different conditions. Application to the effects of soot on climate.

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Soot particles appearing due to human activity are known to play important role in Earth's climate system. Soot (black carbon) is a distinct type of carbonaceous material with unique combination of physical properties. The soot aerosol in atmosphere absorbs incoming solar radiation and scatters it. Soot deposition on glaciers causes surface dimming and melting. It reduces snow albedo, causing more solar radiation to be absorbed. These factors lead to atmospheric warming and global temperature increase [1].

An accurate data of soot optical properties is necessary for reliable estimates of climate models. However, a wide variation of soot properties is observed in dependence on formation conditions. In this study, soot nanoparticles were synthesized by ethylene, acetylene and propylene combustion in a flat premixed flame and by pyrolysis of the same hydrocarbons in a shock tube at temperatures of 1800–2000 K and a pressure of 3–4 atm. The absolute value of the refractive index functions of soot nanoparticles E(m,1064) at wavelength 1064 nm, the ratio of the refractive index functions at two laser wavelengths of 1064 nm and 532 nm were studied in dependence on soot primary particle size. It was found that soot refractive index function increases with soot particle size as decaying exponential function and does not exceed value of 0.55.

Internal structure of soot particles was analyzed by transmission electron microscope to found parameters causing the soot optical properties changes. Such parameter appeared to be interlayer spacing between the graphene fringes in the soot basic structural units. An interlayer spacing decrease is resulted by soot graphitization and soot primary particles growth process.

It was found that optical properties and an extend of soot graphitization is strongly affected by type of hydrocarbons used for synthesis and by the primary particle size. At the same time, it slightly depends on the type of reactor and, consequently, on the temperature and pressure in the investigated range of parameters.

The data obtained in this study can improve climate models by applying the E(m) of soot as a function of particle size instead of constant value.

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References

1. T.C. Bond, S.J. Doherty, D.W. Fahey, et al, *J. Geo-phys. Res. Atmos.* 118 (2013) 5380–5552. DOI: 10.1002/jgrd.50171.

Soot formation during ethylene pyrolysis with biofuels

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The study of alternative fuels (e.g. biofuels) is an urgent task both from the limited fossil fuels and environmental problems associated with harmful emissions into the atmosphere. Currently, various oxygen-containing biofuels are widely studied. Its production has a «zero carbon footprint», and the oxygen presence in composition should lead to an increase in the oxidation processes efficiency, which in turn could reduce the amount of polycyclic aromatic hydrocarbons (PAHs) and soot nanoparticles formed due to incomplete fuel combustion.

PAHs are mainly formed from incomplete combustion processes and generally considered as precursors for soot particles [1]. The linear and cyclic esters: furan C_4H_4O (F), tetrahydrofuran C_4H_8O (THF), diethyl ether $C_4H_{10}O$ (DEE), dimethoxymethane $C_3H_8O_2$ (DMM)) and alcohols: methanol CH_3OH (M) and butanol C_4H_9OH (B) are of high-potential biofuels representatives [2, 3]. Therefore, it is of particular interest to study their effect on the PAHs and soot formation due to their composition and structure.

At the investigation, experimental study of the effect of listed biofuel additives on the PAHs and soot formation processes during ethylene C_2H_4 pyrolysis diluted in Ar behind reflected shock waves range was carried out. Laser induced fluorescence (LIF) was used to detect polycyclic aromatic hydrocarbons formed during pyrolysis. To induce PAH fluorescence, a Nd:YAG laser at wavelength of 266 nm was used. Besides that laser extinction at 633 nm was used to control the condensed phase appearance and measure its volume fraction. Soot-particle size was determined *in situ* by laser induced incandescence (LII) method using a Nd:YAG laser at a wavelength of 1064 nm and *ex situ* by transmission electrons microscopy (TEM) analysis.

The obtained temperature dependences of carbon nanoparticles sizes and volume fraction in the ethylene mixture have had a well-known «bell» shape [4] with the maximum in the range T_5=2200-2250 K. It was also found that M and B slightly increase soot formation and particle sizes at T_5 = 2000-2200 K; F greatly increases soot formation and particle sizes and expanded the temperature range of its formation; THF also increases soot formation and particle sizes at T_5 = 2240 – 2510 K. The DEE addition results a shift in the soot formation processes to higher temperatures relative to ethylene mixture and slightly increase soot volume fraction and DMM has no any effect on soot formed but increases the soot particle sizes at T_5=2200-2300 K.

Acknowledgement

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References

1. H. Wang.Proc. *Combust. Inst.* **2011**, 33, 41-67
2. S. Jesak et al. *Fuel*. **2016**, 184, 334–343.
3. R. Estevez et al. *Catalysts.* **2019**, 9, 1033.
4. G. Agafonov et al. *Kin. Kat.* **2016**, 57, 557-572.

Indenyl radical self-reaction study

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When theoretically considering the mechanism of the reaction of two indenyl radicals, the first step is to find and refine the energies, structures of the reactants, intermediate and transition states, and products using non-empirical quantum mechanical methods of density functional theory, in this case B3LYP / 6-311G **. The results of theoretical studies of the reaction of five-membered carbon rings C_5H_5 and C_5H_4 by the G3(MP2, CC)//B3LYP methods, leading to the formation of two-ring PAHs, have already been presented in[1–3], as well as data from a previous work showing the pathways for the formation of multi-ring PAHs and their energy profitability, which served as the goal and basis for further study of the formation of four membered ring PAHs and their kinetics. Vibrational frequencies and zero-point energies E(ZPE) were also calculated by a similar method. The final energy refinement was based on a modified combined scheme: E[G3] = E[CCSD(T)/6-311G**] + E[MP2/G3Large] - E[MP2/6-311G**] + E(ZPE), where CCSD(T) is the paired cluster method with the 6-311G** basis, and MP2 is the Möller-Plesset second-order perturbation theory method with the 6-311G** and G3Large basis sets.

The interaction of two radicals firstly forms a $C_{18}H_{14}$ complex, where further abstraction of hydrogen from the five-membered ring of one bicyclic indenyl system leads to the barrier-free formation of the i1 isomer, the energy of which is 23.6 kcal/mol higher than the energy of the reagents. In the future, a similar abstraction of a hydrogen atom can immediately lead to the formation of a product p1 of the dibenzofulvalene type with an energy of 66.6 kcal/mol. Isomerization can occur in two ways, one of which is the creation of a three-membered compound between the rings to form a spiro structure with an energy i1-1 of 37.4 kcal/mol. Subsequently, this three-membered compound breaks with an energy of 72.3 kcal/mol to form a six-membered ring, obtaining a four-ring spiran structure. Similarly, the last five-membered ring grows into a six-membered one. Further, after the detachment of hydrogen from i4-2, the product p3 is formed with an energy of 29.9 kcal/mol of the tetraphene type.

It is also possible to create a four-membered ring bond in the i1-2 intermediate with an energy of 70.0 kcal/mol. This compound involves the creation of a larger carbon ring (i2-2; 43.3 kcal/mol). The detachment of hydrogen can lead to the formation of a product p2 of the dibenzoazulene type with a relative energy of 67.8 kcal/mol. Also, like in the first route, it is also possible to obtain the i4-22 isomer with a relative energy of 13.1 kcal/mol. Removal of hydrogen will lead to the formation of the p4 product of the chrysene type with a relative energy of 27.4 kcal/mol. However, by getting rid of the intercarbon bond in c i4-22, it is possible to create a twelve-membered ring in the center, in which another bond can be made to create a sequential four-ring structure. As a result, after the removal of hydrogen from intermediate i5-2 (36.3 kcal/mol), the product p5 of the “tetracene” type can be formed with a relative energy of 38.5 kcal/mol. These results allow us to begin work on the study of reaction rate constants and relative yields of products to determine the energy preference.

References

1. Kislov V.V., Mebel A.M. *The Journal of Physical Chemistry A*. 2007. V. 111(38). P. 9532-9543.
2. Mebel A. M., Landera A., Kaiser R.I. *The Journal of Physical Chemistry A*. 2017. V. 121(5). P. 901-926.
3. Krasnoukhov V.S., Zagidullin M.V., Zavershinskiy I.P., Mebel A.M. *The Journal of Physical Chemistry A*. 2020. V. 124(48). P. 9933-9941.

Potential energy surfaces for the Reaction of the Methylidyne Radical (CH $X^2\Pi$) with the Propionitrile C_2H_5CN ($X^1\Sigma^+$) Molecule

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The reaction of the methylidyne (CH; $X^2\Pi$) radical with ethyl cyanide (C_2H_5CN; $X^1\Sigma+$) molecule was studied at a collision energy of 4.0 kJ/mol with ab initio calculations of the potential energy surface (PES). At low temperatures in deep space, a large amount of nitriles are present in the atmosphere of Saturn's moon Titan [1, 2], as well as in interstellar molecular clouds. Reactions of nitriles with the methine radical CH are of interest, as potencial initial step in the study of biological molecules. In particular, in the course of the reaction with cyanide molecules, a nitrogenous base, structural blocks in DNA chains, can be formed. In addition, the formation of linear and cyclic radicals is possible with the release of the corresponding products: atoms, molecular particles, ethylene, etc.

Geometries and potential energies of reactants, products, intermediates and transition states for the reaction were found by means of ab initio quantum chemical method ωB97xd/cc-pVTZ [3, 4] and the higher-level corrections were evaluated at the CCSD(T)-F12 level of theory[5, 6, 7] with the cc-pVQZ-f12 (E_1) basis set [8, 9].

Those results were utilized in Rice−Ramsperger−Kassel−Marcus calculations of the product branching ratios at the zero pressure limit – common approach in modelling of the cold molecular clouds chemistry. Mechanism identified emphasizes importance of the $CH+C_2H_5CN$ reaction as an important supplier of the initial bricks for building heterocyclic hydrocarbons in extreme environments [10, 11].

References

1. R.I. Kaiser, A.M. Mebel, V.V. Kislov, S.J. Klippenstein, L.B. Harding, M.C. Liang, and Y.L. Yung. Acrossed molecular beams study on the formation of the exotic cyanoethynyl radical in titan’s atmosphere x. Gu1, / astrophysical journal V. 701, – i 2, – 2009, – p. 1797-1803
2. X.Gu, Y.S. Kim, R.I. Kaiser, A.M. Mebel, M.C. Liang, Y.L. Yung Chemical dynamics of triacetylene formation and implications to the synthesis of polyynes in Titan’s atmosphere // Proceedings of the National Academy of Sciences of the United States of AmericaV. 106, – I. 38, – 2009, – P. 16078-16083
3. D. Xu and D. Li, «CH as a molecular gas tracer and c-shock tracer across a molecular cloud boundary in Taurus» Astrophys. J., 2016, 833, 90.
4. Frisch, M.J. «Gaussian 09 (Revision A.1): Gaussian, Inc., Wallingford (CT)». – 2009. https://gaussian.com
5. Werner, H.-J. MOLPRO, Version 2010.1, A «Package of Ab Initio Programs MOLPRO.NET: University of Cardiff, UK». – 2010. – URL: https://www.molpro.net/info/release/doc/manual/index.html
6. Adler, T.B. «A simple and efficient CCSD(T)-F12 approximation» The Journal of Chemical Physics. – 2007. – Vol. 127(22). – P. 1-4.
7. Knizia, G. «Simplified CCSD(T)-F12 methods: Theory and benchmarks» The Journal of Chemical Physics. – 2009. – Vol. 130(5). – P. 1-21.
8. Chai, J.-D. «Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections» Physical Chemistry Chemical Physics. – 2008. – Vol. 10. – P. 6615-6620.
9. J.-D. Chai and M. Head-Gordon, «Systematic optimization of long-range corrected hybrid density functionals» Physics Chemical Journal. – 2008. 128 – 084106.
10. Marcus, R.A. «Unimolecular reactions, rates and quantum state distribution of products Philosophical Transactions of the Royal Society» A. – 1990. – Vol. 332. – P. 283-296.
11. P. J. Robinson, K. A. Holbrook, «Unimolecular Reactions», Wiley: New York, 1972.

Formation mechanism of 1- and 2-propanols in reaction CO and C_2H_5

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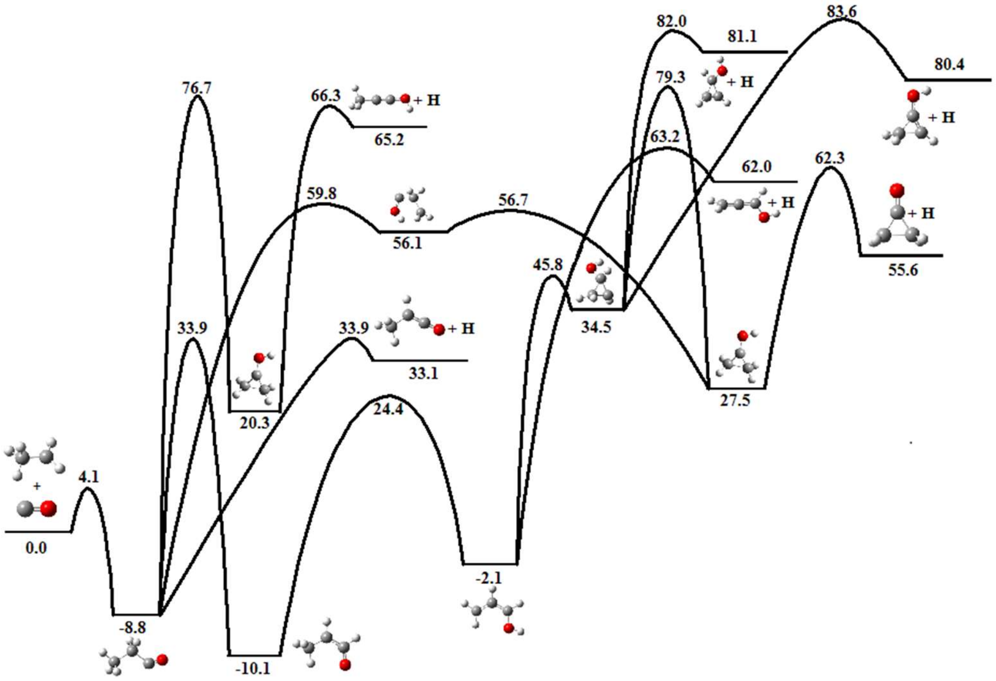
The synthesis of organics in molecular clouds and in star forming regions such as the Taurus Molecular Cloud (TMC-1) and Sagittarius B2, respectively, has been linked to the processing of low temperature (10 K) ice-coated nanoparticles (interstellar grains) by ionizing radiation such as the internal ultraviolet photon field and galactic cosmic rays (GCRs) in cold molecular clouds and in star forming regions. Interstellar grains represent carbonaceous and/or silicate-based nanoparticles coated with ice mantles a few hundred nanometers thick consisting of mixtures of at least water (H_2O), methanol (CH_3OH), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), formaldehyde (H_2CO), and ammonia (NH_3). The densest parts of these molecular clouds undergo gra-vitational collapse ultimately leading to star forming regions. In these environments, heating raises temperatures up to 300 K thus leading to a (partial) sublimation of the complex organic molecules into the gas phase, where they can be searched for and detected by radio telescopes with star forming regions resembling memory records of cold molecular clouds. Since the transition from a cold molecular cloud to star forming regions depends strongly on the molecular composition, it is imperative to unravel the basic processes of how key classes of organics are formed in those environments.

This study proposes a mechanism for the formation of 1- and 2-propanols through the reaction of carbon monoxide and ethane radical, which, in turn, may be present or formed from components of space ice. The energies and molecular parameters of the local minima and transition states involved in the reaction were computed at the B3LYP/6-311G(d,p) level of theory with a chemical accuracy of 0.01–0.02 Å for bond lengths as well as 1–2° for bond angles.



Potential energy surface (PES) for the ethyl reaction with carbon monooxide. This PES was calculated at the B3LYP/6-311G(d,p) level of theory.The relative energies are given in kCal/mol.

Combustion of Ti-Si-C powder system with infiltration by molten copper

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In [1] it was shown, that placing the Cu powder briquette between two adjacent charge briquettes 3Ti+1,25Si+2C for the self-propagating high-temperature synthesis (SHS) or combustion synthesis of MAX-phase of Ti_3SiC_2, it was possible to use a large heat effect of SHS for melting of Cu and spontaneous infiltration of Ti_3SiC_2 porous skeleton by this melt to prepare the Cu-Ti_3SiC_2 composite. However, this experimental scheme significantly limited the size of the resulting composite within a few centimeters. In addition, due to the lack of combustion energy for melting copper in a volume sufficient to fill the entire volume of pores, such a scheme did not allow to create a homogeneous composite with minimal residual porosity.

In this work, a new scheme was tested with the immersion of Ti_3SiC_2 hot skeleton after a certain pause after the SHS end in melts of copper or alloys Cu-10%Si or Cu-20%Sn at a melt temperature T=1120 ºC [2]. At a pause of 6-8 s, partial impregnation of Ti_3SiC_2 skeletons with copper-based melts was observed, which was evident from the significant residual porosity. At the same time, microstructure analysis showed traces of Ti_3SiC_2 plates in samples partially impregnated with Cu-10%Si and Cu-20%Sn alloys and almost complete absence of traces of Ti_3SiC_2 when impregnated with pure copper.

In order to reduce the cooling rate of SHS skeletons, a new approach was considered, in which a charge powder briquette Ti-Si-C of cylindrical shape with a length of 200 mm and a diameter of 22 mm was horizontally placed on a sand base, and the copper melt was prepared separately in a melting furnace in the required volume, after which the copper melt was poured into a sand mold so that direct contact with the end of horizontal charge briquette was provided. The initiation of the combustion of the charge briquette Ti-Si-C occurred at a distance of 40 mm from the place of contact with the copper melt, which caused two combustion fronts moving in opposite directions of the charge briquette. This was done to provide a temporary pause between the combustion front, moving in the opposite direction from the melt, and the infiltration front, which began to move at the moment of reaching the second front of the combustion end of the charge briquette in contact with the copper melt. But the pure copper melt was not infiltrated in Ti_3SiC_2, probably due to insufficient melt temperature, and as a consequence poor wetting. The addition of 10% Si to copper, which reduces the melting point of copper to ~830 ºC, made it possible to impregnate the cylindrical Ti_3SiC_2 skeleton by ~90 mm in length. In the resulting composite, a different phase composition along the length was observed. In general, the addition of 10% Si to copper contributed to spontaneous infiltration of Cu melt and, at the same time, ensured the preservation of Ti_3SiC_2 in the area from 40 to 90 mm. The resulting composite is highly brittle, probably due to saturation of the copper matrix with oxygen, which, according to chemical analysis, reached up to 1% by weight.

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References

1. A.P. Amosov, E.I. Latukhin, A.M. Ryabov, E.R. Umerov, V.A. Novikov. *J. of Physics: Conf. Series.* **2018**, 1115 (4), 042003. DOI :10.1088/1742-6596/1115/4/042003.
2. A.P. Amosov, E.I. Latukhin, E.R. Umerov. *Pat. 2733524 (RF)*. **2020**.

Influence of carbon forms on the synthesis of highly dispersed titanium carbide by combustion in aluminum melt

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Cast aluminum-matrix composite materials reinforced with a dispersed phase of titanium carbide have considerable strength with a small mass and a high value of the elastic modulus and therefore belong to the group of the most promising materials. Traditionally, they are manufactured according to the ex-situ methods, when the carbide phase particles are manufactured separately and only then introduced into the aluminum melt. However, in the case of highly dispersed (less than 1 μm) ceramic particles, this is difficult to do because of their tendency to agglomeration and poor wetting by melt, as well as contamination with impurities. More promising are the in-situ methods, which implie the formation of a carbide phase directly in the matrix. For this purpose, the use of a simple resource-saving method of self-propagating high-temperature synthesis (SHS), which is based on an exothermic combustion reaction between titanium and carbon powders Ti+C=TiC, is of undoubted interest and, as shown in numerous studies [1,2], can be successfully implemented in a matrix aluminum melt. However, most studies using SHS are carried out using traditional forms of carbon: carbon black and, in some cases, graphite and charcoal [3]. At the same time, new polymorphic modifications of carbon materials, including nanostructured ones, have been discovered in recent years. In this regard, the purpose of this work was to compare the effect of various types of carbon forms on the formation of highly dispersed titanium carbide during the implementation of SHS in Al and Al-5%Cu melts. In the course of the study, the following carbon forms were studied: activated carbon of BAU and AG-2 grades, colloidal graphite of C-1grade, carbon black of T-900 and P-701 grades, carbon multilayer nanotubes (CNTs) of "Taunit" grade.

Experimental studies have shown that all the considered forms of carbon are reactive and, when a mixture of Ti+C powders is introduced into an aluminum melt at a temperature of 900 ° C, they lead to a combustion reaction that can result in the formation of particles of both the target phase TiC and the side phases Al_3Ti and Al_4C_3. However, a full-fledged SHS reaction with the formation of highly dispersed particles of one target phase of block-shaped titanium carbide without impurities of side phases was recorded only in cases of the use of P-701 carbon black in the Al melt and the use of P-701 and CNT "Taunit" in the melt of the Al-5%Cu alloy. In general, the results of experimental studies show that the use of carbon forms such as activated carbon, colloidal graphite and carbon nanotubes does not give advantages over the use of carbon black for SHS of titanium carbide in the melt of aluminum and its alloys, therefore, for practical use in the production of aluminum matrix composites of the Al-TiC system by the SHS method, the use of carbon black is recommended.

References

1. S.L. Pramod, S.R. Bakshi, B.S. Murty, *J. of Mat. Eng. and Perfomance*. **2015**, 24(6), 2185-2207.
2. M. S. Song, *Mat. Sc. and Eng*. **2008**, A 473, 166-171.
3. A.P. Amosov, A.R. Luts, A.D. Rybakov, E.I. Latukhin, *Russian J. of Non-Ferrous Met*. **2020**, 61 (5), 500–516.

Review of advances in the field of methane-hydrogen mixtures application in industrial gas turbines

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Recently, more and more materials have been published in Russia and abroad about renewable energy sources and the use of hydrogen instead of conventional (hydrocarbon) fuels in order to reduce CO2 emissions. A number of countries have already developed and adopted roadmaps to reduce greenhouse gas emissions. One of the main sources of CO2 emissions are gas turbine power plants designed for gas transmission and power generation.

Currently, there is a global trend towards a systematic reduction in direct CO2 emissions, which now average 500 g of CO2 per 1 kWh. In the foreseeable future, it is planned to reduce CO2 emissions to 340 g CO2 per 1 kWh and to 100 g CO2 per 1 kWh over the long term. The natural gas that is currently used in gas turbine power plants, mainly composed of methane (CH4), is already the lowest "C" containing fuel, so the reduction of "C" atoms in the fuel seems only by the use of hydrogen (H2). Moreover, it is an additive to natural gas at the initial stage, and in the future it is the main fuel with only water vapor remains in the combustion products while burning.

As part of this paper, a review of modern technologies for the gaseous fuels combustion with a high hydrogen fraction was carried out, problems of using hydrogen as a fuel and ways to solve them were mentioned.

Alkali Plasmas: from equation of state to thermodynamics physical characteristics

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It the given report, we show the analytical equation of state for pure alkali metals (lithium, sodium, potassium, rubidium and cesium) in gas phase known also as alkali plasmas. The given equation has a simple form, generalizes the equation of state for a perfect gas and is universal for all alkali elements. It correctly reproduces the experimental data for the equilibrium gas phase over a wide range of pressures (up to ~10 000 Pa) and temperatures (up to 3 000 K). On the basis of this equation of state, expressions for the thermal and caloric coefficients as well as for other physical characteristics are obtained. The results confirm feasibility of the principle of corresponding states in relation to the group of alkali elements [1].

The computational part of this study is supported by the Theoretical Physics and Mathematics Advancement Foundation “Basis” (Project No. 20-1-2-38-1).

References

[1] A.V. Mokshin, *Physics Letters A*, 2022, 424, 127819.

Measurement of activation energy of combustion of methane-air mixture using the thin-fiber pyrometry method

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This paper presents the latest results of the experimental measurement of activation energy of methane-air mixture. The thin-fiber pyrometry method is used. The experimental plant includes the flat porous burner which position can be regulated vertically, the gas mixture leaking from the burner, thin filament made of silicon carbide (SiC) to measure the gas temperature, and the thermal imager OPTRIS PI. The flow rate of the gas can be adjusted by Bronkhost Elflow controllers.

By measuring the gas temperature dependence on the height above the burner, it is possible to determine the maximum flame temperature, which is close to the temperature of adiabatic combustion (Fig.1). According to the formula [1]

$$M = A \exp\left(-\frac{E_a}{2RT}\right), \tag{1}$$

changing the mass flow of the gas M and measuring the maximum temperature T it is possible to find the activation energy E_a for certain methane concentration in the mixture as a slope of the line (Fig.2). This experiment was carried out for various methane-air mixtures with different φ – ratio of methane to air. The results are compared with the numerical calculation which uses the GRI 3.0 method [2] (Fig.3).

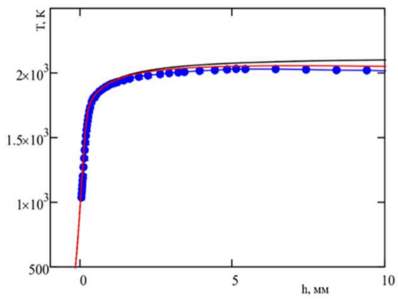

Fig.1. Temperature dependence on the height. Blue dots - experiment, red line - numerical calculation, black line - adiabatic combustion.

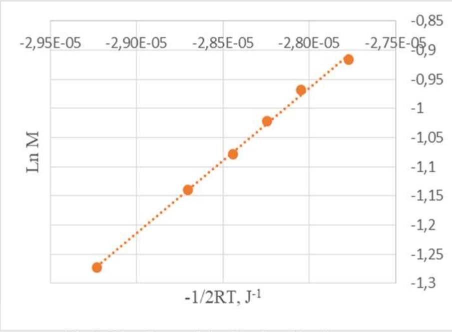

Fig.2. The slope of the line is activation energy

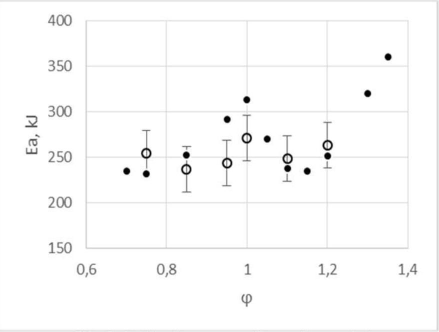

Fig.3. Activation energy for various mixtures

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References

1. Зельдович Я.Б., Баренблатт Г.И., Либрович В.Б., Г.М. Махвиладзе Г.М. *Математическая теория горения и взрыва*, М.: Наука, **1980**
2. G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R.K. Hanson, S. Song, W.C. Gardiner, Jr, V.V. Lissianski, Z. Qin, *Gri-mech 3.0*, **1999**

Investigation of a detonation chamber for possible use in perspective aerospace propulsion systems

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A numerical simulation of the operation of the experimental installation (Fig. 1) was carried out for various initial parameters, such as: the initial temperature of the mixture, the initial pressure, the concentration of the supplied mixture.

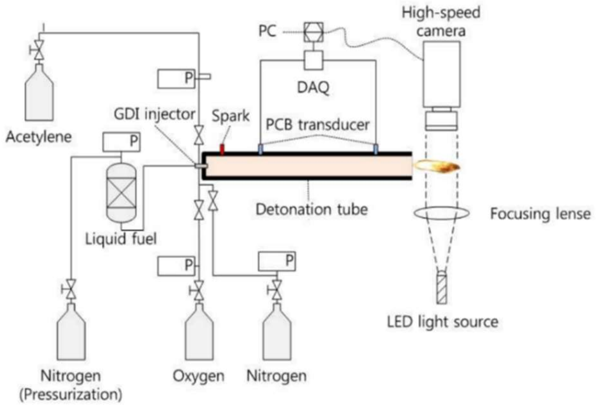

Figure 1. Scheme of the combustion chamber, its injection system, and measurement and control systems on the test bench.

The mathematical model includes a system of balance equations for transient 3D multi-component gas dynamics with chemical reactions considering a presence of a dispersed phase with low or medium density, and a RANS turbulent model. To calculate the phase of particles suspended in the supporting gas phase, a Lagrange approach is used; a group of model particles represents all the dispersed phase. The model particles are affected by the state and velocity of the gas in their vicinity, turbulent fluctuations, determined by the distributed parameters of the RANS model. The dispersed phase influence on gas is modeled by source terms in the balance equations, thus the whole model is two-way coupling one. Using a relatively small set of representative particles, a huge number of real particles are modeled so that each model particle corresponds to tens of thousands of real ones that have similar properties and are located approximately in the same place. Each model particle is determined by its position, velocity, size, temperature, the number of corresponding real particles, as well as the parameters that determine the turbulent properties of the gas in its vicinity.

The dispersed fuel is inserted via injectors on the bottom edge of the combustion tube. After some delay it is ignited, and a detonation may occur in the tube. Products of detonation and combustion are ejected via the opposite side producing thrust force. Then, the products of reaction are displaced by inert gas, then filled with a fresh mixture, thus the process is repeated. The work describes the most important part of this cycle: ignition, combustion, and detonation of the flammable mixture.

This work was supported by the subsidy of the Ministry of Science and Education of Russian Federation on the topic: “Investigation and development of detonation combustion chambers being used in perspective aerospace propulsion systems” (No. 075-15-2021-1385).

Combustion modes during the synthesis of ZnO from aqueous solutions of zinc nitrate with various fuels

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Recently, much attention has been paid to the study of a simple, energy-saving method for producing nanopowders of oxides, promising for industrial use, based on the synthesis during combustion of reagent solutions of highly exothermic redox reactions (Solution Combustion Synthesis – SCS) [1, 2]. In the case of the synthesis of zinc oxide nanopowder ZnO, the most common use is as an oxidizer of zinc nitrate $Zn(NO_3)_2$, and as a fuel of urea $CO(NH_2)_2$, glycine $C_2H_5NO_2$ or citric acid $C_6H_8O_7$, which are soluble in water, have low decomposition temperatures, are available and inexpensive [3, 4]. The equations of ZnO synthesis reactions using these fuels have the following form:

$$Zn(NO_3)_2+\frac{5}{3}\varphi CO(NH_2)_2+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{10}{3}\varphi H_2O+\frac{5}{3}\varphi CO_2+(\frac{5}{3}\varphi+1)N_2, \quad (1)$$

$$Zn(NO_3)_2+\frac{10}{9}\varphi C_2H_5NO_2+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{25}{9}\varphi H_2O+\frac{20}{9}\varphi CO_2+(\frac{5}{9}\varphi+1)N_2, \quad (2)$$

$$Zn(NO_3)_2+\frac{5}{9}\varphi C_6H_8O_7+\frac{5}{2}(\varphi-1)O_2=ZnO+\frac{20}{9}\varphi H_2O+\frac{10}{3}\varphi CO_2+N_2. \quad (3)$$

In these equations, the dimensionless criterion φ, characterizing the ratio of fuel and oxidizer, shows whether excess oxygen is released or, conversely, the oxygen missing for complete oxidation of the elements is consumed from the surrounding gas environment during synthesis in combustion of reagents aqueous solution. This paper presents the results of an experimental study of the types and characteristics of combustion during the solution synthesis of ZnO nanopowder according to equations (1)-(3) when heating a vessel with the solution on a hot plate. First, there is a relatively slow process of heating the solution from the initial temperature to the boiling point and subsequent boiling off of the main amount of solvent, as a result of which a viscous mixture of reagents (gel) is formed. Then the temperature of the gel increases rapidly due to the beginning of a chemical reaction with intense heat and gas release, which leads to various types of combustion: 1) flameless combustion without the formation of luminous zones, 2) smoldering with the formation of focus and frontal luminous zones, 3) spontaneous ignition and slow volumetric combustion with the formation of flame, 4) spontaneous ignition and very rapid explosive combustion with the formation of flame. In the first three cases, combustion leaves behind a loose or dense cake of solid combustion products in the vessel, and in the fourth case, explosive combustion leads to the ejection of the reacting mixture and combustion products from the vessel, so that practically nothing remains in the vessel. For the used fuels, along with combustion type determination, such combustion characteristics were found as: 1) delay time of the combustion start, 2) duration of combustion, 3) the coefficient of conservation of the mass of the product as the ratio of the mass of the combustion product remaining in the reaction vessel after the experiment to the theoretical mass of the product calculated by the reaction equation. Combustion types and characteristics dependences on the value of the criterion φ, the volume (layer thickness) of the solution and the heating rate of the solution on the hot plate were determined.

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References

1. K.C. Patil, M.S. Hegde, T. Rattan; S.T. Aruna Chemistry of Nanocrystalline Oxide Materials. Combustion Synthesis, Properties and Applications. *Singapore: World Scientific*, **2008**, 364 p.
2. A. Varma, A. Mukasyan, A. Rogachev, K. Manukyan *Chem. Rev.* **2016**, 116, 14493.
3. N. Riahi-Noori, R. Sarraf-Mamoory, P. Alizadeh, *J. Ceram. Proc. Res.* **2008**, 9, 246.
4. Z.K. Bolaghi, M. Hasheminiasari, S.M. Masoudpanah. *Ceram. Int.* **2018**, 44, 12684.

Pyrolysis of mixed and slurry fuels

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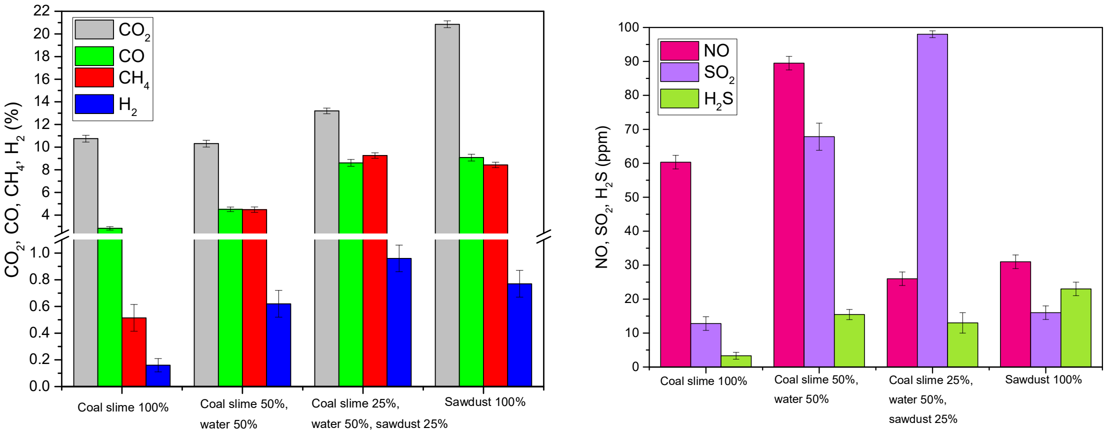
Gasification and pyrolysis are environmentally promising waste treatment technologies, as they produce less pollution in comparison with combustion, in particular, by SO_x and NO_x emission. Currently, a significant number of studies have been carried out on pyrolysis and gasification of conventional energy sources such as coal and biomass. However, the methods of thermal conversion of mixed waste-derived fuels to obtain fuel gas and other valuable pyrolysis products (char, oil) are less studied. This research presents the results of experimental studies on the pyrolysis of mixed and slurry fuels prepared based on wastes of different origins.

Typical biomass (sawdust), coal processing wastes (coal slime) and mixtures based on them were considered as fuel components. The experimental setup included sealed electric furnace (temperature range 20–700 °C), control unit (regulator), gas analyzing system Test 1 («Boner», Novosibirsk), personal computer and service equipment (holders, scales and others).

Fig. 1 shows the concentrations of gas components during the pyrolysis process of biomass, coal slime in dry and wet state and their mixture (coal slime 25 wt%, sawdust 25 wt%, water 50 wt%).



(*a*) (*b*)

Fig. 1. Average values of gas concentrations during fuels pyrolysis: (*a*) CO_2, CH_4, CO, H_2; (*b*) NO, SO_2, H_2S

According to the obtained data (Fig. 1), the pyrolysis of the coal slime 50 wt%, water 50 wt% intensified the gas output in comparison with the coal slime 100 wt% in dry state. The water in slurries promoted an increase in the gas yield. At fast heating, water reacted with volatiles or coal, contributing to the formation of additional gaseous products. The concentration of CO, H_2 и CH_4, increased by 33%, 89% and 75%, respectively. The water promoted the water gas shift reaction. However, it was found that when replacing 25% of the coal slime with sawdust, it is possible to additionally increase the concentration of combustible gases up to 2 times. Pyrolysis of sawdust in its pure form was also characterized by high concentrations of combustible gases, but CO_2 emissions were 1.5 times higher than the established values for coal slime 25 wt%, sawdust 25 wt%, water 50 wt%. This allows us to conclude about the efficiency of utilization of industrial wastes and biomass in the composition of mixed and slurry fuels their pyrolysis.

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Micro-explosive dispersion of gel fuel composition ignited in a high-temperature air medium

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At present, investigations into the ignition and combustion of gel fuels are relevant for the development of the combustion theory of condensed substances [1]. By their state of matter, gel fuels take an intermediate position between the common liquid and solid fuels, combining their advantages in terms of relatively high energy and environmental characteristics, as well as safety indicators for storage and practical application [2]. Due to the multi-component structure of gel fuels, their combustion mechanism differs greatly from that of widespread liquid fuels [3]. When oil-filled cryogels are melted, the liquid components of the fuel separate. A film of molten gellant is formed on the droplet surface with a combustible liquid beneath it. Due to such structure of the gel fuel melt droplet, its heating is accompanied by the processes not typical of the ignition of a single-component combustible liquid droplet: a great number of bubbles emerge in the near-surface layer of the droplet; bubbles increase in number and size, significantly changing the droplet shape; bubbles collapse, and the initial droplet is dispersed to produce a group of much smaller droplets (with a size 1–2 orders of magnitude smaller than the initial fuel particle size); the previous process occurs with a release of combustible liquid vapors into the oxidizer medium through the thickener layer (external envelope) when the droplet breaks up; under threshold conditions, the gas-phase ignition takes place in the vicinity of the droplet.

Unlike it is with liquid single-component fuels, combustion is initiated not in the immediate vicinity of the droplet but in a rather large area. At the moment of the gel fuel ignition, the flaming starts around one or several small fragments which separated and moved away from the droplet surface as a result of a micro-explosion. The temperature of these fine droplets is quite low. When they move around the initial droplet, evaporation proceeds at a relatively low rate. In this area, the temperature of the emerging gas-vapor mixture is lower than that of the ambient hot air. As the fine droplets are moving away from the initial droplet surface, the ambient temperature increases to the initial temperature of heated air, enhancing evaporation. Under critical conditions, the fuel vapors are ignited around the moving fine droplet or a group of droplets. Then, the exothermic reaction is spread from this area all over the volume of the combustible gas-vapor mixture that was formed during the induction period around the gel fuel melt droplet from the outer boundary into the deep layers. Micro-explosions, accompanied by the droplet dispersion, intensify both the ignition and burnout of the fuel due to considerable growth of the surface area of liquid component evaporation [4, 5].

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References

1. M.B. Padwal, B. Natan, D.P. Mishra, *Progress in Energy and Combustion Science.* **2021**, 83, 100885.
2. H.K. Ciezki, K.W. Naumann., *Propellants, Explosives, Pyrotechnics*. **2016**, 41, 539.
3. Q. Cao, W. Liao, W.-T. Wu, F. Feng., *Experimental Thermal and Fluid Science*. **2019**, 103, 377.
4. D. Glushkov, G. Kuznetsov, A. Nigay, V. Yanovsky, O. Yashutina. *Powder Technology.* **2020**, 360, 65.
5. D.O. Glushkov, A.O. Pleshko, O.S. Yashutina, *International Journal of Heat and Mass Transfer*. **2020**, 156, 119895.

Fluorene formation in the reaction of phenyl and benzyl radicals theoretical study

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Up to nowadays combustion reactions of various hydrocarbons is still remaining as a main source of energy. Due to inefficient conditions of the process, in flames appear products of incomplete combustion, such as polycyclic aromatic hydrocarbons (PAH), that eventually lead to soot formation — a strong pollutant. The key for the solution of this problem is to understand properly the mechanisms that lie behind the PAHs formation and growth. As so, the possible mechanism for third ring formation by addiction of phenyl and benzyl radicals was suggested.

The study of this reaction was performed by using ab initio methods of quantum chemistry. The geometries of reagents, intermediates, transition states and products were calculated using the B3LYP/6-311G**. At the same level of theory the values of vibrational frequencies and zero vibration energies, as well as the estimated energies of the molecular systems entering the reaction, were obtained. The refinement of energies to achieve chemical accuracy is carried out by G3(MP2, CC)//B3LYP composite method.

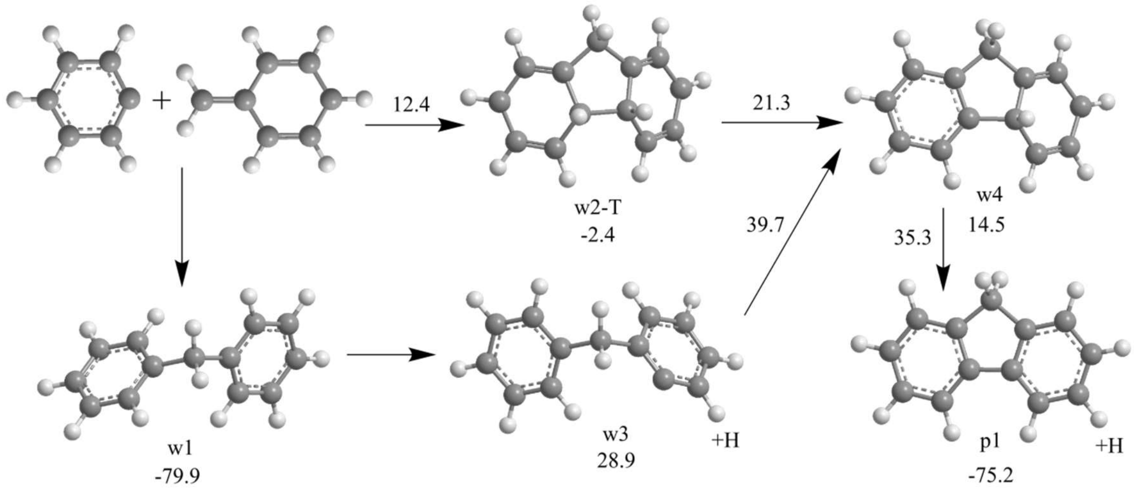

Figure 1 — one of the possible reaction’s pathways. Energies is listed in Kcal/mol relative to the ones of the reagents

The path through w1 implies the usual barrier-free connection of reagents with further step-by-step separation of atomic hydrogen and closure into a ring. The separation of molecular hydrogen at once is expected to be less profitable, due to a higher barrier. Alternatively, the case when the reagents are combined in a triplet state (w2-T) is also possible. This way is more profitable because of lower barriers, as well as fewer intermediate steps, since the closure of the ring goes immediately.

Experimental study of the effect of hydrogen addition to fuel on combustion instability

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Perspective development of aircraft gas turbine engines and gas turbine power plants created on their basis are associated with the creation of low-emission combustion chambers. The most promising approaches for reducing the pollutant emissions in exhaust gases are the combustion of an "ultra-lean" fuel-air mixture and the use of alternative fuels with a lower carbon fraction. In the coming decades, such a fuel will be a methane-hydrogen mixture.

The main problem in the development of combustion chambers that implement the above concepts is the instability of their operation due to occurring of high-amplitude pressure pulsations. The lack of methods that allow predicting the occurrence of self-oscillations with high accuracy leads to the use of predominantly experimental methods for studying the instability of combustion chambers. Therefore, this paper is devoted to an experimental study of the hydrogen addition effect in methane-hydrogen fuel on the pulsation parameters of the combustion chamber. Pressure pulsations in the combustion chamber were recorded using a Kistler 6021A high-temperature dynamic pressure sensor.

The spectra of pressure pulsations obtained as a result of the study showed a significant fuel composition effect on both the amplitude and the frequency of gas self-oscillations.

C_3H_2 oxidation by molecular oxygen: a theoretical study

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Propynylidene is one of the commonly found in interstellar space particles. In addition, propynylidene can occur as intermediates in the hydrocarbon fuel's combustion. This particle can have several forms: singlet propynylidene may be in a cyclic and linear form, and triplet propynylidene has linear form. The low stability makes it difficult to study the transformations of propynylidene under combustion conditions by experimental methods. We have studied the interaction of triplet propynylidene with molecular oxygen in a wide range of temperatures and pressures by theoretical methods using quantum chemical calculations.

Geometries of the reactants, products, transition states, and reaction intermediates in the reactions of triplet propynylidene with molecular oxygen have been optimized using the wB97XD method with the 6-311G** basis set. Vibrational frequencies have been computed at the same level of theory to characterize stationary points as local minima or transition states, to obtain zero-point vibrational energy corrections (ZPE), and to be utilized in partition function calculations. Further, the wB97XD optimized geometries were used to refine single-point energies by the MOLPRO package. Temperature- and pressure-dependent rate constants for the reactions considered were evaluated within the framework of RRKM theory in combination with the Master Equation approach (RRKM-ME).

Based on the results of the study, the potential energy surface (PES) of the reaction of triplet propynylidene with molecular oxygen was constructed, and the rate constants of this interaction were determined. The calculated rate constants at different pressures were fitted by the modified Arrhenius expressions, which are proposed for kinetic modeling of propynylidene reactions in combustion.

Choice of a kerosene surrogate for prediction of the emission of carcinogenic polycyclic aromatic hydrocarbons

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The component composition of kerosene is very complex and depends on the brand, feedstock and manufacturer, for this reason, model fuels are used in calculations - surrogates consisting of several well-studied substances. The paper validated 14 surrogates of aviation kerosene, which can be used to predict the emission of carcinogenic polycyclic aromatic hydrocarbons (PAH) using the kinetic model of the Samara University "A17". The surrogates were verified using experimental data for normal flame propagation velocity, low-temperature pyrolysis, and combustion of pre-evaporated kerosene. The obtained results show the significance of reproduction of molar mass and carbon number by surrogates. The use of trimethylbenzene, methylnaphthalene, tetralin and xylene isomers in surrogates contributes to a better description of the low-temperature oxidation of kerosene aromatic compounds. Predicting the concentrations of combustion products showed that the Liu and Drexel surrogates describe the concentrations in the front better than others, but the concentrations of the equilibrium products can be overestimated. Surrogates UM1 and su4 more accurately predict concentrations in the post-flame zone. As a result of the review, the su4 surrogate was chosen for use in future computational work in the region of high and low temperatures.

Burning of two-phase fuel droplets in weightlessness

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In the present paper physical and mathematical models are developed, allowing to consider the effect of multiphase fuel (liquid + solid combustible materials) on the conditions of ignition and modes of propagation of combustion in poly-dispersed non-uniform mixtures. In this case, the combustion of different droplet fractions occurs in different modes: the volatile fraction evaporates and burns in the gas-phase mode, and the solid fuel fraction reacts with the oxidizer in the heterogeneous mode. The effect of the presence of a solid fraction in droplets reacting in a heterogeneous regime on the evaporation rate of the volatile fuel component is studied. The effect of tightness due to the presence of other droplets on the evaporation rate of each droplet is taken into account. The problem is acute for the fire safety in space studies. As it was shown in experiments conducted under strongly reduced gravity conditions, the burning of some structural materials is accompanied by evaporation of low temperature boiling components, which causes the vapor expansion and ejection of material droplets into the vicinity of the burning surface. Those droplets form clouds of droplets near the burning surface surrounded by combustible vapors, which could preserve this state for a long time in microgravity contrary to terrestrial conditions under which gravity makes droplets fall down thus preventing from formation of hazardous aerosol clouds. While in weightlessness such clouds of droplets can exist for long times characterized by combustible vapor concentration exceeding the burning limit. Thus, the clouds of rich mixture could stay in the heated atmosphere of reaction products for some time after flame extinguishing. An incidental air flow caused by switching on ventilation, or just moving of some crew members, could bring to increasing the oxidant concentration in the cloud and accidental volume ignition. The droplets of combustible materials thermally ejected from the surface and injected into the atmosphere have a complex composition, as a rule. In particular, one can distinguish in those droplets volatiles (substances forming a gaseous phase and burning in the contact with gaseous oxidant) and solid combustible particles (substances remaining solid and burning in a heterogeneous regime due to surface contact with an oxidant). The presence of two different types of substances within one agglomerate introduces serious peculiarities in combustion of such droplets. The existing models for evaporating droplet or solid particle combustion cannot be used directly for determining the burning rate.

The developed mathematical model showed that in the presence of condensed fuel in the droplet, the evaporation of the liquid is faster due to the additional energy release because of a heterogeneous reaction on the surface. When only the solid residue remains, the rate of mass consumption decreases abruptly, but then increases rapidly due to an increase in the temperature of the condensed residue due to energy release in heterogeneous reaction.

When the flame propagates in a poly-dispersed mixture, the thickness of the front reaches a dozens of centimeters. Then, as the flame approaches the walls of the chamber, the thickness of the front increases.

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Numerical simulation of combustion processes in combustion chamber of hybrid solid fuel engine

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Hybrid solid-propellant engines, which use fuel mixture components in various states of aggregation, are very attractive. This type of engine has a number of advantages over liquid or solid propellant engines. For example, compared to solid fuel engines, it has greater safety due to the storage of fuel components separately from each other. It also allows you to control the traction of the device. Compared to liquid fuel engines, hybrid engines are simpler in design and easier to maintain. One of the fastest and relatively cheap ways to develop such engines, as well as other engines, is computer simulation. Carrying out predictive computational modeling of such devices due to its rather high complexity is difficult without the use of high-performance computing systems and the development of parallel algorithms and programs.

In this work, a three-dimensional numerical simulation of the processes occurring in the combustion chamber of a solid-fuel engine, into which the oxidizer enters in gaseous form at supersonic speed, was done. Gaseous oxygen and air were used. It is assumed that in the course of chemical reactions occurring on the surface of a solid fuel as a result of interaction with the oncoming flow, a gaseous combustible substance, decomposition product of a solid fuel, is released into the chamber, which also begins to mix and react with the oncoming flow of the oxidizer. The HTPB (Hydroxyl-terminated polybutadiene) and PMMA (Polymethyl methacrylate) solid fuels were used. Modelling the release of gaseous fuel through a solid fuel surface was done by near-wall functions calculated on the basis of the parameters of the medium near the wall surface obtained in the course of numerical calculation. The characteristic dimensions of the engine are based on experimental data from the work [1,2]. A specialized author's program code was developed for the simulation. The numerical model is based on the MUSCL method of flow interpolation, the AUSMP method for compression conditions on a uniform cubic grid and the semi-implicit Novikov method for a rigid system of kinetic equations. An increase to the second order of accuracy was carried out according to the McCormack method. Wilcox's k-ω turbulence model was used. In the course of the study, a comparison with experimental data was done. A series of test computational experiments was carried out to determine the distributions of physical parameters inside the combustion chamber. The diffusion mode of the combustion process in the combustion chamber, large flow turbulence, vortex formation and strong process asymmetry have been obtained.

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References

1. A. Ben-Yakar, B. Natan, A. Gany, *Journal of Propulsion and Power* **2015**, 14 (4) 447–455.
2. X. Sun, H. Tian, Y. Li, N. Yu, G. Cai, *Acta Astronautica* **2016**, 119, 137–146.

Threshold intensities for laser spark in pure O_2, N_2 and CH_4

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The laser impact on combustible mixtures is one of the possible ways to initiate chain reactions [1-3]. This is especially relevant now, when the initiation of combustion must be carried out under conditions of high pressures, fast compression rates and lean fuel mixtures. Initiation by a laser spark has a number of advantages over traditional methods: ease in management of time and place of ignition, absence of electrodes, the possibility of implementing multi-point ignition, etc.

In the present study, we performed measurements of threshold intensities for laser spark in the air/CH_4 mixture at different pressures. Laser radiation was provided by a tunable dye laser Sirah Precision Scan PSCAN-D-18-EG pumped by the second harmonic of a Nd:YAG laser Quanta-Ray PR0-290-10E. The dye laser was set at wavelength λ=761 nm. The laser spark was initiated in a 180 mm length quartz tube with an inner diameter of 8.5 mm, covered with nichrome thread, which allowed heating the gas up to 1000 K. The quartz tube was installed into the stainless steel chamber with two windows for input and output of the laser beam and a third one for visual observation of the spark. The experimentally obtained threshold intensities for laser spark on pressure of oxygen, nitrogen and methane are presented in Figure 1 at room temperature. The leftmost values in the figure indicate the minimum pressures at which a spark occurred. The slight wavelength variations in the range of 750–770 nm did not lead to noticeable changes. In addition, the high temperature experiments (up to 1000 K) in N_2 and O_2 did not reveal the dependencies of threshold intensity by temperature.

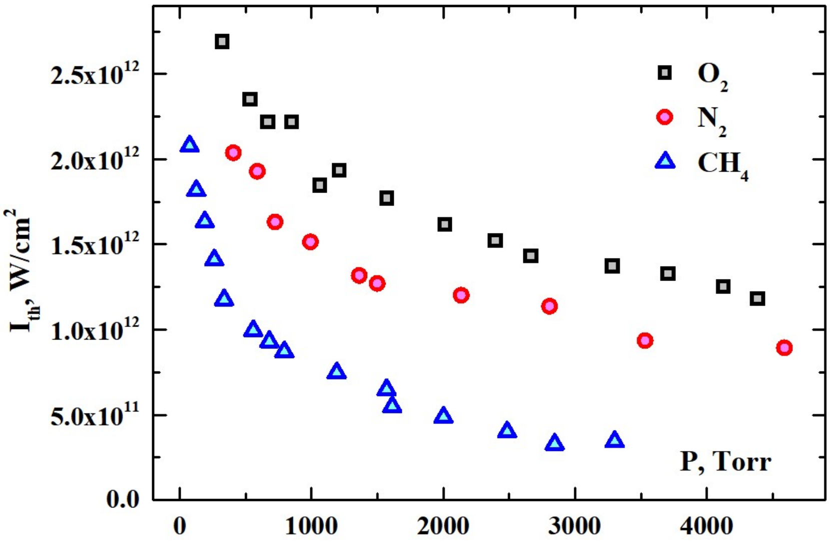

Figure 1 – Threshold intensities for laser spark in three gases at λ=761 nm and T=297 K

References

1. T.X. Phuoc. *Optics and Lasers in Engineering*. **2006**. 44(5). P. 351-397.
2. Y.E. Gamal et al. *Physics of Plasmas*. **2017**. 24(10). P. 103503.
3. T.Endo et al. *Combustion and Flame.* **2017**. 178. P. 1-6.

NO_2 production in a dielectric barrier discharge in air-CH_4 mixtures

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Dielectric barrier discharge (DBD) is of particular interest in the field of accelerating chemical processes in lean fuel-air mixtures and plasma stabilization of combustion due to the relative simplicity of technical implementation and the ability to be easily integrated into various gas flow configurations [1,2]. To develop and verify the existing kinetic models of DBD plasma-associated combustion, all possible experimental data on the composition of the gas mixture in the discharge afterglow are required.

Figure 1(a) shows measured number densities of NO_2 in the afterglow of DBD as a function of power input at a constant pressure 1 atm and air flow rate 4 L/min in the absence of methane. The DBD system used in the experiments is described in detail in [3]. NO_2 number densities were measured using tunable diode-laser absorption spectroscopy at a wavelength near 404.3 nm. It was found that nitrogen dioxide was present in the afterglow of the barrier discharge only when a certain threshold value of the discharge power was exceeded, and then NO_2 number density increased linearly with power. The value of the nitrogen dioxide production threshold in the barrier discharge was determined to be 46.5 ± 0.5 W using the linear approximation of the experimentally obtained data. The measured threshold value corresponds to an energy input into the gas of 580 ± 6 J/g.

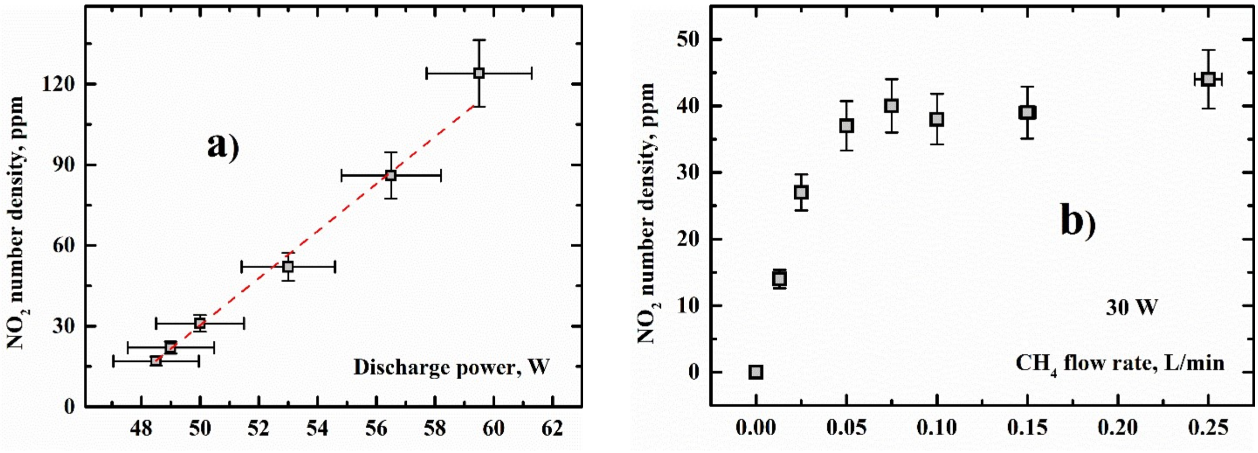

Figure 1. The measured number densities of NO_2 in the DBD afterglow at constant pressure 1 atm and air flow rate 4 L/min as a function of: (a) discharge power W; (b) CH_4 flow rate.

Figure 1(b) shows the dependence of the NO_2 number densities in the DBD afterglow on the methane flow rate at a constant air flow rate 4 L/min for a discharge power input equal to 30 W, which was below the NO_2 production threshold. However, nitrogen dioxide was observed in the discharge afterglow with the slightest addition of methane into the mixture (0.3%) and reaches a plateau at a 2.5% content of CH_4 in the air.

References

1. M. Dong et al. *Energy*. **2020**, 199, 117463.
2. Chen Y. et al. *Aerospace Science and Technology*. **2020,** 99, 105765.
3. Mikheyev P. A. et al. *Plasma Sources Science and Technology*. **2020,** 29, 015012.

Combustion synthesis of Ti_3SiC_2 skeleton with infiltration by tin melt

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In this paper, the possibility of using combustion for simultaneous synthesis of ceramic compound of MAX-phase Ti_3SiC_2 in the form of a porous skeleton and spontaneous infiltration of its pore body with liquid tin to obtain the Ti_3SiC_2-Sn cermet according to the author's method [1, 2]. The synthesis of the Ti_3SiC_2 skeleton by combustion was carried out from a mixture of titanium (~300 µm), silicon (~5 µm) and graphite (~15 µm) powders taken in the ratio 3Ti+1Si+2C. The combustion process was characterized by a temperature of over 2000 °C, the velocity of the combustion wave ~ 6 mm / s, and the structure formation of the target compound Ti_3SiC_2 after the passage of the combustion wave could take up to 6-8 seconds. Taking into account the fact that the process of secondary structure formation continues in an already burnt and rapidly cooling SHS skeleton, which is able to spontaneously absorb the metal melt due to the action of capillary wetting forces immediately after combustion, it was necessary to study the effect of the presence of tin melt in the pores of the hot skeleton on the ongoing process of secondary structure formation of Ti_3SiC_2.

Within the framework of this work, a technique for producing Ti_3SiC_2-Sn cermet was developed, which ensures the combination of the combustion process and the completion of the formation of the Ti_3SiC_2 skeleton together with high-temperature infiltration by tin melt. Melts of pure tin and Sn-10%Pb alloy were not infiltrated into the Ti_3SiC_2 skeleton at a melt temperature of 400 °C. However, the tin melt is spontaneously impregnated by ~120 mm if the melt temperature is increased to 800 °C. It was found that, firstly, the tin melt does not destroy the MAX phase of Ti_3SiC_2, and secondly, the premature ingress of tin melt into the SHS skeleton practically does not interfere with the process of Ti_3SiC_2 structure formation.

A study of the density distribution of the obtained cermet along the length showed a stable decrease in density from the beginning of the sample in contact with the tin melt to the end from 6.02 g/cm^3 to 4.49 g/cm^3, which indicates a corresponding increase in residual porosity from ~ 0% to ~ 25.1%. The study of the microstructure showed the presence of a significant number of Ti_3SiC_2 plates along the entire length of the cermet. According to the XRD analysis data, the phase composition is Sn, Ti_3SiC_2 and TiC.

Thus, it was found that the temperature of the tin melt significantly affects the possibility of infiltration into the hot porous skeleton of the MAX phase Ti_3SiC_2. It was also found that the tin melt does not exhibit destructive chemical activity in relation to the 3Ti-Si-2C powder system, that is, it does not prevent the formation of Ti_3SiC_2 and does not destroy it.

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References

1. A.P. Amosov, E.I. Latukhin, E.R. Umerov. Method of obtaining ceramic-metal composite materials. *Pat. 2733524 (RF)*, **2020**.
2. A.P. Amosov, E.I. Latukhin, E.R. Umerov Applying infiltration processes and self-propagating high-temperature synthesis for manufacturing cermets: a review. *Rus. J. Non-Ferr. Metals*, **2022**, 63 (1), 81.

Experimental study and quantum-chemical calculation of C_3H_7I initial dissociation kinetics and its thermodynamic properties in a wide temperature range

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Iodine-containing halocarbons and halohydrocarbons are widely used in various fields of the chemical industry, firefighting, and medicine. At the same time, scientific interest in such substances remains extremely high at the present time. In particular, the C_3H_7I molecule due to presence of the weakest bond of halogen atom with the carbon atom (C-I bond), is the most suitable precursor for the alkyl radical C_3H_7. This substance, as is known, are formed in significant quantities at the combustion and pyrolysis processes of normal alkanes, and without the correct prediction it is impossible to build physically consistent models of real hydrocarbon fuels combustion. That is why this work is aimed at studying the kinetic and thermodynamic C_3H_7I dissociation properties.

The n-C_3H_7I + Ar → n-C_3H_7 + I + Ar reaction at the temperatures 800-1200 K and pressures 3.5± 0.5 bar behind reflected shock waves using the atomic resonance absorption spectroscopy (ARAS) technique on a resonant line of atomic iodine at 183.04 nm have been studied. The initial concentration of n-C_3H_7I in Ar was varied from 0.8 to 1.1 ppm.

As a result, the first direct experimental data on the n-C_3H_7I thermal unimolecular decomposition were obtained. Time profiles of iodine atom concentration were used to determine the rate constant temperature dependence and its activation energy. Based on the data, the dissociation rate constant n-C_3H_7I was obtained in the two-parameter Arrhenius form for further using in kinetic databases.

At the same time, using modern methods of quantum chemical calculations at the level of the B3LYP/cc-pVTZ-PP theory, individual characteristics of n-C_3F_7I, i-C_3F_7I molecules, their products, and transition states were calculated. Among them, optimized geometry, harmonic frequencies, rotational constants, total electron energy, zero-point energy, etc were obtained. The data made it possible, in the ideal gas approximation, to determine the standard enthalpy of dissociation and isomerization reactions, as well as all necessary thermodynamic properties, such as enthalpy, entropy, and isobaric heat capacity in the temperature range from 200 to 5000 K.

And finally, based on quantum chemical calculations, the theoretical calculation of the monomolecular n-C_3H_7I dissociation rate constant was performed using the Rice-Ramsperger-Kassel-Marcus (RRKM) model in a wide thermodynamic parameters range ($T = 300–3000$ K, $p = 10^{-4}–10^{2}$ bar). For this substance, Arrhenius dependences of the rate constants in the high and low pressure limit are presented, as well as the central broadening factor. Comparison of the theoretical and experimental results with literature data confirmed their reliability. The RRKM calculations has allowed to conclude, under the studied conditions, the n-C_3H_7I dissociation rate constant is close to the high-pressure limit; nevertheless, at elevated temperatures (above 900 K), the effect of pressure still remains significant.

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