Innovations in combustion technologies for propulsion

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Motivation

- Combustion of variable fuels (gaseous, solid, and liquid) is in the heart of the modern propulsion systems including aero and rocket engines and energetic machines.
- Enhancement of combustion makes it possible to reduce the fuel consumption and pollutant emission and to improve the flight characteristics of the aircrafts and rockets.
- For past decades great attention was paid to exploring the possibility of combustion intensification by chemical and physical techniques.

Background of the methodology

- The ignition and combustion of the majority of the mixtures (hydrogen/air, hydrocarbon/air and others) occur by chain-branching reactions.
- The common principal stages of chain process:
  - Chain initiation
    \[ A \rightarrow r + D: \]
    \[ H_2 + O_2 \rightarrow H + HO_2 \]
  - Chain propagation
    \[ r + A = C + r \ (l=1,2,...) \]
    \[ H + O_2 = OH + O \ (l=2) \]
    \[ O + H_2 = OH + H \]
  - Chain termination
    \[ r + r = r_2 \]
    \[ H + O_2 + M = HO_2 + M \]
    \[ 2OH + M = H_2O_2 + M \]

In order to intensify the ignition and combustion it is needed to accelerate
- reaction of chain initiation
- reaction of chain propagation
or decelerate the reaction of chain termination

One can distinguish a few classes of methods for combustion enhancement:

- Gas dynamic methods
  - preheating the mixture
  - shock induced combustion
- Chemical method
  - admixture of the species which can produce highly reactive radicals in the course of their decomposition (promoters): \( H_2O_2 \rightarrow 2OH \)
- Physical methods
  - dissociation of reacting molecules by means of ionized radiation, electron beam, laser photons, electrical discharge (10-10^3 eV/molecule)
  - excitation of vibrational and electronic states of reactive atoms and molecules by means of electron impact, resonance laser radiation (0.1-2 eV/molecule)
Control of combustion processes by selective excitation of internal degrees of freedom of reacting molecules

- Among the physical methods of exerting on ignition and combustion only two approaches can be considered as the most pronounced and the least energy consuming ones

- Exposure of target molecules to resonance laser radiation
  1. \( \text{O}_2(\Sigma^1\text{g}) + h\nu (\lambda = 762 \text{ nm}) = \text{O}_2(b^3\text{g}) \)
  2. \( \text{O}_2(000) + h\nu (\lambda = 9.6 \mu \text{m}) = \text{O}_2(001) \)
  3. \( \text{O}_2(\Sigma^1\text{g}) + h\nu (\lambda = 193.3 \text{ nm}) = \text{O}(\text{P}) + \text{O}(\text{D}) \)

- Activation of reacting molecules by electron impact in a specially arranged electrical discharge
  1. \( \text{O}_2(\Sigma^1\text{g}) + e(E = 5 \text{ eV/molecule}) = \text{O}(\text{P}) + \text{O}(\text{P}) \)
  2. \( \text{O}_2(\Sigma^1\text{g}) + e(E = 0.98 \text{ eV/molecule}) = \text{O}_2(a^1\text{g}) \)
  3. \( \text{H}_2(V=0) + e(E = 0.5 \text{ eV/molecule}) = \text{H}_2(V=1) \)
  4. \( \text{N}_2(V=0) + e(E = 0.2 \text{ eV/molecule}) = \text{N}_2(V=1) \)

Accelerating of chemical reactions

The experimental data revealed that chemical reactions with vibrationally and electronically excited molecules occur much faster than those with non-excited ones

1. Vibrational excitation
   \( \text{Light} \rightarrow \text{O}_2(X^3\Sigma^1\text{g}) \rightarrow \text{O}_2(X^3\Sigma^1\text{g}) + h\nu \rightarrow \text{O}_2(a^3\Sigma^1\text{g}) \)
   The rate of reaction with \( \text{O}_2(a^3\Sigma^1\text{g}) \) is by a factor of 10^3 higher than with normal oxygen \( \text{O}_2(X^3\Sigma^1\text{g}) \)

2. Electronic excitation
   \( \text{O}_2(a^3\Sigma^1\text{g}) + \text{H} = \text{OH} + \text{O} \)
   At \( T=300 \text{ K} \) the rate constant of the reaction with \( \text{O}_2(a^3\Sigma^1\text{g}) \) is thousand fold greater than that with normal oxygen \( \text{O}_2(X^3\Sigma^1\text{g}) \)

Vibrational and electronic energy of molecules is much more effective than translational and rotational energy in overcoming the barriers of endoergic reactions
Excitation of O₂ Molecules to the σ⁺Δ_u and σ⁺Σ_g States by 
Resonant Laser Radiation

Scheme of the electronic terms of oxygen molecule Excitation:
CH₄/O₂ mixture in low pressure subsonic flow (self-sustained discharge).

Resonant Laser Radiation

Measurement: concentrations of O₂(σ⁺Δ_u) + O₂(σ⁺Σ_g) (spontaneous emissions
at λ=1,268 μm and 762 nm, respectively), OH(v) - LIF; temperature -
CARS.

Singlet oxygen-assisted combustion

Flow reactor

Plasma-chemical assisted combustion in 
subsonic flow by self-sustained discharge

The schematic of the test facilities to investigate influence of singlet delta and singlet 
sigma oxygen molecules on the enhancement of ignition/combustion of H₂/O₂ and 
CH₄/O₂ mixture in low pressure subsonic flow (self-sustained discharge).

Measurements: concentrations of O₂(σ⁺Δ_u), O₂(σ⁺Σ_g) (spontaneous emissions
at λ=1,268 μm and 762 nm, respectively), OH(v) - LIF; temperature -
CARS.
Singlet oxygen-assisted combustion

The geometrical characteristics of the induction length shortening

Spontaneous emissions of oxygen plasma

Spectra of the oxygen plasma at different values of discharge current density

Singlet oxygen-assisted combustion

The photo of the flame in H2/O2 fuel rich mixture (H2/O2=5/2) at Vf=17 m/s in reactor the temperature of reactor wall is as small as 780 K for two cases: (1) free diffusion flame; (2) the singlet oxygen-assisted flame

Kinetic Model

Electronically Excited Species: O(5Σg-) (1), O(5Σg-) (3), O(3P)

Electronically Unexcited Species:

• for H2/O2 mixture: H2, O2, H, O, OH, H2O, HO2, H2O2, O, N, N2, NO, NO2, N2O

• for CH4/air mixture: H2, O2, H, O, OH, H2O, HO2, H2O2, O, C, CO, CO2, CH4, CH3, CH2, CH2O, CH3O, CH3OH, CH3O2, CH3O2H, N, N2, NO, NO2, N2O

Vibrationally Excited Modes:

• di-atomic molecules: O2(3Σg-), F, O(1Σg-), F, O(3Σg-), F, H2(1Σg), OH(1Σg), CO(1Σg) N2(1Σg)

• Tri-atomic molecules: H2O(F2,F3,F4), H2O(F2,F3,F4), NO(F2,F3,F4), NO(F2,F3,F4), CO(F2,F3,F4)

• Multi-atomic molecules H2O2(F2,F3,F4,F5,F6), CH2O(F2,F3,F4), CH3OH(F2,F3,F4)

Processes

• intramode vibrational-vibrational exchange

\[ \chi_e^{s}(T,T') = k_e(T)\chi_e(T,T') \]
In recent years, much attention has been concentrated on studying the processes of ignition and combustion stabilization in a supersonic flow. This is due to the prospect of designing new engines for high-speed vehicles.

- The key question in this problem is how to shorten the induction and energy release zones in organizing combustion.

- To solve this problem several approaches have been considered:
  - Purely gas-dynamic approach based on the creation of flow zones with a higher temperature and reduced gas velocity behind bluff bodies (stabilizers).
  - Generation of an oblique shock. Disadvantages: in order to ignite the mixture at appropriate distances from the front (~1 m) the shock intensity must be fairly high. At small angles of inclination of the front to the free-stream velocity vector ($\beta < 35^\circ$) and substantial gas velocities (Mach number $M_0 = 5–7$) even a hydrogen-air mixture cannot be ignited at a distance smaller than 10 m.

In singlet oxygen-assisted combustion, both the experiments and modeling exhibit a strong influence of the presence of singlet oxygen molecules in the oxygen plasma on the induction zone length and even on the ignition temperature. The predictions are consistent well with experimental data and demonstrate great potentialities of the approach based on the excitation of $O_2$ molecules to enhance the combustion.

Parameters in flow reactor:
- $V_f = 17$ m/s, $T_{in} = 780$ K, $P_0 = 10$ torr.
- The values of input energy $E_{in} = 0; 59; 107; 246$ J/mol are related to $T_{axis} = 780; 730; 700; 675$ K at $x = \infty$.

Both the experiments and modeling exhibit a strong influence of the presence of singlet oxygen molecules in the oxygen plasma on the induction zone length and even on the ignition temperature. The predictions are consistent well with experimental data and demonstrate great potentialities of the approach based on the excitation of $O_2$ molecules to enhance the combustion.
Shock induced combustion in a supersonic flow at high Mach numbers, low levels of pressure and temperature

- Flow conditions: \( M = 5 - 6 \), pressure \( 10^3 - 10^5 \) Pa, \( T = 300 - 600 \) K

- Excitation of internal degrees of molecules of the reacting species as the method of solution of the ignition and combustion problems

**Flow conditions:**

\[ M = 5 - 6, \quad \text{pressure} \ 10^3 - 10^5 \ 	ext{Pa}, \quad T = 300 - 600 \ 	ext{K} \]

**Excitation of internal degrees of molecules of the reacting species as the method of solution of the ignition and combustion problems**

Thermally non-equilibrium effects in combustion

- Shock-induced combustion
- Plasma-assisted combustion: abundance of electronically and vibrationally excited species: \( \text{H}_2(v), \text{N}_2(v), \text{O}_2(X^\Sigma_g^+,v), \text{O}_2(a^1\Delta_g,v), \text{CO}(v) \)
- Laser-induced combustion: \( \text{O}_2(X^\Sigma_g^+,v=0)+h\nu(678 \ \text{nm})=\text{O}_2(b^1\Sigma_g^+,v=1) \);
  \( \text{O}_2(000)+h\nu(96 \ \text{nm})=\text{O}_2(001) \);
  \( \text{O}_2+h\nu(243 \ \text{nm})=\text{O}_2(a^1\Delta_g,v)+\text{O}(3P) \)

- Thermally equilibrium chemical kinetic model
  \[ T=T_{rot}=T_v \]
- Thermally non-equilibrium model: \( T=T_{rot} \neq T_v \)

Plasma-chemical initiation of detonation in a supersonic flow

The schematic of the flow

- **Discharge**
- **Mixing zone**
- **Induction zone**
- **Shock wave front**

The system of equations describing the flow behind shock wave front

\[ \frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0 \]
\[ \frac{\partial \rho u}{\partial t} + \frac{\partial (\rho u^2)}{\partial x} = -\frac{\partial P}{\partial x} + \frac{\partial (\rho u v)}{\partial x} \]
\[ \frac{\partial \rho \phi}{\partial t} + \frac{\partial (\rho \phi u)}{\partial x} = \frac{\partial (\rho \phi v)}{\partial x} + \frac{\partial}{\partial x} \left( \frac{\rho \phi}{X_0} [X_0 - X_0^0] \right) \]

Kinetic schemes

- **\( \text{H}_2/\text{O}_2 \) mixture** - 78 reactions, 11 species:
  \( \text{H}_2, \text{O}_2, \text{H}, \text{O}, \text{OH}, \text{H}_2\text{O}, \text{HO}_2, \text{O}_3, \text{O}_2(\sigma^1\Delta_g) \), and electronically excited oxygen molecules \( \text{O}_2(a^1\Delta_g), \text{O}_2(b^1\Sigma_g^+) \)
- **\( \text{CH}_4/\text{O}_2 \) mixture** - 307 reactions, 31 species:
  \( \text{H}_2, \text{O}_2, \text{H}, \text{O}, \text{OH}, \text{H}_2\text{O}, \text{HO}_2, \text{O}_3, \text{O}_2(\sigma^1\Delta_g), \text{O}_2(\alpha^1\Delta_g), \text{O}_2(\epsilon^1\Delta_g), \text{O}_2(3\Sigma_g^+), \text{C}, \text{C}_n\text{H}_m (n=1,2), \text{CH}_n\text{H}_m (m=1-4), \text{CH}_3, \text{CH}_2\text{O}, \text{CHO}, \text{CH}_{3}\text{O}, \text{CH}_{3}\text{OH}, \text{CH}_{3}\text{O}_2\text{H} \)

Ignition behind oblique shock wave in \( \text{CH}_4/\text{air} \) mixture

Evolution of gas temperature behind oblique shock (\( T_0=300 \ \text{K}, P_0=10^5 \ \text{Pa}, M_0=10, \beta=30^\circ \))

- **1** thermally equilibrium chemistry: \( L_w=5.65 \ \text{m} \)
- **2** thermally non-equilibrium chemistry: \( L_w=15.7 \ \text{m} \)

The neglect of non-equilibrium excitation of molecular vibrations of reagents results in significant underestimation of predicted induction zone length (by a factor of three)
Preliminary excitation of molecular vibrations of $\text{N}_2$ leads to a significant decrease in the induction zone length (by a factor of 10-12) due to exclusion of the thermally non-equilibrium delayed excitation of $\text{N}_2$ vibrations behind the oblique shock front.

Thermally non-equilibrium chemistry

Evolution of vibrational and transitional temperatures behind oblique shock front

Thermally non-equilibrium effects behind shock wave

Evolution of vibrational, $\text{H}_2$, and translational temperatures behind the incident shock ($M_0=5.77$) in $\text{H}_2/\text{O}_2$ ($\phi=0.13$) mixture predicted by thermally equilibrium and thermally nonequilibrium models.

There is no consistency between data predicted using the thermally equilibrium kinetic model and measurements. This model underestimates the ignition delay time. Thermally non-equilibrium model predicts more reliable results ($\tau_{\text{ign}}=23 \mu s$).

Discharge model

The self-consistent 1D model is based on:
- Kinetic Boltzmann equation for EEDF in standard quasi-stationary approximation
- Kinetic rate balance equations for charged and neutral species: $e$, O, O$^+$, O$_2$($^3\Sigma_u^+$), O$_3$($^1\Sigma_g^+$), O$_4$($^1\Sigma_g^+$), O$_5$(X$^1\Sigma_g^+$), O$_6$(A$^3\Delta_g$), O$_7$(B$^1\Sigma_u^+$), O$_8$(C$^3\Sigma_u^-$), O$_9$(D$^3\Sigma_g^-$), O$_{10}$($^1\Delta$), including vibrationally excited O$_{11}$(X$^3\Sigma_g^-$) molecules
- 1D gas dynamic equations

Activation of molecular oxygen in electrical discharge

Predicted concentration of the main species and temperature at the discharge outlet for different $E_\gamma$ values at $E/N=1.1 \times 10^{-10}$ V cm$^2$, $T_0=300$ K, $P_0=5 \times 10^3$ Pa, $M_0=5$.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_\gamma$ [J/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2(X^3\Sigma_g^-)$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>$3.521 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{O}_4(A^3\Delta_g)$</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{O}_5$</td>
<td>$3.18 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\text{O}_6$</td>
<td>$3.521 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{O}_7$</td>
<td>$6.43 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{O}_8$</td>
<td>$7.663 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{O}_9$</td>
<td>$1.55 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{O}_{10}$</td>
<td>$1.596$</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>$400$</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>$868$</td>
</tr>
<tr>
<td>$\text{O}_2(X^3\Sigma_g^-)$</td>
<td>$985$</td>
</tr>
<tr>
<td>$\text{O}_4$</td>
<td>$1596$</td>
</tr>
</tbody>
</table>
Plasma-chemical initiation of detonation in a supersonic flow of H₂/O₂ mixtures

Heating the gas – dashed lines. Activation of O₂ molecules in electrical discharge – solid lines

Variation of the gas temperature behind the oblique (β=15°) shock front in stoichiometric H₂O₂ (P₀=0.1 bar, M₀=6) at different values of the specific energy deposited to the oxygen in electrical discharge: Eₛ=3⋅10⁻² (1) and 6⋅10⁻² J/cm³ (2).


Plasma-chemical combustion initiation in a supersonic flow behind oblique shock wave

Premixed flow of CH₄/O₂ stoichiometric mixture

Evolution of the species mole fractions along the flow behind the shock front at P₀=10⁴ Pa, M₀=6, β=25°, Eₛ=3⋅10⁻³ J/cm³.

Excitations of oxygen molecules to the a¹Δg and b¹Σg⁺ electronic states is much more efficient in shortening the induction zone length than the heating the gas.

Kinetic Mechanisms of Combustion Initiation in H₂+O₂ Mixture

1. Without excitation of O₂ molecules
2. With excitation of a¹Δg, b¹Σg⁺ electronic states of O₂ molecules

Combustion enhancement in CH₄-O₂ mixture

• Singlet oxygen-assisted combustion in a supersonic flow

The excitation of O₂ molecules to the singlet electronic states makes it possible to increase the fraction of chemical energy that may be converted to thermal energy during combustion as compared to initiation of combustion by heating the mixture. The gain in terms of ΔHch may be as large 50%.

Gas-Dynamic Parameters of the Initial Mixture and Combustion Exhausts; Energy Input to the Gas and Chemical Energy Converted to Heat


Method of combustion initiation

Method

Exploitation of O₂ molecules

Heating of the mixture

P₀ (kPa)
Mₐ (kJ/kg)
ΔHch (kJ/kg)
Eₘ (kJ/cm³)

394
3468
691
1.65
3273
190
750
3382
286
2.78
2214
502

The excitation of O₂ molecules to the singlet electronic states makes it possible to increase the fraction of chemical energy that may be converted to thermal energy during combustion as compared to initiation of combustion by heating the mixture. The gain in terms of ΔHch may be as large 50%.
The effect of non-equilibrium excitation of molecular vibrations behind shock front

Schematic of the flow and computational domain

\[ \text{H}_2/\text{O}_2, T_0 = 600 \text{ K} \]
\[ P_0 = 5 \times 10^3 \text{ Pa} \]
\[ M_0 = 6 \]

\[ \text{LD} = 7.8 \text{ m} \]
\[ \text{LD} = 11.4 \text{ m} \]

Equilibrium kinetic model
\[ I_d = 7.8 \text{ m} \]
\[ T_1 = T_0 = 600 \text{ K} \]

Nonequilibrium kinetic model
\[ I_d = 11.4 \text{ m} \]
\[ T_1 = T_0 = 600 \text{ K} \]

Pressure fields in the flow of \( \text{H}_2/\text{O}_2 = 2/1 \) mixture \((P_0 = 5 \times 10^3 \text{ Pa}, T_0 = 600 \text{ K}, M_0 = 6)\)

The effect of non-equilibrium excitation of molecular vibrations behind shock front

Plasma-assisted initiation of detonation over the wedge

\[ \text{H}_2 + \text{O}_2 \]
\[ T_0 = 400-600 \text{ K} \]
\[ P_0 = 5 \times 10^3 \text{ Pa} \]
\[ M_0 = 6 \]

\[ \text{O}_2(\Delta g), \text{O}_2(\Sigma_g^+), \text{O}, \text{O}_3 \]

The principal scheme of the flow for simulation of plasma-chemical initiation of detonation in supersonic flow over the wedge

Without activation:
\[ E_s = 0, L_d = 2.6 \text{ m} \]

With activation:
\[ E_s = 0.03 \text{ J/cm}^3, L_d = 1 \text{ m} \]

Flow parameters: \( P_{\text{out}} = P_{\text{in}} = 5 \times 10^3 \text{ Pa}, M_{\text{out}} = M_{\text{in}} = 6, T_{\text{out}} = 500 \text{ K}, T_{\text{in}} = 354 \text{ K} \)

Predicted pressure fields for a \( \text{H}_2/\text{O}_2 \) supersonic flow over the wedge for following cases:
(a) the inner \( \text{O}_2 \) flow does not contain excited oxygen molecules \((T_{\text{in}} = 354 \text{ K})\); (b) the inner flow is activated by electrical discharge \((E_s = 3 \times 10^{-3} \text{ J/cm}^3)\).

At \( E_s = 0.03 \text{ J/cm}^3 \) and \( T_{\text{out}} = 500 \text{ K} \) the activation of molecular oxygen in the region with \( d = 5 \text{ cm} \) leads to shortening the induction and detonation zone lengths
Plasma-assisted detonation initiation over the wedge

Nonpremixed flow with and without activation of oxygen in electrical discharge

The temperature in the \( \text{O}_2 \) inner flow is 354 K, \( P_{\text{in}}=5\cdot10^3 \text{ Pa}, M_{\text{in}}=6 \). The temperature in the outer flow is 400 K, \( P_{\text{out}}=5\cdot10^3 \text{ Pa}, M_{\text{out}}=6 \).

Predicted temperature field for the flow of the \( \text{H}_2/\text{O}_2 \) mixture under activation of molecular oxygen

Detonation wave initiation by laser-induced excitation of oxygen molecules


Initiation of a detonation wave above a wedge: species concentrations in irradiation zone

Concentration of excited \( \text{O}_2 \) molecules in the irradiation zone depends on the radiation energy absorbed by single \( \text{O}_2 \) molecule

\[
E_t = 
\frac{l}{l_0} \frac{k_l}{k_0} \frac{dt}{dt_0}
\]

Variation of the species mass fraction and gas temperature with distance in irradiation zone.

Flow parameters: \( \text{H}_2/\text{O}_2=2/1 \) mixture, \( M_0=6, P_0=10^4 \text{ Pa}, T_0=600 \text{ K} \).

Laser radiation: \( \lambda_l=762 \text{ nm} \).

\( E_s = 0.01 \text{ eV/(molecule } \text{O}_2 \) (black lines)

\( E_s = 0.05 \text{ eV/(molecule } \text{O}_2 \) (red lines).

Initiation of a detonation wave above a wedge: static pressure fields

Flow parameters: \( \text{H}_2/\text{O}_2=2/1 \) mixture, \( M_0=6, P_0=10^4 \text{ Pa}, T_0=600 \text{ K} \).

Laser radiation: \( \lambda_l=762 \text{ nm}, \gamma = 2 \text{ cm} \)
Flow scheme: diffusion mode of combustion

As compared to the homogeneous flow, the mixing influences the ignition delay length and in the case of pre-excitation of reactive molecules can decrease the concentration of excited molecules due to their quenching at the longer length.


\[\text{component} \quad E_s, \text{J/cm}^3\]

<table>
<thead>
<tr>
<th>Component</th>
<th>0</th>
<th>1.3 \times 10^{-2}</th>
<th>2 \times 10^{-2}</th>
<th>2.6 \times 10^{-2}</th>
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</thead>
<tbody>
<tr>
<td>O(\text{X}, ^3\Sigma_g^-)</td>
<td>0.9817</td>
<td>0.9732</td>
<td>0.9636</td>
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<tr>
<td>O(\text{D})</td>
<td>5.64 \times 10^{-10}</td>
<td>7.45 \times 10^{-10}</td>
<td>9.82 \times 10^{-10}</td>
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</tr>
<tr>
<td>\text{O}_2</td>
<td>9.1 \times 10^{-10}</td>
<td>1.41 \times 10^{-9}</td>
<td>1.92 \times 10^{-9}</td>
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<tr>
<td>\text{O}_3</td>
<td>2.44 \times 10^{-9}</td>
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</tr>
<tr>
<td>\text{O}(\text{a}^1\Delta_g)</td>
<td>1.43 \times 10^{-4}</td>
<td>2.14 \times 10^{-4}</td>
<td>2.85 \times 10^{-4}</td>
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<tr>
<td>\text{O}_2(\text{b}^1\Sigma_g^+)</td>
<td>3.31 \times 10^{-7}</td>
<td>4.95 \times 10^{-7}</td>
<td>6.59 \times 10^{-7}</td>
<td></td>
</tr>
</tbody>
</table>

Temperature, K: 300, 325, 339, 352
Pressure, bar: 0.1, 0.111, 0.117, 0.123

- An increase in the value of the input specific energy results in a noticeable growth in the concentration of excited oxygen molecules.
- The concentrations of O atoms and O3 molecules in the oxygen plasma at such discharge parameters are considerably smaller than those for \text{O}_2(\text{a}^1\Delta_g) and \text{O}_2(\text{b}^1\Sigma_g^+) molecules.

Discharge parameters

Plasma-assisted combustion in a supersonic flow

\(E_s = 1.3 \times 10^{-2} \text{ J/cm}^3\)

\(E_s = 2 \times 10^{-2} \text{ J/cm}^3\)

\(E_s = 2.6 \times 10^{-2} \text{ J/cm}^3\)

Predicted water vapor mass fraction fields for \(T_0=750 \text{ K} \) at \(d=1 \text{ cm}\).
Ignition delay length (in cm) versus the transversal dimension of excitation region of for air temperature of 750 K and different values of $E_s$.

<table>
<thead>
<tr>
<th>Type of influence</th>
<th>$d$, cm</th>
<th>$E_s$, J/cm$^2$</th>
<th>0</th>
<th>0.013</th>
<th>0.02</th>
<th>0.026</th>
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<tr>
<td>discharge</td>
<td>0</td>
<td>9855.6</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>9594.9</td>
<td>1374.0</td>
<td>703.3</td>
<td>332.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9195.4</td>
<td>256.3</td>
<td>117.2</td>
<td>81.6</td>
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<tr>
<td>heating</td>
<td>0.5</td>
<td>9594.9</td>
<td>9490.0</td>
<td>8399.2</td>
<td>9331.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9195.4</td>
<td>9081.1</td>
<td>9075.1</td>
<td>9029.5</td>
<td></td>
</tr>
<tr>
<td>discharge without O atoms</td>
<td>0.5</td>
<td>9594.9</td>
<td>2145.3</td>
<td>1221.8</td>
<td>734.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>9195.4</td>
<td>475.5</td>
<td>225.3</td>
<td>141.2</td>
<td></td>
</tr>
</tbody>
</table>

Plasma-assisted combustion in a supersonic flow

One of the most important fundamental characteristics in combustion science is the velocity of laminar flame propagation.

- An increase of burning rate is an extremely important problem in creating the prospective combustors.
- The possibility of the flame speed increase by means of electrical discharge was first demonstrated for lean low pressure $H_2-O_2$ mixture by Basevich and Kogarko (Kinetika i Kataliz, 1966). An attempt to explain this phenomenon was undertaken by Basevich and Belyaev (Chem. Phys. Report. 1989).
- The comprehensive analysis of the effect of the presence of the singlet oxygen molecules in $H_2-O_2$ mixture has been done recently by our group (Starik et al. J. Phys. D: Appl. Phys. 2008; Combustion, Explosion and Shock Waves, 2008).

Photo of experimental set up with the discharge chamber and the system to supply $O_2/Ar$ mixture.

Photo of the section for measurement the spontaneous emissions and for occurrence of special diagnostics.

Increase of fame speed
Velocity of flame propagation

**H₂/O₂ mixture**

The predicted laminar flame velocities for hydrogen-oxygen mixtures with 10.5% and 8.5% H₂ at \(P_0=0.068\) bar, \(T_0=329\) K.

<table>
<thead>
<tr>
<th>H₂ volume fraction</th>
<th>(U_n), cm/s</th>
<th>(U_n^{cal}), cm/s</th>
<th>(\Delta U_n/\Delta n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without discharge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_0=329) K</td>
<td>10.5%</td>
<td>17.07</td>
<td>2.14</td>
</tr>
<tr>
<td>8.5%</td>
<td>6.07</td>
<td>16.91</td>
<td>2.78</td>
</tr>
</tbody>
</table>

**Un** without discharge

**Un** with discharge

\(T_0=329\) K

**Un**/\(\Delta n\)

Burning rate increases by a factor of ~2.1 at 10.5% H₂ concentration by a factor of ~2.8 at 8.5% H₂ concentration.

Such a tendency (the flame velocity grows stronger at smaller H₂ concentration in the mixture) was observed in experiments.

Some discrepancy between experimental data and calculations in the values of flame speed may be explained by the fact that the experimental parameters of glow discharge is not known exactly and composition of discharge plasma may be calculated only approximately.

**Velocity of flame propagation**

- In modern combustion technologies the hydrocarbon fuels are widely used. Unfortunately, until now, there were no any researches on the analysis of kinetic mechanisms of the flame speed increase due to the abundance of singlet molecules both in H₂-air and in hydrocarbon-air mixtures.

- It is very important to highlight the principle mechanisms of the influence of activation of oxygen molecules in electrical discharge on the speed of laminar flame propagation in hydrogen-air and methane-air mixtures.

**Comparison of flame propagation in H₂/air and CH₄/air mixture**

<table>
<thead>
<tr>
<th>(\phi)</th>
<th>CH₄/air</th>
<th>H₂/air</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% O₂(a₁Δg)</td>
<td>10% O₂(a₁Δg)</td>
<td>0% O₂(a₁Δg)</td>
</tr>
<tr>
<td>(T_e), K</td>
<td>1496</td>
<td>1542</td>
</tr>
<tr>
<td>(U_n), cm/s</td>
<td>10.1</td>
<td>17.0</td>
</tr>
<tr>
<td>(\Delta U_n/\Delta n)</td>
<td>0.68</td>
<td>0.68</td>
</tr>
<tr>
<td>(\phi=1)</td>
<td>(\phi=1)</td>
<td>(\phi=1)</td>
</tr>
<tr>
<td>(T_e), K</td>
<td>2276</td>
<td>2305</td>
</tr>
<tr>
<td>(U_n), cm/s</td>
<td>72.3</td>
<td>85.5</td>
</tr>
<tr>
<td>(\Delta U_n/\Delta n)</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>(\phi=1.9)</td>
<td>(\phi=1.9)</td>
<td>(\phi=1.9)</td>
</tr>
<tr>
<td>(T_e), K</td>
<td>1772</td>
<td>1827</td>
</tr>
<tr>
<td>(U_n), cm/s</td>
<td>11.1</td>
<td>14.2</td>
</tr>
<tr>
<td>(\Delta U_n/\Delta n)</td>
<td>0.28</td>
<td>0.14</td>
</tr>
</tbody>
</table>

An increase in flame speed may be as large as 70% for fuel lean mixture.
Kinetic processes in flame front region

**CH₄/air mixture**

- The diffusion of CH₃, CH₂O radicals from the high temperature flame region to low temperature zone.
- The presence of O₂(a¹Σg⁺) molecules in the low temperature zone of the flame increases the rates of reactions:
  \[
  \text{CH}_3 + \text{O}_2(a¹Σg⁺) \rightarrow \text{CH}_3\text{O} + \text{O} \]
- Concentration of O atoms is much higher in low temperature region than that without O₂(a¹Σg⁺) molecules in the low temperature zone.
- Due to larger O atom concentration in the low temperature zone the rate of reaction CH₄+O=CH₃+OH increases.

Velocity of flame propagation

**CH₄/air mixture**

- Predicted dependence of \( U_n \) on \( \phi \) for CH₄/air mixture at \( [\text{O}_2(a¹Σg⁺)]/[\text{O}_2+\text{O}_2(a¹Σg⁺)] = 0; 0.05 \) and \( 0.1 \) for \( T_0=300 \) K (a) and 450 K (b) and \( P_0=1 \) atm.
- At \( T_0=450 \) K the flame speed increase due to the presence of 10% singlet oxygen molecules in \( \text{O}_2 \) for fuel lean mixture (\( \phi=0.45 \)) may be ~70% and for fuel rich mixture (\( \phi=1.9 \)) ~30%.
- For temperature (\( T_0=300 \) K) the flame speed growth is slightly smaller.

Clean combustion

**CONTROL OF POLLUTANT FORMATION DURING COMBUSTION BY MEANS OF EXCITATION OF INTERNAL DEGREES OF FREEDOM OF MOLECULES**

- We can change the formation pathways of pollutant due to selective excitation of vibration or electronic states of molecules.

- **1.** \( \text{H}_2\text{O}(001) + \text{NO} = \text{HNO} + \text{OH} \)
  \( \text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{H} + \text{OH} \)
  \( \text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O} \)

- **2.** O₂(X³Σg⁻) + hν(λₑ=762 nm) = O₂(b¹Σg⁺)
  O₂(b¹Σg⁺) + SO₂ = SO₃ + O (3P)
  SO₃ + H₂O = H₂SO₄

- The use of excited molecules to enhance the clusters formation and to stimulate the nucleation at relatively high temperature in the exhaust:
  \( \text{SO}_2 + \text{O}_2(001) = \text{SO}_3 + \text{O} \)
  \( \text{SO}_2 + \text{H}_2\text{O}(001) = \text{H}_2\text{SO}_4 \)
  \( \text{nH}_2\text{O}(001) + \text{H}_2\text{SO}_4 = \text{H}_2\text{SO}_4(\text{H}_2\text{O})_n \)

Aviation combustor

- Aero-engine test rig combustor configuration and CFD predicted CO mass concentration field inside the combustor. A one million cell sector geometry is used. The k-ε turbulence closure model is used.
Summary

- Excitation of \( \text{O}_2 \) molecules makes it possible to initiate the detonation wave in a supersonic flow over the wedge at 1 m distance from the wedge apex for a small specific energy deposited to the gas \(-3 \cdot 10^{-2} \text{ J/cm}^3\).

- The intensification of ignition and full-scale combustion is caused by the acceleration of the formation of highly reactive atoms and radicals mainly due to abundance of electronically excited oxygen molecules \( \text{O}_2(a^1\Delta_g) \) and \( \text{O}_2(b^1\Sigma_g^+) \) in the mixture and has a non-thermal character.

- For initiation of oblique detonation wave over a wedge, it is sufficient to activate molecular oxygen in a narrow near-axis region, i.e. in a thin layer adjacent to the wedge apex.

- The excitation of \( \text{O}_2 \) molecules in electrical discharge may be an efficient approach to initiate the diffusion combustion in a \( \text{H}_2(\text{CH}_4) \)-air mixture supersonic flow for small input energy \( (E_s=0.03\text{ J/cm}^3) \) at extremely narrow \( \text{O}_2 \) excitation region \( (d=0.5 \text{ cm}) \).

- The abundance of singlet oxygen molecules in the \( \text{H}_2 \)-air and \( \text{CH}_4 \)-air mixtures in amount of 5-10% of the total concentration of molecular oxygen, can considerably affect the speed of laminar flame propagation.

We certainly underhand that our researches are only a starting point in the solving the problem of combustion enhancement and development of novel combustion concepts, but we believe that we have found a true way to do it.

Plasma-chemical initiation of detonation in a supersonic flow of \( \text{H}_2/\text{O}_2 \) mixtures

The \( \text{O}_2 \) activation by electrical discharge results in the formation of electronically excited oxygen molecules and \( \text{O} \) atoms that intensifies the chain mechanism of combustion.

This work was supported by International Scientific Technical Center (ISTC), Russian Foundation for Basic Research (RFBR), the Research Program of Russian Academy of Science and INTAS.

Also I am grateful to the co-workers of my Research Center “Physics of Non-equilibrium Processes and Novel Combustion Concepts”

Many thanks for your attention
Plasma-chemical initiation of detonation in a supersonic flow of H₂/O₂ mixtures

Flow parameters:
- β = 20°
- M₀ = 6
- P₀ = 10⁴ Pa

Variation of the vibrational temperatures of the modes of molecules, Tᵦ, and translational temperature, T, downstream the shock front at deposited energy Eₘ = 6 ⋅ 10⁻² J/cm³.

The effect of non-equilibrium excitation of molecular vibrations behind shock front

Pressure fields in the flow of H₂/O₂ = 2/1 mixture (P₀ = 5 ⋅ 10³ Pa, T₀ = 600 K, M₀ = 6).

In thermally non-equilibrium kinetic model the induction and transition zone lengths are essentially larger than those in the thermally equilibrium model.

Initiation of a detonation wave above a wedge:

Initiation zone length

Under heating the mixture induction zone length cannot be stabilized within 2.5 m from the tip at any Ye.

At given value of Eₘ there exists the quantity of critical transversal dimension Ye of the irradiation region, beginning of which the lengths of induction and detonation zones changes only slightly.

Induction and detonation zone lengths vs. transversal dimension of the excitation region.

Flow parameters: H₂/O₂ = 2/1 mixture, M₀ = 6, P₀ = 10⁴ Pa, T₀ = 600 K.
Laser radiation: λ = 762 nm, Eₘ = 0.05 eV/molecule O₂.
Dashed lines - mere laser heating;
Continuous lines - laser excitation of O₂ molecules into b¹Σ⁺ state.
An increase in the concentration of singlet oxygen molecules in the mixture and in the temperature leads to the growth of the flame speed.


Laser-induced excitation of O₃ molecular vibrations

Excitation: O₃+hv(λ≈9.7 μm)=O₃(001)

\[ \lambda = \text{9.69483} \mu \text{m}, \lambda = \text{9.69486} \mu \text{m} \]

This transition is allowed in dipole approximation, Amn=10.64 s⁻¹,
P₀=10⁴ Pa, I₀=50 kW/cm²

\[ \tauₐ=10^{-6} \text{ s}, \tauₕ=3 \cdot 10^{-5} \text{ s} \]

The scheme of low vibrational levels of O₃ molecule. Solid and dashed arrows depict the induced transition and collisional pathways of vibrational energy relaxation (V-V' and V-T processes).

Laser-induced excitation of O₃ molecular vibrations intensifies the thermal explosion mechanism of O₃ photolysis and chain-branching mechanism of H₂/air mixture combustion
The principal scheme of the chain mechanism development CH$_4$+O$_2$ mixture upon the activation of O$_2$ molecules by electrical discharge ($E/N=1.1 \times 10^{-16}$ V cm$^{-2}$) (a) and at the heating the gas (b) at low temperature (T<1200K).

The effect of non-equilibrium excitation of molecular vibrations behind shock front

- Behind shock front the vibrational temperatures are smaller than the translational temperature $T_v < T$
- Increase of flow velocity and density in a supersonic flow
- Reduction of a collision number
- Increase of reaction zone length
- Decrease of chemical reaction rates
- Decrease of gas temperature and density in a supersonic flow
- Increase of flow velocity in a supersonic flow
- Increase of reaction zone length
- Heat transfer from translational to vibrational degrees of freedom behind shock front

The reason of increase of the length at which ignition front forms for thermally non-equilibrium chemical kinetic model as compared to equilibrium model:

1. Increase of flow velocity
2. Reduction of a collision number
3. Decrease of chemical reaction rates
4. Increase of reaction zone length