Analysis of the effect of boron-containing compounds and combustion catalysts on paraffin combustion rate in an oxidizer flow

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Abstract. The paper addresses to the experimental investigations of the combustion of test samples of solid fuels based on paraffin and boron-containing compounds and combustion catalysts in the gaseous oxygen subsonic flow. Tests were carried out at the atmospheric pressure and oxygen flow velocity from 27 to 31 m/s. The mass combustion rate of the samples increased by 28% when ammonia borane was added to paraffin, and by 16% when sodium borohydride with a bit of solid oxidizer was added. The biggest amplification of the mass combustion rate using the catalyst reached 5%.

1. Introduction
Today, developers of rocket engines, of both solid (SPRE) and liquid propellant (LPRE), have reached a high level of their technological achievements. A supersonic combustion ramjet engine (SCRAMJET) is a promising area in the rocket engine industry [1–3]. Works with SCRAMJET applied to the creation of high-speed tactical weapons are performed in many countries (USA, China, EU, etc). In spite of massive efforts, the success is modest yet. High flight speeds (M > 10) of the aircrafts with the SCRAMJET has not been demonstrated yet. A large number of works are devoted to solid fuel ramjet engines [4–9]. A promising direction of increasing the energy characteristics of solid fuels is the addition of boron [10, 11].

The hybrid rocket engine (HRE) working on solid fuel and liquid or gaseous oxidizer [12–19] are a breakthrough technology in the developing rocket-engine technology to provide the long-term high-speed flight. It is predicted that hybrid engine systems are going to find wide application, including the control in orbital flight on upper stages, tactical and strategic rocket systems. Hybrid rocket engines combine the advantages of SPRE and LPRE and, at the same time, do not have many disadvantages. The specific energy-mass characteristics of the hybrid rocket engines put them in between the LPRE on cryogenic fuels and SPRE. At the same time, the hybrid rocket engines demonstrate higher values of the specific pulse than SPRE owning to the fuels with the bigger energy store. The most important advantage of the hybrid engine is the wide range of thrust module control and the possibility of multiple engine ignition and
cutoff during one flight. Utilization of thermoplastic materials as the major component of the fuel for the hybrid engines enables to use modern additive technologies for the development and production of charges for these engines, which essentially decreases the cost of the development and production of these engine charges. All these advantages make the hybrid engines very promising in for the rocket equipment in the XXI century.

Creation of the energy-intensive oxygen-free solid propellants with high combustion rate and provision of their effective combustion efficiency in the gaseous oxidizer flow is a key challenge in the HRE development. In this work we investigate the effect of energy-intensive additives such as boron-containing hydride compounds and transition metal coordination compounds containing organic ligands and nitrate (or perchlorate) anions as combustion catalysts on the combustion rate of paraffin in the gaseous oxygen flow.

2. Experimental setup for investigation of solid fuel combustion in the gaseous oxidizer flow

The experimental setup of ITAM SB RAS was used to perform experimental investigations on the definition of the rate of combustion of experimental samples of solid fuel in the gaseous oxidizer flow; the setup configuration contains the combustion chamber as an open working part. This configuration provides the optical access to the sample surface and permits observing the liquid film of melted paraffin. The setup schematic is shown in figure 1. The setup sketch is shown in figure 2. The outlook of the setup is shown in figure 3. The prechamber and input nozzle are purposed to create a uniform oxidizer flow with the specified pressure and velocity at the combustion chamber (CC) entrance. In the combustion chamber, on the pylon, there is the sample 5 of the studied solid fuel made as a cylinder of 21 mm in diameter and 40 mm in length. Ahead of the sample there is the elliptical cowl to form the uniform flow around the sample. To initiate the combustion process, the flame heater is used; some hydrogen (1 g/s) is supplied into the prechamber for the short-time flow temperature jump at the nozzle exit up to 2000 K. It has been found experimentally that for the reliable ignition of almost any polymer material, 200 ms work of the flame heater is enough. Then the flame heater is cutoff, and the gaseous oxygen of room temperature is supplied to the combustion chamber entrance, and then the self-sustaining combustion of solid fuel takes place in the oxidizer flow. Combustion and carry-away of the solid-fuel sample mass occur only on the external surface of the sample. The typical time of combustion is 1 s, which is sufficient to determine the variation of the sample mass, the sample size variation is insignificant and makes almost no effect on the flow parameters on the sample surface.

3. Gas-dynamic calculation of the flow in the model combustion chamber

To evaluate the consumption and velocity characteristics of the experimental setup, the flow was numerically modeled with no regard to the combustion. The calculation was performed by integrating the system of Navier–Stokes equations describing the spatial flow of a viscous compressible gas. Adiabatic wall condition was used. The model k-ε was chosen as the model of turbulence where k is the turbulence kinetic energy and ε is turbulent dissipation. Mesh consisted of 28 489 fluid cells and 6013 partial cells. On the left boundary of the computational domain, the condition of the oxygen mass flow rate was preset, on the right boundary, the static pressure \( P = 99 900 \) Pa was preset. The calculation was carried out for the oxygen flow rate of 20 g/s with temperature \( T = 300 \) K. Velocity distributions have been obtained in the combustion chamber. The schematic of the calculation configuration and calculation results as the velocity distribution are presented in figure 4. The calculation results show that this configuration provides the formation of the uniform oxidizer flow around the sample, which is important for the analysis of the combustion on the surface of the solid fuel material.
4. Method of experimental result processing

4.1. Determination of working gas flow rates at the flame heater input

The flow rates during the experiment are found by the varying pressure drop in the working gas bottles. To determine the flow rate, there is the equation for the calculation of the pressure dependence on time at the adiabatic gas outflow from a container of the known volume $V$ through the critical hole with the flow area $F^*$ for the known values of the initial pressure $P_0$ and initial temperature $T_0$ in the container (the initial gas temperature equals to the room temperature):

$$P(t) = P_0(1 + Bt)^{-\frac{2\gamma}{\gamma - 1}},$$

where

$$B = \frac{\gamma - 1}{2V} Rm F^* \sqrt{T_0},$$

Figure 1. Schematic of the experimental setup: 1—flame heater; 2—prechamber; 3—subsonic nozzle; 4—elliptical cowl; 5—solid fuel sample; 6—pylon; 7—suction system.

Figure 2. Sketch of the experimental setup.
\[ m = \left[ \gamma \left( \frac{2}{\gamma + 1} \right)^\frac{\gamma + 1}{\gamma - 1} \right]^{1/2} \sqrt{\frac{1}{R}}. \]  

(3)

$R$ is a specific gas constant; $\gamma$ is the adiabatic index. It is accepted that the process of working gases outflow is adiabatic, since the tie of the working mode does not exceed 2 s. During the calculation, the area $F^*$ of the output hole varies in such a way that the pressure drop graph in the bottle measured with a pressure gage coincides with the calculation graph. The example of the measured and calculated pressure dependence in the bottle with oxygen is shown in figure 5. When the area of the critical section is found, the current gas flow rate is detected by the next formula:

\[ G(t) = G_0 (1 + Bt)^{\frac{\gamma + 1}{\gamma - 1}}. \]  

(4)

This method permits determining the working gases flow rates with the error no more than ±0.5%.
4.2. Average solid fuel flow rate during the experiment

The average mass flow rate of the sample within one regime is defined as

$$Q = \frac{\Delta m}{t_{\text{comb}}},$$

where $\Delta m$ is the variation of the sample mass within the regime, $t_{\text{comb}}$ is the sample combustion time. The variation of the sample mass $\Delta m = m_1 - m_0$ is determined by means of the control weighting of the sample on the laboratory balance with an accuracy of 0.02 g, $m_0$ and $m_1$ is the sample mass before and after the experiment respectively.

The sample combustion time is preset by the oxidizer supply time in the combustion chamber.

5. Results of solid fuel combustion tests in the oxygen flow

The tests were carried out at the atmospheric pressure and oxygen flow velocity at the exit of nozzle from 27 to 31 m/s. The mass combustion rate of solid fuel samples from different materials was found experimentally. The test materials were: polymethylmethacrylate (PMMA), paraffin (Pf), ceresin. Experimental samples are based on paraffin with different energy admixtures such as combustion catalysts and boron-containing hydride compounds. The following coordination compounds based on glycine ($C_2H_5NO_2$, Gly) and aminoguanidine nitrate ($C_7N_5O_3$, AGHNO$_3$) were used as combustion catalysts: $Fe_3O(NH_3CH_2COO)_6(H_2O)_3(ClO_4)_{17}3H_2O$ (designated as $Fe\text{Gly}(ClO_4)$), $Ni(NH_2NHC(= NH)NH_2)_2(NO_3)_2$ (designated as $Ni\text{AG(NO}_3$)), compound prepared by slow evaporation of water solution of glycine, nitrates of copper and iron at the addition of aqueous ammonia (designated as $CuFe\text{Gly(NO}_3)(NH_3)$) [20], and compound prepared by slow evaporation of water solution of glycine, nitrates of lanthanum, iron and copper (designated as $LaFeCu\text{Gly(NO}_3$)) [21]. The mass fraction of the catalysts in every sample was 5%. Sodium borohydride $NaBH_4$ [22] and ammonia borane $NH_3BH_3$ [23] were used as the boron-containing energy admixtures. These compounds are the source of gaseous hydrogen and boron. Additively the samples of paraffin-based solid fuel with small amount of solid oxidizer were tested.

The collective results of the tests are listed in table 1. It is found that the mass combustion rate of pure ceresine is 30% lower than the mass combustion rate of pure paraffin. And the PMMA mass combustion rate is 4.5 times lower than paraffin. Addition of catalysts of different compositions to paraffin does not increase the combustion rate, except for $Ni\text{AG(NO}_3$); with
Table 1. Experimental test results.

| Sample                          | Run | $t_{comb}$ (s) | $m_0$ (g) | $m_1$ (g) | $\Delta m$ (g) | $Q$ (g/s) |
|--------------------------------|-----|----------------|-----------|-----------|---------------|-----------|
| PMMA                           | 10  | 1.15           | 12.98     | 12.52     | 0.46          | 0.40      |
| Pf                             | 19  | 1.2            | 23.58     | 21.38     | 2.20          | 1.83      |
| Pf                             | 31  | 1.2            | 23.72     | 21.6      | 2.12          | 1.77      |
| Ceresine                       | 14  | 1.2            | 22.64     | 21.1      | 1.54          | 1.28      |
| Pf + CuFeGly(NO$_3$)(NH$_3$)    | 16  | 1.2            | 22.76     | 20.64     | 2.12          | 1.77      |
| Pf + FeGly(ClO$_4$)            | 18  | 1.2            | 22.6      | 20.62     | 1.98          | 1.65      |
| Pf + NiAG(NO$_3$)              | 20  | 1.2            | 24.34     | 22.06     | 2.28          | 1.90      |
| Pf + LaFeCuGly(NO$_3$)         | 21  | 1.2            | 22.3      | 20.1      | 2.20          | 1.83      |
| Pf + NaBH$_4$                  | 22  | 1.2            | 23.6      | 21.4      | 2.20          | 1.83      |
| Pf + NaBH$_4$ + LaFeCuGly(NO$_3$) | 23 | 1.2          | 24.12     | 21.94     | 2.18          | 1.82      |
| Pf + NaBH$_4$ + oxidizer       | 29  | 1.2            | 24.86     | 22.34     | 2.52          | 2.10      |
| Pf + LaFeCuGly(NO$_3$) + oxidizer | 28 | 1.2         | 24.02     | 21.7      | 2.32          | 1.93      |
| Pf + oxidizer                  | 30  | 1.2            | 24.62     | 22.26     | 2.36          | 1.97      |
| Pf + NH$_3$BH$_3$              | 24  | 1.2            | 23.06     | 20.24     | 2.82          | 2.35      |
| Pf + NH$_3$BH$_3$              | 33  | 1.2            | 23.28     | 20.54     | 2.74          | 2.28      |
| Pf + NH$_3$BH$_3$ + oxidizer   | 34  | 1.2            | 23.96     | 21.42     | 2.54          | 2.12      |

This material, the mass combustion rate rose by 5%. Addition of FeGly(ClO$_4$) led to the mass combustion rate decrease by 10%. Sodium borohydride without catalyst and with it did not influence the sample mass combustion rate either. Addition of 10% solid oxidizer increases the sample mass combustion rate, and the biggest increase is reached when the solid oxidizer is added to the paraffin and sodium borohydride sample (16%). When adding the solid oxidizer to pure paraffin, the mass combustion rate increased approximately by 10%. The biggest mass combustion rate was reached for the samples consisting of paraffin and ammonia borane, the average amplification in two runs was 28%. Adding the solid oxidizer to this composition decreased the rate, and the amplification in respect to pure paraffin was only 17%.

Thus, in accordance with the results, the most effective way to increase the paraffin-based solid fuel combustion rate is addition of boron-containing compounds combined with some solid oxidizer (in the case of NaBH$_4$). Utilization of energetic coordination compounds as a paraffin combustion catalysts in the oxidizer flow turned out to be low-effective. It may be related with the fact that a liquid film occurs on the paraffin surface during its combustion, the film holds the catalyst particles and does not allow them to get in the combustion zone. Investigations with the solid fuels based on other polymer materials such as polyethylene, polyurethane, resin, etc are necessary.

During the experiments, high-speed video recording of the sample combustion process was carried out using a Sony RX10 camera. The camera was located perpendicular to the axis of the experimental setup in a horizontal plane at a distance of 1.5 m. The frequency was 500 fps, exposure 1/10 000, ISO 200, resolution 1920 $\times$ 1080. The video record of the paraffin-based sample combustion shows the essential influence of the gravity force on the flow of the liquid paraffin film. The example of three random shots is presented in figure 6. The significant part (up to 25%) of the melted paraffin flows down from the sample surface, having no time to evaporate or to be captured as drops by the flow. It may result from the fact that the tests are carried out at the atmospheric pressure, since the pressure in the combustion chamber of the rocket engine highly exceeds the atmospheric one, and hence the Reynolds number on the sample
surface in these tests was insufficient for the melted paraffin liquid film to lose its steadiness, and liquid paraffin to be atomized into the oxidizer flow.

Figure 6. Video snapshot.
6. Conclusion
Experimental samples of paraffin-based solid fuels with the addition of B-containing compounds and combustion catalysts in a stream of gaseous oxygen were studied experimentally. The tests were carried out at the atmospheric pressure and oxygen flow velocity from 27 to 31 m/s. The mass combustion rate of the samples increased by 28% when amino-borane was added to paraffin and by 16% when sodium borohydride with a bit of solid oxidizer was added. Utilization of energetic transition metal coordination compounds as paraffin combustion catalysts in the oxidizer flow turned out to be low-effective, the biggest rate amplification with the catalyst was 5%. Addition of FeGly(ClO$_4$) led to the mass combustion rate decrease by 10%. Addition of 10% solid oxidizer increases the sample combustion rate, the biggest increase is reached 16% in case of paraffin and sodium borohydride and 10% in case of pure paraffin. The essential influence of the gravity force on the flow of the liquid paraffin film was revealed, up to 25% of the melted paraffin drop from the sample surface.

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References
[1] Goldfeld M A and Starov A V 2017 Combust., Explos. Shock Waves 53 24–31
[2] Starov A V and Goldfeld M A 2017 AIP Conf. Proc. 1893 030157
[3] Goldfeld M A, Nalivaichenko D G, Starov A V and Timofeev K Yu 2016 AIP Conf. Proc. 1770 030112
[4] Frolov S M, Zvegintsev V I, Ivanov V S, Aksenov V S, Shamshin I O, Vnuchkov D A, Nalivaichenko D G, Berlin A A, Fomin V M, Shipluky A N and Yakovlev N N 2018 Int. J. Hydrogen Energy 43 7515–24
[5] Vnuchkov D A, Zvegintsev V I, Nalivaichenko D G, Smolyaga V I and Stepanov A V 2018 Thermophysics and Aeromechanics 25 605–11
[6] Frolov S M, Zvegintsev V I, Ivanov V S, Aksenov V S, Shamshin I O, Vnuchkov D A, Nalivaichenko D G, Berlin A A and Fomin V M 2018 Combust., Explos. Shock Waves 54 357–63
[7] Vnuchkov D A, Zvegintsev V I, Lukashevich S V and Nalivaichenko D G 2017 Gorenie i Vzryv 10 51–6
[8] Aul’chenko S M and Zvegintsev V I 2017 Gorenie i Vzryv 10 57–62
[9] Kartovitskii L L, Levin V M and Yanovskii L S 2018 Combust., Explos. Shock Waves 54 170–8
[10] Rashkovskii S A, Milekhin Y M and Fedorychev A V 2017 Combust., Explos. Shock Waves 53 652–64
[11] Ermolaev G V and Zaitsev A V 2018 Combust., Explos. Shock Waves 54 442–9
[12] Potapkin A V and Lee T S 2004 Combust., Explos. Shock Waves 40 386–92
[13] Arkhipov V A, Zhukov A S, Tolotorev N N, Perfil’eva K G and Bondarchuk S S 2017 Combust., Explos. Shock Waves 53 634–40
[14] Arkhipov V A, Zharova I K, Zhukov A S, Kozlov A M, Zarko V E, Aksenenko D D and Kurbatov A V 2016 Combust., Explos. Shock Waves 52 497–513
[15] Risha G, Boyer E, Wehrman R, Evans B and Kuo K A 2003 AIAA Pap. 4593
[16] Netzer D, Gany A, Karadimitris A and Scott C 1991 J. Propul. Power 7 341–7
[17] Nakagawa I and Hikone S 2011 J. Propul. Power 27 1276–9
[18] Chandler A, Jens E, Cantwell B J and Hubbard G S 2012 AIAA Pap. 3961
[19] Dunn C, Gustafson G, Edwards J, Dunbrack T and Johansen C 2018 Aerosp. Sci. Technol. 72 371–9
[20] Simagina V I, Komova O V, Odegova G V, Netskina O V, Bulavchenko O A, Pochtar’ A A and Kayl’ N L 2019 Russ. J. Appl. Chem. 92 20–30
[21] Komova O V, Simagina V I, Mukha S A, Netskina O V, Odegova G V, Bulavchenko O A, Ishchenko A V and Pochtar’ A A 2016 Adv. Powder Technol. 27 496–503
[22] Netskina O V, Ozerova A M, Komova O V, Odegova G V and Simagina V I 2015 Catal. Today 245 86–92
[23] Gorlova A M, Kayl N L, Komova O V, Netskina O V, Ozerova A M, Odegova G V, Bulavchenko O A, Ishchenko A V and Simagina V I 2018 Renewable Energy 121 722–9