Probe Method of Sampling of Combustion Products of Solid Rocket Propellant at Temperatures and Pressures Typical of Combustion Chamber of Rocket Motor

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Introduction
The combustion processes of modern solid rocket propellants (SRP), occurring in combustion chamber of rocket motor, are characterized by pressures about 4 - 8 MPa and temperatures ~ 3000 K. The peculiarity of studying of these processes is that at such temperatures the products of combustion are in partly dissociate state and present a complex multicomponent gas mixture, which can exist without essential changes only at the temperature of combustion. The burning rates of propellants in such conditions are high – 10 - 40 mm/s, so the used methods should be fast enough. At present authors doesn’t know methods, enabling to determine the composition of combustion products in considered conditions without distortion. The known CARS method [1] is complex, expensive and difficult and it does not allow measuring such important combustion products as CO₂ and H₂O. The most universal methods of flame structures investigation are the probe ones. Previously authors used the method of molecular-beam mass-spectrometric sampling of combustion products of ammonium dinitramide at pressures 0.3 and 0.6 MPa [2], providing good freezing the sample. But the using of time-of-flight mass-spectrometer (TOFMS) in that method does not allow to distinguish between CO and N₂. The method utilizing the “sonic” probe was previously used by the authors in [3] and gave good results in determination the composition of combustion products of double base at pressure 2 MPa and temperature 2670K. The purpose of the present study is the improvement of this method and it’s application to the analysis of composition of combustion products of SRP at 4 - 8 MPa and 3000K.

Results
1. Single-stage sampling technique.

Primarily, this method [3] with the probe usage, manufactured from stainless steel with inner opening angle being 40°, was applied for determination the composition of composite SRP combustion products at the pressure of 4 - 8 MPa. At the outlet of the probe the pressure of the sample was reduced to 0.1 MPa, after which the sample entered the inlet system of mass-spectrometer or was extracted into the balloon for further analysis by the chromatograph. The composition of gaseous phase of N₂, CO₂, O₂, CO, H₂ and NO was determined in percentage of the total volume of the sample, the temperature of combustion products in the place of sampling was measured with the help of W+5%Re-W+20%Re thermocouple 12-14 µm thick, taking into account the correction for radiation. The measured composition of combustion products was compared with thermodynamically equilibrium compositions at temperatures 3148K and 2870K (see Table 1).

Table 1. Composition (in mole fractions) of combustion products of propellant of stoichiometric composition: ammonium dinitramide (ADN) - polycaprolacton (pCLN) at 4 MPa

<table>
<thead>
<tr>
<th>T, K</th>
<th>H₂O</th>
<th>N₂</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
<th>NO</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation</td>
<td>3148</td>
<td>0.415</td>
<td>0.339</td>
<td>0.092</td>
<td>0.047</td>
<td>0.027</td>
<td>0.014</td>
</tr>
<tr>
<td>Calculation</td>
<td>2870</td>
<td>0.445</td>
<td>0.35</td>
<td>0.11</td>
<td>0.03</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>Experiment</td>
<td>2870±25</td>
<td>0.48*</td>
<td>0.358</td>
<td>0.109</td>
<td>0.008-0.013</td>
<td>0.011</td>
<td>0.006</td>
</tr>
</tbody>
</table>

* Calculated based on material balance equation.

Thermodynamically equilibrium temperature of combustion products appeared to be 280 degrees higher than measured ones, that indicates about the incompleteness of propellant combustion. As it is seen from Table 1, thermodynamically equilibrium concentration of CO at temperature 3148K is equal to 4.7%, that is 3 - 5 times higher than the value of CO concentration obtained in the experiment. This contradiction stimulated the search of the ways of increasing the accuracy of CO concentration determination. The possible reasons of
distortion of sample composition are insufficient freezing of chemical reactions in the probe and possible proceeding of chemical reactions at shocks inside the stage as they cross the gas sample. To eliminate these defects the new construction of probe device was designed. The cone with maximum inner opening angle was applied as the probe. The skimmer was located after the probe enabling to extract the sample from the region before the Mach disk. Unlike molecular-beam system of sampling [2], in which molecular beam is introduced directly into the ion source of mass-spectrometer, in the described construction the flow behind the skimmer mixes with surrounding gas and then enters the inlet system of mass-spectrometer. It allows performing the additional operations with the sample, for example, separation of CO and N₂ in the sample composition. The designed device is simpler and cheaper in comparison with molecular-beam system of sampling.

2. Two-stage probe device.

The probe device (Fig. 1) consists of two chambers. Chamber 1 is located between the probe and the skimmer, while chamber 2 – between the skimmer and the diaphragm (Fig. 2).

The diaphragm serves to inlet the gases into TOFMS. At pressure in combustion chamber equal to 4 MPa the following pressures are established in chambers 1, 2: 20 - 30 torr - in chamber 1 and 3 - 7 torr - in chamber 2. According to the estimations the Mach disc is located
at the distance of ~3.1 mm from the probe orifice. To check that the chosen position of skimmer location lies in the region before the Mach disc the measurements of the dependence of the pressure behind the skimmer $P_2$ on the pressure $P_1$ in chamber 1 have been performed. Fig. 3 shows that the pressure $P_2$ starts to “feel” external pressure only with the increase of $P_1$ up to the value about 28 torr. In our experiments the pressure $P_1$ was equal to 18 - 19 torr, providing the skimmer location in the region before the Mach disc.

3. The simulation of sample flow and chemical reactions inside the probe.

The probe influences the sample in several ways: freezes it, reduces its pressure and distorts the streamlines of the flow. As a result the sample composition can be distorted. The estimations of these distortions were performed numerically. The mentioned above gas mixture – combustion products of SRP (stoichiometric mixture of ADN/pCLN) thermodynamically equilibrium composition of which corresponds to the relation $41.5\%H_2O + 9.2\%CO_2 + 33.9\%N_2 + 4.7\%CO + 3.7\%OH + 2.7\%H_2 + 1.9\%O_2 + 1.4\%NO$ was chosen as the object of investigation. This mixture entered the probe at temperature 3148K and pressure 4 MPa.

The simulation of gas dynamic parameters of the flow in chamber 1 was performed by the numerical solution of full set of unsteady Navier-Stokes equations for axially symmetric flow of compressible gas with the help of original algorithm, the main features of which are as follows. 1) The hybrid difference grid is applied, when pressure, density and temperature are determined in the center of the cell, while the components of velocity – in the middle of corresponding borders of the cell. 2) The difference equations are resolved implicitly with the help of known method of splitting into physical processes and spatial variables. 3) The continuity equation is approximated according to the scheme, providing conservativity at reaching the steady solution (or at explicit resolving of the equations). 4) The symmetrical approximation of difference operators provides second order of accuracy over spatial variables at uniform grid. 5) The algorithm is characterized by low viscosity introduced by the scheme, that essentially widens the region of Reynolds numbers accessible for modeling.

The simulation of the gas flow was performed applicable to the chosen construction of two-stage probe device (Fig. 1) for the region along the axis from 0.6 mm upstream the probe orifice to 6.3 mm downstream it. At first the two-dimensional problem of perfect gas flow through the probe was solved, the presence of skimmer in the flow field being not considered. In Fig. 4 the flow field of density inside the stage 1 for the distances $\geq 0.3$ mm behind the probe orifice is presented. In Fig. 5 the axial distributions of temperature and
pressure are illustrated (the dashed line shows the location of the skimmer). Then for the axial streamtube the system of equations of chemical kinetics accounting for 17 chemical reactions was solved. As the result the axial distribution of concentrations of separate components was obtained. In Table 2 the composition of combustion products upstream the probe and calculated sample composition at the distance of 0.3 mm behind the probe orifice, where the composition freezing take place, are presented. As it is seen, in the process of flame sampling and passing the sample through the probe the concentration of the majority of stable gas components changes in the range of 2 - 3%, while H₂ and O₂ ~ 12%.

Fig. 4. Flow field of gas density inside the probe (dashed line shows the chosen location of the skimmer).

Fig. 5. Axial distributions of pressure and temperature in chamber 1 (dashed line shows the location of the inlet of the skimmer).

Table 2. Calculated composition of combustion products at the distance 0.6 mm upstream the probe orifice and inside the probe at the distance 0.3 mm behind the orifice.

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>N₂</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
<th>NO</th>
<th>O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream the probe orifice</td>
<td>0.414</td>
<td>0.3392</td>
<td>0.092</td>
<td>0.0463</td>
<td>0.0266</td>
<td>0.0147</td>
<td>0.0189</td>
</tr>
<tr>
<td>Inside the probe</td>
<td>0.4234</td>
<td>0.3400</td>
<td>0.0938</td>
<td>0.0453</td>
<td>0.0233</td>
<td>0.0147</td>
<td>0.0211</td>
</tr>
<tr>
<td>Deviation from the initial value (%)</td>
<td>2.27</td>
<td>0.23</td>
<td>1.7</td>
<td>-2.2</td>
<td>-12.4</td>
<td>0</td>
<td>11.6</td>
</tr>
</tbody>
</table>

For the analysis of possible distortion of sample composition in chamber 2 the simulation of the flow in the region after the skimmer utilizing the marching method of solving the parabolized Navier-Stokes equations [4] was performed. The simulation have shown that growth of temperature and pressure at mixing of high-enthalpy supersonic flow with surrounding gas (Fig. 6) does not lead to initiation of chemical reactions, which could distort the sample composition.

The measurements of CO and CO$_2$ concentrations in the combustion products of propellant ADN/pCLN were performed at the setup shown in Fig.2. Strands with diameter 6 mm and length 10 mm were located in the chamber of constant volume in the atmosphere of argon at pressure 4 MPa along the axis of the probe at the distance ~ 3 mm from the probe orifice. Concentration of CO was determined based on the data of the analysis from the following experiments. In the first one the combustion products directly entered the inlet system of TOFMS. In the second ones the flow of oxygen was added to the products and resulting mixture was passed through the reactor with catalyst CuO, heated to the temperature ~ 870K. In this case CO at the catalyst was oxidized into CO$_2$. The relation between CO and CO$_2$ concentrations in combustion products was determined from the analysis of mass-spectrometric data. The average values of CO and CO$_2$ concentrations were found to be equal to $\alpha_{\text{CO}}=3.1\pm0.6\%$, $\alpha_{\text{CO}_2}=10.8\pm0.6\%$. The CO concentration obtained by two-stage probe device (3.1%) is essentially higher, than that obtained by single-stage probe (~1%). Besides, the obtained value of CO concentration correlates well with the value of CO concentration in thermodynamically equilibrium gas composition at experimentally determined temperature 2870K (see Table 1).

The developed method can find application in diagnostics of combustion chambers of rocket motors, aircraft engines and internal combustion engines.

Acknowledgements

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References