**Use of Thermochemical Conversion in Pulse Detonation Engine**

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To create pulse detonation engine thermochemical conversion is proposed. There is shown that thermochemical conversion prepares new modified fuel and as result the possibility to use fuel-air mixtures in pulse detonation engine appears. Moreover, the thermochemical conversion is shown to provide the temperature of the wall of combustion chamber below the spontaneous combustion value. The analysis of heat capacity and cooling resource of hydrocarbon fuels and ammonia is done.

The main type of the devices in contemporary subsonic and supersonic aviation is turbo-spiral and turbo-jet engines of different modifications that works on thermodynamic circle with heat supply on $P=\text{const}$ (Briton's circle). The improvements of the parameters of such kind of engines is realized by means of gas maximum temperature increase and summary degree of pressure increase (in aircollector and compressor) in Briton's circle. Since there is no possibility now to develop such kind of circles it seems actually interesting to study the possibility to create the aviation engines of non traditional type. It is known that isochoric thermodynamic process has the thermal performance coefficient exceeding those of the circle $P=\text{const}$ on the same maximum temperatures and degrees of pressure increase, however this circle means the periodically pulsed regime in combustion chamber.

The attempts to build pulsejet engine based on circle $V=\text{const}$ were not successful. So far only the mechanical valve systems were used. Recently the possibility to arrange periodically pulsed regime that based on so-called gasdynamical valve was shown. The use of gas detonation instead of ordinary combustion is the most advanced technology to create the engines based on circle $V=\text{const}$. As theoretical and numerical investigation show [1, 2], the pulse detonation engines provide essential advantages comparing with available aviation and jet propulsion. The gas temperature behind the detonation wave is more than in combustion case, the degree of pressure increase can attain the factor of 150-200 and therefore it can provide higher expansion degree of combustion products. The velocity of detonation wave exceeds the velocity of combustion at two orders of magnitude. It allows projecting the engines with high specific power that can achieve few thousand MW/m$^2$. According to this value the contemporary oxygen-hydrogen fluid jet propulsiones are less effective than pulse detonation engine in the one order at least.

One of the most important problems, however, is the big heat release on the walls of the device. At detonation of the methane-oxygen mixture with frequency 1-3 [s$^{-1}$] the heat release $(\alpha)$ attain the value of 40% of all the heat emitted in the detonation tube with 16 mm diameter and 1.5 m length. The walls absorbs 1.3 kJ for one circle of detonation [3]. As a result, the wall temperature increases, that causes the spontaneous ignition. In this case it is impossible to control the detonation frequency. If the frequency increases up to 40-50 [s$^{-1}$] the heat outgoing to the wall $(\alpha)$ during the one circle decreases down to 28% of the total quantity, but it increases for time units. Corresponding density of the heat flow is equal to 0.6 MW/m$^2$ and it can increase up to 2-2.5 MW/m$^2$ using the pulse frequency of 200 [s$^{-1}$] (which seems to be the best one). Thus, the problem of cooling can be stated by two general conditions, specific for the pulse detonation engines:
1) limitation of the specific cooling resource \( (C_\Sigma^R) \) divided by heat-producing capacity \( (Q) \):

\[
C_\Sigma^R = \frac{C_\Sigma}{Q} \geq \alpha
\]

\( \alpha \) - coefficient is supposed to be minimized that depends on the construction of the detonation combustion chamber, \( C_\Sigma \) - the total quantity of heat that is consumed by fuel while it is heated up to temperature of spontaneous combustion, by phase transitions and chemical transformations before combustion.

2) extremely high heat load must be removed on the wall temperature \( T_w \) that should not exceed the spontaneous combustion temperature of air-fuel mixture \( T_{si} \):

\[
T_w < T_{si}
\]

\( T_{si} \) - the temperature, corresponding the induction period of mixture combustion reaction longer than the time of detonation circle. \( C_\Sigma^R \) of the fuel (for liquid hydrogen 0.12) cannot be enough even if the absolute value is very high, that can be seen from the Table. 1 where thermophysical properties of possible fuels are presented. Hence not only physical, but also chemical cooling resource should be used (heat absorption in the endothermic reactions) for cooling of detonation combustion chamber.

The problems of the heat protection and thermochemical transformation of hydrocarbon fuels are presented in the frame of the concept "AJAX". The heat protection system carries out not only usual function, providing the thermal conditions of aviation construction, but it works as preliminary producing system to prepare new modified fuel containing molecular hydrogen. Such a system can also be used for pulse detonation engine cooling. One of the cases is the hydrocarbon stream conversion, for example:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} - 6\text{MJ/kg} \quad (1)
\]

\( C_\Sigma^R \) of the reaction is 0.34 at 100% conversion. Comparing with the heavier hydrocarbons methane allows decrease the deposition of carbon on the catalytic surface. Produced synthesized gas is supposed to be the mixture of \( \text{H}_2, \text{CO}, \text{CO}_2, \text{CH}_4, \text{H}_2\text{O} \), the exact composition depends on conversion degree. The thermodynamics of the reaction is that it is possible to attain higher degrees of the conversion only at the wall temperature \( T_w \) close to the limit of construction materials capacities (1100-1300 K) and good catalytic properties of the surface [5].

Another way of thermochemical cooling of pulse detonation engine is to use the ammonia decay reaction:

\[
2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2 - 2.7 \text{MJ/kg} \quad (2)
\]

Ammonia is widely used in cooling devices as cooling agent due to its very good properties, the yield of hydrogen is the same as at methane conversion and \( C_\Sigma^R \) is 0.29 if the dissociation is completed (other properties are given in Table. 1). Dissociation equilibrium degree of ammonia is equal to 96 % under pressure of 20 atm and temperature of 800 K. If \( T_w \leq 1500 \text{ K} \) the rate of dissociation is quite high on catalytic wall.

Based on the experiment [6] of heat transfer to dissociating \( \text{NH}_3 \) and methane conversion [5] one can conclude that the heat flows of density up to 1-2 MW/m\(^2\) can be removed from the walls of detonation chamber. That means it is possible to work with pulsation frequency \( f \) up to 200 [s\(^{-1}\)]. However, the practically available degree of conversion \( (Z) \) does not exceed the value of 70 %. The main problem is to decrease \( T_w \) because it should be below 1000 K, since the fuel in both cases is hydrogen (Fig.1, numerical solution was done using software CHEMKIN II and data GRI-Mech 3.0). The reaction \( 2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2 - 2.7 \text{MJ/kg} \) is more preferable because it
does not lead to catalytic poisoning by carbon under low $T_w$. The main side process, nitriding of the walls by atomic nitrogen, does not lead to decrease of catalytic properties (in [6] stainless steel was used).

Table 1.
The thermophysics properties of various fuels for pulse detonation engines. The initial data taken from [7,8]. $T_b$ - boiling temperature, $\rho_{fe}$ - fluid density at $T_b$, $C_{\Sigma}$ - total cooling resource, $C_{\Sigma R}$ - total specific cooling resource. The products of reaction propeties is calculated for conversion degree 70%.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>$H_2$</th>
<th>$CH_4$</th>
<th>$NH_3$</th>
<th>Reaction products:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_b$, °C</td>
<td>-253</td>
<td>-161.5</td>
<td>-33</td>
<td>$CH_4+H_2O\rightarrow3H_2+CO$</td>
</tr>
<tr>
<td>$\rho_{fe}$ [kg/l]</td>
<td>0,07</td>
<td>0,42</td>
<td>0,68</td>
<td></td>
</tr>
<tr>
<td>$C_{\Sigma}$ [MJ/kg]</td>
<td>14,5</td>
<td>3,0</td>
<td>3,6</td>
<td>7,8</td>
</tr>
<tr>
<td>$Q$, [MJ/kg]</td>
<td>120</td>
<td>50</td>
<td>24</td>
<td>27,8</td>
</tr>
<tr>
<td>$C_{\Sigma R}$</td>
<td>0,12</td>
<td>0,06</td>
<td>0,15</td>
<td>0,28</td>
</tr>
</tbody>
</table>

In conclusion it is necessary to state that the conversion product is hydrogen which detonation capacity is better than those the initial substance has. For instance, the critical energy of direct initialization of spherical detonation of hydrogen-air mixture is at factor of 1000 less than the energy of methane-air mixture [9]. Therefore the opportunity of the hydrogen-air mixtures use in pulse detonation engines arises. Though endothermic fuels can be used to create more effective ways of cooling, heat capacity of products is less at factor of 1.5-2 comparing to air-kerosene ($Q = 45$ MJ/kg), however is more than rocket fuel has ($Q = 13$ MJ/kg for composition $2H_2 + O_2$). To increase this value, liquid hydrogen can be also used additionally as cooling agent. For example, the combination of 80% $NH_3 + 20%$ $H_2$ gives $C_{\Sigma R} \approx 0.2$ and heat of combustion close to those of kerosene.

![Figure 1](image-url)

The allowed wall temperature ($T_w$) and heat flux density to the wall of detonation chamber ($q_w$) in dependence on detonation frequency $f$. The calculation correspond to ctoicheometric (by hydrogen) mixtures with air at initial pressure 1 bar. The degree of conversion (dissociation) is 70%.
References:

4. Korabelnikov A.V., Kuranov A.L. Thermochemical conversion of hydrocarbon fuel under the concept 'AJAX' // AIAA 99-4921