A study reported in the present note was focused mainly on possibilities to control the autoignition delay in the GT combustion chamber using the plasma discharge. An extensive activity on the plasma assisted combustion is underway, which concerns the boiler ignition and the gas turbine combustion stability. Three approaches to the plasma assisted GT combustion have been theoretically analyzed using the plasma-chemical and chemical kinetic modelling: Methane pyrolysis; Plasma ignition of the lean CH4/air mixture; Methane pre-reforming (partial oxidation) in a rich CH4/Air mixture.

The plasma discharge in reactive gases and gas mixtures initiates a physical process, which generally comprises three main phases as follows: Electric breakdown and plasma formation. During this phase the free electrons are accelerated in the imposed electric field and gain high kinetic energy, which depends on the field intensity and the gas density and initiate plasma-chemical reactions. Also, a fraction of the kinetic energy is dissipating into the thermal energy of the heavy particles; hence, the gas is heated up. As it is seen in the following Figure 1 a minimum of heat production exists. This minimum corresponds to the maximum of the radicals production in the plasma and the maximum of the discharge chemical efficiency, at $E/n \sim 250–300$ Td. Below that level, the electron energy is not sufficient to dissociate the molecules and initiate the chemical reaction, above that level almost all the energy is spent to ionization of the gas, which has a lower efficiency of the chemical chains initiation in comparison to dissociation. Chemical efficiency of order of 45% can be potentially reached.

Discharge afterglow may last up to several microseconds at elevated pressure conditions ($P \sim 20$ atm) all the excited radicals and ions enter the chemical reactions and create chemically active radicals. During this phase the gas is further heated up due to energy release in the reactions of the electron/ion recombination and radicals association.

During the chemical relaxation phase the metastable mixture produced during discharge phase is relaxing towards a thermo-chemical equilibrium, which may be or might not be reached depending on the actual process duration (in our case we should compare the time before the fuel is mixed with the air in a burner and the characteristic time of the reactions, which depends on the gas temperature and pressure). The
latter one is determined by the mixture temperature in the afterglow as well as by the heat effect of the corresponding relaxation processes and the radicals production in the discharge phase.

Three general applications of the plasma for GT combustion are considered in the present report (see Figure 2). In general the oxygen content in the mixture is the major differentiator.

Figure 2: Three approaches to the plasma assisted combustion; the numbers correspond to the modeling variants described in Table 1 and Table 2.

1. Methane pyrolysis. No oxygen in the mixture. This process results in the mixture of methane, hydrogen and higher hydrocarbons, which is more reactive and exhibit lower delay of autoignition after being mixed with the hot air. Chemical pyrolysis is a promising technology of hydrogen production from methane. Plasma is an effective method of rapid energy injection into the gas and generation of the chemically active species, which expedite the chemical relaxation, at least at its initial phase. Soot formation is the major risk for the possible in-situ implementation of plasma assisted pyrolysis.

2. Direct ignition of the lean methane-air mixture. Amount of oxygen exceeds the stoichiometric level. From the literature it is known (see, for instance, [1,2]) that the plasma discharge arranged directly in the combustible mixture may significantly expedite the autoignition. Therefore it can be used not only as an ignition plug (which is a state-of-the-art in the aero energies), but also to stabilize the flame. The discharge device has to be located in the direct vicinity of the area, where the flame has to be ignited. The major problems related to the possible application of this technology in large GT combustion are as follows:
   a. The need to control the relatively large volume(s) by the discharge, which makes difficult use of such plasma technologies as dielectric barrier discharge (DBD), streamer corona etc., which rely on very high local electric fields especially at high pressures.
   b. Possible intense NOx generation in the high temperature plasma discharge in presence of air. Use of thermal or quasi-thermal discharges leads to extremely high local temperatures (>6000K in case of DC arc, 1500-2000K in case of gliding arc or plasma of intermediate temperatures (PIT), which results in the rapid formation of the thermal NOx.

3. Plasma methane pre-reforming. An intermediate case between the previous two. Amount of oxygen is sufficient to initiate a pronounced oxidation process, but still much below the stoichiometric level. Hence, no “normal” combustion takes place. The idea is to form a rapidly reactive mixture of methane, hydrogen and carbon monoxide (syngas). There exist three general methods of CH4 reforming:
   a. Steam methane reforming (SMR), which is based on the schematic reaction CH4+H2O→CO+3H2. This reaction is endothermic, hence, requires a significant energy
input and may be insufficiently fast for our purposes due to relatively low gas temperatures. Water plays a role of the oxygen source.

b. Dry methane reforming in the presence of carbon dioxide. The reaction scheme is CH4+CO2→2CO+2H2. It is endothermic as well as it is based on the reduction of the carbon dioxide as the source of oxygen for partial methane oxidation.

c. Methane partial oxidation in the rich CH4/air or CH4/O2 mixtures (under the conditions of oxygen deficiency compared to the stoichiometry). The reaction scheme looks like CH4 + (1/2)O2→ CO+H2. This reaction is an exothermic one and is self-accelerating provided that the amount of oxygen is sufficient to support it. On the other side if the initial oxygen content is closer to stoichiometry of higher, the process evolves towards formation of water and carbon dioxide (combustion instead of partial oxidation).

Based on the previous studies, it can be expected that ~5% of methane or more must be reformed, in order to achieve a noticeable effect on the autoignition delay. In order to realize the partial oxidation process, a kind of in-situ reactor has to be arranged, which would comprise the mixing area, plasma discharge zone and a sufficient space for the post-discharge chemical relaxation.

It is worth noting, that there may exist a chemo-ionization supported plasma process, in which the charged particles are generated in chemical reactions in the combustion zone and the plasma discharge is supported by the external electric field. For the moment this approach is not considered in the Plasma assisted GT combustion program.

**Methane pyrolysis**

**Plasma-chemical reactions**

During the discharge phase the collisions between accelerated electrons and the methane molecules cause dissociation and appearance of free radicals:

\[
\text{CH}_4 + \text{e} \rightarrow \text{CH}_3 + \text{H} + \text{e} \quad \text{(Activation energy 431kJ/mol)} \quad (1)
\]

\[
\text{CH}_4 + \text{e} \rightarrow \text{CH}_2 + \text{H}_2 + \text{e} \quad \text{(Activation energy 468kJ/mol)} \quad (2)
\]

Amount of the radicals created by the discharge can be seen in the following Figure 3. Due to the difference in the energy threshold the former reaction goes approximately as twice as fast compared to the latter one. CH3, CH2 and H radicals trigger oxidation reaction chains in the afterglow and further.

Discharge afterglow and chemical relaxation

The major reactions in afterglow are as follows:

\[
\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \quad (3)
\]

\[
\text{CH}_4 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2 \quad (4)
\]

\[
\text{CH}_4 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (5)
\]

\[
\text{CH}_4 + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_7 + \text{H}_2 \quad (6)
\]

….further down to high hydrocarbons and C.
These reactions drive the system into the non-equilibrium metastable state, from which is relaxing towards the chemical equilibrium. How far the process continues in the direction of equilibrium and whether it will be achieved depends on the mixture temperature (which determines the reaction rate), pressure, the time available, and the termination reactions:

\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6
\]
\[
\text{CH}_3 + \text{H} \rightarrow \text{CH}_4
\]

… which lead to stable molecular products formation.

From set of reactions (3)-(6) one sees that, unlike the conventional thermo-chemical pyrolysis process, the gas mixture exited by the plasma discharge enters the dehydrogenation process at several “gates” simultaneously. Nonetheless, the chemical relaxation part of the process is relatively slow. At the temperatures suitable for our purposes (say, below 1300K) generation of a noticeable amount of H2 or C2+ hydrocarbons requires tens or hundreds of milliseconds Error! Reference source not found., which might not be available in the in-situ GT fuel reforming.

Reaction times required for the noticeable coke formation are, presumably, of the same order of magnitude. Therefore, if the time available for chemical relaxation is relatively small (for instance, the discharge is initiated shortly before the fuel injection into the air/hot gas stream), the coke formation may be theoretically avoided. Nonetheless, as the deposition of solids may be considered a potential technology killer, this risk remains a special subject to theoretical and experimental investigation.

Therefore, it may be assumed that the plasma reforming process would yield the amount of rapidly reacting products (H2 and C2+) corresponding to the amount of H*, CH3*, CH2* radicals at the end of afterglow, recombining then into metastable molecules.

Overall, plasma-induced methane pyrolysis may produce a noticeable effect on the autoignition time of the air/fuel mixture if the discharge energy exceeds 2000 kJ per kg of CH4. In order to avoid coke formation as well as due to thermo-mechanical limitations, the discharge should be applied shortly or directly before the fuel injection into the air/hot gas stream or the mixture has to be quenched by the injection of a cold gas soon after the discharge.

---

**Figure 3:** Amount of radicals created by the discharge in CH4 (per J of the discharge energy) and their molar fraction at 20bar.
**Plasma Ignition**

In this paragraph a plasma assisted process is considered, when the plasma plays a role of an ignition plug. The discharge is initiated in the lean methane/air mixture. The reaction scheme should take into account reactions (1)-(6) and reactions with oxygen and nitrogen:

Discharge

*Dissociation:*

\[
O_2 + e \rightarrow O(3P) + O(1D) + e \quad (7)
\]

*Excitation of nitrogen:*

\[
N_2 + e \rightarrow N_2(C) + e \quad (8)
\]

*Quenching of excited levels:*

\[
N_2(C) + O_2 \rightarrow N_2 + O(3P) + O(1D) \quad (9)
\]

Reactions in plasma afterglow:

\[
\begin{align*}
CH_4 + O(3P) & \rightarrow CH_3 + OH \quad (10) \\
CH_4 + O(1D) & \rightarrow CH_3 + OH \quad (11) \\
CH_4 + N_2(C) & \rightarrow CH_3 + H + N_2 \quad (12) \\
CH_3 + O_2 & \rightarrow CH_2O + OH \quad (13)
\end{align*}
\]

**Combustion**

Products of reaction (7)-(13) as well as the heat release initiate the regular combustion kinetic chain, which evolves according to the known chemical kinetics.

Amounts of O*, CH3*, H*, CH2* and H2 particles (related to the discharge energy) are shown in the following Figure 44, where the radical production is shown per 1J of the discharge energy. For instance, if the amount of energy injected with the plasma discharge was 1MJ per kg of CH4 the corresponding amount of radicals (related to the initial molar quantity of CH4) would be 2.3% for O* and ca. 0.9% for H*, H2, CH3*, CH2* particles. This amount is sufficient to expedite significantly the autoignition reaction.
Figure 4: Amount of radicals generated by the plasma discharge in 4.7% CH4/Air mixture (per J of the discharge energy).

Reactions with non-thermal O* radicals

Immediately after the event of dissociation the radicals are not in the statistical equilibrium with the gas. Dissociation of molecular oxygen results in appearance of species with the energy significantly exceeding the average translational energy of thermalized particles. After the event of dissociation the particle is thermalized in a series of elastic or inelastic collisions with the other molecules (in our case this process would need of order of 5-20 collisions). Some of the “fast” particles may have kinetic energy exceeding the activation level of reaction (14) and, therefore, may contribute into the NOx formation during the active phase of the plasma discharge. Due to the high level of the energy at impact, the difference between the activation energies of reactions (14) and (16) is not that critical as in case of thermalized radicals, hence the methane might not play a role of effective inhibitor of nitrogen oxidation.

It should be noted, however, that the reactions of “hot” O-atoms with methane are accelerated as well. Figure 5 shows the ratio between the ignition delay time calculated for mechanism with “thermally-equilibrium” atoms formation ($\tau_1$) and ignition delay time, calculated taking into account the translational nonequilibrium and TT-relaxation of atomic oxygen and hydrogen ($\tau_2$). In the mixture with methane translational non-equilibrium of both H and O atoms is important. “Hot” O atoms in this system can effectively use its excessive translational energy to overcome the reaction energy threshold. High rate of TT-relaxation of O atoms leads to their fast thermalization; despite of this, approximately 25% of “hot” O atoms will react with methane before thermalization in stoichiometric methane-air mixture. “Hot” H atoms can react both with oxygen and methane molecules. As a result, the methane-air stoichiometric mixture demonstrates almost the same sensitivity as hydrogen-air mixtures to atoms production with excessive translational energy, even at high temperatures [4].
Overall, only gas discharge phase of the plasma assisted process may contribute into the production of additional NOx on the top of that, which is normally generated by the lean premix combustion. It is worth emphasizing that these considerations are valid solely for the “cold” and distributed in space discharges, for which the arc (contraction with the subsequent overheating) does not take place. In these discharges the typical energy price of O-atoms production is about 4.5 eV/atom, while the energy price of N-atoms production is about 40 eV/atom.

**Methane Plasma pre-reforming**

The rich methane-air mixture with the air-to-CH4 ratio below 4 at the temperatures exceeding ca. 850K tends to evolve towards formation CO and H2 [5-6]. At higher air/CH4 ratios due to increasing quantity of oxygen the equilibrium shifts towards formation of water steam and carbon dioxide. The process of partial oxidation is exothermic and is accompanied by the heat release due to formation of CO, which in its turn accelerates the kinetics.

If the energy input from the discharge suffice to initiate the reaction in the rich mixture and to assure the temperature level, which is required for the reasonably fast chemical conversion, one may expect a partial reforming of the fuel into the one with higher reactivity prior to its injection into the mixing and combustion area, hence the reduction of the autoignition time may be expected. The process of an in-situ fuel pre-reforming (pre-oxidation) could comprise the following steps:

1. Pre-heating of methane;
2. Admixture of the air ($\lambda < 0.4$) into the fuel; Rich mixture is formed.
3. Discharge and plasma-chemical relaxation in the rich mixture;
4. Chemical relaxation = reforming = partial oxidation;
5. Mixing with the air ($\lambda = \text{ca. 2}$). Lean mixture is formed.
6. Autoignition of the pre-activated lean fuel/air mixture
Plasma-chemical reactions in the air/methane mixture.

Corresponding reaction schemes look like as follows:

Discharge

\[ \text{Dissociation:} \]
\[ \text{O}_2 + e \rightarrow \text{O}(3P) + \text{O}(1D) + e \]
\[ \text{CH}_4 + e \rightarrow \text{CH}_3 + \text{H} + e \]
\[ \text{CH}_4 + e \rightarrow \text{CH}_2 + \text{H}_2 + e \]

\[ \text{Excitation:} \]
\[ \text{N}_2 + e \rightarrow \text{N}_2(\text{C}) + e \]

\[ \text{Quenching:} \]
\[ \text{N}_2(\text{C}) + \text{CH}_4 \rightarrow \text{N}_2 + \text{CH}_3 + \text{H} \]
\[ \text{N}_2(\text{C}) + \text{CH}_4 \rightarrow \text{N}_2 + \text{CH}_2 + \text{H}_2 \]
\[ \text{N}_2(\text{C}) + \text{O}_2 \rightarrow \text{N}_2 + \text{O}(3P) + \text{O}(1D) \]

Reactions in plasma afterglow:

\[ \text{CH}_4 + \text{O}(3P) \rightarrow \text{CH}_3 + \text{OH} \]
\[ \text{CH}_4 + \text{O}(1D) \rightarrow \text{CH}_3 + \text{OH} \]
\[ \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \]
\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{OH} \]

…..and the relaxation towards the chemical equilibrium.

The amount of converted fuel is increasing with the initial oxygen content in the mixture up to the air/methane ratio of ca. 3 (λ < 0.32). The same time the temperature after the discharge afterglow of the process (which is close to the “frozen” gas temperature after the discharge) is lower for mixtures with higher air content at the same specific discharge energy (in MJ/kg of CH4). So will be the reaction rate of the chemical relaxation during chemical relaxation phase. This is illustrated by Figure6 and Figure7, where the temperature dynamics at the latent and the rapid phases of the after-discharge chemical relaxation and the duration of the chemical phase (defined at the temperature peak) and the relaxations time are shown. It is seen that the relaxation time is exponentially reduced with the increase in discharge energy. Concentration of the reactive species after 100ms of the process is shown in Figure8 for different values of the discharge energy. If the available relaxation time is not sufficient for the “rapid” relaxation to take place, the concentration of the rapidly reacting species like H2, CO and C2+ hydrocarbons is low. If the “rapid” relaxation takes place, concentrations of H2/CO are much higher and they are slightly increasing with the discharge energy according to the final gas temperature, so will be effect on the autoignition time, when the mixture is finally injected into the air/hot gas.

It is worth noting that unlike the frozen temperature of the plasma-processed mixture the equilibrium one is increasing with the oxygen content due to increasing heat release of hydrocarbon oxidation.
Figure 6: Influence of the discharge energy on reaction kinetics, $5\text{J/cm}^3$=ca. $2\text{MJ/kg CH}_4$

Figure 7: Duration of the chemical relaxation vs. discharge energy

Comparison of plasma reforming of different fuel mixtures

*Calculations with the fixed discharge energy (per volume of mixture) and fixed pre-ignition hot gas temperature (after mixing)*

The analysis of the present investigation is based on a set of modelling cases, which are summarized in the following Table 1.

All cases were calculated for the gases at 20 bar with the electric field strength of 250 Td (approximately two times above the breakdown threshold). Initial gas temperature was 500 K (except the case 7, i.e the ignition of the lean methane-air mixture). The discharge energy density in the feeder ($10 \text{ J/cm}^3$) and the
gas flow in the feeder remains the same in all cases. Thus, the total electrical energy consumption remains the same in all cases, but the chemical energy is very different. In the case of diluted mixtures (2-6) total chemical energy is much lower than in the case of mixtures (1) and (7). For example, the chemical energy of the mixture in the case (4) is 3 times lower than in the case (7).

For the cases 2-6 the same value of the volumetric discharge energy of 10 J/cm was assumed. This assumption results in similar temperature levels at the end of the afterglow phase, hence – in the comparable reaction rates. This allows one to reveal the effect of the gas composition on the combustion dynamics after the fuel processing. It is worth noting that the mass specific energy input (per kg of the pure methane) in this case is different for all the variants.

![Discharge energy vs. Mole Fraction](image)

**Figure 8**: concentration of reactive species at 100ms vs. discharge energy for 2:1 air/CH4 mixture, P=20bar, T_0=500K, 5J/cm^3=ca. =2MJ/kg_CH4

**Resulting gas composition depending on available relaxation time**

As it was mentioned above, the volumetric energy input during the discharge was the same (10 J/cm³) for variants 1-6 and the temperature difference in the after the afterglow phase of the process can be attributed mainly to the different molar heat capacities of the initial mixtures and, to the less extent – to the radical concentration after the plasma relaxation in afterglow (Figure 9). It is seen that after the plasma relaxation afterglow phase the process is nearly over for the pure methane (1), methane with low oxygen content (2 – 1/8:1 Air/CH4) and the Steam/CH4 mixtures (6). For the 1:1 and 2:1 air/CH4 and 1:1:1 air/steam/CH4 mixtures after the latent relaxation phase the process enters the rapid relaxation one. This phase is nearly over after ca. 7 ms for the 2:1 Air/CH4 mixture and continues beyond 10 ms for the other two.
The gas compositions are shown in Figure 10 for the relaxation times of 1, 10 and 100 ms respectively. At 1 ms all the mixtures have similar content of H2, C2+ and/or CO (as discussed above, there is nearly no carbon monoxide in Steam reforming). At 10 and 100 ms the rich air/steam mixtures become the obvious front-runners, from which the most pronounced effect on the further combustion process may be expected.

Table 1: Modelling variants

<table>
<thead>
<tr>
<th>Variant</th>
<th>Mixture composition (Vol %)</th>
<th>Total CH4/air, %</th>
<th>Description</th>
<th>Discharge energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Per volume in the feeder, J/cm³</td>
</tr>
<tr>
<td>0</td>
<td>4.76 CH4+76.19 N2+19.05 O2</td>
<td>4.76</td>
<td>Conventional autoignition, no plasma</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>100 CH4</td>
<td>4.76</td>
<td>Pure Methane modification</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>87.5 CH4+10 N2+2.5 O2</td>
<td>4.165</td>
<td>Methane with air admixture</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
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<td>2.38</td>
<td>Methane-air 1:1</td>
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<tr>
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</tr>
<tr>
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<tr>
<td>7</td>
<td>4.76 CH4+76.19 N2+19.05 O2</td>
<td>4.76</td>
<td>Discharge in high-T zone</td>
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</tr>
</tbody>
</table>

**Influence of resulting gas composition on the autoignition of lean fuel/air mixture**

In order to quantify the effect of the plasma fuel pre-treatment, the temperature evolution during the autoignition process is shown in the following Figure 11 for the ignition temperature of 1400 K and 1200 K respectively. All the mixtures were set to the same temperature conditions at fuel injection just to reveal the pure effect of the gas composition.

An apparent difference in the initial temperature of variant 7 (discharge in the lean mixture) is due to the fact that in the modelling the discharge and the autoignition process in this case were not separated in time and the mixture was heated directly during the process.

Duration of the pre-reforming process was assumed to be 100 ms (which is definitely too much for the feasible in-situ process, but still shows the maximum possible effect).
Figure 9: Evolution of temperature in afterglow and chemical relaxation zone for different gas mixtures, a) – all mixtures time 0...1ms, b) – 1:1 and 2:1 air/CH4 and 1:1:1 Air/Steam/CH4 mixture, time 0…10ms, P=20bar
Figure 10: Plasma reforming of mixtures 1-6 (see Table 1); a, b, c – available after-glow relaxation times are 1, 10 and 100 ms respectively.

As discussed earlier in section 0 of the present report, the direct plasma ignition of the lean mixture is a very effective way of controlling the autoignition process as the free radicals generated by the discharge immediately enter the combustion reaction chain. Nonetheless one sees that the mixtures with the pronounced conversion of the methane (in our case – 1:1 and especially 2:1 Air/CH4 ones) may also exhibit similar autoignition behaviour.

Figure 11: Influence of the plasma discharge on the autoignition process for different initial fuel mixtures; a) $T_{\text{ign}} = 1400$ K, b) $T_{\text{ign}} = 1200$ K
Effect of the discharge energy on the pre-reforming process and auto-ignition delay

Effect of the discharge energy on the autoignition delay is illustrated in the following Figure 12 (referring to Figure 6 and Figure 7 as well). Reduction of the autoignition delay is pronounced only if the combustion phase relaxation time was sufficient to reach the rapid conversion process step (in this case it happened when the discharge energy is above 5.5 J/cm$^3$ of mixture (ca. 2.2 MJ/kg CH$_4$).

![Figure 12: Effect of the discharge energy in 2:1 air/CH$_4$ mixture on the autoignition time of the lean mixture, T$_{\text{ign}} = 1200$ K](image)

Calculations with the fixed (fuel mass-specific) discharge energy and initial hot gas temperature.

Plasma treatment changes not only the gas composition, but also thermodynamic conditions after the fuel mixing with the air/hot gas (different fuel enthalpy and amount of admixing gas and, to the less extent, different heat capacity of the reformed fuel mixture). This also affects the resulting autoignition dynamics. In order to demonstrate that, the same gas mixtures were modelled assuming the same methane-air ratio (2.96% CH$_4$ in air, See Table 2).

The discharge energy density in the feeder (10 J/cm$^3$) in the feeder remains the same in all cases, but the gas flow was adjusted to keep the same methane consumption. Thus, the chemical energy remains the same in all cases, but the total electrical energy consumption is very different. In the case of diluted mixtures (2-6) total discharge energy is much higher than in the case of mixtures (1) and (7). For example, the discharge power in the case (4) is 3 times bigger than in the case (7).

The gas temperature in the beginning of autoignition phase was calculated according to the actual enthalpies of the mixing components. Unlike the cases considered in the previous paragraph, in these calculation runs the temperatures of the treated fuel-air mixtures were different.

Resulting autoignition dynamics is shown in Figure 13. It is seen that the effect of plasma-induced reforming is now more pronounced. With the initial air-to-methane ratios between 1 and 2 the autoignition delay of the pre-reformed methane is comparable (of even smaller) than that of the lean mixture directly ignited by the plasma and it is noticeably shorter than that in the reference case of no plasma. The same time, steam reforming makes the process even longer that in the reference case. This is due to lower temperature of the resulting mixture as significant amount energy was channelled into the water dissociation.
It is worth emphasizing that variation of the autoignition delay for different variants with regard to the reference case may exceed an order of magnitude and only a small portion of the effect is to be attributed to the changes in the initial mixing temperature (compare with results of Figure 11). For instance, initial temperature difference of 100 K would result in the ca. two-fold reduction in the autoignition delay between variants 6a and 4a, whereas the overall effect is as high as 30 times.

Table 2: Modelling variants considered

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<td>7*</td>
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<td>Discharge in high-T zone</td>
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</tr>
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</table>

Summary

A study reported in the present note was focused mainly on possibilities to control the autoignition delay in the GT combustion chamber using the plasma discharge.

Three approaches to the plasma assisted GT combustion have been theoretically analyzed using the plasma-chemical and chemical kinetic modelling.

- Methane pyrolysis;
- Plasma ignition of the lean CH4/air mixture;
- Methane pre-reforming (partial oxidation) in a rich CH4/Air mixture;

Results of the analysis can be formulated as follows:

1. Pyrolysis:
   - High energies/temperatures are required to achieve the effect, immediate quenching after the discharge is needed in order to avoid soot deposition. Potentially the pyrolysis can be realized just before the fuel injection into the stream. The highest energy consumption for the same ignition delay time reduction;
2. Plasma ignition of the lean mixture:
   - Significantly reduces the autoignition time due to intense O, O(1D), H and CH3 radicals formation in the discharge;
   - The plasma discharge in the air-fuel mixture would inevitably generate additional NOx during the discharge phase of the process. Because of different dissociation threshold of O2, CH4 and N2 molecules by electron impact the energy consumption per one O atom is approximately 4.5 eV, while for N atom it is about 40 eV. This difference in the energy efficiency in O and N atoms production prevents NOx formation and makes the low-temperature nonequilibrium plasma a good tool for the ignition control. Low temperature in the discharge zone guarantee the low rate of reactions O+N2→NO+N because of its high energy threshold. Presence of unburnt CH4 in the plasma after-glow and the area of chemical relaxation effectively blocks formation of additional NOx during chemical relaxation phase. Overall amount of the additional NOx generated in the plasma fuel pretreatment likely to be acceptable;

3. Pre-reforming:
   - With the appropriate combination of Air/CH4 ratio and plasma discharge energy pre-reforming may significantly reduce the autoignition time after the mixing with the main hot gas stream;
   - Efficient process requires significant relaxation time (>1ms, hence- lengthy reaction zone) and high temperatures, which may be hard to realize in design. The temperature increase in the discharge and discharge afterglow zone could decrease the required discharge energy. The process produces very small amount of NOx because of low N2 and O2 concentration in the mixture;
   - Air/H2O mixtures unlikely to be suitable for the in-situ plasma pre-reforming due to lower temperatures after the discharge, too low reaction rates and endothermic nature of the chemical relaxation.

Figure 13: Influence of the plasma discharge on the autoignition time delay: same discharge energy per mass of the fuel, fixed hot gas temperature BEFORE injection of fuel mixture; T\_hg\_init = 1400 K
References


