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Evolution of Hydrocarbons Ignition Delay Time Over HTAC (High Temperature Air Combustion) Conditions

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Abstract. In this investigation, ignition processes of the methane and the propane using a high-temperature oxidizer ($T_{oxi} > T_{ai}$) with a varying oxygen concentration z_{O2} - the HTAC (High Temperature Air Combustion) conditions, applying a constant-volume bomb (CVB) was investigated. The influence of the initial temperature of the oxidizer T_{oxi} was analyzed and discussed. It is shown that in order to achieve an effective reaction of ignition the oxidizer temperature needn't be maximized. Detailed evolution of ignition delay time with equivalence ratio τ_{ig} was presented. It can be concluded that increment of oxygen concentration z_{O2} in oxidizer results in decrease of τ_{ig}. Trials with propane are characterizing lower values of ignition delay time τ_{ig} in comparison with methane.

Keywords. Ignition delay time, HTAC, methane, propane.

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1 Introduction

As it is known the reserves of natural gas resources (and other fuels) are subject to two constraints, namely: capital invested in the exploration and drilling technologies used to discover new reserves. The natural gas scarcity factor, i.e. ratio between available reserves and natural gas consumption, is around 300 years for the last 50 years [1]. The new discovery of natural gas reserves has given rise to a new energy strategy based on natural gas.

The HTAC (High Temperature Air Combustion) technology or FLameless OXidation (FLOX) [2] or Mild (Moderate and Intensive Low-oxygen Dilution) combustion [3] is probably the most important achievement of combustion technology in recent years. Within a decade or two, it has been developed from laboratory tests to industrial an application which certainly is an extraordinary progress as for an energy technology. A comprehensive review paper summarizing both the development and current status of this technology does not exist although some information can be found in [3–6]. The essence of this technology is that fuel is oxidized in an environment that contains a substantial amount of inert (flue) gases. For clean gaseous fuels that do not contain any fuel-bounded nitrogen this results in very low NO_x emissions even if the combustion air stream is preheated to temperatures in excess of 1273 K. Chemical reactions take place in almost the entire volume of the combustion chamber and uniformity of both the temperature and the chemical species fields are characteristics of this technology. The opposite case occurs in conventional combustion systems where reactions are concentrated in a narrow flame front.

The HTAC has been applied in many industrial furnaces [7] (especially fired with natural gas). Furthermore, it was also proved that this technology may be used for combustion of light liquid fuels [8] and biogas [9]. Also, the first trials have been made to burn solid fuels under HTAC technology [10–12]. However, HTAC is still a new promising combustion technology. So, it is still a subject of scientist's research in many countries. Previously, many of the characteristics of high-temperature air combustion have been investigated in laboratory-scale systems [13, 14]. The knowledge of the gaseous fuel ignition phenomenon under high temperature and various concentrated oxidizers conditions is still an example of the gap in the research of HTAC. Ignition delay time is an important parameter in the most modern and advanced combustor concepts designed for low-NO_x emission. Rapid spontaneous ignition and complete reaction of fuel are required to achieve efficient combustion. Past experimental works of the ignition delay time can be divided into two groups: flow reactors [15] and bombs [16], and heated and unheated shock tubes [17–19] and rapid compression machines [20].

In this paper, the ignition delay time τ_{ig} was assumed as parameter characterizing the process of ignition under analyzed conditions. The experimental investigation of the gaseous fuels ignition process at different type of high-temperature oxidizer and analysis of chemistry of the ignition delay time are the main goals of the research.

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φ	oxidizer	methane	propane
		T_{oxi}, K	T_{oxi}, K
1.43	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1186
1.25	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
1.11	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
1.00	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
0.91	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
0.77	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
0.63	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055
0.50	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	960, 989, 1005, 1034, 1055, 1085, 1104, 1134, 1186, 1206, 1234	803, 833, 853, 883, 903, 933, 960, 989, 1005, 1034, 1055

Table 1. Experimental matrix

2 Methods and Materials

The impact of the following variables: type of gaseous fuel, initial temperature of oxidizer T_{oxi} (for methane eleven values from the range of oxidizer temperature $T_{oxi} = 960$–1234 K and for propane also eleven values from the range of $T_{oxi} = 803$–1055 K – see Table 1), equivalence ratio $\phi = 0.50$–1.43 (eight values from this range – see Table 1) and volumetric composition of oxidizer {four types of oxidizers: atmospheric air ($z_{O2} = 0.21$ and $z_{N2} = 0.79$), oxidizer 1 ($z_{O2} = 0.15$ and $z_{N2} = 0.85$), oxidizer 2 ($z_{O2} = 0.10$ and $z_{N2} = 0.90$) and oxidizer 3 ($z_{O2} = 0.05$ and $z_{N2} = 0.95$)} on the ignition process under HTAC conditions were investigated. Full experimental matrix is presented in Table 1.

An example of the way of determining the ignition delay time τ_{ig} is presented in Figure 1 [21].

Point "0" is interpreted as the moment of the gas injection and the start of ignition (and moment of opening the electric valve). The time from the moment of opening the electric valve (point "0") to the achievement of the maximum temperature is assumed as the ignition delay time τ_{ig}. The maximal value of standard deviation of ignition delay time τ_{ig} is equal to $\sigma_{\tau ig} = 0.017$ s. The signals from thermocouples were collected every 0.001 s. The oxidizer temperature T_{oxi} was measured with an enlarged uncertainty equal to $\delta T_{oxi} = 2$ K [22]. Error of calculations of the equivalence ratio $\delta\phi$ was equal to $\delta\phi = 0.02\,\%$.

2.1 Experimental Apparatus

In the studies the experimental cylindrical (Figure 2) combustion chamber (2) with constant volume (CVB) made of steel with the total volume approximately 400 $cm^3$was used [23].

The oxidizers in the reaction cylinder were initially heated by heating coils (3) with the total heating power of $1.7 \cdot 10^3$ W. The oxidizers with different oxygen concen-

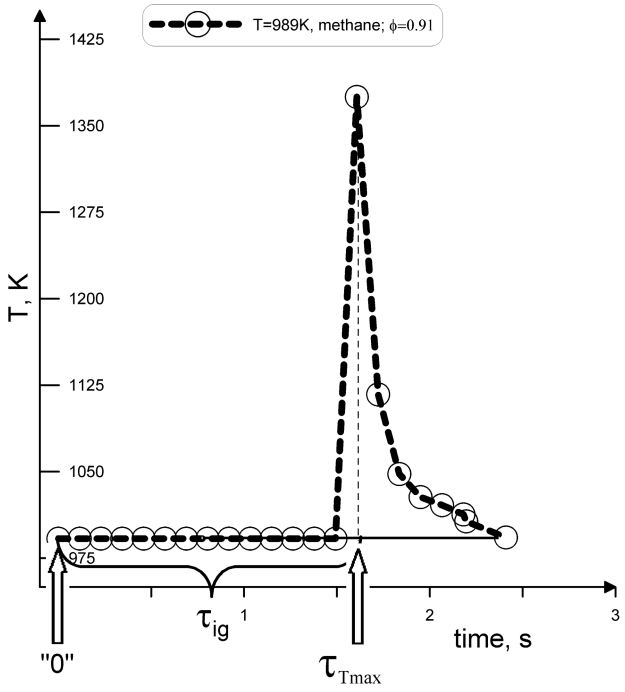

Figure 1. Example of the ignition delay time τ_{ig} as a function of the duration of the test.

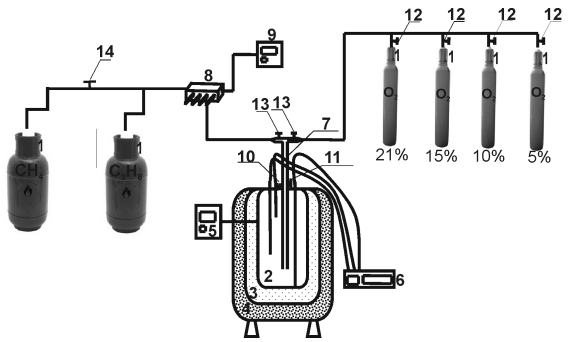

Figure 2. Scheme of constant volume bomb (CVB); 1, gas cylinders, 2, reaction chamber, 3, heating coil, 4, thermal insulation, 5, microprocessor control unit, 6, digital recorder, 7, conduit supplying gas, 8, electric valve, 9, control unit, 10, safety vent, 11–14, valves.

tration were taken from the gas cylinders (1) equipped with standard reducing valves and valves (12) to cut off stream of oxidizer. The combustion chamber is insulated with ceramic fibre (4). Fuels from the proper gas cylinders (1) with reducing valve, through electric valve (8) (controlled by microprocessor control unit (9)) and pipe supplying gas (7) were injected into the reaction chamber. Fuels with room temperature were injected to stationary oxidizer. Switching between of analyzed gases is done by opening and closing of valve (14). The pipe supplying gas with an internal diameter of $3 \cdot 10^{-3}$ m is equipped with four holes with an internal diameter of $5 \cdot 10^{-4}$ m situated around the axle of the pipe. It is equipped with valves (11) and (13), thanks to whom it is possible to switch between of dosage of oxidizer and fuel. In the upper cover, there is a safety vent (10) as well as three holes, through which three thermoelements type S (PtRh10-Pt) are installed and connected with a digital recorder (6). The temperature of hot oxidizer inside the reaction chamber is controlled by a microprocessor control unit (5) integrated with a thermoelement of the type K (NiCr-NiAl).

3 Results and Discussion

In Figure 3 the ignition delay time τ_{ig} as a function of the oxidizer temperature T_{oxi} for both analyzed fuels and for equivalence ratio equal to $\phi = 0.91$ is shown.

It can be observed for each test, initially the ignition delay time decreases at the beginning with a growth of oxidizer temperature T_{oxi}. It is connected with the relationship that with the growth of the oxidizer temperature T_{oxi}, the reaction rate and frequency of particle collision are increasing both. As it can be observed in this Figure, there is value of oxidizer temperature T_{oxi}, in which the ignition delay time reaches its minimum. As can be observed, for the value of T_{oxi} in which $\tau_{ig} = \tau_{min}$, the ignition delay time in the case of propane is lower than in the case of methane. As it is generally known, more complicated chemical complex structure of the propane molecule favors the easier ignition of propane than in methane. Above the

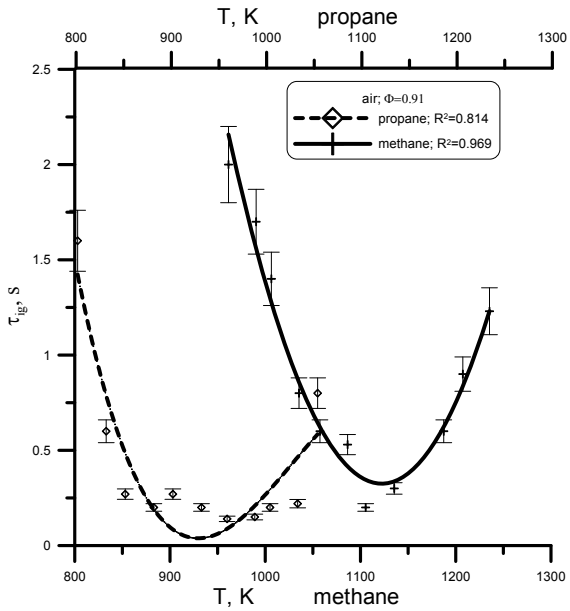

Figure 3. Dependence of ignition delay time τ_{ig} as a function of oxidizer temperature T_{oxi}.

value of T_{oxi} in which the ignition delay time reaches its minimum (τ_{min}), this parameter is increasing due to smaller level of density (concentration) of reacting gases at constant pressure (chamber is not hermetic). It can be concluded, that despite the fact that increment of oxidizer temperature T_{oxi} favors of growth of reaction rate, the decrease of gas density is much stronger. As a result, above the value of T_{oxi} in which $\tau_{ig} = \tau_{min}$, this parameter is increasing. It seems that preheating oxidizer above this value of temperature oxidizer equal approximately to: in the case of methane $T_{oxi} \approx 1100$ K and in the case of propane $T_{oxi} \approx 950$ K is unsubstantiated. This opinion is correct when the HTAC technology is appreciated from point of view of ignition delay time τ_{ig}. Similar diagrams have been plotted for all analyzed (see Table 1) values of equivalence ratio but it is well known that most combustion properties have simple minima in the neighborhood of $\phi = 1$.

In Figure 4 the ignition delay as a function of equivalence ratio for both analyzed fuels and for $T_{oxi} = 903$ K (in the case of propane) and for $T_{oxi} = 1104$ K (in the case of methane) is presented.

The evolution of τ_{ig} with Φ can be described by three branches, thereafter qualified by:

1. very lean: $\Phi \leq 0.15$;
2. lean, up to stoichiometric: $\Phi \in [0.15, 1.0]$;
3. rich: $\Phi > 1.0$

Methane and propane as majority of alkanes inhibits its own ignition [24] when rate of branching of chain branching (as essential reaction for the high temperature combustion) is higher than rate of tearing off of chain branching. Hydrogen atoms °H and alkyl radicals (the most important products of chain branching) in different conditions are characterized by different properties. It can be noticed on Figure 4, that for rich mixtures ($\phi > 1$), alkanes are inhibitors of ignition reaction due to important rerouting of hydrogen atoms from chain branching reaction. This feature is predominating over ignition, so ignition delay time increases with growth of ϕ. For lean mixtures ($\phi < 1$), not very often collisions between oxidizing and reducing species (small presence of fuel) are limiting the rerouting of hydrogen atoms (favorable factor). Here alkanes behave like promoters of its own ignition. In this case, ignition delay time decreases with growth of the ϕ. For values ϕ in which τ_{ig} reaches its minimum, there is a balance between amount of reactive radicals and not very well reactive hydrogen atoms.

In Figure 5 it can be clearly observed that increment of oxygen concentration z_{O2} in oxidizer results in line decrease of τ_{ig}. Trials with propane are characterizing lower values of ignition delay time τ_{ig} in comparison with methane.

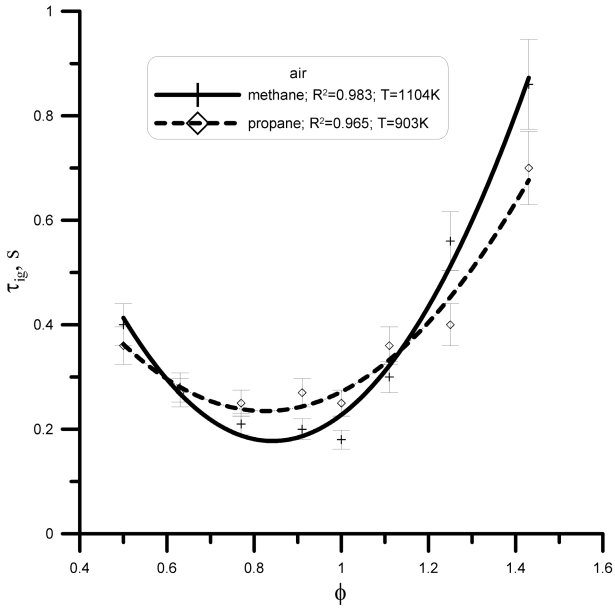

Figure 4. Dependence of ignition delay time τ_{ig} as a function of equivalence ratio ϕ.

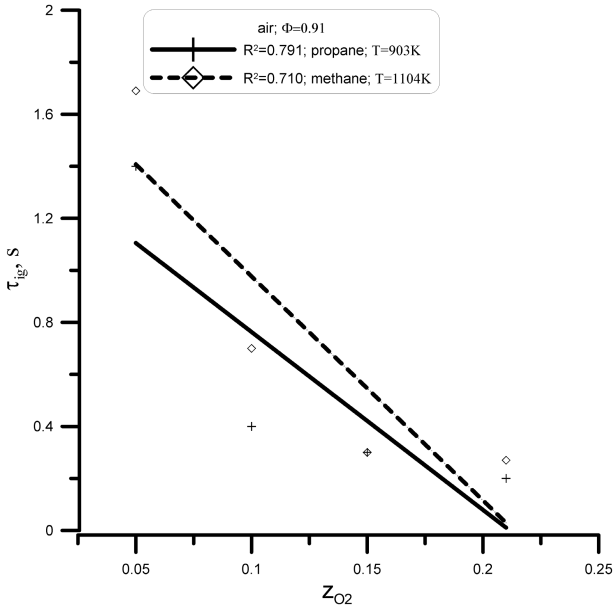

Figure 5. Ignition delay time τ_{ig} as a function of molar fraction of oxygen in oxidizer z_{O2}.

4 Conclusions

In this work ignition of methane and propane under HTAC technology condition were investigated. Different high temperature oxidizers were used. Constant volume bomb (CVB) was applied. Taking into consideration analyzed parameter (τ_{ig}), it seems that preheating the oxidizer without limits seems to be unsubstained. There are the values of temperature oxidizer (for methane $T_{oxi} \approx 1100$ K and for propane $T_{oxi} \approx 950$ K) in which the ignition delay time

reaches its minimum. The increment of oxygen concentration z_{O2} in oxidizer results in line decrease of τ_{ig}. Trials with propane are characterizing lower values of ignition delay time τ_{ig} in comparison with methane. It is caused by more complicated chemical complex structure of the propane molecule in comparison with methane. As a result, propane is characterizing by easier ignition in comparison to methane.

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