A Constant-Volume Bomb and Co-Flow Reactor Investigation of Ignition Phenomenon of Hydrocarbon Fuels in High Temperature Oxidizer*

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Abstract

The paper presents results of experimental studies on the methane and propane ignition process in various volumetric compositions of oxidizers heated to temperatures higher than the ignition point of analyzed fuels (HTAC conditions – High Temperature Air Combustion conditions). The increment of temperature ΔT and the ignition delay time τ' are parameters characterizing the process of ignition under these conditions. These parameters are the function of air excess ratio λ, temperature of the oxidizer t_{oxi} and the volumetric composition of oxidizer z_i. In order to achieve the minimum ignition delay time τ' and the maximum increment of the temperature ΔT, the oxidizer temperature need not be maximized. There is an interval of t_{oxi} in which the parameters mentioned above reach their extreme values.

Keywords: High Temperature Air Combustion, ignition, methane, propane.

1. Introduction

HTAC (Tsuji at al., 2003) is probably the most important achievement of the combustion technology in recent years. This technology is also known as Excess Enthalpy Combustion (EEC) (Wilk, 2002) or FLameless OXidation (FLOX) (Wünning and Wünning, 1997) in Germany or MILD (Moderate and Intensive Low-oxygen Dilution) Combustion (Cavaliere and de Joannon, 2004) or Diluted Combustion (Milani, 2001) in Italy.

The basic principles of this technology are as follows (Wilk, 2002):

1. The temperature of oxidizer t_{oxi} has to be higher than the autoignition point t_{au} of the combustible mixture. In such conditions the phenomenon of combustion is in its character similar to a volumetric and flameless combustion. Thanks to this, the temperature level inside the combustion chamber is relatively uniform, and temperature peaks ($t \geq 1400^0 C$), at which thermal nitrogen oxides are formed, can be avoided.
2. The fuel nozzles are positioned away from the air nozzles supplying the gas fuel into the hot flame gases.
3. Strong recirculation of hot exhausted gases to the reaction chamber is required.
4. HTAC is controlled simultaneously by mixing fuel and the oxidizer and by means of chemical kinetics.

The main advantages of applying HTAC technique are as follows (Wilk, 2002):

1. Thanks to the strong recirculation of combustion gases, HTAC burners permit to increase the average temperature and obtain a more equalized temperature in the combustion chamber, avoiding temperature peaks and thermal NO_x formation.
2. The intensive circulation of hot combustion gases reduces the local concentration of oxygen, retarding the mixing of the fuel with the oxidizer, so that the formation of prompt NO_x and via N_2O may be prevented.
3. The heat radiation is more effective.
4. The increase of the average temperature in the combustion chamber and the heat radiation improves the thermal efficiency of the system and thus also reduces the consumption of fuels and the emission of NO_x and CO_2. The final results are a reduction of the operating cost.
5. The construction of the combustion chamber is very compact; in comparison with a classical combustion system it is much smaller, resulting in lower capital costs.

The HTAC technology has been applied in many industrial furnaces (Yokomori at al., 2007) (especially fired with natural gas). Furthermore, it has also been proved that this technology may be used for the combustion of light liquid fuels (Wilk et al., 2002). Also, the first attempts have been made to burn solid fuels applying the HTAC technology (Weber at al., 2005; Schaffel at al., 2009). However, HTAC technology is still a new and promising combustion technology. So, it is still a subject of scientists' research in many countries.

The present paper deals with the results of experimental investigations concerning the ignition of methane and propane in various volumetric compositions of superheated oxidizer in a combustion chamber with a constant volume (CVB). Experiments in a co-flow reactor (CFR) were also done. The main task of this research was to test the research technology in conditions similar to actual industrial furnaces.

2. Experiment

A full experimental matrix is presented in Table 1. Main properties of investigated fuels are presented in Table 2. Eight different values of air excess ratio (as a ratio of volume of oxidizer in chamber to volume

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Table 1. Experimental matrix.

λ	CVB				CFR	
	Methane		Propane		Propane	
	t_{oxi}, ^{o}C	Oxidizer	t_{oxi}, ^{o}C	Oxidizer	t_{oxi}, ^{o}C	Oxidizer
0.7	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
0.8	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
0.9	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
1.0	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
1.1	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
1.3	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
1.6	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air
2.0	687, 716, 732 761, 782, 812 831, 861, 913 933, 961	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630, 660 687, 716, 732 761, 782	Air Oxidizer 1 Oxidizer 2 Oxidizer 3	530, 560, 580 610, 630	Air

of injected gas) were investigated. Various oxidizers were taken into consideration: 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). Oxidizers were initially preheated up to pre-set temperatures t_{oxi}. Lower values for analyzed intervals of t_{oxi} are higher than the autoignition temperature of the combustible mixture (see Table 2). This fundamental experimental assumption indicates the main requirements of HTAC technique, which demands preheating the oxidizer above autoignition point and strong gas recirculation (low level of volumetric composition of oxygen) into the combustion chamber.

Table 2. Main properties of investigated fuels (Bartok and Sarofim, 1989).

	Methane	Propane
Chemical formula	CH_4	C_3H_8
Flammability limits in the air mixtures, % vol.	5.0-15.0	2.0-9.5
Autoignition temperature t_{au} of the combustible mixture with air, ^{0}C	595.0	493.0

2.1 Experimental rigs-CVB

Figure 1 shows the diagram of the stand for experimental investigations of the ignition of gaseous fuels and its fundamental elements (Werle and Wilk, 2007). A experimental cylindrical combustion chamber (2) (CVB) made of steel with a total volume of approximately 400 cm^3 was used. The oxidizers in the reaction cylinder were initially heated by heating coils (3) with a total heating power of 1.7 kW. Oxidizers with different oxygen concentrations were taken from gas cylinders (1)

equipped with standard reducing valves and valves (12) to cut off the stream of the oxidizer. The combustion chamber is insulated with ceramic fibre (4). Fuels (at room temperature) pass from the proper gas cylinders (1) with a reducing valve, through an electric valve (8) (controlled by a microprocessor control unit (9)) and the gas supply pipe (7) and were injected into the reaction chamber. The analyzed gases are switched on and off by opening and closing the valve (14). The gas supply pipe with an internal diameter of 3 mm is equipped with four holes with an internal diameter of 0.5 mm, situated around the axis of the pipe. It is equipped with valves (11) and (13), thanks to which it is possible to adjust the dosage of oxidizer and fuel.
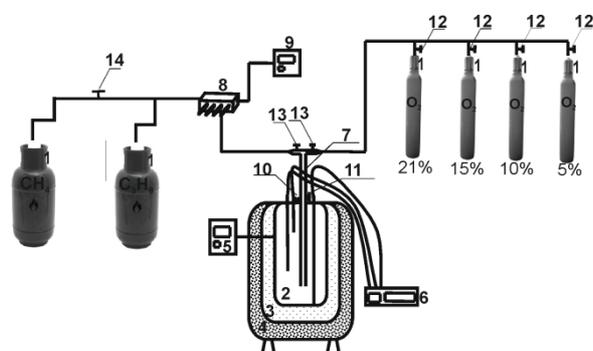

Figure 1. Scheme of constant volume bomb (CVB); 1, gas cylinders, 2, reaction chamber, 3, heating coil, 4, thermal insulation, 5, microprocessor control unit, 6, digital recorder, 7, conduit supplying gas, 8, electric valve, 9, control unit, 10, safety vent, 11-14, valves.

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 the hot oxidizer inside the reaction chamber is controlled by a microprocessor control unit (5) integrated with a thermoelement of the type K (NiCr-NiAl).

Procedure of measurements:

1. The steady oxidizer is electrically heated up to the pre-set constant temperature t_{oxi}.
2. The electric valve is opened (the time of opening is connected with the air excess ratio).
3. Gas - in amounts corresponding to the air excess ratio equal to λ =2.0, 1.6, 1.3, 1.1, 1.0, 0.9, 0.8 and 0.7 - is passed into the vessel.
4. An ignition of the mixture occurs in the reaction vessel, which is proved by a rise in the temperature registered on the recorder and by a distinct audible explosion inside the vessel.

2.2. Experimental rigs-CFR

The main task of this research was to test the research technology in conditions similar to actual industrial furnaces and to compare the results obtained at different conditions of combustion (CVB and CFR reactors) (Werle and Wilk, 2010). The tests were performed on a special stand (Fig. 2), consisting of a ceramic chamber (2), heated by heating coils with a total heating power of 1.7 kW. The temperature inside the reaction chamber is controlled by a microprocessor control unit (3) integrated with a thermoelement of the type K. The reactor chamber is provided with rolled stainless steel, a spiral tube (4) with an internal diameter of 4 mm. The oxidizer (atmospheric air: z_{O2}=0.21 and z_{N2}=0.79) taken from the cylinder (1) flows inside the heated pipe and is initially preheated to the pre-set temperature. A stream of gas from the cylinder (1) at room temperature in an amount equal to that predicted and at a controlled value for the equivalence ratio is supplied into the hot flowing oxidizer.

Ignition (and the flame (5)) and the increment of the temperature recorded on a digital recorder (6) are observed.

The temperature of the mixture after its reaction is measured using two thermoelements type K, situated on both sides of the injection point connected with a digital recorder (6). The final value of the increment of temperature is the result of the arithmetic mean taken from the two thermocouples.

2.3. Definition of main parameters

The increment of temperature ΔT, ignition delay time τ', volumetric fraction of oxygen in the oxidizer z_{O2} and type of the gas are parameters characterizing the process of ignition under conditions of superheating of oxidizer. These parameters are the function of air excess ratio λ and the temperature of the oxidizer t_{oxi}. Figure 3 provides an example of the increment of temperature ΔT and the way of determining the ignition delay time τ' (Werle and Wilk, 2008). Similar diagrams have been plotted for other temperatures of oxidizers t_{oxi} as well as for other values of air excess ratio λ. Point A is interpreted as the moment of the gas injection (the moment of the opening of the electric valve) and the start of ignition (beginning of the process). The height between point A and the point B is determined as the increment of temperature ΔT. The time from the moment of opening the electric valve (point A) to the achievement of the maximum temperature (point B) is called the ignition delay time τ'. The maximum value of standard deviation of the increment of temperature ΔT is equal to $\sigma_{\Delta T}$=6.22K and the ignition delay time τ' is equal to $\sigma_{\tau'}$=0.017s. The signals from thermocouples were collected every 0.001 s. The oxidizer temperature t_{oxi} was measured with an enlarged uncertainty equal to δt_{oxi}=2K. The temperature inside the reaction chamber (after gas injection) was measured with an uncertainty equal to δT=1.2K. The error of calculations of the air excess ratio $\delta\lambda$ was equal to $\delta\lambda$ =0.02%.
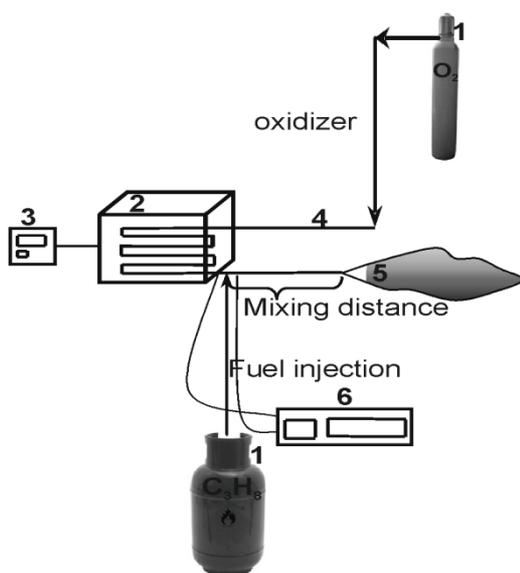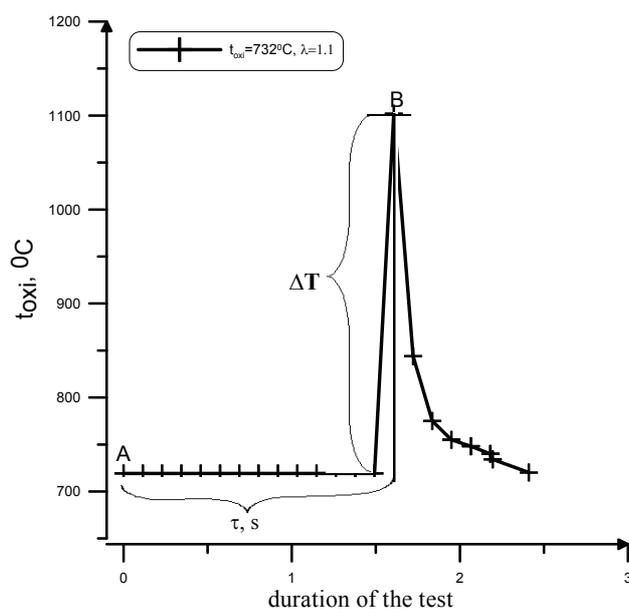

Figure 2. Scheme of co-flow reactor (CFR), 1, fuel/oxidizer cylinders, 2, reactor chamber, 3, microprocessor control unit, 4, stainless steel, spiral tube, 5, flame, 6, digital recorder.

Figure 3. Example of the increment of the temperature ΔT and the ignition delay time τ, as a function of the duration of the test; methane; t_{oxi}=732⁰C; λ=1.1.

3. Results

Figure 4 illustrates the dependence of the increment of temperature ΔT as a function of the air excess ratio for various values of volumetric composition of oxidizer (both for methane and propane). Four cases are presented in this Figure – the results with four different values of volumetric fraction of oxygen in superheated oxidizer. There are only two examples ($t_{oxi}=861^0C$ in the case of methane and $t_{oxi}=660^0C$ in the case of propane) but similar diagrams have been plotted for other temperatures of oxidizers for both gases. The highest values of the increment of temperature are for an interval of air excess ratio equal to $\lambda=1.0-1.1$. It is well known that most combustion properties have simple maxima or minima in the neighborhood of $\lambda=1$. On the one hand, it was ascertained that the highest values of ΔT were achieved for the test with volumetric fraction of oxygen equal to
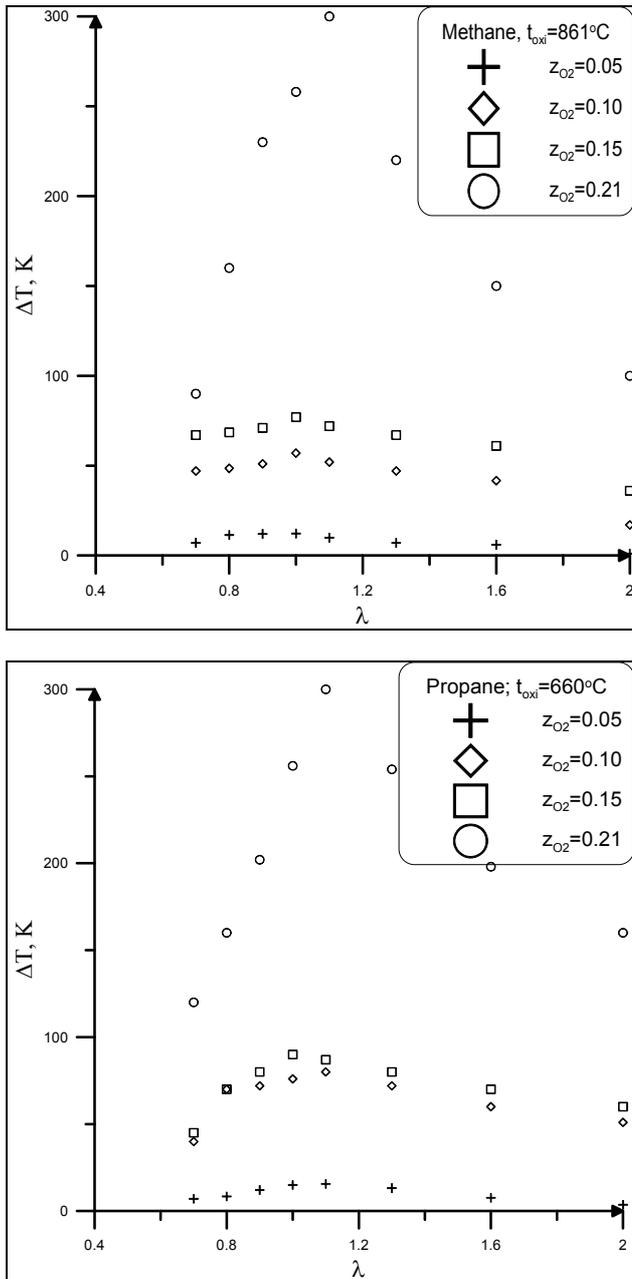
$z_{O2}=0.21$ and on the other hand, the lowest values of ΔT were for $z_{O2}=0.05$. This is caused by the low concentration of oxygen and high level of mixture dilution. It is worth pointing that, irrespective of the volumetric composition of oxidizer, the ignition reaction always takes place. Irrespective of considered cases, there is an interval of air excess ratio ($\lambda=1.0-1.1$) in which the increment of temperature reaches its maximum. Above the value of air excess ratio in which the increment of temperature reaches it's maximum, this parameter is decreasing due to smaller level of gas density at constant pressure (in a chamber with a security hole so it is not hermetic).

Figure 5 illustrates the dependence of the increment of temperature ΔT as a function of the initial oxidizer temperature t_{oxi} for various volumetric compositions of oxidizer. There are only two examples – for $\lambda=1.0$ for both gases. The same dependences have been tested for remaining values of air excess ratio λ.
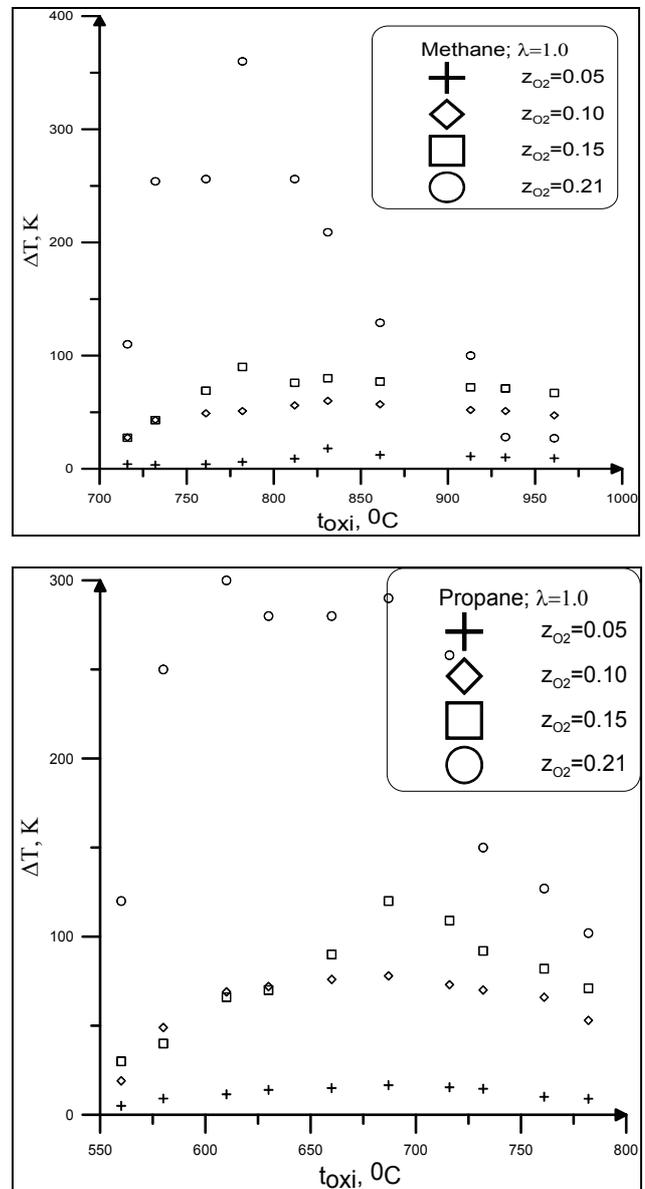

Figure 4. Dependence of the increment of the temperature ΔT as a function of the air excess ratio λ for various volumetric compositions of oxidizer; methane and propane.

Figure 5. Dependence of the increment of the temperature ΔT as a function of the air temperature t_{oxi} for various volumetric composition of oxidizer; methane and propane.

There is an interval of the oxidizer temperature (in the case of methane $t_{oxi} \approx 780\text{-}850^{o}C$ and in the case of propane $t_{oxi} \approx 630\text{-}680^{o}C$), in which the increment of temperature reaches its maximum. And, similar to the Figure 4, the highest values of ΔT are for volumetric fraction of oxygen equal to $z_{O2}=0.21$ and the lowest for $z_{O2}=0.05$. The difference between those maximum values is quite high. Nevertheless, irrespective of the considered cases, a clear ignition effect was achieved. It can be observed that with the growth of the oxidizer temperature t_{oxi} the reaction rate and frequency of particle collision are increasing. It is connected with the Arrhenius equation. It is well known that an increase of the temperature causes an increase in the velocity of particles. As a result, the number of particles collisions (and probability of the reaction) also increases. Above the value of t_{oxi} in which $\Delta T = \Delta T_{max}$ this parameter decreases due to a lower level of concentration (density) of the reacting gases at constant pressures (chamber is not hermetic). It may be concluded that despite the fact that the increment of the oxidizer temperature favors the reaction rate, the decrease in the gas density is much more intensive.

The next Figure (Fig. 6) illustrates the dependence of the ignition delay τ' as a function of the air excess ratio λ for various volumetric compositions of oxygen in the preheated oxidizer. The ignition delay time τ' depends
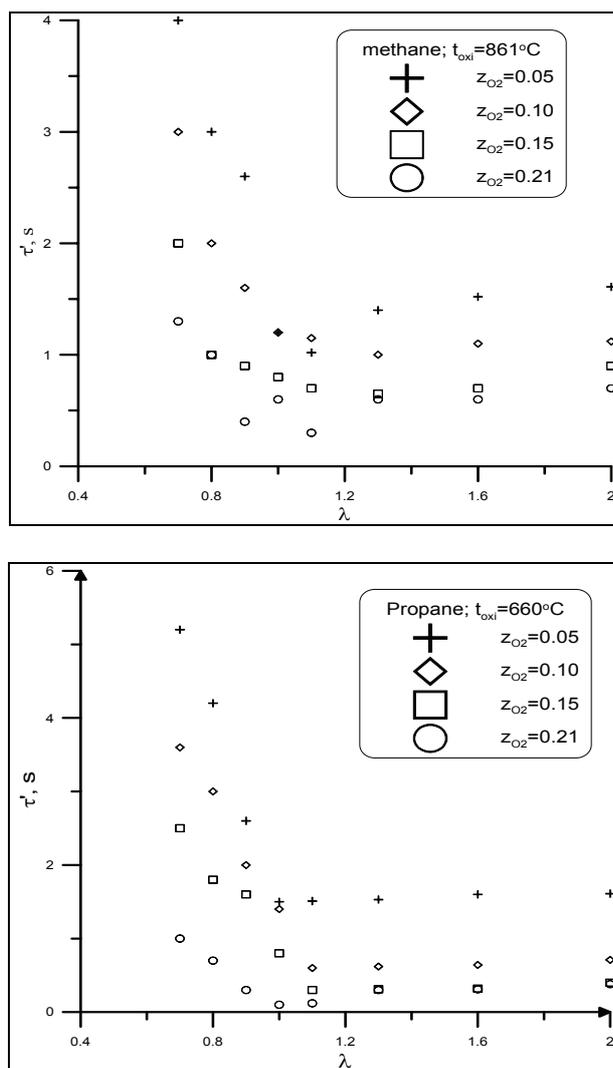

Figure 6. Dependence of the ignition delay time τ', as a function of the air excess ratio λ for various volumetric composition of oxidizer; methane and propane.

parbolically on air excess ratio λ. It can be observed in this figure that it decreases with growth of air excess ratio. The lowest measured values of the ignition delay parbolically on air excess ratio λ. It can be observed in this figure that it decreases with growth of air excess ratio. The lowest measured values of the ignition delay time are observed-independently of considered cases-for the air excess ratio equal to $\lambda=1.0\text{-}1.1$. Analyzing these diagrams, it has been noticed that the lowest values of the ignition delay time τ' are for tests with volumetric fraction of oxygen in the oxidizer equal to $z_{O2}=0.21$, but it is very important that the differences between the values of $z_{O2}=0.21$, $z_{O2}=0.15$ and $z_{O2}=0.10$ are not as strong as in the case of $\Delta T=f(t_{oxi})$ (Fig.5). It is probably caused by comparable values of reaction rate in these three cases. In the case of propane, the ignition delay time is a little bit lower than it is for methane. It is connected probably with the reactivity of propane, which is characterized by, for example, a much lower autoignition temperature and more complex molecule structure in comparison with methane.

It can be noticed in Fig. 6, that in the case of lean mixtures $(\lambda>1)$, alkanes are inhibitors of the ignition reaction due to the important rerouting of hydrogen atoms from the chain branching reaction. This feature is predominating over ignition, so the ignition delay time increases with the growth of λ. In the case of rich mixtures $(\lambda<1)$ rarely occurring collisions between oxidizing and reducing species limit the rerouting of hydrogen atoms (favorable factor). Here alkanes behave like promoters of their own ignition. In this case, the ignition delay time decreases with the growth of λ. For values λ in which τ_{ig} reaches its minimum, there is a balance between the amount of reactive radicals and poorly reactive hydrogen atoms.

Figure 7 illustrates the dependence of the ignition delay time τ' as a function of the oxidizer temperature t_{oxi}. There is an interval of the oxidizer temperature (in the case of methane $t_{oxi}=850\text{-}890^{o}C$ and in the case of propane $t_{oxi}=650\text{-}675^{o}C$) in which the ignition delay time reaches its minimum. Above this interval, it is observed a growth of the ignition delay time τ'. It is caused mainly due to smaller level of gas density (concentration) in constant pressure condition (reaction chamber with security hole). Analyzing these diagrams it has also been found that the lowest values of the ignition delay time τ' are for tests with the volumetric fraction of oxygen in the oxidizer equal to 0.21, and also differences between the values of the ignition delay for $z_{O2}=0.21$, $z_{O2}=0.15$ and $z_{O2}=0.10$ are rather low.

3.1 CVB versus CFR reactor

Comparison between some results achieved in CVB reactor and CFR were presented in Fig. 8. As mentioned in the experimental matrix, propane as a fuel was investigated. A wide interval of air preheating temperature t_{oxi} was investigated. Analyzing this figure, it can be seen that the increment of temperature for CFR reactor is higher than in CVB due to a higher level of homogeneity of the mixture. It is observed in the Figure that it is possible to compare results achieved in CVB and CFR reactor and confirms the similar tendency of the interdependence between increment temperature ΔT and air excess ratio λ.
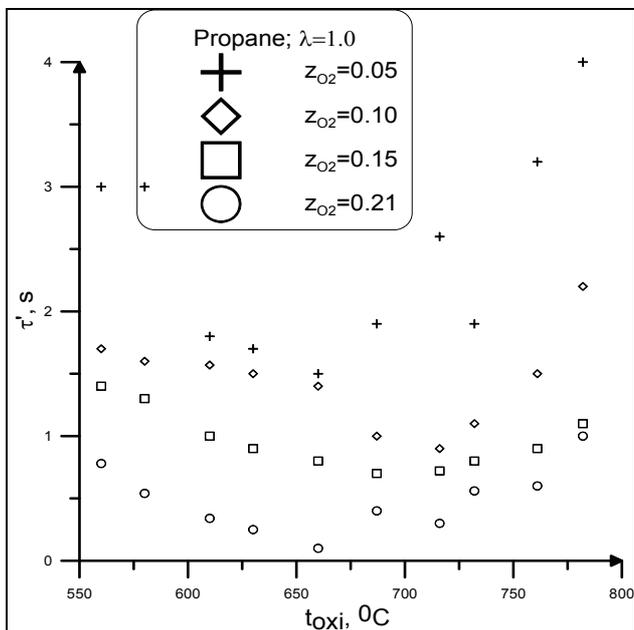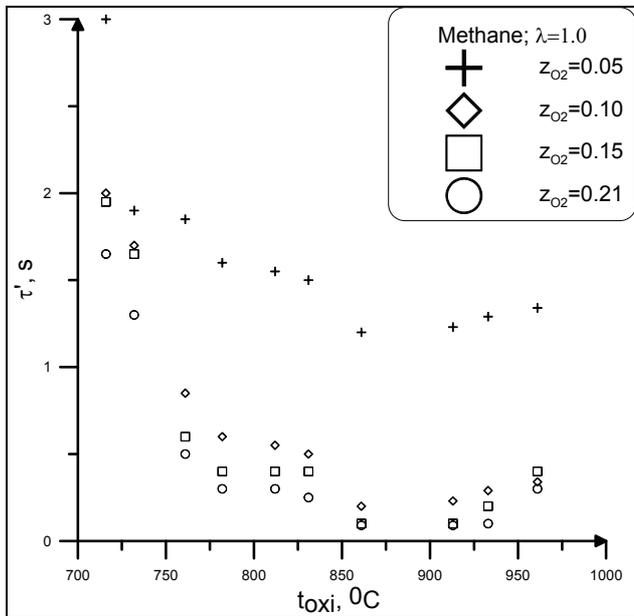
Figure 8. Comparison of the results for CVB and CFR reactor.

intensity of mixing and other factors. However, experiment in CFR reactor gives possibility to say that it is probably possible to transfer results from CVB reactor into real installations.

Nomenclature
t , T   Temperature [^{0}C], [K],
z   Molar/volumetric fraction of gas.

Greek letters:
δ Uncertainty of measurement,
σ Standard deviation,
λ Air excess ratio,
Δ Increment,
φ Equivalence ratio,
τ '   Ignition delay time [s].

Subscripts
au   Autoignition,
ig   Ignition,
oxi   For oxidizer,
max   Maximum,
min   Minimum.

Figure 7. Dependence of the ignition delay time τ', as a function of the oxidizer temperature for various volumetric compositions of oxidizer; methane and propane.

4. Conclusion

In order to achieve the minimum ignition delay time τ' (the maximum reaction rate) and the maximum of increment of temperature ΔT, the oxidizer has to be preheated to a temperature t_{oxi} about 780-890°C (in the case of methane) and 630-680°C (in the case of propane). It seems that preheating of the oxidizer above this interval is unsubstantiated. Additionally, it is important to keep the interval of air excess ratio approximately equal to 1.0-1.1.

Beyond this interval of t_{oxi} and λ in which τ'$\rightarrow$min and $\Delta T \rightarrow$max, analyzed parameters are going to increase (τ') or to decrease (ΔT). It is mainly caused by the smaller level of gas concentration in constant pressure conditions

The optimum value of the oxidizer temperature is probably a function of the combustion chamber type, the
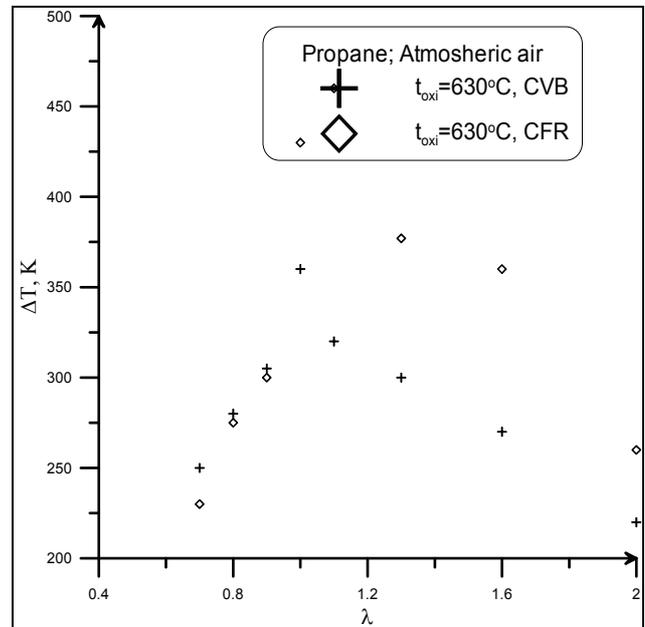
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