





THESIS WORK

# FOR DUAL MASTER'S DEGREE

# ITBA Mag. in Energy and Environment

KIT M.Sc. in Mechanical Engineering

# EXPERIMENTAL INVESTIGATION OF THE COMBUSTION PROPERTIES OF CO2 DILUTED CO-O2 MIXTURES WITH VARIATION OF INITIAL TEMPERATURE AND PRESSURE

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> Karlsruhe 15/03/2022

# Declaration of self-employment

I, Eugenio Torres de Ritter, hereby declare that I have written this thesis independently and without external help. Only the sources explicitly stated in the thesis have been used. I assure that all texts in which the ideas of others have been taken over, either literally or in essence, have been marked as such.

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Karlsruhe, March 15th

# Acknowledgments

I would like to express my gratitude to the people who guided and supported me throughout the time I worked on this thesis, whose encouragement and inspiration allowed me to complete one more step in my professional life in times of adversity.

To Dr. Cecilia Smoglie at ITBA Institute in Buenos Aires and Dr. Ferdinand Schmidt at KIT.

To my thesis supervisors Prof. Dr. Thomas Jordan and Prof. Dr. Thomas Schulenberg.

To Anke, Andreas and Mike, who helped me in countless occasions with dedication and patience.

To the technicians and researchers in KIT-ITES institute, who have collaborated so attentively with me. Especially to Matthias and Jeremi for their immense help.

To my colleagues, Federico, Macarena and Juan.

And most especially, to my family and friends.

# Table of Contents

Declaration of self-employment	1
Acknowledgments	2
Abstract	5
Nomenclature	6
1. Introduction	8
2. Theoretical Background	12
2.1 Theory of Carbon Monoxide combustion	12
2.2 Laminar Burning Velocity	14
2.3 Constant Volume Bomb Method	18
3. Experimental Setup and Procedure	20
3.1 Experimental Layout	20
3.1.1 Explosion bomb	21
3.1.2 CO/O <sub>2</sub> /CO <sub>2</sub> intake and exhaust system	21
3.1.3 Ignition System	22
3.1.4 Optical system	23
3.1.5 Data acquisition and control system	25
3.1.6 Heating system	30
3.2 Experimental Matrix	32
3.3 Experimental Procedure	34
4. Results and Discussion	36
4.1 Flame speed through optical results	36
4.1.1 Optical Visualization	36
4.1.2 Optical Method	47
4.1.3 Numerical Results of Visual Method	52
4.2 Flame speed through pressure analysis	55
4.2.1 Constant Volume Bomb Method	55
4.2.2 Numerical Results of Constant Volume Bomb Method	56
4.3 Flame speed results comparison	59
4.4 Maximum pressure	65

4.4.1 Reproducibility	65
4.4.2 Obtention of the parameters	67
4.4.3 Maximum pressures	68
4.5 Maximum temperature	72
5. Summary and outlook	77
References	80
List of Figures	82
List of Tables	87
Appendix	88
Appendix: Video Recording Distance Calibration	88
Appendix: Standard Error Calculation	91
Appendix: CANTERA Simulation for Constant Volume Bomb Method	93

# Abstract

With the increasing relevance of energy transition, synthetic fuels have arisen as an alternative to storage green energy. In the processing of this fuels, carbon monoxide is widely used. Understanding the behaviour of the combustion of this gas is of high importance. To date, very limited knowledge is available on how combustion of carbon monoxide behaves alone or diluted with carbon dioxide as much focus were given towards mixtures that included hydrogen and water. The focus of this work is to investigate the combustion of carbon monoxide in dry ambient and characterize the flame speed of the combustion through two different methods, the Shadowgraph Method and the Constant Volume Bomb Method.

For this purpose, combustion experiments in an explosion bomb were conducted. An experimental matrix of nine different initial pressures-temperature combinations and five different mixtures of  $CO-O_2-CO_2$  were tested.

# Nomenclature

Symbol	Unit	Description			
А	m²	Surface area			
B <sub>2</sub>	bar/s <sup>3</sup>	Polynomial coefficient of the correlation of the experimental pressure-time history			
Cp	kJ/kgK	Specific heat capacity at constant pressure			
Cv	kJ/kgK	Specific heat capacity at constant volume			
К	1/s	Stretch rate			
L <sub>M</sub>	m	Markstein length			
Р	bar	Pressure			
Pini		Initial pressure			
R		Internal radius of the explosion chamber			
r <sub>b</sub>	m	Instantaneous flame radius or burnt gas radius			
r <sub>o</sub>		Ignition position			
SL	m/s	aminar burning velocity			
$S_{L,s}$		Stretch-free laminar burning velocity			
S <sub>s</sub>		Visible flame front velocity			
Tini	°C	Initial Temperature			
$T_{b}$		emperature of burnt gas			
T <sub>u</sub>		Temperature of unburnt gas			
u <sub>b</sub>	m/s	Velocity of burnt gas			
uL		Flame velocity			
u <sub>u</sub>		Velocity of unburnt gas			
α	m²/s	Thermal diffusivity			
δ	m	Flame front thickness			
γ <sub>b</sub>	-	Specific heat ratio for the burnt gas			
γu	-	Specific heat ratio for the unburnt gas			
К	W/m²K	Thermal conductivity			
ρ <sub>b</sub>		Density of burnt gas			

Ρ <sub>u</sub>	kg/m³	Density of unburnt gas fuel			
σ	-	Expansion factor			
$\tau_{b}$	S	Characteristic reaction time			

# 1. Introduction

The usage of fuels throughout history has been continuously increasing. This progressed to the point that today-world's activity is mainly based on fossil fuels as a source of primary energy and as an energy carrier. Although fossil fuels are a finite and scarce resource, the demand for them has increased with the constant increasing necessity of energy. In addition, and not less important, greenhouse gas (GHG) emissions produced from fossil fuel combustion present a serious and increasing global environmental problem [1]. Figure 1 shows the increasing  $CO_2$  emissions through historical records.



Figure 1 Global mean annual concentration of carbon dioxide in atmosphere [2]

As a consequence of the increased GHG presence in the atmosphere, the global average temperature is estimated to increase by more than 3 °C by 2050 (compared to 2013), which will cause unavoidable climate change and have considerable economic and social impacts [3].

To mitigate the effects of GHG emissions, research and developing technologies that utilize alternative and carbon-free energy resources have been intensified in the last decades.

Among the renewable energy sources (RESs) those that produce electricity and with current bigger exploitation are solar and wind power. As disadvantage, they are characterized by intermittency, with a consequent mismatch between production and demand. This forces to find an energy storage solution [4].

One of the most promising systems for storing large quantities of energy over long time periods seems to be the conversion of the RESs surplus of electricity into hydrogen by means of the electrolysis process. Also, in a second step, hydrogen can be transformed into fuels (e.g., methane). These processes are called power-to-fuel, which consist of obtaining synthetically

produced fuels using the surplus that may exist in the RESs and using sustainable carbon sources.

Other options using the power-to-fuel concept are being investigated and developed to generate alternative fuels that are useful in the transition to clean energy sources.

In this way, research is focused on replacing fossil fuels with zero carbon footprint fuels. One of the advantages of these fuels is that they do not increase  $CO_2$  presence in the atmosphere and at the same time maintain the infrastructure already in place for various industries (e.g., transportation).

One of the strategies being investigated is to capture  $CO_2$  directly from the air in the atmosphere and then convert it, together with hydrogen, into a fuel that releases the same amount of  $CO_2$  molecules to the ambient when burnt [5].

Following this direction, the KEROGREEN Project studies fuel for the aviation sector since it is a difficult sector to decarbonize due to the high energy density requirements of aircrafts. The main goal of the project is to produce green kerosene, synthesized from air and water, powered by renewable electricity and recapturing the carbon emitted from the atmosphere, creating a closed carbon fuel cycle [6].

One of the advantages of this would be that existing infrastructure for storage, transport, filling of aircraft and jet engine technology can be kept unchanged. The conversion route is based on plasma-driven dissociation of air captured CO<sub>2</sub>, solid oxide membrane oxygen separation, and Fischer-Tropsch (F-T) kerosene synthesis. In Figure 2 a flow diagram of this cycle is shown.



Figure 2 Flow diagram of the kerosene production cycle with power-to-fuel process, proposed by Kerogreen [6].

The plasma serves to split  $CO_2$  into CO and  $O_2$  at high conversion ratio by employing microwave technology [7].

$$2 CO_2 \rightarrow 2 CO + O_2$$
 ( $\Delta H^\circ = 282,97 \, kJ/mol$ ) (1)

The emerging gas mixture of the reaction (equation (1)) is then purified to CO by a Pressure Swing Adsorption unit. Then part of the CO stream is diverted to a Water Gas Shift reactor to produce  $H_2$  (equation (2)) and then  $H_2$  is mixed with the remaining CO stream, forming synthesis- or syngas. Syngas serves as the starting point for the kerosene synthesis based on the Fischer-Tropsch reaction (equation (3)).

Watergas-Shift-Reaction (WSR) to obtain H<sub>2</sub>[8]

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H^\circ = -41.2 \text{ kJ/mol})$$
 (2)

Fischer-Tropsch (F-T) used for kerosene synthesis [9]

$$n CO + 2n H_2 \rightarrow (CH_2)n + n H_2O$$
 ( $\Delta H^\circ = -164,96 \text{ kJ/mol}$ ) (3)

Kerosene is the fraction of crude oil composed of several hydrocarbons  $C_{12}H_{26} - C_{15}H_{32}$  (ASTM aviation standard).

As shown above, one of the main reactants involved in this process is carbon monoxide. However, there is little information about its reactivity in the presence of oxygen and the most recent studies on the subject, conducted with air and  $N_2$  mixtures, date back from the 1960s [10] and 1970s [11]. In order to provide information on the dissociation, it was decided to study the inverse reaction to equation (1), the combustion of carbon monoxide.

Therefore, the purpose of the present work is to experimentally investigate the combustion behavior of carbon monoxide using the explosion bomb facility present in the ITES-KIT laboratory. For this purpose, the combustion of carbon monoxide was carried out using a  $CO+O_2$  mixture in stoichiometric ratio with  $CO_2$  as diluent. To observe influences in laminar flame speed and flammability limits, the experiments were performed with different mixture compositions, in particular with regard to the different concentration, and under variation of the

initial pressure and temperature. The combustion reaction was visualized by the shadowgraph method using a high-speed camera. In parallel the analysis was also performed with pressure measurements implementing the Constant Volume Bomb Method.

It should be noted that since these experiments have no precedents, it is not possible to compare them with the literature. Instead, some theoretical calculations were carried out to obtain parameters for comparison.

# 2. Theoretical Background

In this chapter, an introductory theory about CO combustion is described. In addition, the theory of flame acceleration and burning phenomena with its characteristic parameters are explained. To finalize one of the used methods to calculate the laminar flame speed, the "Explosion Bomb" method, is presented.

## 2.1 Theory of Carbon Monoxide combustion

Combustion is a chemical reaction that occurs between a fuel and an oxidizing agent that produces energy, usually in the form of heat and light. Combustion is considered an exothermic chemical reaction. In the current work fuel is carbon monoxide and the oxidizer is oxygen. The ignition source can be a spark, a flame, or a hot surface. In this work only sparks are used.

Regarding the autoignition temperature, which is the minimum temperature at which the substance would burn without external ignition source, carbon monoxide presents a relatively high temperature of 605°C.

Another characteristic to be considered is the minimum ignition energy (MIE). The MIE is defined as the minimum electrical energy stored that, when discharged, is sufficient to ignite the most ignitable mixture of fuel and air under specified test conditions [12]. In case of the CO the MIE is less than 0.3 mJ [13]. To put this in perspective the MIE of petrol, methane, ethane, propane, butane, and benzene are usually in the order of 0.1 mJ [14] and in the case of hydrogen around 0.019 mJ [15]. This means that CO is less ignitable than the above-mentioned components.

Regarding flammability limits, carbon monoxide shows a lower limit of 12.5% (vol) and an upper limit of 74.2% (vol) in air at 20°C and 1bar [16].

Considering that air is formed of 20,95% (vol) of oxygen and that the rest of the components as nitrogen or argon are non-reactive gases and taking in consideration as dilutant all species out of the stoichiometric reaction of CO, then the maximum dilution for flammable stoichiometric  $CO/O_2$  mixtures would be approximately 74,96% (vol).

#### CO combustion process

The mechanism related to the burning of CO is still not conclusively determined [17]. Some authors suggested steps involving chain carriers, oxygen atoms and electronically excited carbon dioxide ( $CO_2^*$ ) [18], but this was refuted in later experimentation [10]. Despite the fact

that the high influence that water and hydrogen presence has in the burning mechanism was largely tested, no dry burning mechanism was conclusively proved [18].

Taking in consideration the above mentioned, the mechanism for the burning of hydrogen-free mixtures of carbon monoxide and oxygen was proposed as it is shown in Figure 3, but it requires further research. It was proposed that burning initiates through nearly thermoneutral reaction and then continues with thermal releasing steps. "M" refers to a third body species.

$$co + o_2 \xrightarrow{k_i} co_2 + o$$

with subsequent heat release due to

$$O + CO + M \rightarrow CO_2 + M$$

 $O + O + M \rightarrow O_2 + M$ 

and

#### Figure 3 Postulated reaction mechanism for hydrogen-free CO burning [10]

For the purpose of this work, the CO burning mechanism was simulated with Cantera Software. Using the library GRI-30 the same steps showed in Figure 3 were found and an extra step (reaction 122). These are shown in the next equations,

Reaction 1, three body reaction,

$$20 + M \leftrightarrow 02 + M \tag{4}$$

Reaction 12, falloff reaction,

$$0 + CO(+M) \leftrightarrow CO2(+M) \tag{5}$$

Reaction 31,

$$02 + CO \leftrightarrow O + CO2 \tag{6}$$

Reaction 122,

$$C + O2 \leftrightarrow O + CO \tag{7}$$

As already mentioned, the reaction is greatly accelerated by water or hydrogen, even in small traces [10]. This represents an extra technical challenge when it comes to dry experimentation.

Regarding former experiments about CO burning, they were conducted around the first half of 20th century and dry combustion conditions was not easy to be achieved [10].

The net reaction of CO combustion, which is in fact the reverse of equation (1), reads as follows.

$$CO(g) + \frac{1}{2}O_2(g) \to CO_2(g) \quad ; \quad \Delta H = -283.0 \ kJ/mol$$
 (8)

As the net enthalpy of the reaction is negative the reaction is defined as exothermic.

#### 2.2 Laminar Burning Velocity

There are two types of combustion regimes for pre-mixed systems: deflagrations and detonations. Deflagrations are subsonic flames propagated by heat release from chemical reactions, while detonations are supersonic combustion phenomena. The laminar-flame theories correspond to deflagrations.

In laminar-flame theory, the main interest is to determine the flame speed (also called burning velocity or flame velocity or normal combustion velocity). The laminar-flame speed is defined as the velocity of the unburnt gases normal to the combustion wave surface while these gases move into the combustion front [19].

The laminar flame speed is only unambiguously defined in a one-dimensional (1D) path. In Figure 4 a freely propagating 1D flame is shown. A fuel-oxidizer mixture enters the system at the unburnt side with velocity  $u_u$ . A flame front of thickness  $\delta$  propagates with constant velocity

 $u_{L}$  in the unburnt mixture. The flame front will remain at a fixed position in space only when the gas velocity  $u_{u}$  equals  $u_{L}$  exactly.



Figure 4 Schematic diagram of stationary one-dimensional flame propagation.

Regarding the physical mechanism of flame propagation, it could be described as follows. The burnt matter has higher temperature than the unburnt gas. This drives heat transference to the cold unburnt mixture. The temperature of the unburnt mixture close to the burnt matter increases. The associated transport of radical starts the reaction in the neighbouring layer and some additional energy is released. The released energy is transported by diffusion to the next pre-mixed layer resulting in propagation of the reaction front. Thus, deflagration is the combustion regime, which is due to heat diffusion, the direct transfer of heat from the burning gas to the fresh fuel-oxygen mixture, which is still unburnt [20].

Flame velocity  $u_{L}$  and thickness of a flame front  $\delta$  may be expressed in the following terms [20]

$$U_L \propto \sqrt{\frac{\kappa}{\tau_b \,\rho_u C_p}} \tag{9}$$

$$\delta = \frac{\kappa}{U_L \rho_u C_p} \tag{10}$$

Being the  $\tau_b$  the characteristic reaction time,  $\kappa$  is the thermal conductivity,  $\rho_u$  is the density and  $C_p$  is the specific heat capacity of the unburnt mixture at constant pressure.

Thermal diffusivity  $\alpha$  is defined as

$$\alpha = \frac{\kappa}{\rho_u C_p} \tag{11}$$

Considering the above-mentioned equations, it could be seen that a smaller reaction time would lead to a faster flame. The same effect occurs with higher thermal diffusivity.

#### Nonplanar configuration

For most configurations the flame front is not planar but curved. Flame surface is very susceptible to non-uniformity and instability leading to a curvature in the flame front. Due to these curvatures, flame front presents stretch effect. The stretch rate (K) is defined as the rate of change of the surface area of the flame (A) with time (t) [21]. For 2-D geometry this could be simplified as shown in equation (12).

$$K = \frac{1}{A}\frac{dA}{dt} = \frac{2}{r_b}\frac{dr_b}{dt}$$
(12)

Where  $r_b$  represents the instantaneous flame radius or burnt gas radius, that is the visible radius and could be obtained from visual recordings.

Another important parameter is the visible flame front velocity  $S_s$ , defined in the equation (13).

$$S_S = \frac{dr_b}{dt} \tag{13}$$

Taking in account equation (12) and (13), then

$$K = \frac{2}{r_b} S_S \tag{14}$$

In Figure 5 a schematic diagram of two-dimensional flame propagation with center ignition is shown. The parameters involved are also presented in the same figure.



Figure 5 Schematic diagram of two-dimensional flame propagation with center ignition [11]

Carbon monoxide combustion is an exothermic process, according to equation (8). Flame front experiments thermal expansion as a result of the expansion of the burnt gases.

Then visible flame front velocity  $S_s$  can be related to the stretched laminar burning velocity  $(S_L)$  relative to the unburnt gas, with a factor that relates to the difference in density. This parameter is the expansion factor ( $\sigma$ ), defined as the ratio of the unburnt gas density to the burnt gas density. These relations are shown in equation

$$S_s = \sigma \cdot S_L \quad ; \quad \sigma = \frac{\rho_u}{\rho_b}$$
 (15)

Also it exists a linear relationship between stretched laminar burning velocity,  $S_L$  and flame stretch rate K [21], as shown in equation (16),

$$S_L = S_{L,S} - L_M K \tag{16}$$

where  $S_{L,s}$  is the unstretched laminar burning velocity and  $L_M$  is the Markstein length, which characterizes influence of stretch effect on flame and indicates stability of the flame.

## 2.3 Constant Volume Bomb Method

The constant-volume bomb method [22] has been chosen as main tool for the experimental measurements of burning velocities in this work jointly with the optical method.

In this method, the combustible mixture is ignited at the center of a rigid spherical vessel, which is about 25 cm. As the flame progresses, the expansion of the burnt gas causes both the pressure and the temperature of the burnt gas to increase because of adiabatic compression. The flame velocity increases continuously from the center towards the wall, caused by the temperature increase [19].

In order to determine the burning velocity via this method, the pressure rise should be measured against time at the initial stage of the spherical flame propagation. Because of this, the pressure variations are very accurately measured in a relatively short time. As a solution for this requirement, two pressure sensors with high- and low-pressure resolution are used. The high resolution to sense the very first part of the pressure variation, and the other to cover the whole range of pressure variation during the experiment.

The dependence which takes into account the adiabatic change of pressure and temperature of the unburnt material [23] was used for the evaluation of the laminar burning velocity ( $S_L$ ) as follows:

$$S_{L} = \frac{S_{s}}{\sigma} \left( 1 + \frac{1}{\gamma_{b}} \frac{B_{2} r_{b}^{3}}{(S_{s}^{3} P_{0} + B_{2} r_{b}^{3})} \right)$$
(17)

where,  $B_2$  is the polynomial coefficient of the correlation of the experimental pressure-time history in the form:

$$p(t) = p_0 + B_2 \cdot t^3 \tag{18}$$

where  $p_0$  is the initial pressure,  $r_b$  is the burnt gas radius,  $\sigma = \rho_u / \rho_b$  is the expansion ratio of unburnt to burnt mixture,  $\gamma_b$ ,  $\gamma_u$  are specific heat ratios for the burnt and unburnt gas (being  $\gamma = Cp/Cv$ ) and  $S_s$  is the visual flame velocity given by (19)

$$S_{S} = \left(\frac{B_{2}}{P_{0}} \left(\frac{\gamma_{b}R^{3} + \frac{\gamma_{u}}{\sigma}r_{b}^{3} - \gamma_{b}r_{b}^{3}}{\left(1 - \frac{1}{\sigma}\right)\gamma_{b} \cdot \gamma_{u}} - r_{b}^{3}\right)\right)^{\frac{1}{3}}$$
(19)

where R is the internal radius of the explosion chamber.

# 3. Experimental Setup and Procedure

In the experimental part of this work the combustion behavior of a stoichiometric CO/Omixtures (ratio 2:1) diluted with CO<sub>2</sub> was investigated. The experiments were performed at different initial pressures, temperatures, and dilutions. As ignition source an electric spark between two electrodes was used. The tests were conducted following the constant-volume bomb method (close spherical bomb) (see section 2.3 Constant Volume Bomb Method) [19]. A shadowgraph method with high-speed video recordings was used as optical method. In total 403 ignition tests were conducted and 152 of these showed effective ignition.

# 3.1 Experimental Layout

Figure 6 shows a photo of the experimental setup.



Figure 6 Experimental set up used to conduct combustion experiments with CO/ O<sub>2</sub>/CO<sub>2</sub> mixtures.

The experimental setup consists of:

- 1. a robust steel vessel inwhere the combustion takes place (explosion bomb)
- 2. CO/O<sub>2</sub>/CO<sub>2</sub> intake and exhaust system
- 3. an ignition system
- 4. optical measurement system with a high-speed camera
- 5. data acquisition and control system
- 6. heating system

### 3.1.1 Explosion bomb

The explosion bomb consists of a stainless-steel vessel with a spherical combustion chamber of 25 cm inner diameter (V=8,2 dm<sup>3</sup>). In the Figure 7 a cutaway view of the vessel and its additaments is shown.



Figure 7 Schematic cut of the explosion bomb [21]

The combustion phenomena inside the vessel can be recorded through two optical windows, as shown in Figure 7. These optical windows are made of single cylindrical piece of quartz (visible window size of 50 mm diameter) and are located diametrical opposite to each other, pointing towards the center of the bomb.

The bomb is also equipped with two ports for pressure sensors and two thermocouples to record pressure and temperature during the combustion process. Two separate ports are used for filling and evacuation of the bomb. Additionally, through two threaded ports the ignition electrodes, made from modified spark plugs, were positioned in the bomb.

The shape and dimensions of the bomb were chosen in accordance with the German Standard pnEN1839(B) for the flammability tests [21].

## $3.1.2 \text{ CO/O}_2/\text{CO}_2$ intake and exhaust system

The inlet and outlet of the vessel are highlighted in Figure 8. The procedure for filling and emptying the vessel is described in section 3.3 Experimental Procedure.



Figure 8 Inlet and outlet of the vessel in the upper part, highlighted in red.

To feed the vessel with the test mixture the pre-existing piping had to be adapted. Prior to this work the facility was used to test other mixtures and so additional flow controllers were installed, together with several pipes and valves. Also, due to the toxicity of CO, all pipes, valves and connection were leak-tested several times

The gas components used as filling where CO (purity 99,97%),  $O_2$  (purity 99,998%) and  $CO_2$  (purity 99,995%) from gas cylinder. The pressure regulators of all gas bundles were set to 10 bar for filling.

Observation: To guarantee safety in handling of CO, wearable carbon monoxide alarms with thresholds at 30ppm were always used (Gaswarngerät BW-Clip). Also, static CO detectors (Ei208 CO) were installed in the roof of the test facility and in the cabinet where CO tank was stored. Additionally, all the facility and gas analyzers were evacuated after experiments and an exhaust fan was used in the room where the experiments were conducted.

### 3.1.3 Ignition System

All test mixtures were ignited using an electric spark. The ignition device used to generate the spark is based on modified spark producer, that is fed by a power supply with direct current (between 5 and 10 A) and low voltage (between 10 and 32 V), which is transformed into high frequency alternate current with high voltage. The device can deliver 60 kV at a frequency of 20 kHz.

The ignition device is connected to the vessel through two spark plugs to avoid a short circuit through the steel wall of the explosion bomb. Spark plugs of type NGK BR8ES and BOSCH WR3CC were used.

The spark plugs were extended with electrodes to the center of the vessel. Due to the design of the facility the electrodes meet in an angle of 90°, with the gap between them being positioned in the center of the spherical combustion chamber. The electrodes were made with a TIG welding electrode for stainless steel (316L), that could work continuously without melting.

To avoid sparks between the vessel and the spark plug electrodes, the electrodes were wrapped in an electrical insulator fabricated from glass fiber, as shown in Figure 9. The rolled fiber glass works as electrical insulator and showed good performance in withstanding the temperatures of the combustion tests.



Figure 9 Spark plug and welded electrode fabricated for the experiments.

The spark ignition was activated by a 'trigger' signal that was provided by a relay and a battery of 4.5 V. This allowed to produce sparks with a minimum duration of 10 ms that was the selected duration by default.

## 3.1.4 Optical system

To investigate the early stage of the combustion process, a high-speed shadowgraph set-up using the optical access to the combustion chamber via two quartz glass windows was installed. In the tests a high-speed camera of type Photron FASTCAM-SA1.1 was used (see Figure 10). The frame rate of the high-speed camera was set to 12000 frames/s for all experiments.



Figure 10 High speed camera, Photron FASTACAM-SA1.1

In addition to the high-speed camera, the optical experimental set-up included a light source and a lens array, as shown in Figure 11. The light source of LED basis was developed in house by ITES-KIT staff.



Figure 11 High-speed camera in shadowgraph configuration with lens array (highlighted in red) and LED-based lamp developed by ITES-KIT staff (green and right).

Lens 1 of the lens array was used to focus the image on the sensor of the high speed camara, while lens 2 was used to provide parallel light beams in between the two lenses. In addition, the lens of the high-speed camera was used to focus on the ignition position which is located in the plane of the tips of the electrodes. The configuration used for the shadowgraph technique is shown schematically in Figure 12.



Figure 12 Scheme of the configuration used for shadowgraph video recordings.

### 3.1.5 Data acquisition and control system

To sense the initial conditions of every experiment, pressure, temperature, and gas concentration sensors were used inside and outside the explosion bomb. To control the settings of the facility, heating controllers and valves in combination with flow controllers were used. Different software systems (Signal Express, LabView, FLowView, IMTEC) were used to manage the valves, flow controllers, and to read and record the measured data.

#### 3.1.5.1 Thermocouples inside the bomb

Inside the explosion bomb NiCr-Ni thermocouples (Type K) with a diameter of 1 mm were used. The thermocouples were positioned in different distances to the bomb wall (see Figure 13). Relatively thick thermocouples had to be used to allow them to withstand the high temperatures of the tests despite the negative effect of the thickness on the response time. Anyway, several of the longer thermocouples suffered melting during high temperature combustion tests and had to be replaced.



Figure 13 NiCr-Ni (type k) thermocouples (1 mm), of different length as used in the bomb

The thermocouple signals were recorded via Signal Express, at a frequency of 100 Hz.

### 3.1.5.2 Pressure gauges

During combustion, the signals from two fast pressure gauges connected via short tubes to the explosion bomb were recorded simultaneously with a fast data acquisition card (IMTEC, T112-8) at a frequency of 100 kHz. One pressure sensor (P1, PCB, type 113B28, measurement range 0 -3.5 bar) is used to measure the pressure rise in detail in the very first part of the combustion process inside the bomb.

The second sensor (P2, PCB, type 113B26, measurement range 0 - 35 bar) is used to record the overall pressure behavior during the combustion and to capture the maximum pressure reached in the experiment.

The linearity of both sensors is  $\pm 1\%$  of the full-scale range, according to manufacturer.

Figure 14 shows the position of the two pressure sensors at the bomb already equipped with heating cover.



Figure 14 PCB pressure sensors P1 and P2, highlighted in red at the bomb equipped with heating cover. Also displayed is the air-cooling system surrounding each sensor (yellow dash line).

The pressure sensors could withstand pressures up to 68 bar (P1) and 680 bar (P2) as maximum pressure [24] but in all experiments performed maximum pressures below 68 bar were expected according to theoretical assessments.

Another issue is the maximum temperature of 135 °C allowed for both pressure sensors. Since initial temperatures of up to 300 °C were planned for the test matrix, the sensors had to be separated from the facility by thin tubes. Furthermore, it was necessary to utilize a cooling system, with which flow of pressurized air at ambient temperature was flushed over the sensors during all the tests at elevated temperatures to cool the sensors. The cooling device is shown in Figure 15.



Figure 15 Detail of the air-cooling system for the PCB pressure sensor. The device consists of a pipe with small holes that surround the sensor and flushes it with cool air.

#### 3.1.5.3 Static pressure sensor

Two sensors are used to measure the static pressure during filling and evacuation of the bomb. The first (Jumo dTRANS P30) is used for measuring absolute pressures up to 1.6 bar, with an acceptable pressure of up to 4.6 bar. This sensor is mainly used to measure the low pressures during evacuation. For higher pressures a static pressure sensor, (WIKA S-20, measuring range1 - 9 bar) was used. The two sensors were connected to the pump in a way that they could be chosen depending on the necessity of the pressure to be measured.

#### *3.1.5.4 Thermocouples outside the bomb*

NiCr-Ni (Type K) thermocouples with a diameter of 1 mm were used. Three thermocouples were attached to the outside of the bomb with the aim to sense the temperature of the walls and the heating condition. The signals of these sensors were recorded via Signal Express, at a frequency of 100 Hz.

### 3.1.5.5 Mass flow controllers

The explosion bomb was filled with  $CO-O_2-CO2$  mixtures using three mass flow controllers (Bronkhorst, Series F). All gases were taken from gas bottles that were stored in free field ( $CO_2$  and  $O_2$ ) or in a cabinet with a CO-sensor (CO). The reading and operation of the mass flow controllers was performed using the software FlowView.

### 3.1.5.6 Gas analyzer

To measure the concentration of the three components CO,  $CO_2$  and  $O_2$  in the test mixtures inside the explosion bomb, an NGA 2000 MLT3 gas concentration sensor of Rosemount Analytical (Emerson) was used. In the device an  $O_2$  sensing accessory module from the same series is included.

The MLT3 sensor has an integrated pump, a flow regulator, and a flow meter. The flow rate was kept at point 1 on the flow regulator scale for all measurements since the sensors are sensitive to the flow [25].

The MLT3 pump continuously extracted a part of the gas mixture before the flow entered the explosion bomb. The gas mixture then passed through the various sensors integrated in the MLT3. The device showed the results on a display, which indicated the concentration in volume percentage for each of the gases. The information was also read and recorded via the Signal Express program.

Figure 16 sows that the device is also capable of sensing other gases ( $H_2$ ,  $CH_4$ ,  $H_2O$ ). Because of this, a calibration was needed, to avoid cross sensing. This calibration was done prior to the start of every set of experiments according to manufacturer's manual [25] using  $N_2$  as zeroing gas.

-0.002 0.002 -0.002 0.400 0.06	CH1/CH4 % CH4 CH2/CO % CO CH3/CO2 % CO2 CH3/M20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 CH4/M20 % H20 %	(4) (4) (4) (4) (4)	100 100 100 100	CH1/02/24 0.0003 0 Messbereich:4 Temperatur: 56.6 °C Funktionskontrolle: Nein Wartungsbedarf: Ja oue#3la: Nein	<b>% 02</b>
Auswahi Zustand	Kennung-	Mehr	LCDReset	Anzeige Zustand Menü Ki	anal BasisKal

Figure 16 Display of the Rosemount gas analyzer. The percentages of gases in the measurement flow are shown. Several gases like  $CH_4$ , CO,  $CO_2$ ,  $H_2O$ ,  $H_2$  and  $O_2$  could be detected.

### 3.1.5.7 Data acquisition

The data were recorded with different software systems, which can be summarized as follows:

-The pressure inside the explosion bomb (PCB sensors) and the spark trigger voltage as functions of time were recorded with: IMTEC Software

-The mixture composition as a function of time, from MLT3 sensors: Signal Express

-Temperature inside the bomb as a function of time, from inside thermocouples: Signal Express.

-Temperature on the outer walls of the bomb as a function of time, form outside thermocouples: Signal Express.

-Static pressure during explosion bomb filling as a function of time (Jumo and Wika pressure sensors): Signal Express.

### 3.1.5.8 Control system

Two main control systems were used to perform the experiments.

The mass flow control allowed to adjust the flow of each mixture component into the bomb. This was done with FlowView software that allows to set the desired values in normal liters per minute for every component.

The other control system was the valve control system. For this purpose, a LabView program interface was generated, that allowed to open and close all valves. Physically this was done remotely by relays that released or closed pressurized air to pneumatic actuators in each valve.

From the point of view of the operator this was done with the interface shown in Figure 17





This interface is a representation of the valves that are installed in the facility and indicates whether a valve is open (green) or closed (red) by color.

Also, the relay that triggers the spark is controlled via the interface, where also the time duration of the spark can be adjusted. This trigger is also connected to the IMTEC data acquisition device that was tuned to start recording 0,15 seconds prior to the trigger for a total recording time of 5 seconds.

In Figure 18 a flow diagram of the valves and the facility is shown.



Figure 18 Flow diagram of the test facility [26].

## 3.1.6 Heating system

In order to perform experiments at higher temperatures, it was necessary to install a heating system to the bomb. This consisted of heating strips (Horst fiberglass coated, thickness 3 mm, resistant up to 900°C) wrapped around the bomb that were controlled via heating regulators, as shown in Figure 19.

The heating power of the strips totaled to 3200 W. A 500 W preheater was also added to the gas inlet pipe.



Figure 19 Explosion bomb wrapped in heating strips, highlighted in blue. Highlighted in red is the inlet duct wrapped in a heating strip to preheat the gases. The Horst heating regulators are highlighted in yellow.

In order to adjust the heating power to the desired temperature, Horst HT-31 temperature regulators were used, in which temperature and power level were manually set. Each temperature controller was connected to a thermocouple (NiCr-Ni, type K, thickness 1 mm) installed on the outer wall of the bomb in the vicinity of the heating stripe to be controlled.

The heating stripes and thermocouples were attached to the explosion bomb with a temperature-resistant fiberglass tape.

To prevent heat loss to the environment and to reduce the hazards due to hot surfaces, a fiberglass wool cover, with an aluminum exterior, insulated the explosion bomb and the inlet pipe which was preheated (see Figure 20).



Figure 20 Explosion bomb and inlet pipe, together with heating strips covered with thermal insulation, made of fiberglass wool and aluminum.

Since the explosion bomb is massive and the windows are made from fragile quartz, it was decided to heat up the system slowly to avoid large temperature gradients with related thermal stresses in the materials before reaching the steady state. Because of this the heating procedure was performed in two stages. In the first stage the facility was warmed up to approximately 50 % of the desired temperature at a level of 40 % of the heating power, while in the second stage the desired temperature was approached with 60-70 % of the heating power.

# 3.2 Experimental Matrix

The experimental matrix comprises an array of three different temperatures and three pressures. This results in nine combinations as show in Table 1

25 °C,1 bar	150 °C ,1 bar	300 °C ,1 bar
25 °C <b>,2</b> bar	150 °C <b>,2</b> bar	300 °C <b>,2</b> bar
25 °C ,5 bar	150 °C ,5 bar	300 °C ,5 bar

Table 1 Experimental matrix: pressure and temperature combinations.

The temperatures used were 25 °C, 150 °C and 300 °C. These values were selected to cover ambient temperature and the highest temperature achievable safely with the existing facility. The temperature of 150 °C was selected as a temperature in between.

The pressures selected were: 1 bar, 2 bar and 5 bar. Again, the criterium adopted was to cover atmospheric pressure (1 bar). Whereas the maximum initial pressure aimed to take into account that the pressure during combustion could reach approximately ten times the initial pressure and damage the facility. Since no experiments with the current mixtures have been performed in this facility before, particular caution had to be taken to avoid cracking the quartz glasses with high pressure and/or high temperature conditions. Finally, the 2 bar pressure was selected as intermediate pressure.

In addition, each of the nine cases of the test matrix was tested for stoichiometric mixtures of  $CO+O_2$  and  $CO_2$  dilutions of 0, 20, 40, 60 and 70 % (vol). In some cases, other concentrations were also tested to check especially the lean mixtures behavior (e.g., 65%,67,5% and 80%). So, in total the matrix has 45 (5X9) combinations, not considering some intermediate and leaner dilutions.

Each of the experiments was repeated at least 3 times, creating a set of 135 combustion tests, not considering extra dilution tests and extra repetitions

Considering the measurement uncertainties for each temperature, pressure and concentration used sensors are shown as follows [27] (Table 2).

Initial Parameters and its standard errors						
Pressure [bar]		Temperature [°C]		Concentration [% vol]		
1,000 ±	0,010	25,0 ±	0,5	0,0 ± 20.0 +	0,5 0,5	
2,000 ±	0,010	150,0 ±	0,5	40,0 ±	0,5	
5,000 ±	0,010	300,0 ±	0,5	70,0 ±	0,5 0,5 0,5	

Table 2 Initial parameters and the corresponding standard errors

## 3.3 Experimental Procedure

Prior to any experiment, the complete facility, including the explosion bomb, is evacuated to remaining pressures of less than 5 mbar with a vacuum pump. For pressure control the Jumo pressure sensor is used.

Then the mixture is produced using pre-calculated mass flows for the three components  $O_2$ , CO and  $CO_2$  to obtain the desired mixture composition. The valves that section the inlet of gases are then open filling part of the system, but keeping the valves that communicate to the bomb, the chimney and the composition analyzer closed. When the pressure in the pipes has reached approx. 1.2 bar, the valve that connects these pipes to the chimney is opened, releasing the mixture to the ambient, in a height of 6 m for safety reasons.

When the flow stabilizes and there is no variation in the flow indicators of the FlowVlew program, the valve that is connected to the gas analysis branch is opened. Afterwards the pump in the gas analyzer is turned on and the mixture composition is analyzed by the sensors for O<sub>2</sub>, CO and CO<sub>2</sub>. If necessary, the flow controllers are re-adjusted. When the desired mixture composition is reached, the pump in the gas analyzer is turned off. Then the valve that is connected to the chimney is/are closed together with the valve that connects the Jumo pressure sensor. Finally, the valves to the explosion bomb are opened and the mixture is conducted into the pre-evacuated explosion bomb.

Then the filling begins and continues up to the desired pressure (1, 2 or 5 bar +/- 0.01 bar). This is measured by the Wika static pressure sensor. When the desired pressure is reached, all the valves in the facility are closed at the same time using an extra button programed for this purpose in LabView interface, and the bomb is ready for ignition.

To ignite the mixture the ignition duration (10 ms by default) is set in the LabView interface (see Figure 17) and the button "trigger" is pressed to initiate the spark.

After the ignition and some seconds of delay time, the burnt mixture is released through the chimney to the ambience. This helps to lower the temperature inside the bomb by expansion. Afterwards, the bomb and the pipe system are evacuated again for the next experiment, using the vacuum pump.

With the method described it is possible to generate mixtures of desired concentration values with a good accuracy. To double check the concentrations, once the bomb was filled, some mixtures were not ignited and evaluated in reverse with the gas analyzer. It was observed that the results were coincident to those measured during the inlet flow. Also, a second CO gas analyzer (S-AGM Plus 3006) was used to check the concentration for this component results

and they were coincident with those obtained with the MLT3 analyzer, being the linearity of the sensor S-AGM  $\pm$ 1% of the full-scale range, according to manufacturer.
# 4. Results and Discussion

# 4.1 Flame speed through optical results

As explained above, high-speed recordings were made of the ignition process and evolving flame of carbon monoxide, oxygen, and carbon dioxide mixtures at different initial conditions. The parameters varied were temperature, pressure, and concentration.

# 4.1.1 Optical Visualization

In the following examples for combustion inside the spherical volume of the explosion bomb the effects of different initial parameters are shown.

### 4.1.1.1 Concentration Variation

The examples for concentration variation were made from the case of initial condition of 150 °C and 1 bar.

In the nomenclature throughout this work, the mixture is referred to in terms of carbon dioxide dilution and it is implicitly left that the rest of the mixture corresponds to  $CO+O_2$  in stoichiometric ratio.

Examples of video captures with the following initial conditions are shown in this section:

- I. 150 °C; 1 bar; 0% CO<sub>2</sub> dilution. Figure 21
- II. 150 °C; 1 bar; 20% CO<sub>2</sub> dilution. Figure 22
- III. 150 °C; 1 bar; 40%  $CO_2$  dilution. Figure 23
- IV. 150 °C; 1 bar; 60% CO<sub>2</sub> dilution. Figure 24 and Figure 25
- V. 150 °C; 1 bar; 65% CO<sub>2</sub> dilution. Figure 26
- VI. 150 °C; 1 bar; 70% CO<sub>2</sub> dilution. Figure 27

The first three cases Figure 21, Figure 22 and Figure 23 show similar behavior. In the three mixtures the flame propagates simultaneously in all directions, forming one quasi spherical shape flame front, that grows from the ignition point (spark).

The images (b), (c) and (d) in Figure 21 show the progression of the burning front. One highlight among these images are the images (f) and specially (g) that show a bright blue light resulting from the combustion. This is coincident with the expectations described in literature [28] [29].



(g) (h) (i) Figure 21: Single frames (extracted) from high-speed movies of the combustion of O<sub>2</sub> + CO (stoichiometric) mixture with 0 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 2, (b) 4, (c) 6, (d) 9, (e) 34, (f) 38, (g) 58, (h) 158 and (i) 350 milliseconds after ignition trigger.

In the case of 20 % CO<sub>2</sub> dilution (Figure 22), the light emitted changes its color due to the initial presence of CO<sub>2</sub>. Also, the light released it is not that intense.



Figure 22: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 20 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 2, (b) 5, (c) 6, (d) 9, (e) 13, (f) 55, (g) 71, (h) 111 and (i) 350 milliseconds after ignition trigger.

In Figure 23, images from a high-speed movie of an experiment with 40% CO<sub>2</sub> dilution are shown. It could be observed that the flame front is not that round-shaped at the very beginning, which might be due to the initial influence of the spark and the increasing relative influence of buoyancy. Also, the velocity of the flame front is noticeably lower in comparison with the two previous examples. This could be demonstrated observing images (d) of Figure 21,(e) of Figure 22 and (f) of Figure 23, where the front reaches the edge of the circular window at 9,13, and 25 msec respectively.

In also can be observed a formation of wrinkled structures in the flame when it gets close to the wall. This is shown in images (f) of Figure 21,(g) of Figure 22 and (h) of Figure 23. These wrinkles may be related to the fact that pressure increases as the flame front approaches the

bomb wall [30]. According to Kuznetsov et al. [31] the wrinkles in the flame surface are related to diffusional-thermal instability that also would lead to the acceleration of flame speed. This instability could be evaluated through the sign of the Markstein length,  $L_M$ , included in equation (16). Instability is associated to negative  $L_M$ .



Figure 23: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 3, (b) 4, (c) 7, (d) 13, (e) 17, (f) 25, (g) 138, (h) 175 and (i) 209 milliseconds after ignition trigger.

For dilutions of 60 % and higher it is possible to distinguish a different behavior. This behavior is observed for different initial pressures and temperatures. For instance, an effect of buoyancy is observable. This is related to the density difference between the burnt and the unburnt gas. So, the hot burnt gases move upwards in the vessel. This phenomenon is always present but If buoyancy is larger than combustion velocity the flame lifts up from the ignition source.

Also, with higher dilutions the flame adopts an unpredictable shape and propagates considerably slower than in the experiments with lower dilutions.

In Figure 24 a set of images captured in an experiment with 60% CO<sub>2</sub> dilution is shown. In a first moment an ignition is produced, and the hot gases move upwards to the top of the vessel. 500 ms later, a flame front propagates downwards. This phenomenon can be seen from image (f) to (i). This is coincident with observations in former experiments with lean mixtures of other gases [27].



Figure 24: Single frames (extracted) from high-speed movies of the combustion of  $O_2$  + CO (stoichiometric) mixture with 60 % (% vol) of  $CO_2$  dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 3, (b) 8, (c) 83, (d) 204, (e) 504, (f) 546, (g) 658, (h) 695 and (i) 790 milliseconds after ignition trigger.

In such slow combustions is more difficult and distinguishing the flame boundaries due to weak density gradients [27], as it could be seen in Figure 24.

For this reason, the contrast of the images in the first stages of the combustion was enhanced by image processing. This was also done for the 65% and 70%  $CO_2$  dilution cases, as shown in Figure 25, Figure 26 and Figure 27.

It could be seen that buoyancy and the effect of the spark ignition show more influence in these tests.



Figure 25: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 60 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 3, (b, g) 8, (c, h) 67, (d, i) 83 and (e, j) 204 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment.



Figure 26: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 65 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 4, (b, g) 13, (c, h) 25, (d, i) 89 and (e, j) 126 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment.



Figure 27: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 70 % (% vol) of CO2 dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 4, (b, g) 13, (c, h) 25, (d, i) 67 and (e, j) 101 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment.

For 80% CO<sub>2</sub> dilution no successful ignition was recorded at any initial conditions.

### 4.1.1.2 Pressure Variation

To demonstrate the influence of the initial pressure, the experimental series at an initial temperature of 150 °C with 40%  $CO_2$  dilution was chosen, for initial pressures of 1, 2 and 5 bar.

The examples discussed in this section are the following

- I. 150 °C; 1 bar; 40% CO<sub>2</sub> dilution. Figure 21
- II. 150 °C; 2 bar; 40% CO<sub>2</sub> dilution. Figure 28
- III. 150 °C; 5 bar; 40% CO<sub>2</sub> dilution. Figure 29

The images for case I are already shown in Figure 21, in previous section.

In the images two effects can be observed. It is possible to notice how the shape of the flame loses its quasi-spherical shape as the initial pressure increases. At the same time, also with increasing pressure, more wrinkles develop inside the spherical combustion zone. These wrinkles can be interpreted as different flame fronts possibly resulting from a change in the transport parameters or multiple points of ignition, which is also an indicator of increasing flame instability [27].



(g) (h) (i) Figure 28: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 150 °C and 2 bar. Images taken at (a) 4, (b) 7, (c) 10, (d) 15, (e) 20, (f) 28, (g) 104, (h) 171 and (i) 209 milliseconds after ignition trigger.



Figure 29: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 150 °C and 5 bar. Images taken at (a) 4, (b) 11, (c) 20, (d) 29, (e) 76, (f) 173, (g) 257, (h) 443 and (i) 668 milliseconds after ignition trigger.

Finally, it can also be seen that the higher the initial pressure, the higher the intensity of the light emitted during the combustion, which is an indicator of the higher energy released during the experiment.

#### 4.1.1.3 Temperature Variation

For the discussion of the effect of the initial temperature on the combustion behavior, the series 2 bar initial pressure with 40%  $CO_2$  dilution for initial temperatures of 25, 150 and 300 °C was chosen.

The examples discussed are the following

- I. 25 °C; 2 bar; 40% CO2 dilution. Figure 30
- II. 150 °C; 2 bar; 40% CO2 dilution. Figure 28
- III. 300 °C; 2 bar; 40% CO2 dilution. Figure 31



Figure 30: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 25 °C and 2 bar. Images taken at (a)7, (b) 11, (c) 20, (d) 32, (e) 42, (f) 125, (g) 214, (h) 247 and (i) 276 milliseconds after ignition trigger.

As can be seen from the figures, the influence of the initial temperature is the opposite to the effect observed while increasing pressure, as described in section 4.1.1.2 Pressure Variation, wrinkling and deformations of the quasi-spherical shape of the flame front are observed at lower temperatures. In addition, with higher initial temperature, less light intensity and stronger uniformity of the flame front can be observed.

Additionally, in the video recordings it is observed that convective flows in the vessel increase with temperature.



Figure 31: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 300 °C and 2 bar. Images taken at (a) 3, (b) 7, (c) 15, (d) 21, (e) 29, (f) 137, (g) 202, (h) 216 and (i) 284 milliseconds after ignition trigger.

### 4.1.2 Optical Method

High-speed videos were recorded for all experiments of the test matrix and all the experiments were repeated three times.

The main aim was to obtain the visible flame speed  $S_S$  by discretizing the equation (14). That means that  $S_S$  is derived from,

$$S_s \approx \frac{\Delta r_b}{\Delta t} \tag{20}$$

With rb being radius of the visible flame cell and  $\Delta t$  being the time difference in between two frames of the high speed video. The video camera recording frequency was 12000 frames per second for all cases. The analysis of the images was performed using ImageJ software.

The principle of this type of measurement was to distinguish the flame front and to follow its progress in time. In the following picture the flame front and a magnified section of it are shown.



Figure 32 Single frames (extracted) from high-speed movies of the combustion of a CO/O<sub>2</sub> mixture with 0% CO<sub>2</sub> dilution. Initial conditions of 150°C, 2 bar. On the left the flame front is shown. On the right a magnified section of the flame front (rectangle in red).

As it is shown in Figure 32 the flame front shows a certain width. During the evaluation of the propagation, the center of the bright section of the front was used in all cases. The average width of this region is 6 pixel with the used camara settings, corresponding to  $0.55 \pm 0.05$  mm.

To measure the spatial progression of the flame, front an analysis method was developed. This method had to take into in account that two challenging characteristics might occur in the video recordings: non round shaped cells and movements of the flame center due to buoyancy effects.

As it was shown in the previous section, both phenomena were observed more often in leaner mixtures while non round shapes are propense particularly to occur at higher pressure.

The method developed for this analysis is utilizing a single pixel vertical line in every frame of each high speed video recording. This line was positioned in between the two spark electrodes, aiming to be coincident with the center of the burning cell, as shown in Figure 33.

Then, using the tool for montage in ImageJ (Image/Stacks/Make a Montage), a montage of all the single pixel line was made. This means that every single frame was cropped as a unitary pixel line and then organized into a stack that shows the changes in this single line. This allows to easily relate the pixel in X-axis with time since one pixel corresponds to one frame and each frame represents a 1/12000 part of a second, according to the recording frequency. On the other hand, the distance in Y axis was measured directly from recording and then converted to actual distance through calibration of the images. The calibration was made according to Appendix: Video Recording Distance Calibration, where basically a known distance was recorded and then the number of pixels implied was used as conversion factor.

In the following Figure 33, Figure 34 and Figure 35 the different steps explained above and how they were used for the analysis are shown.



Figure 33 Left: the frame of a video of the combustion cell and in yellow a line that crosses the image, which width equals to one pixel. Right: the video cut (with "Crop" tool) in a line of one pixel width.



Figure 34Left: the selection panel of the tool to perform the montage with ImageJ. An arrangement of columns and rows can be selected. Right: an example, for a stack that is the result of this selection.



Figure 35 The picture shows a stack of images for a CO+O2 combustion with 0% (% vol) dilution CO<sub>2</sub> at initial conditions of 150 C and 5 bar. The yellow dots were manually placed following the progression of the burn front both up and down.

Figure 35 shows a series of points that are manually added to the image stack. These aims are located in the center of the burning flame front. Once they are located the software allows

to make a table of X and Y coordinates for each point. With these coordinates it is possible to calculate  $\Delta Y$  (corresponding to  $\Delta r_b$ ) and  $\Delta X$  (corresponding to  $\Delta t$ ) between points.

Ten points were added to the top of the burning front and ten to the bottom part as shown in Figure 35. Out of these only the six farthest points from the center of ignition were considered for calculation. This allowed to obtain five pairs of  $\Delta X$  and  $\Delta Y$ , to calculate observable velocity. This has to do with the fact that at the first points, closer to the ignition, the influence of the ignition spark is higher and after several frames the flame speed stabilizes, and it is approximately constant for the considered period. The dispersion of the considered measurements was calculated through standard deviation as an indicator of its validity (see

### Appendix: Standard Error Calculation).

It has to be emphasized that in this method, the combustion front points in the records were measured for both, top and bottom position. Since the filming is done parallel to the floor, the cell tends to rise due to buoyancy. Thus, the upper front velocity will be the observable laminar flame velocity plus the buoyancy velocity and the lower front velocity will be the observable velocity minus the buoyancy velocity. Thus, averaging the two velocities mitigates the effect of buoyancy.

Some examples of real images and images stacks for different initial conditions are shown below.





Figure 36 The picture shows a captured image of the video and the montage for a CO+O2 burning at initial conditions of 150°C, 5 bar and (a) 0%, (b)20%, and (c)40% (% vol) dilution CO2. The yellow dots were manually placed in each case following the progression of the burn front both up and down. The auxiliary red lines illustrate the correspondence of each single-pixel frame with the stack of images.

For very diluted CO+O2 mixtures and for higher pressures, the mixtures loose their circular symmetry when burnt (for instance see Figure 37 and Figure 38). Thus, it was not possible to measure flame front progression with the video method for these cases since they presented strange geometric anisotropy. If measured under these conditions, a local velocity could be taken which does not represent the phenomenon in general terms.



Figure 37 The picture shows a captured image of the video and the montage for a CO+O2 burning at initial conditions of 150°C, 2 bar and 60% (% vol) dilution CO2



Figure 38 The picture shows a captured image of the video and the montage for a CO+O2 burning at initial conditions of 150°C, 5 bar and 40% (% vol) dilution CO2

The burning velocities obtained with this method are discussed in detail in the section 4.3 where they are also compared with the results obtained from the method using pressure sensors to calculate the laminar flame speed. The complete spectrum of results is furthermore shown in section 4.1.3.

### 4.1.3 Numerical Results of Visual Method

The data obtained according to the method described in the previous section are shown in Table 3. In this table the initial concentrations, pressures and temperatures of the experiments that could be processed with the visual method are presented. In addition, the observable flame speed,  $S_S$ , obtained directly from the processing of the frames and the laminar velocity,  $S_L$ , calculated with equation (15), are shown. The values of the expansion ratios provided by CANTERA were used for this purpose and are also shown in the table. Calculation of the standard deviation and standard error was done according to "

# Appendix: Standard Error Calculation", for each experiment.

Table 3 Values of visible flame speed (Ss) obtained trhough processing odf high-speed videos, with the use ofvisual method. Laminar flame speed ( $S_L$ ) calculated from Ss is also show. Initial conditions and expansion ratio for each experiment is also displayed. Standard deviation and the standard error of each experiment was calculted and also displayed.

CODE	INITIAL CONC. CO2%	INITIAL P [BAR]	INITIAL T [°C]	Ss [m/s]	Ss STD DEV	Ss STD ERROR +/- [m/s]	Expans. ratio	SL [m/s]	SL STD ERROR +/- [m/s]
25-1-1	0	1	25	2,06	0,15	0,07	8,269	0,249	0,008
25-1-25	0	1	25	2,30	0,23	0,10	8,269	0,279	0,012
25-1-7	20	1	25	1,09	0,14	0,06	7,539	0,144	0,008
25-1-8	20	1	25	1,08	0,14	0,06	7,539	0,143	0,008
25-1-9	20	1	25	1,08	0,13	0,06	7,539	0,143	0,008
25-1-93	40	1	25	0,32	0,06	0,03	6,738	0,047	0,004
25-5-42	40	1	25	0,31	0,08	0,04	6,738	0,046	0,006
25-1-3	40	1	25	0,63	0,08	0,04	6,738	0,093	0,006
25-1-4	40	1	25	0,52	0,09	0,04	6,738	0,076	0,006
25-1-5	40	1	25	0,49	0,07	0,03	6,738	0,072	0,005
150-5-33	40	1	25	0,46	0,12	0,05	6,738	0,068	0,008
25-1-11	60	1	25	0,14	0,09	0,04	5,520	0,025	0,007
25-1-15	60	1	25	0,28	0,13	0,06	5,520	0,051	0,010
25-1-19	60	1	25	0,21	0,05	0,02	5,520	0,037	0,004
25-2-14	0	2	25	2,58	0,15	0,07	8,428	0,307	0,008
25-2-15	0	2	25	2,70	0,18	0,08	8,428	0,320	0,010
25-2-16	0	2	25	2,65	0,12	0,05	8,428	0,315	0,006
25-2-11	20	2	25	1,37	0,07	0,03	7,660	0,179	0,004
25-2-12	20	2	25	1,62	0,07	0,03	7,660	0,212	0,004
25-2-13	20	2	25	1,49	0,04	0,02	7,660	0,195	0,003
25-5-41	40	2	25	0,39	0,06	0,03	6,815	0,057	0,004
25-2-1	40	2	25	0,65	0,04	0,02	6,815	0,096	0,003
25-2-2	40	2	25	0,72	0,05	0,02	6,815	0,105	0,003
25-2-3	40	2	25	0,56	0,07	0,03	6,815	0,082	0,005
25-2-7	60	2	25	0,08	0,07	0,03	5,535	0,014	0,005
25-5-36	0	5	25	2,05	0,33	0,15	8,642	0,237	0,017
25-5-37	0	5	25	2,01	0,52	0,23	8,642	0,233	0,027
25-5-39	0	5	25	1,93	0,13	0,06	8,642	0,223	0,007
25-5-35	20	5	25	1,22	0,22	0,10	7,820	0,156	0,012
25-5-34	20	5	25	1,16	0,06	0,03	7,820	0,148	0,003
25-5-38	20	5	25	1,20	0,07	0,03	7,820	0,154	0,004
25-5-04	40	5	25	0,45	0,05	0,02	6,913	0,065	0,003
25-5-06	40	5	25	0,72	0,05	0,02	6,913	0,104	0,003
25-5-19	40	5	25	0,45	0,05	0,02	6,913	0,065	0,003
25-5-40	40	5	25	0,46	0,04	0,02	6,913	0,066	0,003
25-1-61	60	5	25	0,30	0,10	0,04	5,551	0,053	0,008
150-1-1	0	1	150	3,51	0,24	0,11	5,898	0,596	0,019
150-1-2	0	1	150	3,50	0,26	0,12	5,898	0,593	0,020
150-1-3	0	1	150	3,42	0,42	0,19	5,898	0,580	0,032
150-1-4	20	1	150	0,80	0,13	0,06	5,388	0,148	0,010
150-1-5	20	1	150	1,93	0,17	0,08	5,388	0,358	0,014
150-1-6	20	1	150	1,93	0,16	0,07	5,388	0,359	0,013

150-1-7	20	1	150	1,90	0,14	0,06	5,388	0,353	0,012
150-1-8	40	1	150	0.69	0.07	0.03	4.839	0.142	0.007
150-1-9	40	1	150	0.85	0.10	0.05	4.839	0.176	0.009
150-1-10	40	1	150	0.90	0.06	0.03	4.839	0.186	0.005
150-1-11	40	1	150	0.90	0.07	0.03	4.839	0.185	0.007
150-1-13	60	1	150	0.37	0.08	0.03	4.035	0.092	0.008
150-1-14	60	1	150	0.22	0.10	0.04	4.035	0.055	0.011
150-1-23	65	1	150	0.56	0.08	0.04	3,742	0.150	0.010
150-2-1	0	2	150	3 47	0.18	0.08	6 012	0 577	0.014
150-2-3	0	2	150	3.05	0.18	0.08	6.012	0.508	0.014
150-2-4	0	2	150	3,05	0.17	0,00	6.012	0,500	0.013
150-2-5	20	2	150	1 96	0.11	0.05	5 476	0 358	0,019
150-2-6	20	2	150	1 72	0.07	0,03	5 476	0 314	0,005
150-2-7	20	2	150	1 69	0.07	0,03	5 476	0,314	0.005
150-2-8	40	2	150	0.88	0,07	0.04	4 896	0,300	0,005
150-2-9	40	2	150	0,86	0,05	0,04	4,896	0,100	0.005
150-2-10	40	2	150	0.83	0.06	0,03	4,896	0 170	0,005
150-2-11	40	2	150	0,85	0,00	0,05	4,850	0,176	0,000
150-2-11	60	2	150	0,80	0,10	0,03	4,000	0,170	0,005
150-2-12	60	2	150	0,10	0,05	0,01	4,045	0,035	0,005
150-2-15	60	2	150	0,15	0,03	0,02	4,049	0,038	0,003
150 1 45	00	<u>۲</u>	150	1.67	0,38	0,17	6 166	0,030	0,042
150 5 29	0	5	150	2.00	0,04	0,02	6 166	0,270	0,003
150 5 20	0	5	150	2,09	0,20	0,12	6 166	0,339	0,019
150-5-59	0	5	150	2,05	0,09	0,04	6,100	0,529	0,007
150 1 46	20	5	150	2,02	0,09	0,04	5 502	0,423	0,000
150-1-40	20	5	150	1,00	0,05	0,01	5,592	0,160	0,002
150 5 27	20	5	150	1,42	0,13	0,00	5,592	0,233	0,011
150-5-57	20	5	150	1,22	0,07	0,03	5,592	0,219	0,005
150-5-35	20		150	1,00	0,08	0,04	3,392	0,287	0,000
150-5-40	40	5	150	0,53	0,09	0,04	4,970	0,107	0,008
150-5-22	40	5	150	0,58	0,02	0,01	4,970	0,118	0,002
150-5-32	40	5	150	0,67	0,09	0,04	4,970	0,134	0,008
300-2-35	0	1	300	1,20	0,24	0,11	4,420	0,270	0,024
300-2-36	0	1	300	1,03	0,20	0,09	4,420	0,234	0,021
300-1-09	0	1	300	1,90	0,24	0,11	4,420	0,430	0,024
300-2-32	20	1	300	0,78	0,11	0,05	4,048	0,191	0,012
300-2-33	20	1	300	0,79	0,09	0,04	4,048	0,195	0,010
300-1-08	20	1	300	1,05	0,17	0,08	4,048	0,259	0,019
300-2-02	20	1	300	1,19	0,08	0,04	4,048	0,295	0,009
300-2-30	40	1	300	0,40	0,09	0,04	3,657	0,110	0,011
300-2-31	40	1	300	0,46	0,05	0,02	3,657	0,127	0,006
300-1-01	40	1	300	0,80	0,08	0,03	3,657	0,220	0,009
300-2-37	0	2	300	1,29	0,16	0,07	4,506	0,286	0,016
300-2-01	0	2	300	2,01	0,10	0,04	4,506	0,446	0,009
300-2-20	0	2	300	1,98	0,10	0,04	4,506	0,439	0,009
300-2-34	20	2	300	0,78	0,10	0,05	4,116	0,189	0,011
300-2-21	20	2	300	1,14	0,07	0,03	4,116	0,277	0,008
300-2-29	40	2	300	0,39	0,08	0,03	3,703	0,106	0,009
300-2-04	40	2	300	0,67	0,06	0,03	3,703	0,180	0,007
300-2-05	40	2	300	0,66	0,07	0,03	3,703	0,178	0,008

300-2-06	60	2	300	0,14	0,05	0,02	3,126	0,046	0,007
300-2-07	60	2	300	0,16	0,07	0,03	3,126	0,050	0,011
300-5-15	0	5	300	1,77	0,07	0,03	4,623	0,382	0,006
300-5-16	0	5	300	1,77	0,05	0,02	4,623	0,382	0,005
300-5-17	0	5	300	1,97	0,06	0,03	4,623	0,426	0,006
300-5-12	20	5	300	1,11	0,04	0,02	4,205	0,265	0,004
300-5-13	20	5	300	1,09	0,05	0,02	4,205	0,259	0,005
300-5-14	20	5	300	1,14	0,07	0,03	4,205	0,271	0,008
300-5-09	40	5	300	0,48	0,05	0,02	3,762	0,129	0,006
300-5-10	40	5	300	0,49	0,04	0,02	3,762	0,130	0,005
300-5-11	40	5	300	0,48	0,04	0,02	3,762	0,128	0,005

# 4.2 Flame speed through pressure analysis

For this series of tests, the experimental principles derived from the "Constant Volume Bomb" Method", which was described in section 2.3, were used.

# 4.2.1 Constant Volume Bomb Method

In order to calculate the experimental laminar flame velocity,  $S_L$ , and the visual flame velocity,  $S_S$ , according to the equations of the Constant Volume Bomb Method (17),(18) and (19), an accurate pressure progression against time is needed. The method used by Kuznetsov et al. [32] has been applied.

The pressure and the respective time series are those recorded by the more sensitive pressure sensor P1 showed in Figure 14 (PCB113B28). This has to do with the fact that the initial pressure rise is the most important part and better resolution can be achieved with this sensor.

The experimental pressure-time history of a combustion process is showed as an example in Figure 39.



Figure 39: Example of pressure-time history processing (initial conditions: T=25°C;P=1bar;20% dilution CO2 [%vol)] Left: Experimental pressure-time history of a combustion process. Middle: zoomed view of initial part of the pressure-time history. Right: its linear approximation.

The parameters needed in the equations for the determination of  $S_L$  and  $S_S$ , were obtained using CANTERA software [32] and all mixtures and initial conditions used in the experiments were considered. In "Appendix: CANTERA Simulation for Constant Volume Bomb Method" a table with all scenarios simulated is listed together with the coefficients obtained.

Only the initial part of the pressure record (less than  $0.02*P_{max}$ ) is used for laminar flame velocity evaluation. It could be seen in Figure 39 (b), that this part of the curve can be linearly approximated as the cubic root of the pressure vs. time (equation (18)). From the equation of the linearization, the coefficient B<sub>2</sub> could be obtained with which the visible flame velocity, Ss, and laminar flame speed, S<sub>L</sub>, can be calculated according to equation (17) and (19) respectively.

The whole spectrum of results is shown in the section 4.2. 2. The numerical results of the flame velocity calculations are compared with the results obtained from the visual method in section 4.3.

## 4.2.2 Numerical Results of Constant Volume Bomb Method

The data obtained according to the Constant Volume Bomb Method are shown in Table 4. In this table the initial concentrations, pressures and temperatures of the experiments that were processed through pressure-time history are presented. In addition, the observable flame speed,  $S_s$ , and laminar flame speed  $S_L$ , calculated with equations (17) and (19), are shown.  $R^2$  is the factor that measures the quality of the linear fit performed for each experiment to obtain  $B_2$ , through equation (18).

Table 4 Values of visible flame speed (Ss) and laminar flame speed (S<sub>L</sub>) obtained trhough processing pressuretime history, with the use constant volume bomb method. calculated from Ss is also show. Initial conditions and linear fittin factor  $R^2$  used to determine  $B_2$  for each experiment is also displayed.

INITIAL T [	INITIAL P [bar]	n	INITIAL %CO2 [%v/v]	Ss [m/s]	Ss STD ERROR +/- [m/s]	SL [m/s]	S <sub>L</sub> STD ERROR +/- [m/s]	R2
25	1	1	0	2,40	0,13	0,294	0,016	0,9995
25	1	25	0	2,57	0,14	0,316	0,017	0,9984
25	1	9	20	1,23	0,06	0,166	0,008	0,9968
25	1	7	20	1,26	0,06	0,170	0,008	0,9979
25	1	3	40	0,61	0,03	0,098	0,004	0,9923

25	1	4	40	0,63	0,03	0,095	0,004	0,9972
25	1	11	60	0,14	0,00	0,025	0,001	0,9812
25	1	19	60	0,15	0,01	0,027	0,001	0,9924
25	2	14	0	2,57	0,14	0,309	0,017	0,9991
25	2	16	0	2,53	0,14	0,304	0,017	0,9985
25	2	11	20	1,39	0,07	0,185	0,009	0,9991
25	2	12	20	1,58	0,08	0,209	0,010	0,9984
25	2	2	40	0,66	0,03	0,099	0,004	0,9981
25	2	3	40	0,60	0,03	0,090	0,004	0,9984
25	2	7	60	0,14	0,00	0,025	0,001	0,9931
25	2	8	60	0,15	0,01	0,028	0,001	0,9939
25	5	36	0	1,82	0,10	0,213	0,012	0,9997
25	5	37	0	1,91	0,11	0,224	0,013	0,9996
25	5	34	20	1,12	0,06	0,145	0,007	0,9998
25	5	38	20	1,22	0,06	0,159	0,008	0,9999
25	5	4	40	0,46	0,02	0,068	0,003	0,9996
25	5	6	40	0,64	0,03	0,095	0,004	0,9997
25	5	18	60	0,11	0,01	0,020	0,001	0,9970
25	5	24	60	0,07	0,01	0,013	0,001	0,9948
150	1	1	0	4,42	0,17	0,759	0,029	0,9930
150	1	3	0	4,39	0,17	0,755	0,029	0,9997
150	1	6	20	2,52	0,09	0,475	0,017	0,9992
150	1	5	20	2,48	0,09	0,466	0,016	0,9995
150	1	9	40	1,13	0,04	0,237	0,007	0,9996
150	1	10	40	0,97	0,03	0,204	0,006	0,9935
150	1	12	60	0,19	0,01	0,047	0,001	0,9961
150	1	14	60	0,21	0,01	0,054	0,001	0,9968
150	1	19	65	0,12	0,01	0,032	0,001	0,9750
150	1	20	65	0,17	0,01	0,046	0,001	0,9396
150	1	22	70	0,07	0,01	0,021	0,001	0,9543
150	2	1	0	3,69	0,14	0,622	0,024	0,9992
150	2	4	0	3,07	0,12	0,518	0,020	0,9993
150	2	2	0	3,27	0,13	0,551	0,021	0,9998
150	2	5	20	1,90	0,07	0,351	0,013	0,9992
150	2	/	20	1,/2	0,06	0,318	0,011	0,9993
150	2	9	40	0,89	0,03	0,185	0,006	0,9988
150	2	11	40	0,92	0,03	0,190	0,006	0,9984
150	2	12	60	0,20	0,01	0,050	0,001	0,9972
150	2	15	60	0,22	0,01	0,056	0,001	0,9973
150	2	20	65	0,11	0,01	0,031	0,001	0,9944
150	2	22	65	0,13	0,01	0,036	0,001	0,9947
150	5	38	0	2,04	0,08	0,335	0,013	0,9992
150	5	39	0	2,08	0,08	0,342	0,014	0,9997
150	5	45	0	1,65	0,07	0,272	0,011	0,9994
150	5	36	20	1,36	0,05	0,247	0,009	0,9995
150	5	46	20	0,93	0,03	0,168	0,006	0,9999
150	5	22	40	0,58	0,02	0,117	0,004	0,9997

150	5	25	40	0,66	0,02	0,135	0,004	0,9992
150	5	32	40	0,55	0,02	0,112	0,004	0,9997
150	5	44	60	0,14	0,01	0,034	0,001	0,9991
150	5	41	60	0,13	0,01	0,032	0,001	0,9981
150	5	28	65	0,06	0,01	0,017	0,001	0,9915
150	5	30	65	0,05	0,01	0,014	0,001	0,9947
300	1	9	0	2,17	0,06	0,497	0,014	0,9919
300	1	35	0	1,60	0,05	0,366	0,011	0,9992
300	1	36	0	1,55	0,05	0,355	0,010	0,9993
300	1	8	20	1,24	0,03	0,311	0,008	0,9948
300	1	32	20	0,87	0,02	0,217	0,006	0,9909
300	1	33	20	0,93	0,02	0,232	0,006	0,9916
300	1	30	40	0,50	0,01	0,138	0,003	0,9866
300	1	31	40	0,46	0,01	0,126	0,003	0,9913
300	1	20	60	0,16	0,01	0,052	0,001	0,9825
300	1	2	60	0,26	0,01	0,083	0,002	0,9825
300	1	30	65	0,10	0,01	0,034	0,001	0,9641
300	1	32	65	0,11	0,01	0,037	0,001	0,9727
300	1	33	67,5	0,04	0,01	0,016	0,001	0,9800
300	1	3	70	0,11	0,01	0,038	0,001	0,9673
300	2	37	0	1,47	0,04	0,330	0,009	0,9983
300	2	20	0	2,13	0,06	0,477	0,014	0,9983
300	2	1	0	2,24	0,06	0,503	0,015	0,9996
300	2	34	20	0,93	0,03	0,228	0,006	0,9982
300	2	9	20	1,23	0,03	0,303	0,008	0,9967
300	2	4	40	0,72	0,02	0,197	0,005	0,9972
300	2	5	40	0,70	0,02	0,191	0,005	0,9969
300	2	6	60	0,20	0,01	0,063	0,001	0,9938
300	2	7	60	0,18	0,01	0,058	0,001	0,9930
300	2	22	67,5	0,08	0,01	0,030	0,001	0,9944
300	2	24	67,5	0,08	0,01	0,028	0,001	0,9927
300	2	12	70	0,03	0,01	0,077	0,001	0,9960
300	2	3	70	0,03	0,01	0,078	0,001	0,9887
300	5	15	0	1,81	0,05	0,397	0,012	0,9996
300	5	16	0	1,74	0,05	0,381	0,011	0,9996
300	5	12	20	1,16	0,03	0,280	0,008	0,9997
300	5	14	20	1,12	0,03	0,269	0,007	0,9995
300	5	9	40	0,52	0,01	0,141	0,003	0,9995
300	5	10	40	0,52	0,01	0,139	0,003	0,9995
300	5	6	60	0,14	0,01	0,045	0,001	0,9984
300	5	8	60	0,15	0,01	0,047	0,001	0,9983
300	5	28	67,5	0,07	0,01	0,027	0,001	0,9979
300	5	29	67,5	0,04	0,01	0,015	0,001	0,9844

Taking in account R<sup>2</sup> factor it could be seen that in general the quality of the fitting is lower for bigger dilutions.

# 4.3 Flame speed results comparison

In the following plots the comparison between the visual flame velocities,  $S_L$ , obtained with the above described optical (shadowgraph method) and pressure (constant volume explosion bomb method) method is shown.

The graphs were made with the data grouped according to the possible combinations of initial pressure and temperature provided in the Table 3 and Table 4.

It can be seen that the values obtained with the optical method are consistent with those calculated from the pressure measurements.

The laminar flame velocities obtained from the pressure measurements are plotted in blue and those obtained with the optical method are plotted in orange.

In order to visualize the trend of the set of points, a second order polynomial adjustment was added to the plots, as a dotted line of the same color.

In some cases, it was not possible to measure with the visual method beyond 40% of CO<sub>2</sub> dilution, particularly for the cases of 5 bar initial pressure. This has to do, as explained in the previous sections, with the higher instability of the flame front for higher initial pressures.

The application of the optical method was very difficult in some cases, especially for  $CO_2$ dilutions of 40 % or more and particularly for the experiments at an initial pressure of 5 bar. The reason for these difficulties is connected with the higher instability of the flame front for higher initial pressures, see section 4.1.1.

Furthermore, the laminar flame velocity obtained with the optical method is generally slightly lower than the velocity calculated by the pressure method. However, the trends observed for both methods are consistent with each other.







Figure 40 Series of graphs corresponding to initial conditions of 25 °C and various initial pressures of 1, 2 and 5 bar. In orange the  $S_L$  obtained by the visual method and in blue the  $S_L$  obtained by the explosion bomb method at constant volume. In dotted line the respective trend lines corresponding to a second order polynomial







Figure 41 Series of graphs corresponding to initial conditions of 150 °C and various initial pressures of 1, 2 and 5 bar . In orange the  $S_L$  obtained by the visual method and in blue the  $S_L$  obtained by the explosion bomb method at constant volume. In dotted line the respective trend lines corresponding to a second order polynomial







Figure 42 Series of graphs corresponding to initial conditions of 300 °C and various initial pressures of 1, 2 and 5 bar . In orange the  $S_{L}$  obtained by the visual method and in blue the  $S_{L}$  obtained by the explosion bomb method at constant volume. In dotted line the respective trend lines corresponding to a second order polynomial.

In the following plots the laminar flame velocities,  $S_L$  obtained with the above-described pressure method (constant volume explosion bomb method), are summarized for the same temperature.

In the case of 25°C degrees the series of lower  $S_L$  corresponds to the highest pressure (5 bar). For the cases of 1 and 2 bar, however, the trend is slightly reversed, being the values of the series very close.

For the case of 150°C reduction of  $S_L$  with increasing pressure is more clear.

In the case of 300°C the trend becomes more diffuse with the series having quite close values within the error bands. No conclusive pattern may be derived from these data. More detailed studies should be carried out to see if there is an inflection point where the flame speed trends change with respect to temperature and pressure.



Figure 43 Series of laminar flame speeds obtained with pressure method, initial conditions of 25 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial.



Figure 44 Series of laminar flame speeds obtained with pressure method, initial conditions of 150 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial.



Figure 45 Series of laminar flame speeds obtained with pressure method, initial conditions of 300 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial.

## 4.4 Maximum pressure

The maximum pressure was calculated theoretically and measured experimentally. For comparison purposes, theoretical burning pressure (isochoric complete combustion) from CANTERA was used for analyzing maximum burning pressure.

#### 4.4.1 Reproducibility

Several experiments with the same initial settings were conducted on different days to qualitatively evaluate the reproducibility of the results. Figure 47 shows examples of such experiments. In the graphs the unprocessed pressure signal recorded in three experiments with the same initial conditions are shown for undiluted  $CO/O_2$  mixtures and mixtures with 40 %  $CO_2$  dilution. As can be seen in Figure 47 and Figure 47, the different experiments show good reproducibility.



Figure 46 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar, undiluted CO/O2 mixtures.



Figure 47 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar, diluted mixture with 40 % CO<sub>2</sub>.

The good reproducibility was observed for  $CO_2$  dilutions of 0%,20% and 40% [% vol], but for more diluted mixtures the curves tend to differ one from another as Figure 48 shows. This effect could be related to instable burning close to the flammability limit that leads to a lack of repeatability.



Figure 48 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar.CO/O2 mixture diluted with 40 %. At 0 seconds the signal of 4.5V corresponding to the trigger could be seen.

### 4.4.2 Obtention of the parameters

The theoretical maximum pressure was calculated using CANTERA software with the initial conditions (initial pressure, initial temperature and mixture compositions) as input data. The results for all cases of the test matrix are listed in the "Appendix: CANTERA Simulation for Constant Volume Bomb Method".

The measured maximum pressure was obtained by processing of the pressure sensor signal. For this purpose, a less sensitive pressure sensor was installed to the facility (P2 Figure 14) with a measuring range of 34,5 bar, that correct the complete pressure spectrum observed in the tests.

The maximum experimental pressure was identified as the first local maximum, although in some records a higher absolute maximum was observed at later points in time. This phenomenon is showed in the Figure 49.



Figure 49 Pressure signal of an experiment with initial conditions: 150 °C, 2 bar, 0% CO2 dilution and highlighted local maximum (yellow circle) and absolute maximum (red circle).

This phenomena is particularly observed in lower dilution cases (0% and 20%  $CO_2$  dilution) and was observed already in previous works with the same facility [27]. The reason for this behavior is the way the pressure sensors are mounted to the facility. To separate the sensors from the hot facility (up to 300 °C) they are mounted at the end of small tubes which connect them to the spherical explosion chamber (see Kuznetzov et al. [3]).

#### 4.4.3 Maximum pressures

In the following graphs the maximum theoretical pressures and the maximum experimental pressures for the different dilutions in each of the nine initial pressure and temperature combinations are compared.

Figure 50, Figure 51 and Figure 52 show that the maximum theoretical pressure is always higher than the maximum experimental pressure. This could be explained considering that maximum theoretical pressure is determined for a complete reaction without energy losses. This means that in all the cases the maximum pressure is not achieve because of losses in energy or incomplete combustion.

In this sense, two cases should be distinguished. For  $CO_2$  dilutions of 0% and 20% the lower pressure could be explained as a loss of energy in the system as heat radiation.

In leaner mixtures this effect is also existent but the effect of buoyancy of the mixture is more determining. Buoyancy effect produce the reaction to occur partially in the vessel since it carries the burning flame to the top of the vessel. The higher the dilution, the higher the buoyancy impact since the flame speed becomes slower and that gives time to the combustion cell to be moved towards the top of the vessel, leaving the bottom of the vessel unburnt. This phenomenon is coherent with the experimental results since the higher the dilution the smaller the maximum experimental pressure, revealing increasingly incomplete burning with dilution.

In the first two cases, CO<sub>2</sub> dilutions of 0% and 20%, there is also buoyancy, but due to the higher flame speed the much slower buoyancy cannot influence the combustion behavior significantly and the complete volume is burnt.



Figure 50: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 25 °C series at different initial pressures.


Figure 51: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 150 °C series at different initial pressures.



Figure 52: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 300 °C series at different initial pressures.

### 4.5 Maximum temperature

As it was shown, the thermocouples used in this work had a thickness of 1 mm. This thickness was chosen to resist the exposure to high temperature for several seconds. This was proven since the thermocouple closer to the center was molten and destroyed in some experiments with fuel rich mixtures.

Due to this large thickness and the introduced heat capacity, the thermocouples showed a slow response time. Thus, it was not possible to measure the instantaneous maximum temperature of the reaction accurately. Additionally, the maximum theoretical temperature will only occur in the reaction zone, which has a relative small size compared to the size of the thermocouple. So, the thermocouple measures only a spatial average.

The thermocouples were installed inside the vessel at different distances from the center of ignition and accordingly showed different results. The thermocouple tip closer to the ignition center always showed higher temperatures.

Although the temperature measurement is not accurate to determine the highest temperature, it could be used as an indicator for the temperature behavior. In Figure 53 an example for the temperatures registered by the two thermocouples mounted at two different distances from the ignition center is shown. The figure demonstrates that with higher dilutions the measured maximum temperature is decreasing.

For comparison, the theoretical combustion temperature obtained with CANTERA simulation is depicted in Figure 54. The example shows that the temperatures sensed by the thermocouples are significantly smaller than the theoretical combustion temperature. It also can be seen that the calculated combustion temperature is decreasing with increasing dilution.



Figure 53 Experimental measurements of maximum temperature sensed by a longer (orange) and shorter (blue) thermocouples for different CO<sub>2</sub>-dilutions. Initial conditions of 150°C and 1 bar.



Figure 54 Theoretical combustion temperature for different CO<sub>2</sub>-dilutions. Initial conditions of 150°C and 1 bar.

The following figures demonstrate examples that the maximum temperature increases with increasing initial pressure (Figure 55 and Figure 56). This behavior coincides with the theoretical tendency but as already mentioned, the measured temperatures are significantly lower than the calculated ones.



Figure 55 Experimental measurements of maximum temperature sensed by the longer (orange) and shorter (blue) thermocouples for different initial pressures. Initial conditions of 150°C and 0% CO<sub>2</sub> dilution.



Figure 56 Theoretical combustion temperature for different initial pressures. Initial conditions of 150°C and 0% CO<sub>2</sub> dilution.

Finally, to demonstrate the effect of the initial temperature on the combustion temperature, Figure 57 and Figure 58 are presented. It can be seen that the maximum combustion temperature decreases with increasing initial temperature. Both experimental and theoretical data show the same behavior. Nevertheless, again there is a substantial difference in the data recorded with the thermocouples compared to the theoretical data extracted from CANTERA.



Figure 57 Experimental measurements of maximum temperature sensed by a shorter (blue) thermocouple for different initial temperatures .Initial conditions of 5 bar and 20% CO2 dilution.



Figure 58 Theoretical combustion temperature for different initial temperatures. Initial conditions of 5 bar and 20% CO2 dilution.

In accordance, with the tendencies determined for the initial conditions, the maximum temperature of 2265 °C was registered in an experiment with the initial conditions of 25°C, 5 bar and 0% CO<sub>2</sub> dilution. Coherently, the corresponding theoretical maximum combustion temperature of 3327 °C is also calculated for the same set of initial conditions.

All these trends could be due to their influence on the mixture in terms of the reaction probability in the molecular order. In the case of lowering the initial temperature or increasing the pressure, the density of the initial mixture increases. Thus, there is a higher probability of reaction between the species present, since the average distance between them is smaller. On the other hand, and consistently, concentrating the mixture makes the effective reaction between the CO and O2 molecules more likely.

Also, at macro scale the reaction is defined as exothermic, so an increase in the temperature would rather suppress the reaction. This is coherent with the results determined for temperature variation.

However, further experimentation with alternative techniques should be carried out and a detailed kinetics chemistry should be developed to support such hypotheses.

### 5. Summary and outlook

Within the frame of this work, carbon monoxide flame behavior was experimentally investigated. Carbon monoxide combustions were performed using stochiometric mixtures with oxygen. The stoichiometric mixture was diluted with different concentrations of CO<sub>2</sub>. The combustion experiments were carried out in the ITES-KIT explosion bomb facility.

To investigate tendencies of the initial conditions on the combustion behavior, the experiments were performed with different initial dilutions, pressures and temperatures. The stoichiometric CO and  $O_2$  mixture was diluted with five degrees of  $CO_2$ -dilution (0%,20%,40%,60% and 70% [%vol]). Also 80%  $CO_2$ -dilutions was tested revealing no successful ignition in any initial conditions. The initial pressures were 1, 2 and 5 bar and the initial temperatures 25, 150 and 300 °C. Spark electrodes positioned inside the explosion bomb were used to ignite the test mixtures. The spark was generated in the center of the explosion bomb. All the experiments were conducted without addition of water nor hydrogen to the mixture, as suggested by other authors.

Flame propagation within the explosion bomb was visualized through quartz windows using the shadowgraph method. Shadowgraph enables visualization of the invisible carbon monoxide combustion by casting shadows of the process. The flame propagation was recorded with a high-speed camera at 12000 fps.

Shadowgraph images allow to observe some effects regarding initial concentrations, pressures and temperatures. For the stoichiometric mixtures of CO-O<sub>2</sub> diluted with 0%, 20% and 40% of CO<sub>2</sub> [%V] the combustion occurs simultaneously in all directions, forming one quasi spherical shaped flame front, that grows form the ignition point. It is also possible to observe a bright blue glowing in these cases, expected for CO combustions [29]. For dilutions of 60% CO<sub>2</sub> [%vol] and higher, the flame front develops an unpredictable shape and moves considerably slower than less diluted examples. In these cases of higher dilutions, the effect of buoyancy is relevant and consequently the hot burnt gases tend to move upwards in the explosion bomb and continue burning towards the bottom after reaching its top surface.

Regarding the three initial pressures used (1, 2 and 5 bar) the shadowgraph Method allows to observe that as the initial pressure increases the shape of the flame front loses its quasi-spherical shape and more wrinkles tend to develop. This is an indicator of increasing flame instability. It can also be observed that with higher pressure, also the intensity of the light emitted increases, indicating higher energy release.

Regarding initial temperature variation, the behavior is opposite to that observed for pressure variation. More wrinkles and deformation of the quasi-spherical shaped flame front are observed at lower temperatures. In addition, with increasing temperature, the light intensity observed decreases and also higher uniformity of the flame front is observed.

The shadowgraph Method also allowed to follow the spatial progression of flame front. A visual analysis method was developed to extract a visible flame velocity,  $S_s$ , out of the video recordings and to mitigate the influence of buoyancy. To evaluate the results obtained with this optical method, also the Constant Volume Bomb Method was used in most of the experiments. In this method the experimental pressure recordings of the early stages of each combustion were processed to obtain the  $S_s$  and the laminar flame speed,  $S_L$ . It was shown that the values obtained by the two methods are consistent, and that the trends observed for different initial conditions were followed equally. The range of values obtained for  $S_L$  with Constant Volume Bomb Method is [0,76-0,01] m/s while the one obtained through high-speed video recording is [0,60-0,01] m/s.

It was observed that the laminar flame speed of CO-O<sub>2</sub> mixtures decreases with the increasing CO<sub>2</sub>-dilution for all initial conditions. For different initial temperature the larger S<sub>L</sub> series are observed for 150°C, followed by 25°C and 300°C. For different initial pressures, at the same initial temperature, a clear tendency cannot be observed. For an initial temperature of 150°C increasing velocities are observed as initial pressure decreases. For initial temperatures of 25°C and particularly 300°C, S<sub>L</sub> series show no clear trend when varying initial pressures. Since it is not possible to determine a conclusive pattern with these data, more detailed studies should be carried out in this sense to analyze to behavior of S<sub>L</sub> with change of initial pressure at constant initial temperature.

Analysis about the maximum combustion pressure were also conducted. The theoretical maximum pressure was calculated through combustion simulation in CANTERA software considering the initial conditions of concentration, temperature and pressure listed in the experimental matrix. The maximum experimental pressure was obtained through the processing of the pressure sensor signal. After comparison of these values, it could be seen that the maximum theoretical pressure is always higher than the maximum experimental pressure. For 0% and 20% of CO<sub>2</sub>-dilution the lower magnitude of the experimental maximum combustion pressure, compared to the theoretical maximum pressure, could be explained as a loss of internal energy converted into heat radiation. In leaner mixtures this effect is also existent, but the effect of buoyancy is more determining. Buoyancy effect cause the reaction to occur partially in the vessel. The experimental results show that with increasing dilution the maximum experimental pressure decreases. Also, the difference to the maximum theoretical

80

combustion pressures becomes bigger, revealing increasingly incomplete combustion with  $CO_2$ -dilution.

Finally, the theoretical combustion temperature obtained with CANTERA, and the experimentally measured combustion temperature were compared. It could be observed that the temperatures sensed by the thermocouples are quite smaller compared to the theoretical combustion temperatures. One of the reasons for this behavior could be the slow sensing velocity of the rather thick (d=1 mm) thermocouples used averaging the temperature signal in time and space. Different methods could be used if further experimentation in this field is conducted (e.g. radiation thermometry). Despite this difference, it also could be seen that in both cases theoretical and experimental the combustion temperature is decreasing with higher initial dilution, increasing with higher initial pressure and decreasing with higher initial temperature. This last aspect could be related to the fact that the CO combustion is an exothermic process, so an increase in the initial temperature would discourage the reaction.

With the recorded data collected from the conducted experiments and the laminar flame velocities ( $S_L$ ) calculated through the optical and the pressure methods presented in this report, the flame stability characteristics (e.g., though calculation of  $L_M$ , Markstein length) could be analyzed in future processing, as well as magnitudes of the overall reaction such as the activation energy and the overall reaction order.

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# List of Figures

Figure 1 Global mean annual concentration of carbon dioxide in atmosphere [2]
Figure 2 Flow diagram of the kerosene production cycle with power-to-fuel process, proposed
by Kerogreen [6]
Figure 3 Postulated reaction mechanism for hydrogen-free CO burning [10]13
Figure 4 Schematic diagram of stationary one-dimensional flame propagation
Figure 5 Schematic diagram of two-dimensional flame propagation with center ignition [11]
Figure 6 Experimental set up used to conduct combustion experiments with CO/ $O_2/CO_2$
mixtures
Figure 7 Schematic cut of the explosion bomb [21]21
Figure 8 Inlet and outlet of the vessel in the upper part, highlighted in red22
Figure 9 Spark plug and welded electrode fabricated for the experiments23
Figure 10 High speed camera, Photron FASTACAM-SA1.124
Figure 11 High-speed camera in shadowgraph configuration with lens array (highlighted in red)
and LED-based lamp developed by ITES-KIT staff (green and right)24
Figure 12 Scheme of the configuration used for shadowgraph video recordings25
Figure 13 NiCr-Ni (type k) thermocouples (1 mm), of different length as used in the bomb25
Figure 14 PCB pressure sensors P1 and P2, highlighted in red at the bomb equipped with
heating cover Also displayed is the air-cooling system surrounding each sensor (yellow dash
line)
Figure 15 Detail of the air-cooling system for the PCB pressure sensor. The device consists of
a pipe with small holes that surround the sensor and flushes it with cool air27
Figure 16 Display of the Rosemount gas analyzer. The percentages of gases in the
measurement flow are shown. Several gases like $CH_4$ , $CO$ , $CO_2$ , $H_2O$ , $H_2$ and $O_2$ could be
detected
Figure 17 LabView interface that allows to control the valves in the facility and the ignition
device
Figure 18 Flow diagram of the test facility [26]
Figure 19 Explosion bomb wrapped in heating strips, highlighted in blue. Highlighted in red is
the inlet duct wrapped in a heating strip to preheat the gases. The Horst heating regulators are
highlighted in yellow
Figure 20 Explosion bomb and inlet pipe, together with heating strips covered with thermal
insulation, made of fiberglass wool and aluminum32
Figure 21: Single frames (extracted) from high-speed movies of the combustion of $O_2 + CO$
(stoichiometric) mixture with 0 % (% vol) of CO <sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar.

Images taken at (a) 2, (b) 4, (c) 6, (d) 9, (e) 34, (f) 38, (g) 58, (h) 158 and (i) 350 milliseconds Figure 22: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 20 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 2, (b) 5, (c) 6, (d) 9, (e) 13 , (f) 55, (g) 71, (h) 111 and (i) 350 milliseconds Figure 23: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO<sub>2</sub> dilution . Initial conditions: 150 °C and 1 bar. Images taken at (a) 3, (b) 4, (c) 7, (d) 13, (e) 17, (f) 25, (g) 138, (h) 175 and (i) 209 milliseconds Figure 24: Single frames (extracted) from high-speed movies of the combustion of  $O_2$  + CO (stoichiometric) mixture with 60 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a) 3, (b) 8, (c) 83, (d) 204, (e) 504, (f) 546, (g) 658, (h) 695 and (i) 790 milliseconds after ignition trigger......40 Figure 25: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 60 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 3, (b, q) 8, (c, h) 67, (d, i) 83 and (e, j) 204 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment......41 Figure 26: Single frames (extracted) from high-speed movies of the combustion of O2 + CO(stoichiometric) mixture with 65 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 4, (b, g) 13, (c, h) 25, (d, i) 89 and (e, j) 126 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment......41 Figure 27: Single frames (extracted) from high-speed movies of the combustion of O2 + CO(stoichiometric) mixture with 70 % (% vol) of CO<sub>2</sub> dilution. Initial conditions: 150 °C and 1 bar. Images taken at (a, f) 4, (b, g) 13, (c, h) 25, (d, i) 67 and (e, j) 101 milliseconds after ignition trigger. Upper row: before image treatment; lower row: after image treatment......42 Figure 28: Single frames (extracted) from high-speed movies of the combustion of O2 + CO(stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 150 °C and 2 bar. Images taken at (a) 4, (b) 7, (c) 10, (d) 15, (e) 20, (f) 28, (g) 104, (h) 171 and (i) 209 milliseconds after ignition Figure 29: Single frames (extracted) from high-speed movies of the combustion of O2 + CO (stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 150 °C and 5 bar. Images taken at (a) 4, (b) 11, (c) 20, (d) 29, (e) 76, (f) 173, (g) 257, (h) 443 and (i) 668 milliseconds after ignition Figure 30: Single frames (extracted) from high-speed movies of the combustion of O2 + CO(stoichiometric) mixture with 40 % (% vol) of CO2 dilution. Initial conditions: 25 °C and 2 bar. Images

obtained by the explosion bomb method at constant volume. In dotted line the respective trend lines corresponding to a second order polynomial ......61 Figure 42 Series of graphs corresponding to initial conditions of 300 °C and various initial pressures of 1, 2 and 5 bar. In orange the S<sub>L</sub> obtained by the visual method and in blue the S<sub>L</sub> obtained by the explosion bomb method at constant volume. In dotted line the respective trend Figure 43 Series of laminar flame speeds obtained with pressure method, initial conditions of 25 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial......63 Figure 44 Series of laminar flame speeds obtained with pressure method, initial conditions of 150 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial. ......64 Figure 45 Series of laminar flame speeds obtained with pressure method, initial conditions of 300 °C and various initial pressures of 1, 2 and 5 bar. In dotted line the respective trend lines corresponding to a second order polynomial. .....64 Figure 46 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar, undiluted CO/O2 mixtures. .....65 Figure 47 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar, diluted mixture with 40 % CO<sub>2</sub>......66 Figure 48 Unprocessed pressure signals in Volt vs time in seconds recorded in three different experiments with IMTEC software at an initial temperature of 150 °C and an initial pressure of 1 bar.CO/O2 mixture diluted with 40 %. At 0 seconds the signal of 4.5V corresponding to the Figure 49 Pressure signal of an experiment with initial conditions: 150 °C, 2 bar, 0% CO2 dilution and highlighted local maximum (yellow circle) and absolute maximum (red circle)...67 Figure 50: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 25 °C series at different initial pressures......69 Figure 51: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 150 °C series at different initial pressures.....70 Figure 52: Comparison of theoretical maximum pressures (blue squares) and experimental maximum pressures (green rhombus) for the 300 °C series at different initial pressures......71 Figure 53 Experimental measurements of maximum temperature sensed by a longer (orange) and shorter (blue) thermocouples for different CO<sub>2</sub>-dilutions. Initial conditions of 150°C and 1 bar.....73

Figure 54 Theoretical combustion temperature for different $CO_2$ -dilutions. Initial conditions of
150°C and 1 bar73
Figure 55 Experimental measurements of maximum temperature sensed by the longer
(orange) and shorter (blue) thermocouples for different initial pressures. Initial conditions of
150°C and 0% CO <sub>2</sub> dilution74
Figure 56 Theoretical combustion temperature for different initial pressures. Initial conditions
of 150°C and 0% $CO_2$ dilution74
Figure 57 Experimental measurements of maximum temperature sensed by a shorter (blue)
thermocouple for different initial temperatures . Initial conditions of 5 bar and 20% CO2 dilution.
75
Figure 58 Theoretical combustion temperature for different initial temperatures. Initial
conditions of 5 bar and 20% CO2 dilution75

## List of Tables

Table 1 Experimental matrix: pressure and temperature combinations
Table 2 Initial parameters and the corresponding standard errors 33
Table 3 Values of visible flame speed (Ss) obtained trhough processing odf high-speed videos,
with the use ofvisual method. Laminar flame speed ( $S_L$ ) calculated from Ss is also show. Initial
conditions and expansion ratio for each experiment is also displayed. Standard deviation and
the standard error of each experiment was calculted and also displayed
Table 4 Values of visible flame speed (Ss) and laminar flame speed (SL) obtained trhough
processing pressure-time history, with the use constant volume bomb method. calculated from
Ss is also show. Initial conditions and linear fittin factor $R^2$ used to determine $B_2$ for each
experiment is also displayed56

## Appendix

### Appendix: Video Recording Distance Calibration

The basic idea of the calibration is to correlate a pixel in the image with real distance. For that purpose, a precise sized object was positioned at one each side of the bomb window. The tool used as parameter was a caliper as shown in the next figure.



Three images were taken at each side of the bomb, and they were analyzed and measured through ImageJ software. Also, three measurements at three different points were done to each image.

Images processed with "sharpen" and "find edges" tool were then measure using the tool "measure".

The following showed figures are examples of the mentioned measurements.



The results are displayed in the following table:

POSITION	1	Far from camera close to light
	2	Close to camera far from light

Document name	Position	Image	Angle	Length in pixels
Test 1	1	CAL 1.1	177.491	224,6
Test 1	1	CAL 1.1	178.056	224,8
Test 1	1	CAL 1.1	-3.009	223,9
Test 1 .1	1	CAL 1.2	-5.497	222,7
Test 1 .1	1	CAL 1.2	-6.081	224,2
Test 1 .1	1	CAL 1.2	-5.974	224,6
Test 1 .1 .1	1	CAL 1.3	-0.790	223,7
Test 1 .1 .1	1	CAL 1.3	-0.721	225,2
Test 1 .1 .1	1	CAL 1.3	-0.738	224,9
Test 2	2	CAL 2.1	-8.168	211,1
Test 2	2	CAL 2.1	-9.418	212,4
Test 2	2	CAL 2.1	-9.340	212,2
Test 2 .1	2	CAL 2.2	-4.159	215,4
Test 2 .1	2	CAL 2.2	-5.259	210,0
Test 2 .1	2	CAL 2.2	-4.205	208,6
Test 2 .1 .1	2	CAL 2.3	-0.905	211,0
Test 2 .1 .1	2	CAL 2.3	-0.561	212,6
Test 2 .1 .1	2	CAL 2.3	-0.513	214,0

#### Measured from middle of distortion bands

The average measurement in pixel was 218,1 pixels with an standard deviation of 6,53 (3%). But if each side is considered separate the deviation between the measurements of position 1 and position 2 is 0,3% and 1% respectively. Considering some distortion around the edges of the image of the caliper it is an acceptable measurement. The fact that there is some discrepancy between one side and the other could have to do with some difference in the light from one side and the other showing that it is not perfectly parallel. Nevertheless, the approximation with the average is physically coherent since the images of the burning cells are taken in the middle of the two windows.

Result outcoming of the calibration:

CALIBRATION				
0,02	m	equal to	218	pixels

#### Appendix: Standard Error Calculation

The experimental data presents both systematical (reduced by calibration) and statistical errors, that are more determining in this case.

Statistical errors are calculated through standard deviation  $\sigma$  and the standard error  $\sigma_{\bar{x}}$  (bold typography is used to differentiate the standard deviation from expansion ratio,  $\sigma$ )

The errors in the Excel graphs and in the tables presented were calculated through the standard deviation of the recorded samples.

The standard deviation was calculated with the Excel formula "STDEV", which is obtained as follows:

$$\boldsymbol{\sigma} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \tag{i}$$

Where  $\overline{x}$  is the sample's mean, n the sample size and  $x_i$  is the measured magnitude.

Using the obtained standard deviation, the standard error,  $\sigma_{\bar{x}}$ , was calculated by dividing the value of the standard deviation by the square root of the sample size, as it follows:

$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \tag{ii}$$

The calculation of  $S_L$  and  $S_S$  through the Constant Volume Bomb Method (Pressure Method) and the Shadowgraph Method (Optical Method) depend on other measured variables with their respective errors, Because of this, the calculation of the errors for each method was processed following the error propagation, according to equation (iii)

$$Y = f(x_1, x_2 \dots x_n); \ \boldsymbol{\sigma}_{\bar{Y}} = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial Y}{\partial x_i}\right)^2 * \boldsymbol{\sigma}_{\bar{x}_i}^2}$$
(iii)

The equation (iii) particularly applied to the calculation of  $S_{L}$  for each method are shown in equation (v) for the Optical Method and in equation (viii) for the Pressure Method.

Optical Method standard error calculation,

$$S_S = \frac{dr_b}{dt} \approx \frac{\Delta r_b}{\Delta t}$$
;  $S_L = \frac{\Delta r_b}{\Delta t} \frac{1}{\sigma}$  (iv)

$$\boldsymbol{\sigma}_{\overline{S_L}} = \sqrt{\left(\frac{\partial S_L}{\partial r_b}\right)^2 * \boldsymbol{\sigma}_{\overline{r_b}}^2 + \left(\frac{\partial S_L}{\partial t}\right)^2 * \boldsymbol{\sigma}_{\overline{t}}^2} \tag{V}$$

Pressure Method standard error calculation,

$$S_{s} = \left(\frac{B_{2}}{P_{0}} \left(\frac{\gamma_{b}R^{3} + \frac{\gamma_{u}}{\sigma}r_{b}^{3} - \gamma_{b}r_{b}^{3}}{\left(1 - \frac{1}{\sigma}\right)\gamma_{b} \cdot \gamma_{u}} - r_{b}^{3}\right)\right)^{\frac{1}{3}}$$
(vi)

$$S_{L} = \frac{S_{s}}{\sigma} \left( 1 + \frac{1}{\gamma_{b}} \frac{B_{2} r_{b}^{3}}{(S_{s}^{3} P_{0} + B_{2} r_{b}^{3})} \right)$$
(vii)

$$\boldsymbol{\sigma}_{\overline{S_L}} = \sqrt{\left(\frac{\partial S_L}{\partial P_0}\right)^2 * \boldsymbol{\sigma}_{\overline{P_0}}^2 + \left(\frac{\partial S_L}{\partial B_2}\right)^2 * \boldsymbol{\sigma}_{\overline{B_2}}^2 + \left(\frac{\partial S_L}{\partial R}\right)^2 * \boldsymbol{\sigma}_{\overline{R}}^2}$$
(viii)

The error of R is related to the machinig tolerance of the explosion bomb  $(0,1250\pm0,0001 \text{ m})$ . The error of P<sub>0</sub> is obtained as the statistical deviation of all the initial pressures recorded for each 1,2 and 5 bar. The error of B is obtained as the error for the linear approximation, it is based in minimum squares technic for each pressure rise analysis and it is calculated with Excel function "LINEST". The magnitude is considered constant for this method as well as the theoretical constants obtained from CANTERA.

#### Sources:

https://support.microsoft.com/en-us/office/add-change-or-remove-error-bars-in-a-charte6d12c87-8533-4cd6-a3f5-864049a145f0

http://wwwalt.physnet.uni-hamburg.de/TUHH/Versuchsanleitung/Fehlerrechnung.pdf

	nput para	meter		Mechanisr	igri30.cti	Expansion			ISOC	noric					Isobaric		
Experi	CO2	со				Expans.	Cp[J/(kM	Cv[J/(kM				Dens.	Cp[J/(kM	Cv[J/(kM			Dens.
mont	[Vol %]		T[K]	p[Pa]	Cp/Cv	ratio	ole*K)]	ole*K)]	Cp/Cv	T burn[K]	p burn[Pa]	[ka/m^3]	ole*K)]	ole*K)]	Cp/Cv	T burn[K]	[ka/mA3]
ment	[401./9]	[101 /0]				Tatio	ole kj	ole Kj				[Kg/11-3]	ole kjj				[Kg/11-5]
1	0,0	66,7	298	100000	1,398	8,269	47975,82	39661,36	1,210	3355,2	944724,0	1,184	48286,83	39972,37	1,208	2973,741	0,143
2	20.0	53.3	298	100000	1.370	7,539	53308.81	44994.35	1,185	3017.1	847904.1	1,303	53582.26	45267.80	1,184	2711.980	0.173
2	40.0	40.0	200	100000	1 245	6 729	57941 47	40527.00	1 1 6 9	2644.2	740702.0	1 421	E8024 48	40720.02	1 1 6 7	2207 520	0.211
3	40,0	40,0	298	100000	1,545	0,738	57641,47	49527,00	1,108	2044,5	749793,9	1,421	56054,46	49720,02	1,107	2397,530	0,211
4	60,0	26,7	298	100000	1,324	5,520	60117,43	51802,96	1,161	2105,5	616765,3	1,539	59759,91	51445,45	1,162	1890,381	0,279
5	62.5	25.0	298	100000	1 322	5 305	60077 30	51762.84	1 161	2014 4	594157.2	1 554	59590.07	51275 60	1 162	1802 699	0 293
	02,5	20,0	200	100000	1 210	5,505	50026.76	51/02,01	1,101	4017.2	551257,2	1,551	50017.00	512/3,00	1 1 6 2	1710 505	0,200
6	65,0	23,3	298	100000	1,319	5,076	59936,76	51622,29	1,161	1917,2	569787,4	1,569	59317,38	51002,92	1,163	1/10,505	0,309
7	67,5	21,7	298	100000	1,317	4,835	59692,22	51377,76	1,162	1814,7	543754,3	1,584	58946,00	50631,53	1,164	1615,185	0,328
8	70.0	20.0	298	100000	1 3 1 4	4 586	59343.07	51028 60	1 163	1708.4	516283.0	1 599	58480 48	50166.02	1 166	1518 115	0 349
0	70,0	20,0	250	100000	1,514	4,500	55545,07	51020,00	1,105	1700,4	510205,0	1,555	30400,40	30100,02	1,100	1010,110	0,343
9	0,0	66,7	298	200000	1,398	8,428	48494,50	40180,04	1,207	3458,1	1931640,9	2,368	48//4,61	40460,15	1,205	3052,660	0,281
10	20,0	53,3	298	200000	1,370	7,660	53814,81	45500,34	1,183	3093,2	1727011,4	2,605	54037,51	45723,04	1,182	2771,933	0,340
11	40.0	40.0	298	200000	1 345	6 8 1 5	58215 37	49900 90	1 167	2691 5	1519534.6	2 842	58362 54	50048.08	1 166	2434 228	0.417
11	40,0	40,0	250	200000	1,545	0,815	38213,37	45500,50	1,107	2031,5	1515554,0	2,042	38302,34	50048,08	1,100	2434,220	0,417
12	60,0	26,7	298	200000	1,324	5,535	60225,89	51911,43	1,160	2117,3	1239043,1	3,079	59828,27	51513,81	1,161	1896,805	0,556
13	62,5	25,0	298	200000	1,322	5,314	60153,22	51838,76	1,160	2022,4	1192145,2	3,108	59632,66	51318,20	1,162	1806,572	0,585
1/	65.0	22.2	208	200000	1 210	5 081	50085 /0	51671.03	1 161	1077.7	11/2006 7	3 1 3 8	503/11 20	51026.82	1 163	1712 507	0.618
17	05,0	23,5	200	200000	1,515	5,001	50500,40	51071,05	1,101	1022,2	1142000,7	3,130	50057.07	51020,02	1,105	1/12,007	0,010
15	67,5	21,7	298	200000	1,317	4,838	59720,48	51406,02	1,162	1817,5	1088896,2	3,168	58957,97	50643,51	1,164	1616,189	0,655
16	70,0	20,0	298	200000	1,314	4,587	59357,68	51043,21	1,163	1709,7	1033267,3	3,197	58485,79	50171,33	1,166	1518,540	0,697
17	0.0	66.7	208	500000	1 208	8 642	10101 60	10880.23	1 203	3600.3	4970672.3	5 021	10153.67	11130 20	1 202	3161 340	0.685
1/	0,0	00,7	250	500000	1,350	0,042	49194,09	40000,23	1,203	5000,5	4570072,5	5,521	49493,07	41135,20	1,202	5101,540	0,085
18	20,0	53,3	298	500000	1,370	7,820	54506,36	46191,90	1,180	3196,3	4420569,7	6,513	54660,32	46345,86	1,179	2852,906	0,833
19	40,0	40,0	298	500000	1,345	6,913	58704,79	50390,33	1,165	2752,6	3862447,1	7,105	58787,78	50473,32	1,165	2481,504	1,028
20	60.0	26.7	298	500000	1 324	5 551	60348 49	52034.03	1 160	2130.7	3113132.2	7 697	59903.05	51588 58	1 161	1903 837	1 387
20	60,0	20,7	200	500000	1,024	5,551	60226 75	51022.00	1,100	2100,7	20000270	7,007	505505,05	51363,56	1,101	1010 70	1,507
21	62,5	25,0	298	500000	1,322	5,324	60236,75	51922,28	1,160	2031,3	2990878,9	/,//1	59678,08	51363,62	1,162	1810,704	1,460
22	65,0	23,3	298	500000	1,319	5,087	60037,76	51723,30	1,161	1927,6	2861531,9	7,845	59366,26	51051,80	1,163	1714,784	1,542
22	67.5	217	298	500000	1 317	4 841	59750 15	51435.60	1 162	1820 5	2725881.1	7 910	58970 30	50655.84	1 164	1617 223	1 636
23	07,5	21,7	2.50	500000	1,517	4,041	50750,15	51455,09	1,102	1820,5	2723001,1	7,519	50570,30	50055,84	1,104	1017,223	1,030
24	70,0	20,0	298	500000	1,314	4,588	59372,78	51058,31	1,163	1/11,2	2584979,7	7,993	58491,21	50176,75	1,166	1518,973	1,742
25	0,0	66,7	423	100000	1,388	5,898	47465,39	39150,92	1,212	3320,9	664599,4	0,834	47933,09	39618,63	1,210	2990,302	0,141
26	20.0	52.2	123	100000	1 3/18	5 388	52775 67	44461 21	1 1 8 7	2008 /	508585.0	0.018	53107.86	11883 10	1 1 2 5	2732 707	0 170
20	20,0	55,5	423	100000	1,540	5,500	52775,07	44401,21	1,107	2556,4	556565,5	0,518	55157,80	44003,40	1,105	2732,757	0,170
27	40,0	40,0	423	100000	1,315	4,839	57390,81	49076,35	1,169	2647,6	532469,5	1,001	57706,68	49392,22	1,168	2429,897	0,207
28	60,0	26,7	423	100000	1,288	4,035	60024,04	51709,58	1,161	2151,5	445264,4	1,084	59821,57	51507,10	1,161	1957,491	0,269
20	62.5	25.0	123	100000	1 285	3 804	60061 41	517/6 05	1 161	2067.5	13055/ /	1 005	50737 73	51/23 27	1 162	1875 / 36	0.281
23	02,5	23,0	423	100000	1,205	3,094	00001,41	51740,95	1,101	2007,5	430334,4	1,095	39737,73	51425,27	1,102	1073,430	0,201
30	65,0	23,3	423	100000	1,282	3,742	60003,12	51688,66	1,161	1977,2	414600,3	1,105	59553,04	51238,58	1,162	1788,129	0,295
31	67.5	21.7	423	100000	1.279	3.580	59842.55	51528.09	1.161	1880.7	397388.9	1.116	59268.83	50954.36	1.163	1696.645	0.312
22	70.0	20.0	122	100000	1 276	2 / 11	E0E76 69	E1262.22	1 162	1770.2	270007.2	1 1 2 6	E0000 20	E0E74 02	1 1 6 4	1602 220	0.220
52	70,0	20,0	423	100000	1,270	5,411	39370,08	51202,22	1,102	1//5,2	379007,3	1,120	30003,33	30374,93	1,104	1002,339	0,330
33	0,0	66,7	423	200000	1,388	6,012	47974,57	39660,10	1,210	3422,9	1359201,9	1,668	48420,74	40106,28	1,207	3070,415	0,278
34	20.0	53.3	423	200000	1.348	5.476	53276.77	44962.31	1.185	3075.1	1219643.8	1.835	53658.22	45343.76	1.183	2794.271	0.335
25	40.0	40.0	422	200000	1 215	4 800	5777751	40462.04	1 1 6 9	2607.1	1070912.0	2,002	5005152	40727.06	1 1 6 7	2469.090	0,400
30	40,0	40,0	423	200000	1,515	4,890	57777,51	49405,04	1,108	2097,1	10/9813,9	2,002	58051,52	49737,00	1,107	2408,989	0,409
36	60,0	26,7	423	200000	1,288	4,049	60162,01	51847,55	1,160	2166,8	895526,2	2,169	59915,25	51600,78	1,161	1966,506	0,536
37	62.5	25.0	423	200000	1.285	3.903	60164.19	51849.73	1.160	2078.6	864807.5	2.190	59801.12	51486.66	1.161	1881.360	0.561
20	65.0	22.2	422	200000	1 202	2 749	60074 19	E17E0 72	1 1 1 1	1094.6	021725.2	2 211	F0F02 14	51277.67	1 1 6 2	1701 664	0.500
30	05,0	23,3	423	200000	1,202	5,740	00074,18	51/59,72	1,101	1984,0	031/35,5	2,211	59592,14	51277,07	1,102	1791,004	0,590
39	67,5	21,7	423	200000	1,279	3,583	59887,43	51572,97	1,161	1885,3	796358,2	2,232	59290,58	50976,11	1,163	1698,538	0,623
40	70.0	20.0	423	200000	1.276	3.412	59602.19	51287.73	1.162	1781.6	758896.6	2.252	58900.21	50585.75	1.164	1603.241	0.660
/1	0.0	66.7	122	E00000	1 200	6 166	19666 25	10251 00	1 206	2564.2	24090476	4 171	40000 84	10705 20	1 204	2100 027	0.676
41	0,0	00,7	425	500000	1,300	0,100	48000,35	40551,88	1,200	3304,3	5498947,0	4,171	49099,84	40765,58	1,204	5160,657	0,676
42	20,0	53,3	423	500000	1,348	5,592	53964,49	45650,02	1,182	3179,2	3123604,4	4,588	54289,42	45974,96	1,181	2877,466	0,820
43	40.0	40.0	423	500000	1.315	4.970	58288.28	49973.82	1.166	2761.7	2747345.6	5.005	58501.92	50187.46	1.166	2519.693	1.007
44	60.0	26.7	122	E00000	1 200	4.066	60221 90	E2007.24	1 160	2101 E	2252212.0	E 422	60020.08	E170E 61	1 1 6 1	1076 509	1 224
44	00,0	20,7	423	300000	1,200	4,000	00321,80	32007,34	1,100	2104,5	2235212,0	3,422	00020,08	51703,01	1,101	1970,398	1,554
45	62,5	25,0	423	500000	1,285	3,914	60280,03	51965,56	1,160	2091,2	2172410,0	5,475	59870,12	51555,66	1,161	1887,814	1,399
46	65,0	23,3	423	500000	1,282	3,754	60152,11	51837,65	1,160	1992,8	2086276,4	5,527	59633,67	51319,21	1,162	1795,421	1,472
47	67.5	217	422	500000	1 270	2 5 0 7	59035 43	51620.00	1 1 6 1	1800.3	1995117.1	5 5 70	59212.24	50009 70	1 1 6 2	1700 511	1 555
4/	07,5	21,7	423	500000	1,279	3,367	55555,42	51020,90	1,101	1850,2	1999117,1	5,579	55515,24	30330,78	1,103	1/00,511	1,555
48	70,0	20,0	423	500000	1,276	3,414	59628,90	51314,44	1,162	1784,3	1899550,0	5,631	58911,34	50596,88	1,164	1604,168	1,649
49	0,0	66,7	573	100000	1,370	4,420	46934,93	38620,47	1,215	3296,8	491700.4	0,616	47502,67	39188,21	1,212	3010,441	0,139
50	20.0	52.2	572	100000	1 224	4.049	52107.87	43883.40	1 1 2 0	2088.0	444501.0	0.677	52715 21	44400.85	1 1 9 7	2758 202	0.167
	20,0	33,3	573	100000	1,524	4,040	52157,67	10000,40	1,109	2500,8		0,077	52715,31	11100,03	1,107	2133,233	0,107
51	40,0	40,0	573	100000	1,289	3,657	56865,55	48551,08	1,171	2659,3	398051,7	0,739	57268,48	48954,01	1,170	2469,074	0,202
52	60,0	26,7	573	100000	1,260	3,111	59849,60	51535,14	1,161	2208,4	338831,2	0,801	59804,12	51489,66	1,161	2037,850	0,257
52	62.5	25.0	573	100000	1 257	3.017	59974 10	51659.63	1 161	2133.0	329043.1	0.808	59823.88	51509.42	1 161	1963 514	0.268
55	02,5	23,0	573	100000	1,257	3,017	00000	51055,05	1,101	2133,0	21043,1	0,000	5075040	51333,42	1,101	1002 561	0,208
54	65,0	23,3	573	100000	1,254	2,915	60013,48	51699,01	1,161	2051,4	318408,5	0,816	59750,18	51435,/2	1,162	1883,581	0,280
55	67,5	21,7	573	100000	1,251	2,805	59958,42	51643,96	1,161	1963,6	306857,7	0,824	59579,75	51265,29	1,162	1798,543	0,294
56	70.0	20.0	573	100000	1 748	2 688	59802.16	51487 69	1 161	1869.6	294376.8	0.831	59313.49	50999.03	1,163	1709 372	0 309
50	,0,0	20,0	575	200000	1,270	2,000	47424 52	20120.05	1,101	2000,0	1005047.0	1,001	47000.01	20675.20	1,240	2002.000	0,505
57	0,0	66,7	573	200000	1,370	4,506	47434,52	39120,05	1,213	3398,5	1005847,0	1,232	47989,84	396/5,38	1,210	3092,006	0,273
58	20,0	53,3	573	200000	1,324	4,116	52694,85	44380,39	1,187	3066,4	906217,8	1,355	53181,33	44866,86	1,185	2821,626	0,329
59	40.0	40.0	573	200000	1,289	3,703	57265.74	48951.27	1.170	2711.4	807777.9	1.478	57632.71	49318.25	1,169	2511.075	0.399
60	60.0	26.7	573	200000	1,200	2,120	60024 42	E1700.07	1 1 6 4	2220 4	692409.0	1.001	E0024.00	E1610.00	1.100	2050 606	0.513
60	60,0	26,7	573	200000	1,260	3,126	00024,43	31/09,97	1,161	2228,1	082408,6	1,601	39934,08	51019,62	1,161	2050,696	0,512
61	62,5	25,0	573	200000	1,257	3,028	60113,03	51798,57	1,161	2148,3	661835,2	1,617	59920,06	51605,60	1,161	1972,788	0,534
62	65.0	23.3	573	200000	1.254	2,922	60117.63	51803.17	1,161	2062.7	639607.4	1.632	59816.25	51501.79	1,161	1889.774	0.558
52	63,0	20,0	5.5	200000	1.054	2,040	60020.00	E1710 50	1 4 6 4	1074.0	615640.0	1.002	E0C24 22	E120C.00	1 1 1 2 2	1002.247	0,500
63	67,5	21,7	573	200000	1,251	2,810	00030,98	51/16,52	1,161	1971,2	013040,8	1,647	39021,32	51506,86	1,162	1602,317	0,586
64	70,0	20,0	573	200000	1,248	2,691	59848,38	51533,92	1,161	1874,3	589963,8	1,663	59337,21	51022,75	1,163	1711,448	0,618
65	0.0	66.7	573	500000	1.370	4.623	48116.29	39801.82	1,209	3539.7	2590316.8	3.079	48668.48	40354.01	1,206	3204.548	0.666
60	20.0	50,7	573	E00000	1,070	4.205	E2270.27	45064.04	1 1 0 4	2172.4	2222200.2	2 207	E2021.00	45507.40	1 1 0 2	2007 526	0.005
66	20,0	53,3	573	500000	1,324	4,205	333/9,3/	45064,91	1,184	51/2,1	2322209,3	3,387	55621,89	45507,42	1,183	2907,536	0,805
67	40,0	40,0	573	500000	1,289	3,762	57798,96	49484,49	1,168	2780,1	2057246,9	3,695	58112,50	49798,03	1,167	2565,960	0,982
68	60.0	26.7	573	500000	1 260	3 1 4 4	60232 56	51918 10	1 160	2251.5	1720045.8	4 003	60083.87	51769.41	1,161	2065 504	1 273
00	00,0	20,7	573	500000	1,200	3,144	60232,30	51010,10	1,100	2231,3	1/20045,8	4,005	00003,07	51703,41	1,101	1002.10	1,273
69	62,5	25,0	573	500000	1,257	3,041	60274,32	51959,86	1,160	2166,1	1665417,1	4,041	60027,93	51/13,46	1,161	1983,194	1,329
70	65,0	23,3	573	500000	1,254	2,931	60235,31	51920,85	1,160	2075,3	1606878,1	4,080	59888,36	51573,90	1,161	1896,539	1,392
71	67.5	217	573	500000	1 251	2 815	60110 73	51796.27	1 161	1979 5	1544384.7	4 119	59665.61	51351 15	1 162	1806 340	1 463
71	70.0	21,7	575	550000	1,201	2,015	50110,75	51, 50,27	1,101	1070,0	101104,7	,,110	55555,01	51051,15	1,102	1000,040	2,405

# Appendix: CANTERA Simulation for Constant Volume Bomb Method