Catalytic Ignition of Hydrogen Peroxide for Storable Bipropellant Thrusters

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Abstract

Catalytic ignition of liquid storable bipropellants was obtained in an optical combustor, for space thruster application. The pellet catalyst manufactured for this purpose was an MnO_x active phase deposited onto a silica-doped alumina support. Auto-ignition of the propellants occurred as two n-decane jets interacted with a hot oxidizing plume (700°C) resulting from the complete decomposition of 87.5% hydrogen peroxide. The equivalence ratio was varied from 0.90 to 1.65 for a fixed mass flow rate of 8 g/s. The flame ignition and stabilization processes were recorded in-situ by direct visualization, while the steady performance was characterized by physical measurements and characteristic velocity.

1. Context and objectives

European needs for clean and efficient propulsion technologies are emphasized by the increasing demand in space access. Among the most efficient solutions, storable bipropellant combustion offers a stable, throttleable and high-impulse solution, as currently investigated in Poitiers [1]-[2]. The storable propellants of interest are well-known, e.g. hydrogen peroxide as oxidizer, and alkanes or alcohols as fuels.

As far as storable bipropellant combustion is concerned, the ignitor is a key system that is to be simplified in order to reduce the mass and complexity of the thruster. For this, a catalytic ignitor is considered, by implementing the catalytic decomposition of hydrogen peroxide prior to fuel injection. Thus, no additional reactant is required for ignition, as compared to conventional torch ignitors.

Following this concept, recent work addressed the configuration of a catalytic decomposition chamber upstream of the combustion chamber, especially with hydrogen peroxide as oxidizer. The oxidizing decomposition products were reported to burn efficiently with the fuel [3]-[4], either for ethanol or kerosene fuel. However, such studies are sparse and conducted in opaque combustors, so that the auto-ignition itself is not characterized directly.

Catalytic decomposition of H_2O_2 has been widely studied. Among the catalytic materials investigated, some of them have demonstrated their high efficiency towards the decomposition of high concentrated H_2O_2: (i) metals such as silver, platinum [5] and (ii) metal oxides like manganese oxide [6]. The latter presents the advantage to be a relatively low-cost material. Typically, active phases are dispersed onto a high specific surface area material which is generally based on alumina. Depending on the preparation of this material, the transition of γ-alumina to δ-alumina can occur between 680 and 850°C [7], thus leading to a first decrease of the specific surface area and consequently to a decrease of the catalytic activity. This transition is followed, at higher temperature, by the δ ––> θ and the θ ––> α crystalline phase transitions, which are considered as the main cause of surface loss. Thus, the preparation of the support is crucial since the adiabatic decomposition temperature for 87.5%w HTP is about 695°C, and 953°C for 98 % HTP, assuming that the monopropellant is at ambient temperature at the entrance of the catalytic chamber. Higher temperature can be reached if the monopropellant temperature exceeds the ambient temperature when contacting the catalyst. However, transition can be shifted toward higher temperature with doping methods using, as an example, silicon [8]. This results

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in an enhancement of the heat resistance of the support. For propulsion applications, these high specific surface area materials are shape-formed into pellets or can be washcoated onto monolithic carrier to lower pressure drop.

The present study aims at implementing the decomposition of hydrogen peroxide through a tailored MnO_x active phase catalyst prepared at IC2MP, so as to investigate the auto-ignition of its decomposition products with n-decane – a reference fuel representing kerosene. This phenomenon is to be characterized in-situ within ACSEL optical combustor at PPRIME using physical and optical diagnostics.

2. Experiment and diagnostics

The bipropellant system of interest is composed of storable propellants injected in the liquid phase (see Table 1), namely HTP and decane. ACSEL combustion facility is designed to implement the combustion of such liquid propellants after direct injection in the combustion chamber, as demonstrated recently in the case of ethanol and alkanes [2].

Table 1: Properties of the storable propellants in the liquid phase

	Product	Concentration	Molecular weight (g/mol)	Density (kg/L) at 25°C
Oxidizer	HTP875	87.5%w	30.6	1.376
Fuel	n-decane	99%w	142.3	0.729

2.1. Combustion facility

In the present study, ACSEL optical combustor is fed by the gaseous decomposition products of HTP generated by a catalyst, whereas liquid decane is injected symmetrically through two 0.25 mm nozzles (see Figure 1). The steel combustor is fitted with 2 quartz windows, and pressurized by a 5 mm exit throat. The pressure in the combustor is measured by a piezoresistive sensor (Druck Unik5000, 0.1% uncertainty, 5 kHz bandwidth).
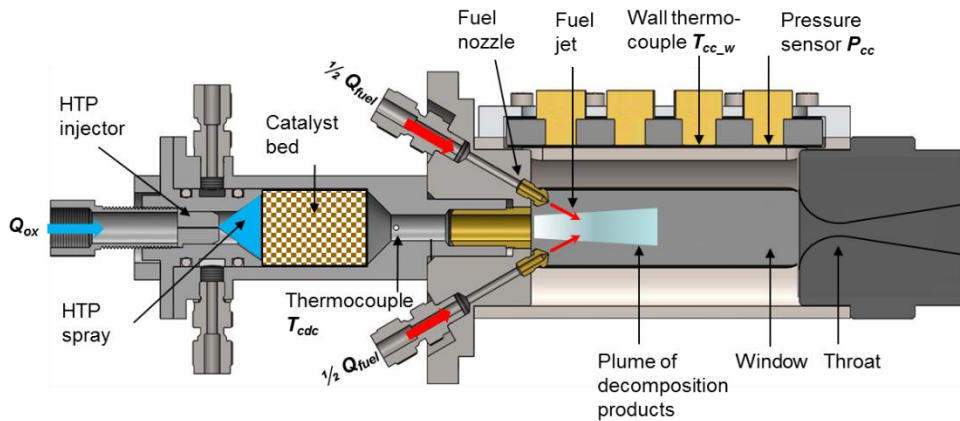

Figure 1: Assembly of the catalytic decomposition chamber on ACSEL optical combustor

The catalytic decomposition chamber (CDC) is a stainless steel vessel filled with catalyst grain between two steel grids; its wall temperature is regulated at 120°C to avoid cold start. It is fed with through a 0.51 mm diameter stainless steel injector. A 1 mm shielded K-thermocouple provides the temperature of the decomposition products at the catalyst exit (mostly H_2O and O_2). For liquid HTP875 at 25°C, this temperature is expected to reach 695°C in the case of adiabatic catalytic decomposition:

$$0.7875 \; H_2O_2 + 0.2125 \; H_2O \rightarrow 0.3938 \; O_2 + 1.0000 \; H_2O \tag{1}$$
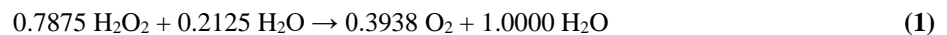
This temperature is expected to yield auto-ignition in the mixing zone where the plume of hot decomposition products of HTP meets the two fuel jets. Imaging of this zone is provided by a CCD camera (Photron AX-200) either by direct visualization of combustion chemiluminescence, or shadowgraphy of the fuel jets interacting with the plume (see Figure 2).

For each propellant, the liquid flow is controlled by a flowmeter (Bronkhorst M15, 0.2% uncertainty), a piezoresistive pressure sensor and a ball valve which actuation provides a finite sequence of operation. The sequence considered in this study begins with ten 300 ms HTP pulses, followed by a 10 s HTP plateau during which a 4 s fuel injection is performed.
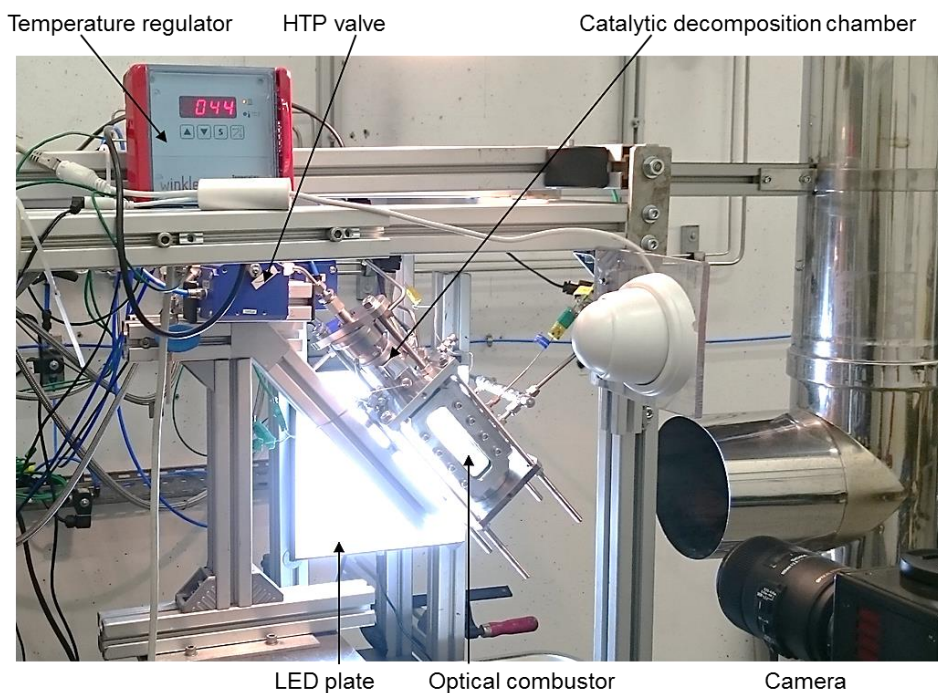
Figure 2: Optical setup

2.2. Catalyst description and preparation

An MnO_x active phase catalyst under the form of pellets was prepared. The pellets chosen for this application were made of alumina doped with silica and obtained from the powdered materials after shape-forming.

The target percentage of the active phase deposited was 10 % in weight in MnO_2 equivalent. For this, a precursor salt of MnOx was dissolved in water. The pellets were then immersed in this solution. Water was then evaporated. This step was followed by a heat treatment. Catalyst was then washed with water and dried.

A picture of the catalytic material thus obtained can be viewed in Figure 3.

Figure 3: Picture of MnO_x-based catalyst

Characteristics of this catalyst are as follows: a specific area of 220 m^2 g^{-1} (measured by nitrogen sorptiometry and using the BET method), and the quantity of MnO_X as determined by gravimetry is 9 %.

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3. Results and discussion

3.1. Characterization of the catalyst operation

The catalyst bed described earlier is inserted inside the CDC. The reference operation sequence is performed, including 10 successive 300 ms HTP pulses, followed by a 10 s HTP plateau (see Figure 4). The efficiency of HTP catalytic decomposition into gaseous products is quantified by T_{cdc}, the gas temperature measured at the exit of the CDC (see Figure 1). T_{cdc} increases during the first 5 successive HTP pulses, thus allowing a pre-heating of the catalyst bed up to around 600°C. The last five HTP pulses exhibit a constant maximum temperature, reaching around 600°C at the end of each pulse. As a result, the HTP plateau occurs in a preheated catalyst that operates in improved conditions, an reaches the optimum temperature target (see dashed line on Figure 4).

The maximum value of T_{cdc} is 710°C, that is slightly higher than the adiabatic catalytic decomposition temperature expected (695°C). Such a high value of T_{cdc} indicates that, although the tank is at room temperature (25°C), HTP has been heated in the liquid phase during its injection through the 0.51 mm stainless steel injector. This is due to the preheating of the CDC (120°C) before the first pulse of HTP.
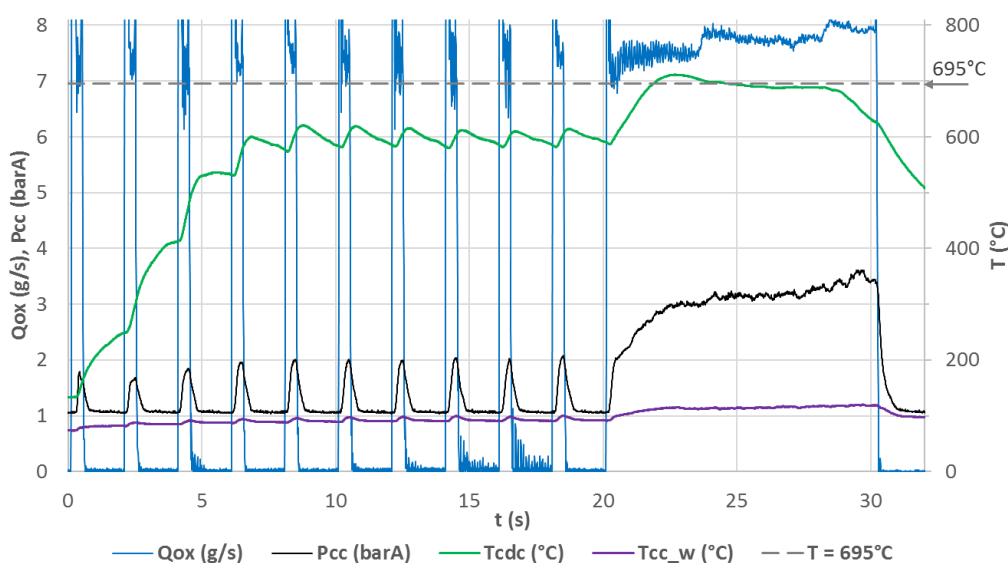

Figure 4: Operation sequence of the CDC with successful decomposition of HTP875

During the plateau, the mass flowrate of HTP increases slightly and is of 7.8 g/s in average. The exit temperature T_{cdc} raises during t = 20–22 s up to 710°C, then slightly stabilizes at 690°C after a few seconds. There is a sudden decrease in T_{cdc} at t = 29 s, i.e. 1 s before the end of the HTP injection plateau, which may indicate a partial saturation of the catalyst bed, that is probably due to the high flow rate of HTP.

3.2. Auto-ignition conditions of n-decane

The experimental sequence described above is designed to yield the auto-ignition of n-decane with the decomposition products of HTP. For this, the auto-ignition delay of the reactants must be compatible with the residence time of gas in the optical combustor.

Auto-ignition is expected to occur when injecting n-decane during the HTP decomposition plateau. Then, the combustion chamber is filled by catalytic decomposition products of temperature around 700°C, and pressure 3 bar due to the 5 mm throat. Therefore, the auto-ignition delay can be computed *ab initio* using chemical kinetics, under assumption that the mixture of n-decane with the decomposition products ($0.2825 \ O_2 + 0.7175 \ H_2O$) is adiabatic and homogeneous in temperature and composition. For this, the chemical scheme developed by Basevich [9] is implemented in Cantera solver and provides the auto-ignition delay as a function of temperature and equivalence ratio ER (see Figure 5).
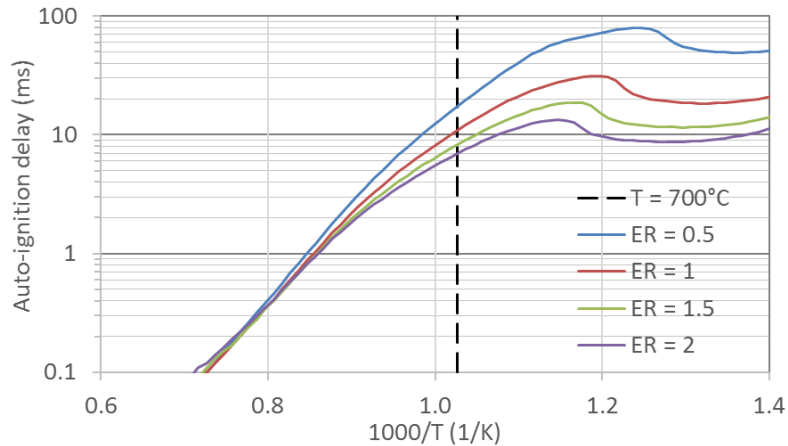
Figure 5: Auto-ignition delay of {n-decane / 0.2825 O_2 + 0.7175 H_2O} mixtures at 3 bar, computed from [9]

In such conditions, the auto-ignition delay for ER = 0.5–2 ranges in 7–17 ms, which is compatible with the average residence time in the combustor fed with 7.8 g/s hot decomposition products at 700°C and 3 bar, i.e. 31 ms. This makes auto-ignition possible in our operating conditions, and the corresponding tests are performed in the next section.

3.3. Combustion of n-decane with HTP decomposition products

The experimental sequence is performed to characterize the operation of the combustor fed with n-decane and HTP decomposition products from the CDC.
A typical test is reported as follows (see Figure 6). The fuel injection occurs 4 s after the beginning of the HTP plateau, and triggers the auto-ignition of n-decane with the decomposition products of HTP. The subsequent combustion phase lasts for 3 s, and leads to quasi-steady conditions in terms of mass flow rates (Q_{fuel} and Q_{ox}) and chamber pressure P_{cc} (see black curve on Figure 6).
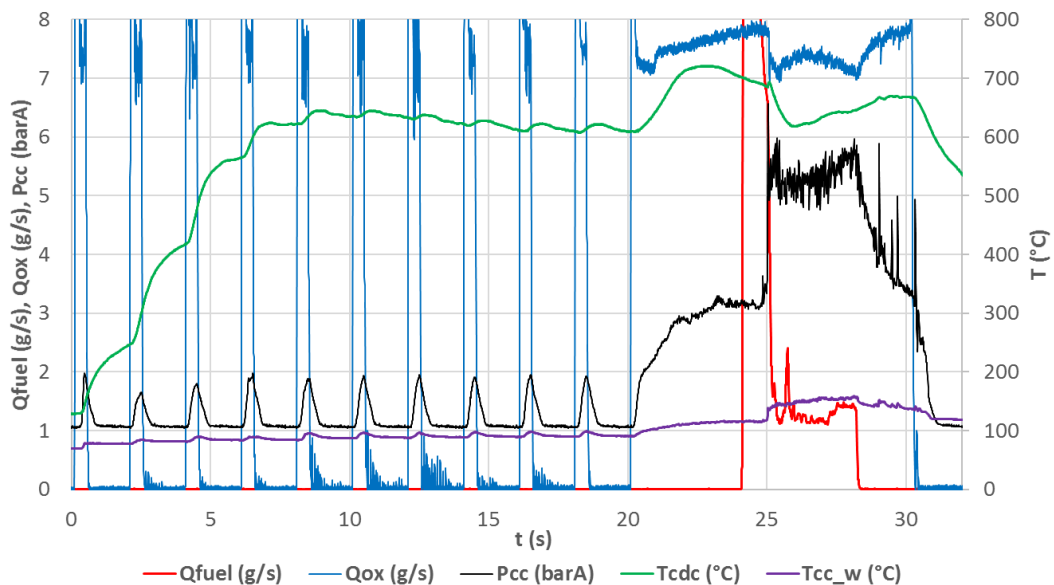

Figure 6: Operation sequence with successful auto-ignition inside the combustor – Test #4

The shadowgraph pictures show that the two fuel jets are sheared by the hot plume of CDC products, either before or after auto-ignition, that is to say during steady combustion (see Figure 7). The combustion process, that takes place downstream, does not seem to influence this mixing zone in the upstream part of the optical combustor, although the deflection of the fuel jets by the hot plume is emphasized after ignition. Chemiluminescence intensity indicates that the flame stabilizes rather in the bottom part of the combustor.

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Plume – fuel jets interaction before auto-ignition | Plume – fuel jets interaction after auto-ignition
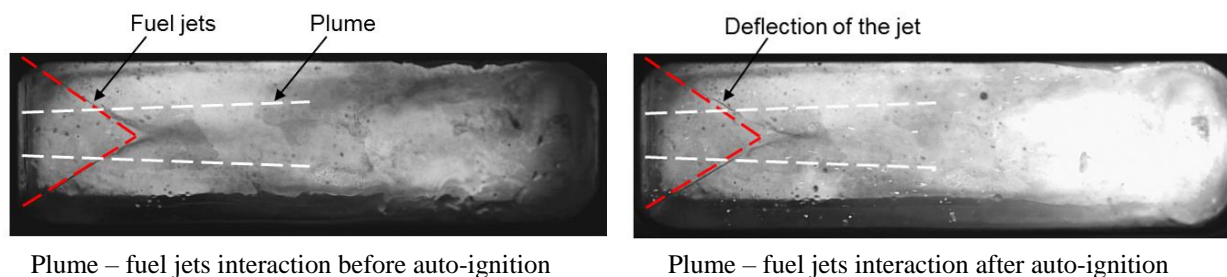
Figure 7: Shadowgraph pictures of the optical combustor during fuel injection

Direct imaging of the flow confirms that, although ignition spreads in the whole combustor (see Figure 8), the self-sustained combustion zone stabilizes downstream of the interaction zone between the oxidizing plume and the fuel jets, whereas chemiluminescence intensity is negligible in the injection region. Recirculation zones seem to be located at the throat corners, thus favouring combustion stabilization.

Picture at ignition | Jets illuminated by the flame shortly after ignition
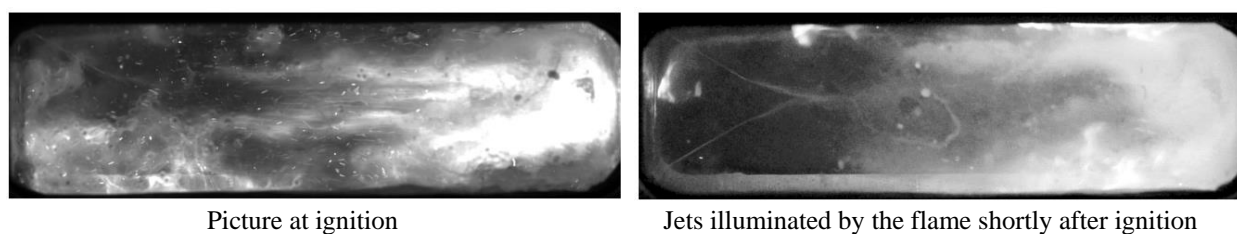
Figure 8: Chemiluminescence pictures of the optical combustor at ignition – Test #4

This experimental sequence is repeated with the same synchronization, and variable equivalence ratio at fixed total propellant flow rate (see Table 2). The behaviour of the CDC is repeatable, and yields hot plume temperatures of around 700°C when ignition occurs. The characteristic velocity c* associated to these tests ranges in 1240–1305 m/s for the conditions investigated. This characteristic velocity is to be compared to its value obtained in the case of bipropellant combustion: c* reaches 1400 m/s during the combustion of liquid n-decane and HTP875 [2] for the same flowrate and pressure, and within the same experimental setup.

Table 2: Experimental results during the combustion phase

Test	Catalyst temperature at auto-ignition T_{cdc} (°C)	Fuel jet velocity (m/s)	Plume velocity (m/s)	Total flow rate Q (g/s)	Equivalence ratio ER	Characteristic velocity c* (m/s)
#2	704	22	108	8.43	1.65	1305
#3	699	12	109	8.09	0.90	1240
#4	688	21	106	8.49	1.57	1292

However, the flame location in the combustion chamber is not the same depending on the equivalence ratio, at fixed total mass flow rate (see Figure 9). The flame is almost anchored to the fuel jets for ER = 0.90, whereas it is obviously detached for ER = 1.57. This lift-off phenomenon is not linked to the auto-ignition ability of the mixture, and may depend on the ER itself, that determines the flame power, as well as on the internal aerodynamics imposed by the injection system. This point deserves further investigation, as well as quantitative measurements. It is noticeable that lifted flames of similar behaviour can be observed in the case of propellants injected in the liquid phase in the combustion chamber [1].
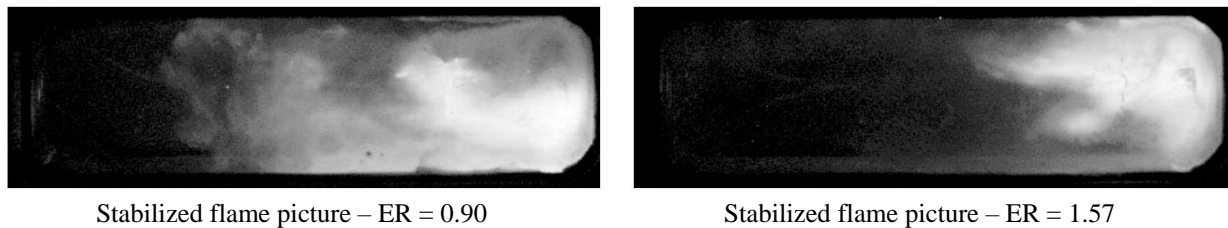
Stabilized flame picture – ER = 0.90   Stabilized flame picture – ER = 1.57

Figure 9: Chemiluminescence pictures of the optical combustor in steady state

4. Conclusion

This study presents recent results concerning the auto-ignition of n-decane in the catalytic decomposition products of HTP875. An MnO_x catalyst under the form of pellets was prepared with an alumina support doped with silica. This catalyst bed proved to decompose efficiently the flow of liquid oxidizer, with an exit temperature of decomposition products as high as 700°C, thus achieving an improved decomposition process. This hot oxidizing flow, associated to the sufficient residence time of gas inside the combustor, led to the auto-ignition of liquid n-decane jets for three values of equivalence ratio 0.90–1.57–1.65, in agreement with auto-ignition delay computations based on Basevich mechanism.
In-situ visualization of the reactive flow provided insight into the combustor dynamics. The shadowgraphy recording of this process revealed the interaction between the two liquid fuel jets and the gaseous plume of oxidizing products. The direct visualization of the reactive flow showed the auto-ignition phenomenon, as well as the stabilization of the flame in the bottom part of the combustor, eventually with a lift-off depending on the overall equivalence ratio.

Acknowledgements

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