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Detailed kinetic computations and experiments for the choice of a fuel-oxidiser couple for hybrid propulsion.

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## Abstract

The choice of a solid reducer for hybrid propulsion is generally based on the quantity of gaseous combustible it can produce (expressed indirectly by the regression rate). For this reason, the studies focus on the use of additives or on the design of grain while the kinetic aspect is rarely of interest despite the chemistry drives the phenomena (chemical induction delay, heat absorption, chemical composition). One-step mechanisms are first considered in this paper to quantify the effect of operating conditions on high density polyethylene -HDPE-, polymethylmethacrylate -PMMA- and hydroxyl termination polybutadiene -HTPB-. Then the chemical composition of pyrolysis products is determined for a large range of operating conditions with highly detailed mechanism for HDPE (1014 species, 7541 reactions). The heating rate applied to the reducer is investigated (from  $1 \text{ K s}^{-1}$  to  $10^7 \text{ K s}^{-1}$ ). Ethylene is found to be the major pyrolysis product. The timescale found over 1250 K and 11.11 bar is in agreement with the requirements of hybrid propulsion. The calculated data are compared to

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experimental ones. Finally, a short combustion study with detailed chemistry (over 700 species and 3000 reactions) is proposed because it impacts directly on the pyrolysis through the generated heat flux. It allows considering the oxidiser decomposition (hydrogen peroxide -H<sub>2</sub>O<sub>2</sub>- and nitrous oxide -N<sub>2</sub>O-). Pure oxygen -O<sub>2</sub>- is considered as reference data. The effect of atmosphere (inert or oxidative) on the pyrolysis is shown. The kinetic computations of N<sub>2</sub>O combustion give higher flame temperatures than for H<sub>2</sub>O<sub>2</sub>. Ignition times, below a few milliseconds, are obtained for all the reducers over 1250 K. Finally, the HDPE/H<sub>2</sub>O<sub>2</sub> and HTPB/N<sub>2</sub>O couples are found to be the most interesting.

## Keywords

Kinetic Study; Pyrolysis; Combustion; Hybrid Rocket Propulsion; Solid Fuels.

## Abbreviations and acronyms

DTG: Derivative Thermo Gravimetry

HTPB: Hydroxyl Terminated PolyButadiene

DSC: Differential Scanning Calorimeter

(HO-((C<sub>4</sub>H<sub>6</sub>)<sub>0.2</sub>-(C<sub>4</sub>H<sub>6</sub>)<sub>0.6</sub>-(C<sub>4</sub>H<sub>6</sub>)<sub>0.2</sub>)<sub>n</sub>-OH)

TGA: ThermoGravimetry Analysis

PMMA: PolyMethylMethAcrylate

HDPE: High Density PolyEthylene ((CH<sub>2</sub>-  
CH<sub>2</sub>)<sub>n</sub>)

((C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>)<sub>n</sub>)

## 1. Introduction

Hybrid technology presents high safety characteristic because of the propellant separation (solid reducer and gaseous oxidiser) [1],[2]. It is a coupled system because the gaseous combustible production is achieved through the solid

pyrolysis under the heat flux generated by the combustion itself [3]. After the engine ignition, the system is self-sustained. A diffusion flame appears in the stoichiometric region between oxidiser flow and diffusing pyrolysis gas products [4]. It is located in the boundary layer and its position depends on the nature of chemical species and on the oxidiser flow. Due to the boundary layer establishment, the distance between the flame and the solid surface can vary spatially. The heat release is received for a part by the solid-gas interface (an additional liquid film can appear when using polymer like paraffin). The propagation of conductive heat transfer inside the solid reducer should be limited to avoid melting or degrading the entire combustible grain. The infrared deep absorption enhances the heat diffusion in the solid. Time variations are possible in the system. The control of injection valve allows modifying the thrust through the adjustment of the oxidiser flow [1],[5]. This thrust directly depends on the momentum increase which can be achieved by those of the burned gases temperature, of their density and of their velocity. Increasing the quantity of burned gases is only possible by the one of oxidiser flow and thus by the one of combustible since the equivalence ratio should be around one. A lean mixture presents the advantage to burn the entire produced combustible but it is of strong oxidative impact for the engine's structure [6]. A rich mixture presents the advantage to limit the structure degradation but it corresponds to a loss of possible propulsive effect. In addition, the limiting step of hybrid technology is currently the production of gaseous combustible [7]. For this reason, numerous studies are

focusing on its enhancement through additives [8], grain design and oxidiser injection [9]-[11].

Nevertheless, rare study exists on the chemical phenomena [12]. Chen et al. considered 13 species and 17 reactions for both combustion and pyrolysis [12], which seems to be the maximum mechanism size used in literature to the authors' knowledge. The pyrolysis of the solid depends on the following parameters: temperature, time, heating rate, pressure and atmosphere. This thermal decomposition can be characterised by: the composition of chemical products, the endothermic effect, the induction delay. Its impact is directly seen on: the chemical diffusion, the auto-ignition delay, the combustion efficiency and the associated heat release. These are visible in the engine by the distance from the surface to the flame, by the heat flux and by their spatial and time profiles inside the combustion chamber. The thrust is the final witness. It is thus obvious that the chemistry fundamentally drives the entire operating parameters in the engine (even if geometrical parameters obviously play a non negligible role). Despite this fact, no studies to the authors' knowledge focus specifically on the kinetics of the pyrolysis and of the combustion. The numerical works found in the literature are either dedicated to equilibrium calculations or they use empirical laws giving the physical displacement of the solid-gas interface (called the regression rate) [10]. The experiments generally focus on the solid surface by optical diagnostics but they never analyse the chemical composition inside the engine by mean of sampling or of non intrusive techniques.

It is experimentally difficult to analyse as a function of time the chemical composition of pyrolysed products and of burned gases in a hybrid engine. Thus, the numerical investigations are the most appropriate, at least in a first step, to predict the time variations of the species concentration. These simulations must be based on detailed chemical mechanisms. These latest can be used under 0-D configuration as a first step to understand and to characterise the chemical phenomena.

A review has been furnished in companion paper [13] to provide an extended view of the chemical processes involved in hybrid engine, particularly during solid fuel pyrolysis. The characteristic timescales and the heat fluxes of all the related phenomena and the effect of operating conditions on the fuel degradation have been presented [13]. Due to the strong coupling with the combustion, both pyrolysis and oxidative processes must be considered. For this reason, it is intended in this paper to present the effect of atmosphere on the solid decomposition and to quantify the combustion characteristics (flame temperature, heat release rate and auto-ignition delay) which modify the pyrolysis. The effect of the detailed chemistry is investigated by comparison with one-step mechanism. Some experimental results are also proposed to support the numerical data which are obtained using mechanisms initially proposed for other application [13]. The decomposition of the oxidisers,  $\text{H}_2\text{O}_2$  and  $\text{N}_2\text{O}$ , is also considered.

## **2. Numerical and Experimental Pyrolysis of the Reducers**

The numerical pyrolysis study aims at evaluating the nature and the quantity of pyrolysis products depending on the initial reducer (section 2.1.). These data are linked to certain parameters like the pyrolysis time and the operating pressure. The experimental work is then presented (section 2.2.). Knowing the species that are produced by pyrolysis as a function of the operating conditions will help to choose a reducer, for example to get the highest specific impulse or the lowest ignition time. This combustion aspect is treated in section 3.

## **2.1. Numerical work**

Most of the transient calculations presented in this work have been achieved with the CHEMKIN program [14] under 0-D homogeneous conditions with either isothermal or isobaric configuration. Few calculations considering a flame development are 1-D. Several detailed kinetic mechanisms are used, as mentioned where necessary. The operating conditions are detailed later for each calculation.

### **2.1.1. Effects of heating rate, of time and of pressure**

Considering the time effect on the pyrolysis can be firstly done by using global Arrhenius law whose coefficients are estimated by experimental data, despite the limitations due to TGA measures [13]. HTPB decomposition is investigated (Figure 1) using kinetic parameters from literature [15],[16]. At each time, the reaction rate is defined as the difference between initial and instantaneous reactant amount and this difference is divided by the initial reactant amount (here:  $\text{Reaction rate} = (n^\circ(\text{HTPB}) - n(\text{HTPB})) / n^\circ(\text{HTPB})$  where  $n^\circ$  and  $n$

represent the initial and current amount of HTPB). The same calculations are conducted for HDPE and for PMMA (parameters from [13] and [17] respectively). The relationship between the heating rate, the temperature of pyrolysis (Figure 1a) and the time (Figure 1b) is clear. The higher the heating rate, the higher the pyrolysis temperature and the lower the associated time. As a consequence, the chemical composition will be strongly different. The reaction pathway under sudden high heat flux generates preferably light molecules instead of heavier ones with moderate heat flux and long residence time [18].

*Figure 1 should be placed here*

The temperature and times for which 99 wt.% of the pyrolysis is reached are given in Table 1 for several values of the heating rate (which corresponds to the time history of the temperature applied to the fluid). When dividing these temperatures by these times, one can obtain kind of absorbed heat rate, which differs from the heating rate because of the chemical induction delay in case of pyrolysis. The pyrolysis temperature and time vary for HTPB from 613 K and 2.7 s at  $10^2 \text{ K s}^{-1}$  to 2500 K and 4.47 ms at  $10^7 \text{ K s}^{-1}$  (Table 1). The time required to heat the reducer (with pyrolysis of less than 1 wt.%) is not counted in the given pyrolysis time because the calculations are made under 0-D configuration. By comparing this time to the residence time of 20 ms [13], the heating rate should be higher than  $10^4 \text{ K s}^{-1}$ . Consequently, the combustion study (section 3.) must answer this point by giving the thermal increase rate for several reducer-oxidiser couples. The flame temperature is reasserted to be important for the choice of the

oxidiser for dynamic purposes. The combustion time should be short enough to get a high heating rate.

PMMA presents a pyrolysis time and temperature at 2.02 bar higher than those of HTPB at  $10^4 \text{ K s}^{-1}$  but these two polymers have similar behaviours when comparing HTPB at 2.02 bar with PMMA at higher pressure (11.11 bar). The pressure rise (from 2.02 bar to 11.11 bar) decreases the pyrolysis time by a factor 2 for PMMA at  $10^4 \text{ K s}^{-1}$  and by more than one order of magnitude at  $10^7 \text{ K s}^{-1}$ . At least qualitatively, this demonstrates a favourable high pressure condition. This is interesting because there are very few results on the pressure effect in hybrid propulsion studies. The studies generally focus on a range of less than 10 bar while much higher pressure could be encountered in hybrid rocket. For the same  $10^4 \text{ K s}^{-1}$  heating rate, the HDPE presents lower pyrolysis temperature and decomposition time than HTPB or PMMA. This means that it is much easier to pyrolyse it compared to the two other polymers.

*Table 1 should be placed here*

### **2.1.2. HDPE pyrolysis by means of detailed chemistry computations.**

In addition to the fuel consumption as presented above, the formation of by-products must be studied for later combustion characterisation. HDPE appears interesting for hybrid propulsion (high density, high combustion enthalpy and regression rate, qualitatively interesting pyrolysis products, short pyrolysis time). The availability of a detailed mechanism for HDPE enables to precisely compute the effect of temperature, pressure and time on the thermal decomposition. It has

not been possible to get a detailed pyrolysis mechanism for PMMA and HTPB, or even a semi-detailed one since none exist to the authors' knowledge. The mechanism of Nemeth *et al.* [19] is used for polyethylene despite the unclear pressure effect consideration. Solid, liquid and gaseous species are considered. No aromatic formation is considered. This pyrolysis scheme (1014 species and 7541 reactions) is initially proposed for recycling purpose and it considers several reaction paths (random scission, H-abstraction). HDPE is modelled by tetracontane ( $C_{40}H_{82}$ ). The pyrolysis time may namely be lower for heavy molecules but the authors validated the mechanism by experimental measures. The Arrhenius parameters are thus appropriate.

The pyrolysis of HDPE can be conducted under two configurations. The first is to consider constant temperature and pressure by assuming the engine is working in permanent state. At 750 K (Figure 2a), the reaction rate percentage after 5 s is lower than 50 % for all the pressure cases. Surprisingly, this percentage increases from 30 % at 1.01 bar to 45 % at 10.1 bar before decreasing regularly to 19 % at 101 bar. This shows that, as the pressure is increased, the product release is reduced. The pressure effect is not monotonous at this temperature and it presents a maximum. At 1250 K (Figure 2b), the reaction rate percentage reaches 99 % for times lower than 1 ms whatever the pressure. For a residence time of 0.1 ms, it is 78 % at 1.01 bar and 98.2 % at 101 bar. Increasing the pressure by a factor 100 makes the time corresponding to 99 % of pyrolysis to be reduced by a factor 10. At this temperature, no pressure singularity is found. It becomes negligible at 2000 K and the time of full pyrolysis is much lower than one

microsecond, which appears to be questionable. This is attributed to the limited validity of the mechanism at high temperature. It can be noted that the initial number of carbon in the polymer formulation is also a source of error [20].

*Figure 2 should be placed here*

The distribution of pyrolysis products remains relatively dependent on the operating conditions (Figure 3). Increasing the temperature from 1250 K to 2000 K (Figure 3a and Figure 3c) makes the ethylene fraction increase from 45 % to 70 %, while it is more or less constant during a pressure increase (Figure 3a and Figure 3b). The methane production decreases with the pressure and with the temperature. It is assumed that, due to the low validity of the mechanism at high temperature, the transformation of pyrolysis products is not sufficiently observed. A larger decomposition of heavy products, like  $C_5H_8$  or  $C_6H_{10}$  for example, should be observed under such high temperature. The final products should be methane, hydrogen with ethylene and acetylene. It can be noted that the sum of the six species with HDPE presented in Figure 3 roughly decreases during the HDPE pyrolysis (from right to left on Figure 3), except at high pressure where this sum increases for HDPE content lower than 20 mol.%. Other compounds are also produced during HDPE pyrolysis and the increase of this sum shows that these 6 major products are favoured.

To conclude on these calculations at constant pressure and temperature, a pressure of at least 10 bar is preferable in terms of chemical composition and pyrolysis time. It is in good agreement with the results of the preceding section.

*Figure 3 should be placed here*

The second way to pyrolyse HDPE is to employ a constant pressure assumption (only). It enables observing the endothermic effect of the decomposition (Table 2). After 5 s, at 1000 K initially, the thermal decrease is about 264 K – 278 K depending on the pressure. It is slightly greater at lower pressure on the range 10.1 bar – 101 bar. A maximum is found at 10.1 bar since the value at 1.01 bar is lower than the one at 10.1 bar. Increasing the initial temperature makes the pyrolysis rate and the endothermic effect to be higher. Similarly at 2000 K, a maximum of 1226 K is found at 10.1 bar.

*Table 2 should be placed here*

## **2.2. Experimental work**

### **2.2.1. TGA apparatus to estimate the heating rate and atmosphere effects**

PMMA decomposition has been studied thanks to thermogravimetric experiments. The aim is to conduct only a few experiments to confirm the preceding numerical results concerning the heating rate effect and then to investigate the atmosphere effect. PMMA has been studied under oxidative and inert atmospheres up to 1273 K at 1 K min<sup>-1</sup>, 10 K min<sup>-1</sup> and 20 K min<sup>-1</sup>. The mass loss fraction of the sample from TGA and the mass loss rate (Derivative ThermoGravimetry signal) are given for several configurations (Figure 4).

The 1 K min<sup>-1</sup> test with Ar shows a DTG peak at lower temperature (593 K) compared to 10 K min<sup>-1</sup> test (663 K) or 20 K min<sup>-1</sup> test (683 K). The relationship between the pyrolysis and the applied heating rate is shown (the higher the heating rate, the higher the pyrolysis temperature). It confirms the numerical

results. It is also observed for Ar conditions that the mass loss shows two steps (Figure 4a). The first decomposition from 473 K to 623 K, represents 15 wt.% of the total mass loss. The second one from 623 K to 723 K, which lasts 4.5 min, corresponds to the remaining 85 wt.%. Contrary to Ar tests, the oxidative one with Air shows only one decomposition step which covers a larger temperature range from 563 K to 703 K and lasts about 7 min. This demonstrates the effect of the atmosphere on the pyrolysis. This clear difference of oxidative test compared to the inert ones is also visible on the mass loss rate (Figure 4b).

*Figure 4 should be placed here*

### **2.2.2. The nature of PMMA pyrolysis products and first kinetic approach through experiments**

The TGA apparatus is linked to a mass spectrometer (Balzers Instruments, ThermoStar GSD 300 T). The PMMA pyrolysis at 600 K ( $10 \text{ K min}^{-1}$ ) shows the following products:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_5\text{H}_{10}$ ,  $\text{C}_6\text{H}_6\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ . They are mainly produced by secondary gas phase reactions while the primary pyrolysis in condensed phase forms MethylMethAcrylate ( $\text{C}_5\text{H}_8\text{O}_2$ ). This is in qualitative agreement with the literature [21]. It can be noted that hydrogen is not detected during the experiments. This can be attributed to its low formation and to its strong volatility, which makes it difficult to be measured in case of slight leakage.

The HSC results [13] and the present experimental data are now compared to literature [21] at 698 K and 1 bar (Figure 5). The data are normalised by the major species found for each set of results. It is obvious that the sets of data are in poor

quantitative agreement. In particular, the limit of equilibrium calculations is visible at low temperature and heating rates.

*Figure 5 should be placed here*

Then, the Arrhenius parameters have been computed thanks to the Kissinger method; with the assumption of a first order reaction, which is suitable for the PMMA pyrolysis (Figure 6). The abscissa corresponds to the inverse of the temperature for which the DTG peak is observed ( $1/T_m$ ). The vertical axis is the logarithm of  $\beta$  (the time derivative of temperature) divided by  $T_m^2$ . The resulting activation energy is  $185.8 \text{ kJ mol}^{-1}$  and the pre-exponential factor is  $3.89 \cdot 10^{12} \text{ s}^{-1}$ . This is in good agreement with data generally observed [17]. This regression analysis presents a correlation coefficient of 0.9942; the strong correlation confirms that the reaction is of first order as has been supposed. The estimated standard deviation is found to be 0.11 on the basis of DSC measures.

*Figure 6 should be placed here*

A Differential Scanning Calorimeter (DSC) has also been used with the Freeman-Carroll method to estimate these parameters by observation of the endothermic decomposition effect. The reaction order is found to be 1.15, the activation energy  $185.13 \text{ kJ mol}^{-1}$  and the pre-exponential factor  $7.09 \cdot 10^{12} \text{ s}^{-1}$ . These results show the difficulty of obtaining reliable data.

### **3. Numerical study of pyrolysis coupled with oxidative reactions**

The combustion of HTPB is often considered with ammonium perchlorate (AP) and it is possible to find semi-detailed numerical schemes to compute

ignition and burning parameters [22]. But this monopropellant is suitable for solid propulsion and not for hybrid propulsion due to solid AP toxicity (Chlorous content). Thus, HTPB, PMMA and HDPE will be considered with the same oxidisers ( $\text{H}_2\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_2$ ). It must be noted that the present combustion work does not involve highly detailed fluid mechanics and heat transfer considerations. This is not a modelling with description of the combustion process but a study of the chemical effect of several compounds on their selection for a hybrid propulsion system.

### **3.1. Thermal decomposition of the oxidiser by detailed numerical mechanism**

Several points have been investigated to provide a characterisation of the oxidisers selected in [13]. First, a phase diagram of the  $\text{H}_2\text{O}_2+\text{H}_2\text{O}$  mixtures has been elaborated depending on the concentration of respective compounds for several pressures. When the pressure is increased, the boiling and the liquefaction curves become closer and are translated toward higher temperatures. Then, the ability of equilibrium calculations to simulate the oxidiser decomposition has been tested. Owing to the unstable behaviour of  $\text{H}_2\text{O}_2$ , the final products from 500 K to 1500 K are  $\text{H}_2\text{O}$  and  $\text{O}_2$  with concentrations corresponding to the equilibrated reaction. The same calculations of  $\text{N}_2\text{O}$  decomposition show an  $\text{N}_2$  and  $\text{O}_2$  formation, while  $\text{NO}$  appears only at temperatures higher than 1500 K whatever the pressure. HSC is judged to be not suitable for such calculations.

Consequently, the thermal decomposition of an  $\text{H}_2\text{O}_2+\text{H}_2\text{O}$  mixture has been computed thanks to a detailed mechanism [23] in order to estimate the

decomposition time (Table 3). The higher the temperature, the pressure and the  $\text{H}_2\text{O}_2$  content (in this order of importance), the lower the decomposition time. The same is observed on the temperature reached after decomposition (Table 3).  $\text{H}_2\text{O}$  is found to act only as a diluter. The final decomposition products are  $\text{H}_2\text{O}$  and  $\text{O}_2$  in direct proportion to the initial H and O content. This is the same as the result obtained by equilibrium calculations. Considering gaseous  $\text{H}_2\text{O}_2+\text{H}_2\text{O}$  mixture and gaseous decomposition products, the heat of decomposition is  $2445 \text{ kJ kg}^{-1}$  at 66 mol.% of  $\text{H}_2\text{O}_2$  and  $2845 \text{ kJ kg}^{-1}$  at 85 mol.% [24]. For one kilogram, this corresponds respectively to a temperature increase of 801 K at 66 mol.% and 1001 K at 85 mol.% (heat capacity of  $3051 \text{ J kg}^{-1} \text{ K}^{-1}$  at 66 % and  $2842 \text{ J kg}^{-1} \text{ K}^{-1}$  at 85 mol.%). These thermodynamic considerations qualitatively verify the numerical results. In the following, if not mentioned, the  $\text{H}_2\text{O}_2$  content to be considered is 85 mol.%.

*Table 3 should be placed here*

To conclude on this sub-section, the decomposition of  $\text{H}_2\text{O}_2+\text{H}_2\text{O}$  mixture is very limited for temperature of less than 800 K. This indicates that at least 800 K must be reached at the inlet of hybrid combustion chamber if  $\text{H}_2\text{O}_2$  is used. This is important for the starting of the engine. In addition, some detailed kinetic computations have been conducted to observe a potential stabilisation effect of  $\text{N}_2\text{O}$  on the  $\text{H}_2\text{O}_2$  decomposition. But  $\text{N}_2\text{O}$  appears to only act as a diluter.

### **3.2. Combustion parameters of selected fuels**

The reaction enthalpies of the thermal decomposition (endothermic) for several reducers, followed by their combustion (exothermic) with some oxidisers, are computed thermodynamically.  $\text{N}_2\text{O}$  ( $-62770 \text{ kJ kg}^{-1}$  with HTPB and  $-34740 \text{ kJ kg}^{-1}$  with PMMA) seems to be a better oxidiser than  $\text{O}_2$  ( $-45070 \text{ kJ kg}^{-1}$  and  $-23890 \text{ kJ kg}^{-1}$  respectively) if the heat release is considered for a complete combustion at the stoichiometry. But using  $\text{N}_2\text{O}$  at the stoichiometry requires a quantity which is twice that of  $\text{O}_2$ . The PMMA conducts to a lower overall heat release compared to HTPB. This result generally justifies the use of HTPB.

Based on the preceding pyrolysis data (section 2), the decomposition products of HTPB and of PMMA are burned in stoichiometric conditions with several oxidisers in adiabatic freely propagating premixed flame at 60 bar (GRI mechanism: 53 species, 325 reactions). The mixing of gaseous compounds, the flame stability and the influence of the O/F ratio are not investigated because they are mainly related to the design and dimensioning of the engine.

The adiabatic flame temperature is higher for both  $\text{N}_2\text{O}$  and PMMA than for  $\text{H}_2\text{O}_2$  and HTPB (Table 4). But the laminar burning velocity is higher for  $\text{H}_2\text{O}_2$  than for  $\text{N}_2\text{O}$  (Table 4). The higher the flame speed, the higher the heating rate and the smaller the length of the combustion chamber. The choice of the oxidiser is a compromise between the flame speed and the temperature.  $\text{H}_2\text{O}_2$  is more interesting for propulsion because its flame speed is about twice that of  $\text{N}_2\text{O}$  and its temperature only 15 % lower. PMMA is slightly more interesting than HTPB because it presents a higher flame speed and temperature. This contradicts the equilibrium calculations. This is attributed to the 1-D flow configurations and to

the fact that equilibrium may not be established. It must be noted that using the equilibrium computation code CEA from NASA (Chemical Equilibrium with Applications), a temperature of 3984 K is found for the HTPB pyrolysis mixture with  $N_2O$ ; the same than used with detailed mechanism (value of 4152 K in Table 4). This discrepancy of 4 % is attributed to the thermodynamic data of species and in less extent to the different reaction products which are taken into account. Nevertheless, for a comparative purpose, these calculations are judged satisfactory for a first approach.

***Table 4 should be placed here***

In order to estimate the combustion of HDPE pyrolysis products (computed in section 2.1.2.), a kinetic mechanism is required. The detailed mechanism of n-heptane combustion (561 species, 2539 reactions [25]), added to the GRI Mechanism, is used to consider the major products which are produced by the pyrolysis of HDPE. The four test cases (and two more at 20.2 bar) presented in Figure 3 are retained with their respective decomposition products compositions at 99 % of pyrolysis. The calculations of the ignition time are made for an equivalence ratio of 1 (Table 5). The differences are mostly attributed to the initial temperature or to the composition of the mixture but only slightly to the pressure.

To specifically investigate the effect of the products composition, several mixtures obtained at various temperatures and pressures of pyrolysis are then considered under the same combustion conditions (1250 K; 20.2 bar). The decomposition products which are obtained at lower temperatures present an ignition time of 1 ms (2 ms for the compounds produced at higher temperatures).

But their maximum combustion temperature is lower. The pressure has a negligible effect on this point. It has been shown (section 2.1.2.) that a pyrolysis level of 99 % is reached for time of much less than 1 ms whatever the pressure. Consequently, it is obvious that the combustion can be the limiting phenomenon and not only the pyrolysis contrary to what is commonly believed. Remembering that with  $\text{H}_2\text{O}_2$ , for example, the time required for the oxidiser decomposition is at least 1 ms (Table 3), the kinetics of the oxidiser should be carefully considered. Furthermore, the use of an HDPE pyrolysis mechanism, based on tetracontane, should not be omitted because this may impact on the pyrolysis time.

*Table 5 should be placed here*

### **3.2. Choice of the reducer-oxidiser couples**

Thanks to the detailed combustion mechanism used above, the three oxidisers are burned with the pyrolysis products of the three reducers (HTPB, PMMA, HDPE) at 1250 K under 1.01 bar for an equivalence ratio of 1 (Table 6). The composition found in [4] at 1073 K is also considered. For all the cases,  $\text{O}_2$  presents the highest temperature, then  $\text{N}_2\text{O}$  and finally  $\text{H}_2\text{O}_2$ . HDPE presents the lowest heat release.

Concerning the ignition time, HDPE and HTPB are relatively similar (the two last columns of Table 6). On this basis, HDPE should be used preferably with  $\text{H}_2\text{O}_2$  due to the much lower ignition time than with  $\text{N}_2\text{O}$  and because the difference on the temperature is moderate. If HTPB is preferable,  $\text{N}_2\text{O}$  should be used because of a temperature 20 % greater than with  $\text{H}_2\text{O}_2$ , even if  $\text{H}_2\text{O}_2$  presents

a shorter auto-ignition time. If comparing the first and third columns of Table 6 (HTPB and HDPE respectively at 1250 K), HTPB presents smaller auto-ignition delays compared to HDPE and for this reason, it could be preferable. Nevertheless, HDPE also presents some advantages in terms of cost, simplicity, density and thermal conductivity [13]. If  $H_2O_2$  is preferred because of Table 4, HDPE should be preferred because of its advantages on HTPB [13].

*Table 6 should be placed here*

These calculations are useful because it is generally admitted that the chemistry (combustion or pyrolysis) present timescales of less than 1 ms (pp 367-4). It is now shown that this depends on the operating conditions and on the reducer and oxidiser.

#### **4. Conclusions**

The importance of detailed chemistry remains often underestimated in hybrid rocket engine technology. The thrust, obtained by the momentum increase through the combustion process, depends on the diffusion flame which is piloted by the diffusion of chemical compounds and by the associated auto-ignition delay. Consequently, instead of using the usual method of trials-and-errors in selecting a couple of reducer and oxidiser, the present study has focused on the computation of some key parameters (pyrolysis and combustion) by means of detailed chemistry. The pyrolysis time, the flame temperature, the flame velocity, the auto-ignition time and the heating rate appear to be the major parameters in selecting a reducer and an oxidiser.

One step mechanisms (for HDPE, PMMA and HTPB) and detailed HDPE pyrolysis mechanism (1014 species, 7541 reactions) have demonstrated the pressure effect. The temperature is confirmed to decrease the pyrolysis time. Depending on the heating rate, the pyrolysis appears at different times and temperatures. This rate must be at least  $10^4 \text{ K s}^{-1}$  to get a pyrolysis time compatible with the average 20 ms residence time in the combustion chamber. Under the same heating rate, HDPE presents lower temperature and time of pyrolysis than PMMA and HTPB. This implies higher possible regression rate. Some experiments have been conducted to confirm the heating rate effect.

The atmosphere (Ar or air) is also found experimentally to influence the pyrolysis. For this reason, the oxidiser has been considered in this study since it impacts on the pyrolysis. Its effect is not only thermal but also chemical. The decomposition time of the  $\text{H}_2\text{O}_2$  oxidiser is reduced at high temperature, high pressure and high  $\text{H}_2\text{O}_2$  content. The limitation of thermodynamic calculations is shown since a higher heat release for HTPB than for PMMA was obtained while the kinetic computations show the opposite. This is due to the higher flame speed and temperature for PMMA, which are not considered by equilibrium computations.

The auto-ignition time is shown to be generally higher than the pyrolysis timescale, while the opposite is often supposed without clear investigation.  $\text{H}_2\text{O}_2$  is found to be more interesting than  $\text{N}_2\text{O}$  because of flame speed notably. Its heating rate is also several orders higher than that of  $\text{N}_2\text{O}$  with HDPE and HTPB. Consequently, the HDPE/ $\text{H}_2\text{O}_2$  couple is estimated to be the most promising for

hybrid technology. For safety reasons, if  $H_2O_2$  should be avoided, HTPB/ $N_2O$  could be considered.

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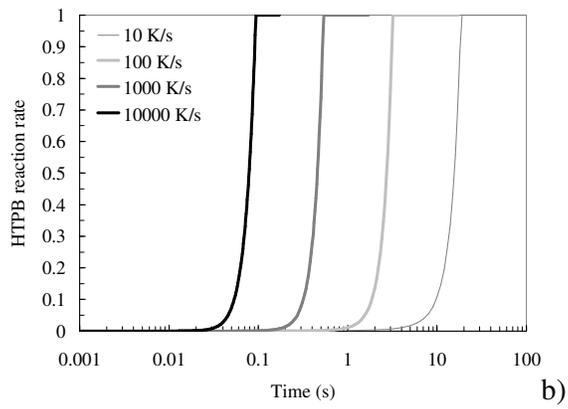
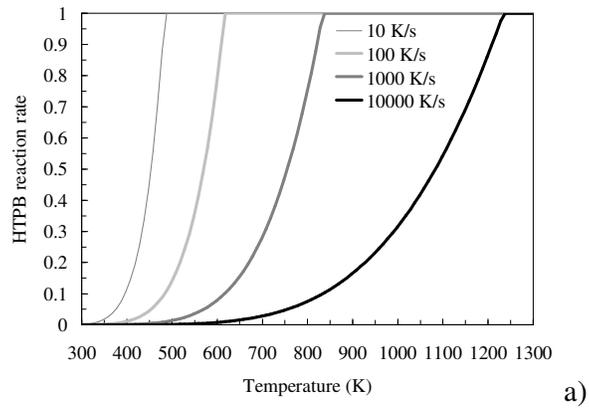
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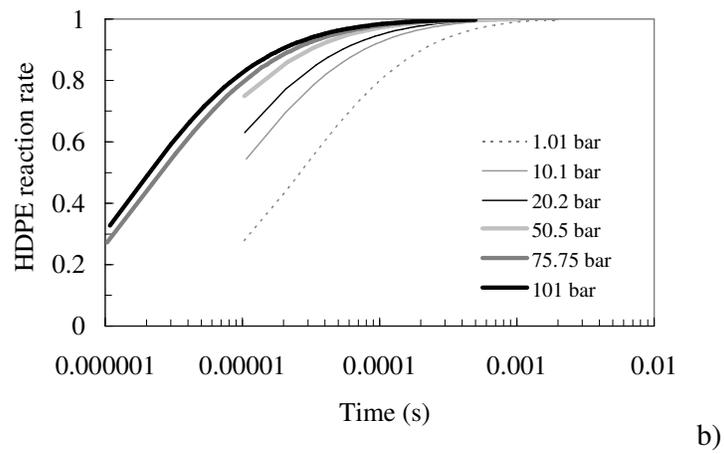
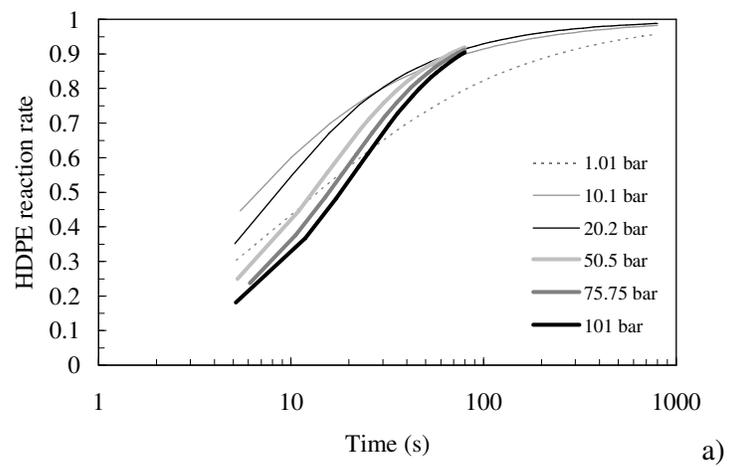
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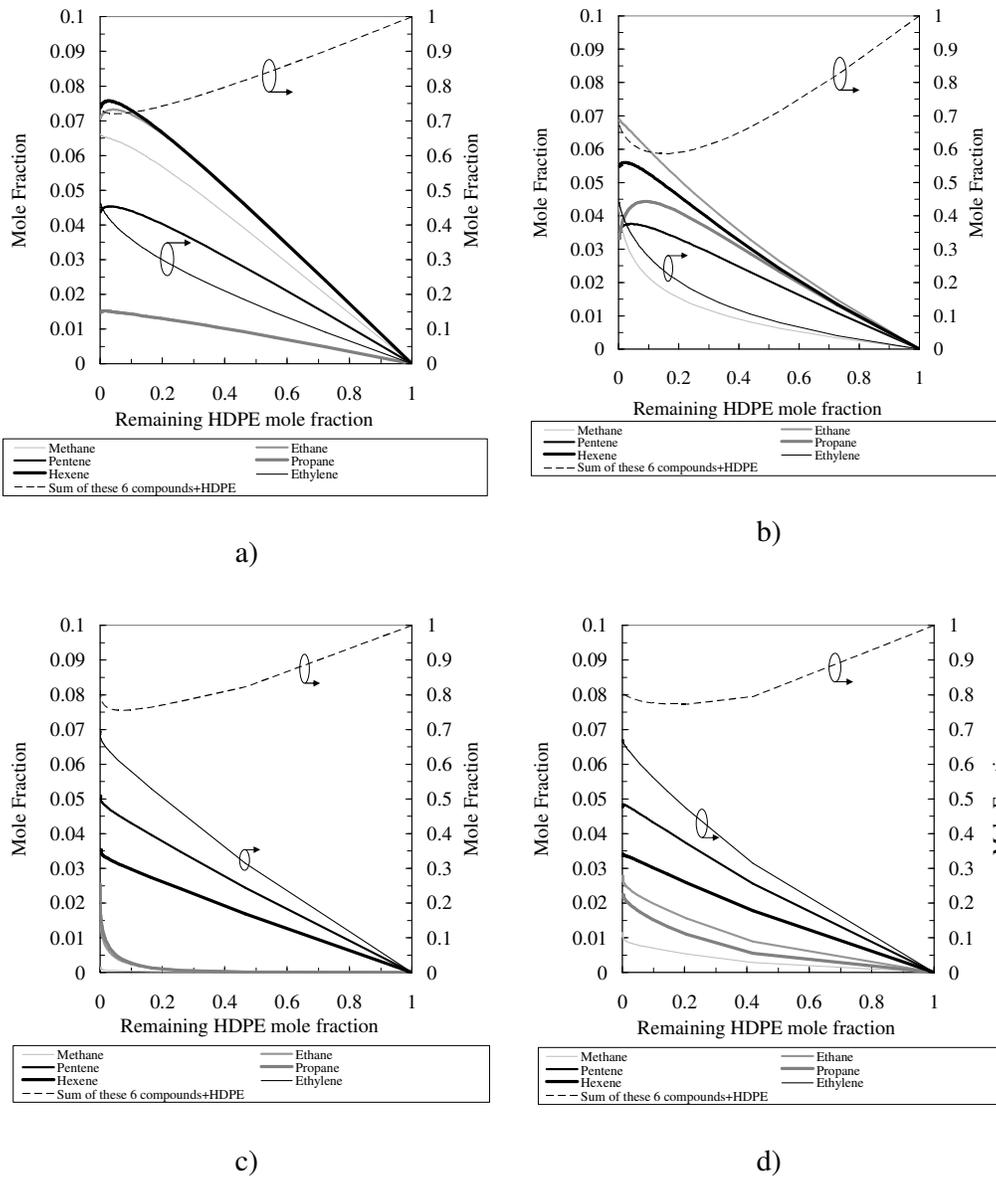
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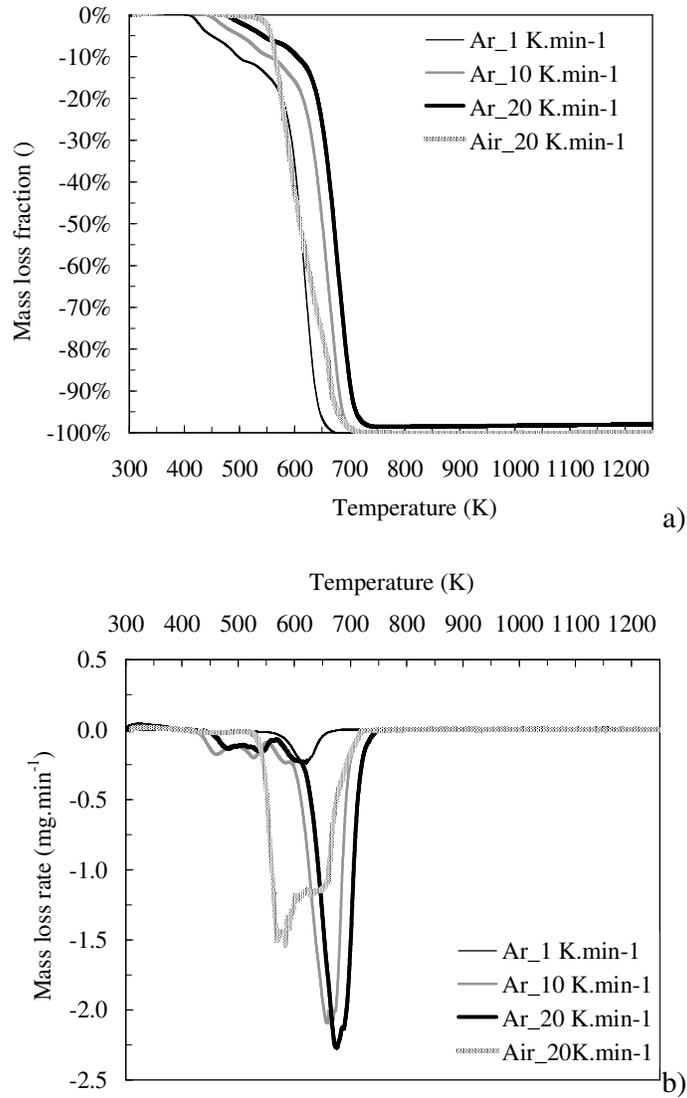
**Figure 1. Impact of heating rate on HTPB pyrolysis depending on the temperature (a) and on the time (b)**



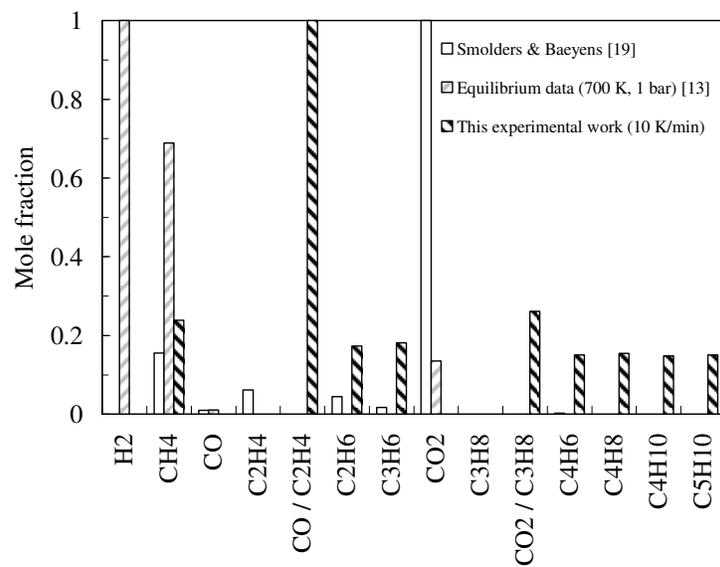
**Figure 2. Effect of temperature (750 K: a; 1250 K: b) and pressure on HDPE pyrolysis.**



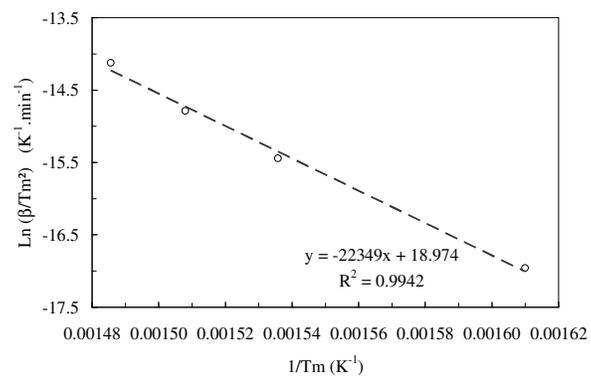
**Figure 3. Pressure and temperature effect on the distribution of six major pyrolysis products: a) 1250 K – 1.01 bar, b) 1250 K – 75.75 bar, c) 2000 K – 1.01 bar, d) 2000 K – 75.75 bar.**



**Figure 4. Mass loss fraction of TGA (a) and derivative of signal -DTG- (b) for several PMMA pyrolysis rates in TGA with inert and oxidative atmosphere.**



**Figure 5. Comparison of normalised pyrolysis results on PMMA between experimental, numerical and bibliographical results.**



**Figure 6. Determination of Arrhenius parameters for the PMMA pyrolysis thanks to the Kissinger method.**

**Table 1. Temperature and time computed by Arrhenius law to reach a pyrolysis of 99 wt.%.**

	Pressure (bar)	1 K s <sup>-1</sup>	10 K s <sup>-1</sup>	10 <sup>2</sup> K s <sup>-1</sup>	10 <sup>3</sup> K s <sup>-1</sup>	10 <sup>4</sup> K s <sup>-1</sup>	10 <sup>7</sup> K s <sup>-1</sup>
HTPB	2.02	460 K 110 s	483 K 17 s	613 K 2.7 s	828 K 430 ms	1223 K 73 ms	2500 K 4.47 ms
PMMA	2.02	750 K 120 s	825 K 17 s	993 K 2.8 s	1268 K 490 ms	1718 K 87 ms	2500 K 5.61 ms
PMMA	11.11	740 K 90 s	823 K 15 s	935 K 2.2 s	1088 K 290 ms	1293 K 43 ms	2500 K 180 μs
HDPE	2.02	783 K 62s	813 K 8s	830 K 1s	865 K 80ms	900 K 10ms	1010 K 15μs

**Table 2. Endothermic effect of the HDPE pyrolysis observed on temperature decrease in 5 s.**

Initial Temperature (K)	Pressure (bar)	1.01	10.1	20.2	50.5	75.75	101
1000	Pyrolysis rate (vol%)	45.4%	54.8%	57.0%	60%	60%	60%
	Thermal decrease (K)	274	278	275	269	264	264
2000	Pyrolysis rate (vol%)	85.1%	88.9%	90.9%	94.5%	95.4%	96.3%
	Thermal decrease (K)	1222	1226	1224	1218	1214	1210

**Table 3. Decomposition time (s) and temperature (K) after exothermic thermal decomposition of 85 mol.% H<sub>2</sub>O<sub>2</sub>+15 % H<sub>2</sub>O and 66.7 mol.% H<sub>2</sub>O<sub>2</sub>+33.3 % H<sub>2</sub>O mixtures.**

Temperature (K)	Decomposition Time (s)			Temperature (K)		
	1 atm	50 atm	50 atm	1 atm	50 atm	50 atm
	85% H <sub>2</sub> O <sub>2</sub>	85% H <sub>2</sub> O <sub>2</sub>	66% H <sub>2</sub> O <sub>2</sub>	85% H <sub>2</sub> O <sub>2</sub>	85% H <sub>2</sub> O <sub>2</sub>	66% H <sub>2</sub> O <sub>2</sub>
800	1.69E-02	1.85E-03	1.88E-03	2191	2229	2021
1000	1.91E-04	9.11E-06	9.77E-06	2315	2380	2181
1300	1.04E-05	3.24E-07	4.02E-07	2480	2600	2419

**Table 4. Adiabatic combustion characteristics of several premixed reducer-oxidiser at 60 bar.**

	Flame temperature (K)		Laminar flame speed (m s <sup>-1</sup> )	
	H <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> O
HTPB	3462	4152	17.63	8.26
PMMA	3613	4306	22.99	11.43

**Table 5. Ignition time (s) of several compositions of HDPE pyrolysis products under their respective different conditions.**

Temperature (K)	Pressure (bar)		
	1.01	20.2	75.75
1250	1.06E-03	1.08E-03	7.29E-04
2000	1.01E-07	1.05E-07	1.04E-07

**Table 6. Maximum temperature, auto-ignition time and heating rates computed during combustion of several reducer-oxidiser couples at 1250 K and 1.01 bar for an equivalence ratio of 1.**

Maximum temperature (K)				
	HTPB	PMMA	HDPE	HTPB at 1073K [4]
O <sub>2</sub>	4613	4305	3698	3899
H <sub>2</sub> O <sub>2</sub>	3524	3504	3025	3195
N <sub>2</sub> O	4349	4232	3190	3789

Auto-ignition delay (s)				
	HTPB	PMMA	HDPE	HTPB at 1073K [4]
O <sub>2</sub>	1.11E-09	1.11E-09	8.88E-05	5.83E-04
H <sub>2</sub> O <sub>2</sub>	5.41E-07	4.29E-07	4.00E-06	4.31E-06
N <sub>2</sub> O	9.69E-07	8.56E-07	4.30E-02	4.07E-02

Heating rate (K.s <sup>-1</sup> )				
	HTPB	PMMA	HDPE	HTPB at 1073K [4]
O <sub>2</sub>	3.04E+12	2.76E+12	2.76E+07	4.55E+06
H <sub>2</sub> O <sub>2</sub>	4.20E+09	5.25E+09	4.43E+08	4.51E+08
N <sub>2</sub> O	3.20E+09	3.48E+09	4.51E+04	6.24E+04