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To cite this version:

Nicolas Gascoin, Philippe Gillard, Alexandre Mangeot, Ana Navarro-Rodriguez. Literature survey for a first choice of a fuel-oxidiser couple for hybrid propulsion based on kinetic justifications. Journal of Analytical and Applied Pyrolysis, 2011, doi: 10.1016/j.jaap.2011.11.006. hal-00649391

HAL Id: hal-00649391

https://hal.science/hal-00649391

Submitted on 7 Dec 2011

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Review

Literature survey for a first choice of a fuel-oxidiser couple for hybrid propulsion based on kinetic justifications.

N. Gascoin[a*], P. Gillard[a], A. Mangeot[a,b], A. Navarro-Rodriguez[a]

[a]University of Orléans

63, avenue de Lattre de Tassigny, 18020 Bourges Cedex, France

[b]CNES

Rond Point de l'Espace, 91023 Evry Cedex, France

Abstract

Hybrid rocket propulsion presents an increasing demand because of safety and cost reasons. Numerous works cover the main related areas (regression rate, oxidiser injection, grain design and additives in solid reducer). Nevertheless, the use of detailed kinetic studies, either experimentally or numerically, remains scarce. In particular, the auto-ignition and pyrolysis delays, the nature of chemical species impacting the diffusion flame and the rate of heat release are some of the important parameters. They are rarely considered when choosing a reducer-oxidiser couple. Understanding these chemical parameters could help choosing, or later improving, the solid reducers which present low regression speeds (limiting step of hybrid engine due to low combustible gas flow rate). Since detailed chemistry is still a foreign field for hybrid rocket studies, a wide review is first

[*] Corresponding author. Tel.: +33.248.238.473; fax: +33.248.238.871. *E-mail address:* Nicolas.Gascoin@bourges.univ-orleans.fr (N. Gascoin)

presented to determine how existing chemical works can be of interest for this propulsion technique. Mechanical and thermal characteristics are also considered in addition to combustion ones. Analytical estimation of the requirements to be met by the reducer-oxidiser couple is proposed (combustion heat release and associated heat fluxes, endothermic pyrolysis effect, chemical induction delays). Moreover, the choice of a reducer depends on the operating conditions under which it is used. For this reason, some equilibrium calculations are also provided to investigate the pressure and temperature effects. Among sixteen solid reducers, only three are finally selected in a first step (high density polyethylene -HDPE-, polymethylmethacrylate -PMMA-, hydroxyl terminated polybutadiene -HTPB-). A similar work for oxidisers is conducted among thirteen compounds and three of them are selected (hydrogen peroxide -H_2O_2-, nitrous oxide -N_2O-, pure oxygen -O_2-).

Keywords

Pyrolysis; Combustion; Hybrid Rocket Propulsion; Solid Fuels; HDPE.

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Abbreviations and acronyms

Isp: specific impulse (s)

TGA: thermogravimetry analysis

AP: ammonium perchlorate (NH_4ClO_4)

GAP: glycidyl azide polymer (CH_2-$CH(CH_2N_3)$-$O)_n$

HAN: hydroxyl ammonium nitrate $(NH_3OH)NO_3$

HDPE: high density polyethylene ($(CH_2$-$CH_2)_n$)

HNF: hydrazinium nitroformate ($N_2H_5C(NO_2)_3$)

HTPB: hydroxyl terminated polybutadiene HO-$(C_4H_6)_n$-OH

LDPE: low density polyethylene ($(CH_2$-$CH_2)_n$)

MMA: methylmethacrylate $CH_2=C(CH_3)(COOCH_3)$

PA6: polyamide $(NH-(CH_2)_5-CO)_n$

PC: polycarbonate $((CO-O-C_6H_5-C(CH_3)_2-C_6H_5-O)_n)$

PE: polyethylene $((CH_2-CH_2)_n)$

PET: polyethylene terephtalate $(CH_2-CH_2-O-CO-C_6H_4-CO-O)_n$

PMMA: polymethylmethacrylate $(CH_2-C(CH_3)(COOCH_3))_n$

PP: polypropylene $(CH_2-CH(CH_3))_n$

PS: polystyrene $(CH_2-CH(C_6H_5))_n$

PVA: polyvinyl acetate $(CH_2-CH(CH_3-COO))_n$

PVC: polyvinyl chloride $((CH_2-CHCl)_n)$

PVDC: polyvinylidene chloride $((CH_2-CCl_2)_n)$

1. Introduction

1.1. Hybrid Rocket Propulsion

Aerospace propulsion can be achieved using several technologies depending on the application. The main selection parameters are the specific impulse (Isp) and the thrust, the flight speed, the simplicity of the technology, the storage ability, the safety and the reliability. With the development of space tourism and with the present ecological considerations, the hybrid rocket is one of the emerging propulsion modes [1-3]. This technology involves a solid fuel contained in the combustion chamber and burned with the injected oxidiser, either liquid or gaseous (heterogeneous combustion). The separation of the propellants produces a very safe engine and a potentially flexible solution. By controlling the injection, via a regulation valve, it is possible to adjust the thrust, to shut the engine down and to reignite it later if necessary. Such a technology could also be useful for creating gas generators for safety devices, for example, like car airbags or slide inflators for airplane evacuation.

At present, numerous solid fuels are being considered, mainly plastic ones such as polyethylene (PE), polypropylene (PP), Polymethyl Methacrylate (PMMA). Polymers are well-known and characterised, easy to handle and to store, and safe under normal conditions. This might even be a way of recycling. The hydroxyl terminated polybutadiene (HTPB) is also largely studied because it is one of the most used in solid propulsion in combination with ammonium perchlorate (AP) as an oxidiser [4]. Other fuels are also presently under investigation because of the current limitations of these solid reducers (low regression rate). Indeed, the addition of metal particles (Al, Li, Mg, Be) and of metal hydrides (AlH_3 and others) is investigated [5]. This generally increases the regression rate by about 10 % (due to higher combustion heat release, up to 60 MJ kg^{-1}). It can also alter the physical properties of the solid reducer (HTPB is generally used as a binder). Due to the major role of radiation heat transfer, the reducer is often charged in carbon black particles to enhance its heating. However, depending on the mission, the hybrid engine could require a regression rate three times higher than it is presently possible [6]. Consequently, the demand of research on solid reducer is veritably a challenging point. The choice of the oxidiser is more limited, mainly in terms of toxicity and safety. The three most used ones are: oxygen (liquid LOx or gas GOx [7]), hydrogen peroxide H_2O_2 [1] and nitrous oxide N_2O [8]. Due to the large number of available reducers and oxidisers, numerous couples have been tested. Some are still under study today [3].

1.2. Phenomena remaining to be investigated

If hybrid rocket technology appeared in the 1930s, the first scientific studies aiming at understanding the phenomenon involved were not found before the 1970s [3]. Nowadays, the fundamentals have been acquired and the physical processes of solid regression with pyrolysis and melting, the diffusion and laminar/turbulent flames with the injected oxidiser are well described and are mainly studied numerically [9,10]. Nevertheless, these studies do not simultaneously consider the detailed chemistry and physics [11] because of the difficulty of solving transient equations in complex geometry with high velocity reactive flows. Thus, the fluid mechanics is often better described while the chemistry is frequently considered using a one-step Arrhenius law or a thermodynamic approach. For the pyrolysis of the reducer, the regression rate is often tabulated [12]. For the combustion, the global heat release measured during the entire combustion, which is proportional to the maximum instantaneous one, can also be used [13,14]. Transient phenomena in combustion, like temperature and pressure oscillations [15,16], could not be observed without pyrolysis kinetics. In comparison with hybrid propulsion, solid propulsion is more widely studied using a detailed kinetic approach [17].

It is absolutely required to consider the detailed chemistry of the pyrolysis to precisely estimate the nature of related products. As a function of their nature, these species will present different diffusion coefficients (considering the detailed approach of multi-component diffusion [18]). This impacts directly the diffusion flame located in the thickness of the boundary layer. The pyrolysis will depend on

the position of this flame toward the solid surface and along the chamber. This is a coupled phenomenon, driven by chemical process with specific and intrinsic time constant. Chiaverini and Kuo [3], whose book is considered as a reference, present one chapter entitled "Solid-Fuel pyrolysis phenomena and regression rate, part 1; mechanisms". Nevertheless, the mechanisms presented in this chapter refer to global one step schemes, to equilibrium cases and to physical regression of the solid-gas interface. The production of pyrolysis products as a function of time or of operating conditions is not proposed. The same can be concluded for the oxidiser thermal decomposition and for the combustion. This highlights the lack of chemical studies in hybrid technology area.

The section 2 and 3 aim at giving a wide vision of all the phenomena related to the choice of a reducer and of an oxidiser.

2. Fuel pyrolysis

Solid fuel pyrolysis happens in two phases. The first one is linked to thermal decomposition in the solid phase with diffusion of light species in the reducer. This is, for example, the case of PMMA (under 773 K), and also of the oxidiser AP [17]. This phenomenon depends on the regression rate of the solid [19]. The second phase, controlled by heat and mass transfers [19], is linked to the melting of the solid surface, whose thickness is about few microns. For example, this appears for PMMA over 773 K. So, the pyrolysis results depend on the initial reducer and also on the method of pyrolysis (low or high heating rate). The references which are considered in this paper generally originate from waste and

recycling purpose. Pyrolysis is also employed as an analysis tool to investigate the chemical formulation of fuels, polymers, composites, ink and rubber. This explains the authors consider restricted operating conditions which do not fit with those of hybrid propulsion. Nevertheless, they can be a good starting point.

2.1. Limitation of the TGA apparatus for experimental work

The relative quantities of gas, liquids and solids produced by pyrolysis depend on the mode of decomposition and on the operating conditions (like temperature, heating rate, pressure and residence time). For example, the pyrolysis of PP appears at 700 K with 2 K min^{-1} and at 780 K at 50 K min^{-1} [20]. For plastic fuels, more liquid is produced at lower temperatures whereas higher temperatures and longer residence times produce more gas. A pyrolysis temperature within a range of 623 K - 723 K is generally the best operating temperature for plastic cracking for recycling purposes in order to obtain valuable liquid petroleum fuels [20]. But this is far from being the range of study for hybrid rocket propulsion, which operates at higher temperatures. In the range of 923 K - 1123 K, a secondary gas phase cracking occurs and the primary devolatilisation products are cracked resulting in a wide spectrum of smaller hydrocarbons (ranging from C1–C9) like alkenes, alkanes, aromatics and gaseous by-products. The high temperature pyrolysis of plastics, which are rich in alkenes, typically produces 65 % - 85 % of gases, 18 % - 22 % of liquid and the rest of soot [21]. However, depending on the pyrolysis conditions, the product composition and concentration can vary [22].

TGA (ThermoGravimetric Analysis) allows the kinetic parameters of the one-step Arrhenius law to be easily and rapidly obtained during decomposition in an inert or oxidative atmosphere [23-25]. However, this is not the most appropriate technique because of gradients lower than 50 K s^{-1}. In the hybrid rocket, the combustion heat release should be of the order of 10^7 K s^{-1} [17]. Flash pyrolysis system allows obtaining several thousand degrees per second by pyrolysing a sample deposited within a very thin electrically heated wire. In these conditions, the results differ widely from those obtained by TGA [26]. For example, PMMA flash pyrolysis only shows two compounds; monomer and carbon dioxide [19], while other TGA studies also present CH_4, CH_3OH and CO [27]. Consequently, pyrolysis must be studied in appropriate conditions using the appropriate experimental apparatus. The use of a CO_2 laser in an inert atmosphere may be a way to get high heating rates to rapidly pyrolyse the surface of the reducer.

2.2. Regression of the reducers under steady state

The regression rate is probably the term most widely used to consider reducer pyrolysis [3]. It quantifies the pyrolysis products, through the reducer mass flow rate, which are generated depending on the operating conditions. To estimate the regression rate, the measurements of mass lost during the pyrolysis can be used [28-29]. Other approaches calculate it using the Arrhenius parameters ($r = A.e^{-\frac{E_a}{R.T}}$) of a one step pyrolysis mechanism; with the pre-exponential factor A expressed in mm s^{-1}. In solid propulsion, the regression rate of the

monopropellant is expressed during the combustion by the *Vieille* or *Saint Robert* law $r = A.P^n$ [30]. Pressure plays a major role on the regression rate because the temperature of combustion mainly depends on the nature of the monopropellant, whereas the pressure is due to the engine design. In hybrid propulsion, the temperature is the most important parameter and it is highly linked to the reducer mass flow rate, through the regression rate.

Table 1 gives a brief overview of the regression rates and the Arrhenius parameter dispersion for some polymers (PMMA, HDPE, PP, HTPB). It must be noticed that the pre-exponential factor is given in s^{-1} because it refers to the variation of mass fraction of the reducer instead of its thickness as it is generally observed in some numerical modelling. When the Arrhenius law is derived from measures of reducer regression by visualizations or ultra-sonic technique, the pre-exponential factor is consequently given in mm s^{-1} because it is related to the solid-gas interface displacement as a function of time. Considering the density of the reducer, the factor could be expressed in g s^{-1}. This is also the case when a weight balance is used to estimate the reducer mass loss during the experiment as a function of time. All these units (s^{-1}, mm s^{-1}, g s^{-1} and even g cm^{-2} s^{-1}) are consistent and only depend on the need of the user. These data fluctuate considerably in the literature; discrepancies up to several orders of magnitude can be found. For example, the activation energy for PP is 222.3 kJ mol^{-1} in [31] and varies from 250 kJ mol^{-1} to 337 kJ mol^{-1} in [32] and even 373.4 kJ mol^{-1} in [23] (Table 1). This is attributed to the different possible ways of producing the polymer (amorphous or crystallography structures) but also on the method of

determination because it is known to impact on the result (isoconversional analysis, Kissinger, Freeman-Carroll,…) and of course on the experiments themselves (non isothermal or isothermal conditions, rate of heating). The accuracy of the values given by the original authors varies within the range 1%-10% roughly. It can be noted that the number of digits in the activation energies is questionable for such an accuracy range.

In the literature, PMMA (density of 1190 kg m^{-3}) is found to regress at a rate of 1.8 g .cm^{-2} s^{-1} while PP (density of 950 kg m^{-3}) shows a value of 0.8 g cm^{-2} s^{-1} [33]. Thanks to the density, these data can be expressed in mm s^{-1} (15.12 mm s^{-1} and 8.42 mm s^{-1} respectively) to be compared to Table 1 (less than 1 mm s^{-1} and 0.02 mm s^{-1} respectively). The results are far from comparable.

Table 1 should be placed here

The regression rate is important from a technological point of view, but it is not uniform inside the combustion chamber due to complex phenomena. For example for PMMA, the rate changes from a factor 2 (0.2 g s^{-1} to 0.5 g s^{-1}) during the ignition due to the temperature [36] (that is to say about 0.42 mm s^{-1} to 1.05 mm s^{-1} for a reducer surface around 4 cm^2). When obtained in "real" conditions, the regression rate depends on other parameters, like the oxidiser flow rate [1], which are not considered or controlled in "lab" conditions. In laboratory, the regression depends on the heating rate, on the heat flux, on the time, on the atmosphere (oxidative or not), on the nature of the polymer samples [37,38] and on its degree of reticulation [39]. Behind these macroscopic parameters, the process of pyrolysis is different from the polymer (end-chain or random initiation)

because of the chemical bonds which are broken [19,40,41]. So, it is important to consider the kinetics of the chemical reactions and not merely a one step mechanism.

2.3. Composition of the gaseous pyrolysis products: difference between reducers

The nature of the pyrolysis products acts on the combustion, thus on the engine's thrust, and their compositions differ widely among the initial reducers. The formation of oligomer during plastic pyrolysis depends on the solid polymer [42]. PMMA forms MMA by a depropagation (unzipping) chain reaction (monomer reversion). HDPE produces various hydrocarbons (alkane, alkene, diene) by random scission followed by beta scission (H-abstraction) mechanism [26,43]. The same trend as for PMMA is found for Polystyrene (PS) while the Polyvinyl Chloride (PVC) pyrolysis through Side Group Scission [26]. Extended details on polymer pyrolysis can be found in [26]. For flash pyrolysis of PMMA (from 653 K to 873 K), the MMA monomer is the major product (> 90 %) and CO_2 the second one [19,27]. These two compounds are the major ones in their respective phases (liquid and gas). CO is the second gaseous product [44]. The results depend on the test conditions and on the nature of the initial PMMA sample [45]. Such experimental results on PMMA pyrolysis products are also available in [3], as well as for PE and HTPB.

A comparative study (at 30 K min^{-1}) shows similar trends for plastics pyrolysis (PE, PP, PS) [46]. From 863 K to 1173 K, the mass amount of tar

decreases and that of gases increases, except at 1173 K, where the formation of coke is much higher and reduces the part of gases. The gas formation is much more important for PE than for PS (at least a factor 2). For PE, the higher the temperature, the more H_2 and CH_4 are formed; which is advantageous for combustion purposes. A very similar trend is seen for PE and PP in terms of compounds and concentrations. These concentrations are 2 to 3 times higher than what is observed for PS. For several PS molar masses, and up to 1073 K, styrene is found to be the major pyrolysis product; others are mainly aromatics [31]. This is amplified by temperature. Considering these data, it should be more appropriate to use PE or PP than PS (despite a high density 1050 kg m^{-3} and a high heat release 43 kJ kg^{-1} [47]).

However, two kinds of PE exist depending on the density. LDPE (Low Density PE) produces light alkanes and alkenes mainly at 1173 K, for a residence time of 0.35 s to 2.5 s. The gas phase represents about 93 wt.% of pyrolysis products with a typical composition of: 4 wt.%-10 wt.% CH_4, 22 wt.%-31 wt.% C_2H_4, 1.5 wt.%-2.7 wt.% C_2H_6, 10 wt.%-14 wt.% C_3H_6, 0.5 wt.%-1 wt.% C_3H_8, 4.8 wt.%-5.6 wt.% C_4H_8, 6 wt.%-7 wt.% C_4H_6 [21]. Methane increases when the residence time is extended at higher temperature, whereas the fractions of C_3 and C_4 compounds decrease. C_2H_4 and C_2H_6 yields are not affected by the residence time. The mono-aromatics are the major compounds in the pyrolysis liquid at high temperature.

The pyrolysis of HDPE shows similar results. At lower temperatures, the main products are solid wax (aliphatic hydrocarbons up to C30) [48] but the

higher the temperature, the lower the quantity of wax [49]. The gaseous part increases with the temperature up to about 90 wt.% at 1053 K. The oil is composed of aromatics. For both LDPE and HDPE, the proportion between paraffin (alkanes), olefin (alkenes) and aromatics are the same in the liquid or gaseous phases during pyrolysis [50]. The atmosphere also impacts on HDPE pyrolysis and it can yield low polycyclic aromatic hydrocarbons (PAH) concentrations and highly energetic compounds [51]. The choice between HDPE and LDPE cannot be made from a reactive point of view but section 4.1 will provide an answer to this problem.

Other pyrolysis studies are available on plastics (polycarbonate: PC, polyvinyl chloride: PVC, polyvinyl acetate: PVA,…) for recycling purposes [52,53]. The data are more limited than those for PE or PMMA. Due to the toxicity of PVC after combustion, which yields to HCl formation [54], (in addition to a low heat release of about 15 kJ kg^{-1} [47]) PVC will not be studied here. Despite an interesting exothermic pyrolysis effect, the same safety issue is applicable to GAP due to its nitrogen content [3]. A very long list of other plastic polymers can be drawn, from which the most common are: PA6, PET, ethylene-vinyl alcohol co-polymer $(CH_2\text{-}CH_2)_n$ $(CH_2\text{-}CH(OH)_m$, PVC and polyacrilonitrile $(CH_2\text{-}CH(CN))_n$. We can notice that PET presents a lower pyrolysis temperature than PE [14]. This may be a good point to allow rapid pyrolysis in the combustion chamber. But due to the lack of studies on PET and on all the others, they will not be considered at present.

Over 643 K and up to 883 K, the flash pyrolysis of HTPB is found to be exothermic, while it is endothermic under 643 K [15,16]. The pyrolysis depends on the liquefaction process under 803 K and on that of desorption over 803 K. A pressure effect is shown, linked to this observation, A sudden change in gaseous products formation is found around 803 K for low pressure while this disappears for higher pressures. This justifies studying pyrolysis under a wide range of pressures and namely under the expected operating pressure of engines.

In this way, the numerical approach is more convenient than an experimental one. Some numerical schemes are notably available for PE (simplified [32,49,55-57] or detailed [58]) and with one step Arrhenius law or semi detailed mechanisms for halogenated polymer [54], for PET [59], PS [31,60] , PP [60], HTPB [15,16]. In the formation of a simplified scheme, the Arrhenius parameters are necessary for the consumption of initial polymer, for example HTPB [61], but also for the formation of pyrolysis products. A maximum of six major gaseous products has been found for HTPB detailed kinetic pyrolysis (Butadiene, 4-vinyl-l-cyclohexene, trans-butadiene oligomers, ethylene, 1,5 hexadiene and cyclopentene) [15,16].

3. General observations on combustion with oxidiser

The pyrolysis of the reducer is not only dependent on the temperature or on the residence time. It is a coupled process with the combustion since this latest provides the heat flux for the pyrolysis. The oxidative atmosphere can play a role in the degradation process. The injection of the oxidiser physically impacts on the

solid fuel regression rate [62]. The axial injector provides a higher regression rate, stability and combustion efficiency compared to the radial injector. This is due to the residence time and to the turbulence [63]. The oxidiser injection also modifies the oxidiser mass flow rate, that is to say the Oxidiser/Fuel ratio. The ignition time is clearly dependent on this point [11]. However, the oxidiser concentration no longer seems to impact on the pyrolysis over a certain value [33] and the phenomena are mainly piloted by the fluid flow. So, the reducer should present a pyrolysis rate in good agreement with the oxidiser mass flow rate. A linear relationship exists between these two parameters [1,36] and also between the burning and pyrolysis rates [64].

3.1. Initiation of combustion and additives for reducer performance increase

The ignition method can impact on the choice of the reducer. For a given technique, firstly a sufficient quantity of gases is required to be produced, in relation with the oxidiser mass flow rate. This is linked to intrinsic parameters, for example the pyrolysis temperature and the decomposition rate, the thermal diffusivity and the infrared absorption of the reducer. Some new methods, such as the CO_2 laser techniques [65,66], may be useful for hybrid combustion chamber because they can reignite the engine after shutting it down during the flight.

Considering the potential of fuels, the addition of metallic compounds is a way to increase their combustive and thermo-mechanical properties (increase of regression rate notably), such as the flame temperature and the density. Using additives with exothermic decomposition will be a benefit [1]. If these additives

are oxidant (such as in solid monopropellant), there is a higher benefit in terms of specific impulse (twice more). With metals, the benefit increases by 30 % [1]. Among these additives, alane (AlH_3) seems promising because it increases the Isp and reduces the throat erosion [67,68]. Other types of fuels are considered, such as silane (Si_nH_{n+2}), because they present higher specific impulse [69]. Nevertheless, no additives will be considered in the present study because they require specific and dedicated work. Some works related to thermodynamic calculations on additives could be mentioned [70] and very rare consider simplified kinetic mechanism [71]. Furthermore, the additives increase the combustion temperature but they do not participate to the thrust because they do not generate directly gas formation, which would increase the momentum quantity. This explains why additives remain limited.

3.2. Potential oxidisers

The oxidisers should be non toxic, safe and present a high burning rate and burning velocity. For toxicity reasons, N_2O_4 is not studied, despite its high energetic performances. This also goes for other nitro compounds and for several fluoro compounds (BrF_5, ClF_3, ClO_3F), even diluted in oxygen. Hydrazinium NitroFormate (HNF) shows a higher heat release during the thermal decomposition than Hydroxyl Ammonium Nitrate (HAN) [72]. They both have a great Isp and density. HAN and HNF are found in mixtures with water, which is undesirable for propulsion applications. HAN, HNF and AP are not considered because of their environment unfriendliness.

Pure oxygen is important to consider. It is the reference used to compare the other oxidiser capacities. But no oxygen based solution will be proposed in this paper due to the storage and handling difficulties of cryogenic liquid oxygen. The gaseous oxygen is not interesting because it has poor density.

H_2O_2 can dissociate spontaneously owing to the temperature. That makes it dangerous because it behaves like a monopropellant. The walls of the tank must be passivated to avoid catalysis effects. Furthermore, it is combined with water (generally 2 vol.% to 15 vol.%) to limit this effect, but the water is a final combustion product and is undesirable for combustion purposes. Nevertheless, these technological problems may be corrected in the future by additives or by mixing H_2O_2 it with other products, thanks to its high miscibility.

N_2O is more interesting than NO or NO_2 in terms of toxicity and energetic performance. It is considered to be relatively safe and non toxic (even used for medical purposes in hospitals). It has a high density (1980 kg m^{-3} when stored at liquid conditions around 35 bar). N_2O could be studied as a monopropellant thanks to a catalyser [8] (H_2O_2 [73], HAN and HNF also [72]). The specific impulse is, for example, expected to be 210 s at 1873 K [8].

When comparing the above polymers in terms of steady-state parameters like the specific impulse, all of them present approximately the same behavior [3]. For example, combustion with N_2O gives an Isp of 247 s for HTPB and PE, 248 s for Paraffin and 252 s with addition of 40 wt.% Al. This is also noted for LO_x. But when regarding the burning rates; that of O_2 is higher than that of H_2O_2 because of the higher combustion temperature and higher combustion efficiency [1]. This

efficiency is linked to the limited mixing of the reducer and oxidiser [1]. Thus, a deeper kinetic study needs to be conducted numerically [74].

4. Additional elements impacting the choice of the reducer

In conclusion to sections 2 and 3, the reducers that present the most interesting properties are HDPE, PMMA and HTPB (due to the nature of pyrolysis gas products and to their solid properties in addition to safety, cost, toxicity and performance point of view). They will be numerically studied in a companion paper [74] in order to help in selecting one of them with the appropriate oxidiser (among H_2O_2, N_2O and O_2).

4.1. Mechanical and physical characteristics of reducers

Reducers also need to be studied with respect to their thermo-mechanical properties. Apart from the reactivity aspects, the characteristics of solid fuels should be considered to ensure they can withstand the high heat load due to the combustion. This kind of consideration is found for gels dedicated to other propulsion techniques [75] but still remains absent for the hybrid rocket. For the thermal resistance, the melting temperature and the thermal conductivity are the most important data. On the basis of the preceding sections, a selection of polymers is observed (Table 2). Only the products without toxicity issues are considered. The LDPE is not given specifically but most of the data can be found for PE independently from its structure (LDPE or HDPE) because the difference is mainly related to the density and not to the reactivity. A direct link exists

between the gasification of solid fuels and their transformation heat [1]. It is preferable to consider solid fuels with low heat capacity and melting latent heat [1]. However, with higher heat capacity, the thermal diffusivity will be lower and the consistency of the reducer is more easily ensured.

Table 2 should be placed here

For comparable reactive behaviours, HDPE (960 kg m^{-3}) is preferable to LDPE (920 kg m^{-3}) and to PP (950 kg m^{-3}). PC is no longer considered due to its low heat release in comparison to HDPE notably and because no numerical pyrolysis scheme has been found. In regards, PMMA is still considered despite a lower heat release because it is more widely studied. More available data can be found to serve as a basis and to go further. HTPB also presents a low heat release but it is commonly used with additives to overcome this drawback. Thus, HTPB will be studied in this paper and in [74], but alone without other compounds in addition. The elastic modulus is relatively comparable between the compounds considered except for that of HTPB, which is very low. Despite this, HTPB is commonly used in solid propulsion and there is not a problem in maintaining the mechanical characteristics.

The maximum temperature that can be sustained by polymers in continuous operating conditions is not considered because it is rapidly exceeded due to the combustion. The cost is not a parameter of choice because these polymers are common enough not to present economic issues. The question of storage ability should, nevertheless, be taken into account. It is well-known that polymers can be altered with time, due to the thermal conditions for example. Aged plastics can

thus pyrolyse at lower temperatures than new ones [42,78]. But this point needs a specific study and the available data in the literature are very sparse. The porosity of solids may also be considered because of its involvement in the chemical process. It also impacts on the thermal and mechanical characteristics.

4.2. Analytical estimation of heat fluxes and characteristic timescales

This section aims at fixing the order of heat fluxes (heating, phase change, pyrolysis and combustion by radiative, conductive and convective transfers) and of timescales (fluid mechanics, heat transfer, pyrolysis time, combustion time) that are expected in the hybrid combustor. They enable to judge if the pyrolysis/combustion times (sections 2 and 3) are suitable for hybrid propulsion.

For a typical residence time of 20 ms [3], the reducer must be heated and pyrolysed, as must the oxidiser if applicable. HDPE is chosen in this section by way of example. The combustion must also be initiated and finished.

If 85 % H_2O_2 mixture is used, for example, it will decompose in 2 ms at 2229 K [74]. To get a stoichiometric combustion with 1 m² of HDPE, a H_2O_2 mass flow rate of 6.76 kg s^{-1} is necessary. This corresponds to an exothermic decomposition flux of 16.22 MW m^{-2} [74]. However, to heat the H_2O_2 from 300 K to 800 K, the required flux is 9.46 MW m^{-2}. Thus, the flux coming from the exothermic oxidiser decomposition is 6.76 MW m^{-2}. By burning 1 mm s^{-1} of HDPE, the heat released is 40.3 MW m^{-2}. Consequently, the overall heat flux generated in the combustion chamber is 47.06 MW m^{-2}. The radiative and convective heat fluxes of the flame toward the solid reducer are respectively

7.5 MW m^{-2} and 1.13 MW m^{-2}. The other part of the incoming heat flux (about 38.43 MW m^{-2}) remains in burned gases to participate in the thrust.

For a pyrolysis time of 1 ms [3, 74], the reducer must be heated up to 1250 K [74]. To increase the solid temperature from 300 K to the melting temperature of 415 K (204 kW m^{-2}), the time required is about 2 ms. With a fusion enthalpy of 1940 J kg^{-1} (with 2000 g mol^{-1}) for HDPE, the heat absorbed for the phase change during this time is 931.2 kW m^{-2}. Considering an endothermic effect of 5 MJ kg^{-1}, the heat flux required for the pyrolysis is 4.8 MW m^{-2}. Heating the pyrolysis products to 1250 K, with the same time order, requires a heat flux of 1.5 MW m^{-2}. Finally, the heat flux dedicated to the reducer is 7.44 MW m^{-2}. A part of the incoming heat flux is conducted through the solid. The conductive flux is 380 kW m^{-2} to increase the solid temperature from 300 K to 1250 K by conduction over 1 mm. The associated time, 4.6 ms, is lower than that of the regression. Thus, the conduction in the solid is not a limiting step.

To conclude, all the heat fluxes computed above are compatible with the hybrid chamber. The choice between the reducer and the oxidiser will not be made on the basis of heat flux, but mainly on the characteristic times (pyrolysis time and ignition time). By adding all the times from this section, a total of 8 ms is found. This is acceptable because the residence time in the combustor is 20 ms.

4.3. Temperature and pressure effects computed by equilibrium approach

The HSC Chemistry software [79] has been used in a first step to conduct thermodynamic equilibrium on a wide temperature and pressure range (323 K to

2273 K and 1 bar to 100 bar) for comparison with kinetic computations. HTPB and PMMA are considered numerically.

For HTPB, a sensitivity study has been conducted to ensure the right representation of decomposition phenomena. Twenty-two compounds are considered as final decomposition products to compute their formation during HTPB pyrolysis (CH_4, C_2H_2, C_2H_4, C_3H_6, C_4H_6, C_4H_8, C_5H_8, C_6H_6, C_6H_8, C_6H_{10}, C_7H_8, C_8H_{12}, C_8H_{14}, $C_{12}H_{14}$, $C_{16}H_{26}$, H_2, O_2, CO, CO_2, CH_2O, C_2H_6O, solid C). This list has been established on the basis of open literature [3,15,61]. Water or methanol are not considered due to their negligible formation, even as products of secondary decomposition mechanism. Furthermore, water could be artificially observed by equilibrium computation. It is better to not consider it than largely over-estimating it.

With HSC, solid carbon and methane are the major decomposition products under 750 K while hydrogen and solid carbon are the major products above 750 K. A CO and CO_2 formation is observed. But the composition of pyrolysis products is different from the literature data, which are obtained experimentally [3]. No C_4H_6 or C_8H_{12} are found around 773 K contrary to [3]. Products with a molar mass of between those of C_2H_4 and C_7H_8 should be found around 1073 K while none is observed numerically. This is due to the thermodynamic approach, which considers an infinite time during which these compounds are unstable. The experimental data are generally obtained at atmospheric pressure, for medium residence time (less than an hour) and "low" temperature (under 1000 K). Both

equilibrium and experimental conditions are incompatible with those of hybrid technology.

But the pressure effect can be investigated properly by thermodynamic calculations (Figure 1). The higher the temperature (from Figure 1a to Figure 1d), the higher this pressure effect. It is also more interesting to have a high operating temperature because of C_2H_2 and H_2 formation at 2000 K replacing the CH_4, which is in majority up to 1500 K. At around 70 bar, C_2H_2 reaches a maximum concentration. This seems to be the optimum operating pressure. This is interesting because the thrust is linked to the internal pressure.

Figure 1 should be placed here

The same thermodynamic approach has been used for PMMA (chemical formula: $(C_5H_8O_2)_n$). After a sensitivity analysis, 26 pyrolysis products are retained, in gas, liquid and solid phases (H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, C_4H_{10}, C_5H_8, C_5H_{10}, CH_3OH, C_6H_6O, CO, CO_2, H_2O (gas and liquid), C_3H_6O, $C_4H_6O_2$, $C_4H_8O_2$, $C_5H_8O_2$, $C_5H_{10}O_2$, $C_5H_{12}O$, C_6H_6O, $C_6H_{12}O_2$, solid C). Comparing to literature at around 800 K [80-82], H_2, CH_4, CO, and CO_2 (Figure 2) are found in similar proportions but no ethylene, propylene or methanol are found. The pressure highly impacts the pyrolysis products' formation, even at 500 K contrary to what is observed for HTPB. Over 1500 K, low pressure (lower than 20 bar) gives high hydrogen content; which is interesting for combustion purposes.

Figure 2 should be placed here

5. Conclusion

Hybrid propulsion is a promising technology from an ecological point of view, as well as considering its simplicity and flexibility. The related phenomena are widely studied except the chemical kinetics for which a strong lack of dedicated work appears. The detailed chemistry enables to transiently estimate the flow rate and the nature of gaseous pyrolysis products. Their combustion must also be studied since it generates the heat flux to pyrolyse the solid fuel. This coupling depends directly on the chemical nature of species (diffusion flame), which drives the phenomena involved in hybrid engine. The time constants induced by the chemistry must be considered and are part of the choice of a reducer-oxidiser couple. Instead of choosing a reducer on the basis of the quantity of gas it can produce (regression rate), the quality of the gas compounds (auto-ignition delay, combustion efficiency, physical properties such as diffusion coefficient and heat capacity) and the way they are produced (chemical induction delay) are at least as important. The solid properties have to be considered since the reducer must meet some criterion in addition to burning capacities.

Through a large review of literature on the chemical behaviour and thermo-mechanical properties of polymers, three reducers (PMMA, HDPE, HTPB) have been selected to be numerically studied in a companion paper [74]. Three oxidisers (H_2O_2, N_2O and O_2) have also been selected for related combustion study. Large variations in Arrhenius parameters, in regression rates and in pyrolysis products composition have been found because of operating conditions of study, of the crystallography structure and of the purity of the samples. This

highlights the difficulty to get reference data for hybrid propulsion purpose. The heat fluxes and the timescales of all the phenomena encountered in hybrid combustion chamber have been estimated analytically. A total time of 8 ms has been estimated for the heat transfers and the chemistry to get completed. The pressure effect on the pyrolysis is shown through equilibrium computations and it increases with the temperature. Ethylene, acetylene and methane are favoured by high pressures. Optimum working temperature of 2000 K and pressure of 70 bar appear for HTPB (1500 K and 20 bar respectively for PMMA). These values must be compared to those from kinetic study [74]. The effect of the time and the composition of products must be investigated since several optimums could exist.

Acknowledgements

The authors would like to acknowledge the Roxel company and the CNES for their support since the present work has been achieved.

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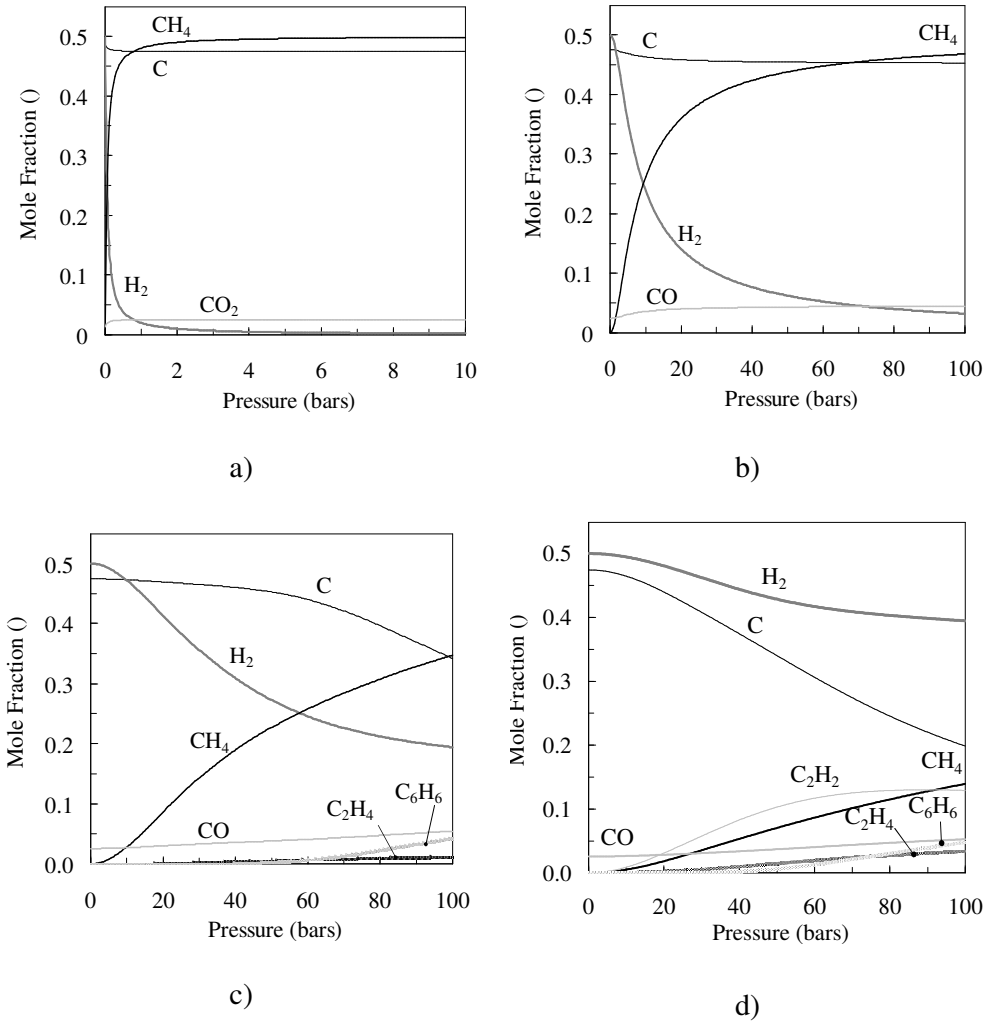

Figure 1. Pressure effect on equilibrium product distribution for HTPB pyrolysis at: a) 500 K, b) 1000 K, c) 1500 K, d) 2000 K.

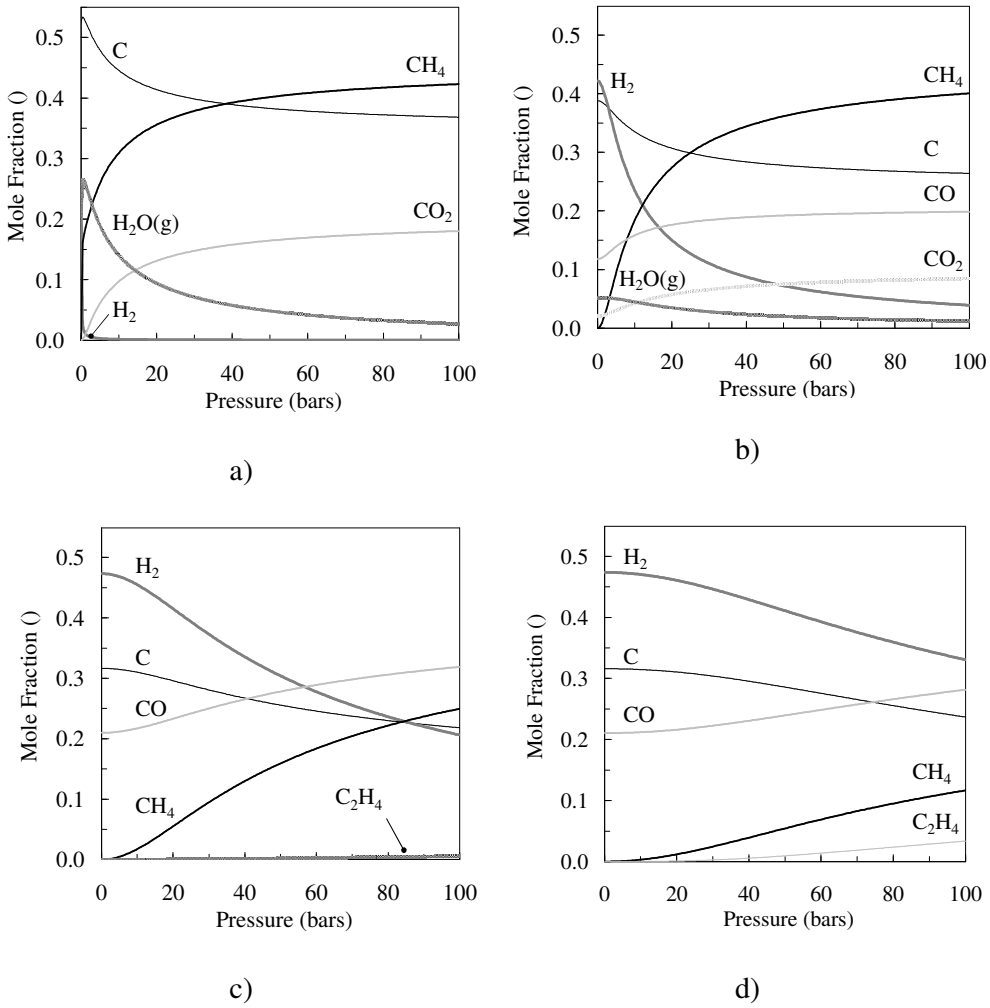

Figure 2. Pressure effect on equilibrium product distribution for PMMA pyrolysis at: a) 500 K, b) 1000 K, c) 1500 K, d) 2000 K.

Table 1. Arrhenius parameters for a one-step mechanism.

	PMMA	HDPE	PP	HTPB
Chemical Formula	$(C_5O_2H_8)_n$	$(C_2H_4)_n$	$(C_3H_6)_n$	$(C_4H_6)_n(OH)_2$
Pre-Exponential Factor (s^{-1})	$5.10^3 – 8.6.10^{19}$ [19]	$4.5\ 10^{28}$ [23]	$3.17\ 10^{24}$ [23]	$1211 – 1.3\ 10^{11}$ [16]
Activation Energy (kJ mol^{-1})	96.14 - 221.5 [19]	445.2 [23]	222.3 - 373.4 [23]	8.78 - 275.9 [16]
Regression rate (mm s^{-1}) at 960K	0.01-1 [34]	0.4 [3]	0.02 [35]	0.35 [3]

Table 2. Properties of polymers [67,76,77]

	PMMA	HDPE	PP	PC	HTPB
Chemical Formula	$(C_5O_2H_8)_n$	$(C_2H_4)_n$	$(C_3H_6)_n$	$(C_6H_4O$-$C3H_6$-$C_6H_4CO_2)_n$	$(C_4H_6)_n(OH)_2$
Density ($kg.m^{-3}$)	1190	960	950	1200	890
Ambient Heat capacity ($J\ kg^{-1}\ K^{-1}$)	1420	1850	1900	1250	2900
Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	0.19	0.4	0.15	0.2	0.14
Melting temperature (K)	450	415	420	500	420
Absolute values of heat release ($MJ\ kg^{-1}$)	25	42	43	30	28.4
Young modulus (Gpa)	1.8-3.1	0.8	1.5-2	2.6	0.0016