Experimental and Numerical Transient Pyrolysis of Supercritical Endothermic Fuel.

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1   Introduction

Hypersonic flight is expected to be achieved with dual-mode-Ramjet, i.e. Ramjet under Mach 6 and Supersonic Combustion RAMJET (SCRAMJET) beyond [1]. Because the total temperature of external air reaches temperatures as high as 4950 K for example at Mach 12, even composite materials could not withstand such large heat load. Thus, an active cooling system has to be used. Furthermore, the time allocated to the combustion in the engine is about 10^{-3} s. These two points lead to use the fuel to cool down the engine's wall and then to burn it in the combustion chamber (C.C.). The principle of SCRAMJET technology, its advantages, and the interest to use hydrocarbon fuel to cool down the engine have been fully studied in the literature [2]. Fuel is expected to be injected near the outlet of the C.C. in a composite channel which surrounds the engine. It flows to the injection in counter-flow to the burned gases. The residence time in this channel is of an order of 1 s. When heated above 800 K, the fuel is pyrolysed and thanks to its endothermic behaviour, it ensures the active cooling of the hot walls. This pyrolysis produces lighter hydrocarbons species; such has hydrogen, methane and ethylene, which are easier to ignite. It is important to note that the expected high pressure in the cooling loop (>3 MPa) causes the fluid to become supercritical in the channel, which leads to some difficulties such as fluid property evaluation and flow rate measurement. Due to the coke deposit along the cooling channel during the pyrolysis process, and due to film cooling through the porous walls, the mass flow rate is slightly different at the outlet of the channel, compared to the one at the inlet. Measuring the flow rate is thus needed to control the engine's thrust and a specific method has to be proposed for a pyrolysed supercritical fluid. Furthermore, it is necessary to identify the relation between pyrolysis and combustion of mixture, and then to provide a measurment method on the pyrolysed fluid to predict its burning capacity.

The present work falls within the framework of the COMPARER project (a French acronym for COntrol and Measure of PArameters in a REacting stReam). It aims at studying coupled phenomena involved in the cooling system such as heat and mass transfer, pyrolysis and combustion. This should help to identify one or two characteristic parameters in order to propose a measurment method about burning capacity of pyrolysed fluid and about mass flow rate under supercritical conditions. For this purpose, an experimental test bench and a numerical code, called RESPIRE (a French acronym for SCRAMJET Cooling with Endothermic Fuel, Transient Reactor Programming), have been developped. A full pyrolysis mechanism [3] is numerically implemented (1185 reactions and 153 species, designed by the French laboratory DCPR). RESPIRE has been deeply validated thanks to experimental, numerical and analytical data on thermal, hydraulic and chemical aspects [4]-[7].

The evaluation of the experimental COMPARER bench ability to furnish suitable data for the analysis of supercritical n-dodecane pyrolysis under transient conditions is the aim of this paper. The RESPIRE code will be used to give a better understanding of results.

2 Experimental test bench

A dedicated experimental test bench is now available in the LEES laboratory since 2006 to study supercritical fuel pyrolysis under stationnary and transient conditions. It aims to provide understanding of coupled phenomena, validation data for the numerical code and evaluation of onboard and real-time measurment methods for industrial use. The conception of the experimental apparatus has been based on the SCRAMJET's operating conditions. The cooling channel is represented by a chemical reactor, the thermal aspect of the combustion chamber by a furnace and the combustion of pyrolysis products by a Bunsen burner. Predimensionning calculations have been performed to define the test bench, thanks to the CFD software Fluent and to the code NANCYNETIK, which has been used for previous studies [4]. The n-dodecane fuel is injected in the chemical reactor thanks to a pump which is limited to a maximum working pressure of 10 MPa and to a maximum mass flow rate of 0.6 g.s^{-1} with dodecane pumped at ambiant conditions. Gradients of mass flow rate can be studied to investigate transient behaviour of the system but only slopes can be obtained even for brutal changes. The furnace, in which is inserted the stainless steal reactor, bears a maximum temperature of roughly 1850 K. Temperature is measured and controlled thanks to a regulator. Various transient temperature profiles can be realised but maximum transient thermal slopes are about 100 K in 600 s. The stabilisation time in the overall furnace is about 1000 s. Pressure is regulated through an automatic valve controlled to vary the operating pressure in transient conditions. Its response time is about fews seconds for pressure decrease. For pressure increase, it depends notably on the pump, on the chemical reactor geometry and on working conditions. A Coriolis mass flowmeter is avalaible at the reactor inlet to measure transient mass flow rate and density.

After the regulation pressure valve, pressure is near the atmospheric one and cooled pyrolysed mixture is gathered in a dedicated phase separator. The gas phase is evacuated thanks to a burner. No combustion study are presently conducted. A specific instrumentation has been settled to characterise phenomena and furnish suitable data for our purpose. A Gas Chromatograph equiped with 10 sampling loops is used to analyse the gas samples at ambiant conditions. Few seconds are necessary to sufficiently sweep the sampling loops during the experiment and to obtain a representative gas sample. Hydrocarbons, liquids at ambiant conditions, are analysed thanks to a coupling Gas Chromatograph - Mass Spectrometer. Liquid samples are collected during the pyrolysis at the phase separator inlet, which needs fews seconds depending on the liquid quantity formed by the process. Study parameters (temperature, pressure, mass flow rate) are obtained thanks to about forty simulatenous measures.

3 Transient pyrolysis results and discussion

Transient behaviour of the process are presented in this paper from a chemical point of view. It would be interesting to study the thermal-hydraulic coupling under transient state, but this could be achieved with standard numerical code and does not need a dedicated experimental bench. The analysis of a transient gradient of mass flow rate is provided in this paper because it is the most possible case for the SCRAMJET engine. Transient pressure variations have demonstrated no influence on the composition of pyrolysis products because pyrolysis is almost pressure independent under supercritical state. Transient thermal gradients have also been investigated but the furnace response time is too low to give interesting data, compared to the thermal dynamics of the SCRAMJET combustion chamber. Chemical compositions at given conditions during the transient evolution could even be obtained with corresponding stationnary data, despite of a limited accuracy.

For a given stationnary test case (6 MPa, 920 K, 0,04 g.s^{-1}), a mass flow rate increase of a factor 2 is studied (Table 1). Molar fractions are given inside the total pyrolysed fluid. Data of a previous corresponding stationnary test case are given in the first column and data of the present transient case are given in the second column at the initial stationnary state of a 0,04 g.s^{-1} flow rate. This corresponds to an experimental time equal to 5870 s. The first two columns of the table 1 are in good agreement for the study. The mass flow rate is suddenly changed to 0,08 g.s^{-1} at a time equal to 5870 s. Pyrolysed fluid composition is studied as a function of time in the next columns. The last one corresponds to a previous stationnary test case for a 0,08 g.s^{-1} mass flow rate. It has to be noticed that stationnary chemical conditions are obtained 5000 s after the transient change, which is difficult to explain for an estimated residence time of an order of 100 s in the chemical reactor of a $4,5.10^{-3}$ m inner

diameter. After severals experiments, this result has been confirmed. The residence time inside the reactor and the conductive heat transfer through the reactor walls could not explain a so long stabilizing time. This point needs to be studied numerically. A maximum gaseification rate, thus a maximum formation of gaseous species, appears during the transient evolution. If the quantitative results (30 %) may be misestimated due to noticeable accumulation inside the process, the qualitative trend is very interesting. It is attributed to the transient combined effect of reactor inertia and convective coefficient increase between the fluid and the reactor. Bidimensionnal effects (thermal gradients and so chemical ones) are also more important and could conduct to such behaviour. We have observed that a 20 K gradient for the fluid could result in a pyrolysis rate discrepancy of about 10 %. This kind of results justify the need to study under transient conditions the fuel pyrolysis. Initial and final values for the transient test, i.e. at stationnary state, are close to the ones corresponding to previous stationnary studies.

Table 1. Transient evolutions of pyrolysed mixture composition with the initial and final corresponding stationnary states.

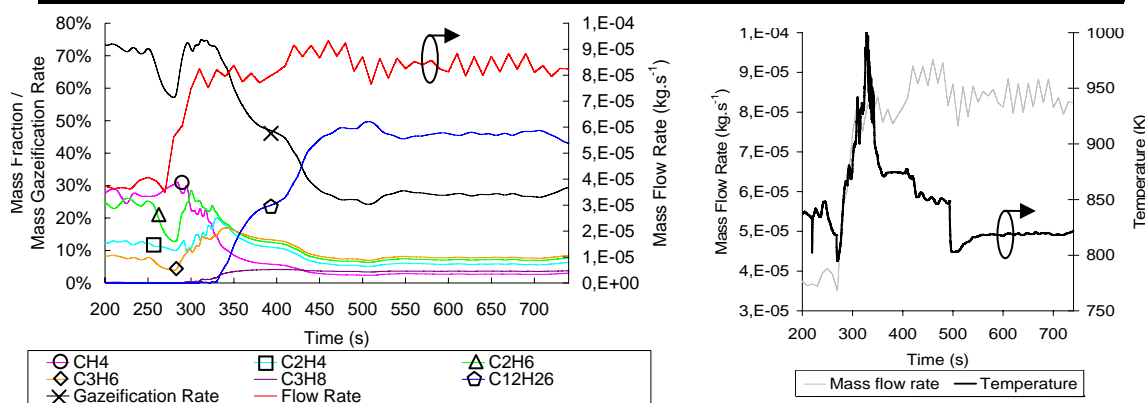|	Stationnary 0,04 g.s^{-1}	Transient					Stationnary 0,08 g.s^{-1}
		5870 s	7090 s	7990 s	9170 s	11000 s	
Maximum furnace temperature (K)	920	929	919	917	917	917	893
H2	0,09 %	0,05 %	0,17 %	0,09 %	0,03 %	0,00 %	0,00 %
CH4	1,83 %	2,21 %	1,42 %	0,67 %	0,14 %	0,02 %	0,03 %
C2H4	0,87 %	1,33 %	0,55 %	0,24 %	0,03 %	0,01 %	0,02 %
C2H6	2,11 %	2,53 %	1,29 %	0,53 %	0,08 %	0,02 %	0,05 %
C3H6	1,66 %	1,71 %	1,07 %	0,32 %	0,04 %	0,01 %	0,03 %
C3H8	1,63 %	1,60 %	1,06 %	0,35 %	0,04 %	0,01 %	0,03 %
Mass Gaseification Rate	10 %	10 %	30 %	14 %	3 %	2 %	6 %

Figure 1. Left : Pyrolysed mixture composition transiently computed with RESPIRE. Right: outlet fluid temperature.

Computations have then be conducted with the RESPIRE code for conditions close to the experimental ones (Figure 1). As the maximum fluid temperature, firstly computed, was near 800 K and because pyrolysis mechanism does not show pyrolysis at this temperature, which is a well-know limitation of the mechanism [3], experimental measurment have been increase arbitrarily by 100 K to serve as boundary conditions for the computation. Thus, the numerical results should only be studied on a qualitative point of view. The maximum temperature of the inside reactor wall is about 1020 K. Outlet fluid temperature (Figure 1, right) increases from 840 K to almost 1000 K because of combined effect of reactor inertia and convective heat transfer increase. This may be slightly overestimated because of the high calculation time step. Nevertheless, this sudden increase can explain the transient one of the outlet gas flow rate, which has been experimentally observed. The chemical composition (Figure 1, left) shows a transient production increase of C_2H_4, C_3H_6 and C_2H_6 before a decrease, whereas CH_4 only decreases and C_3H_8 only increases. This in an interesting transient effect, which justifies the transient study. Due to the mass flow rate increase, the outlet fluid temperature decreases and stabilises near 820 K. This is a lower temperature than the one before the flow rate gradient but because of endothermic effects, this is only a slight difference. The n-dodecane conversion rate passes from almost 100 % to near 50 %. The time needed for this change is about 60 s which is lower than the residence time, around 80 s. It seems to be much more realistic than the time experimentally observed. This conducts to analyse why the experimental bench may not be immediately suitable for transient studies whereas it has furnish really interesting stationnary results.

4   Conclusions

For the COMPARER project, a 1-D transient model has been programmed in order to simulate the SCRAMJET active cooling and to determine the relationship between the pyrolysed mixture composition and its combustion. A complete detailed mechanism with 1185 reactions and 153 species has been used. RESPIRE is quantitatively validated. This model is suitable to simulate the experiment conducted thanks to the dedicted COMPARER test bench, briefly described in this paper. An interesting transient chemical behaviour has been shown. Whereas the experiment is suitable to study the stationnary behaviour of hydrocarbon pyrolysis, possibly at supercritical state, under extreme conditions (8 MPa, 1850 K, 0,6 g.s^{-1}), it should be improved for transient study. Chemical composition of pyrolysis products have been investigated for a mass flow rate increase. The system presents a high inertia, about 2 hours, to obtain stationnay conditions after a transient change in flow rate. This is attributed mainly to the dead volume between the reactor and the products sampling, and to a possible gliding between gas phase and liquid phase in all this volume. If the system is not exactly horizontal, which is tried to be ensured, some liquid accumulation can also appear. And because of low mass flow rate used for this experiment, relatively high residence time does not help to provide a system with a good dynamics response. Finally, the COMPARER experimental test bench could be used for transient study but it needs to be improved. Dead volume between the chemical reactor outlet and the pyrolysis sampling has to be reduced to the minimum, which is required for various measurment apparatus and water cooling system for pyrolysed fluid. A solution is actually under study to take liquid sample and gas sample at the same time. Titanium reactor are presently used to decrease coke deposit and to allow for reducing the cross-section. This latest was increase to delay the reactor filling up by coke. Coupling this solution to an increase of mass flow rate will decrease drastically the residence time, which will be of great interest for transient study, as the response time should be reduced.

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