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SFGP 2007 - Pyrolysis of Supercritical Endothermic Fuel: Evaluation for Active Cooling Instrumentation

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SFGP 2007 - Pyrolysis of Supercritical Endothermic Fuel: Evaluation for Active Cooling Instrumentation*

Nicolas Gascoin, Philippe Gillard, Stephane Bernard, Emeric Daniau, and Marc Bouchez

Abstract

Hypersonic flight is expected to be achieved in the coming years by use of Supersonic Combustion RAMJET (SCRAMJET). One of the main issues is the thermal management of the overall vehicle and more specifically the cooling of the engine. In order to simulate the behaviour of an actively cooled SCRAMJET by use of supercritical endothermic fuel, a one-dimensional transient numerical model has been developed with heat and mass transfer, fluid mechanics and detailed pyrolysis chemistry. A dedicated experimental test bench is now available since 2006 at the LEES laboratory of Bourges to study supercritical fuel pyrolysis under steady-state and transient conditions. It aims to provide understanding of coupled phenomena, validation data for the numerical code and evaluation of onboard and real-time measurement methods for industrial use. A brief overview of the numerical code and a presentation of the experimental bench are proposed in this paper. Experimental results are discussed and a comparison is provided between numerical and experimental data. Discrepancies are shown to be lower than a few percent in terms of molar chemical compositions. This is due to uncertainties on experimental temperature measurement and to 2-D effects, which are not taken into account by the modelling. The numerical code appears to be of great importance in accessing unmeasured data and providing new understanding of coupled phenomena. Experimental and numerical tools are proved to be efficient to test future measurement methods under extreme conditions, especially at supercritical states.

KEYWORDS: endothermic fuel, supercritical state, pyrolysis

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1. INTRODUCTION

Hypersonic flight is expected to be achieved with dual-mode-Ramjet (Fry, 2004), i.e. Ramjet under Mach 6 and SCRAMJET beyond (Curran, 2001), because of its high specific impulse and its capability to be reusable (Falempin, 2002). Because the total temperature of external air reaches temperatures as high as 4950 K for example at Mach 12, no materials (even composite) could withstand such large heat load. Thus, an active cooling system has to be used; but not a dedicated one in order to not increase the vehicle weight. Furthermore, the time allocated to the combustion in the engine is about 10^{-3} s (Shikhman et al., 2001). These two points lead to use the fuel to cool down the engine's wall and then to burn it in the combustion chamber (Figure 1). Fuel is injected in a composite channel (Beyer et al., 2005) which surrounds the engine. It flows to the injection in counter-flow of the burned gases. 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, 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. That leads to some difficulties such as fluid property evaluation and flow rate measurement.

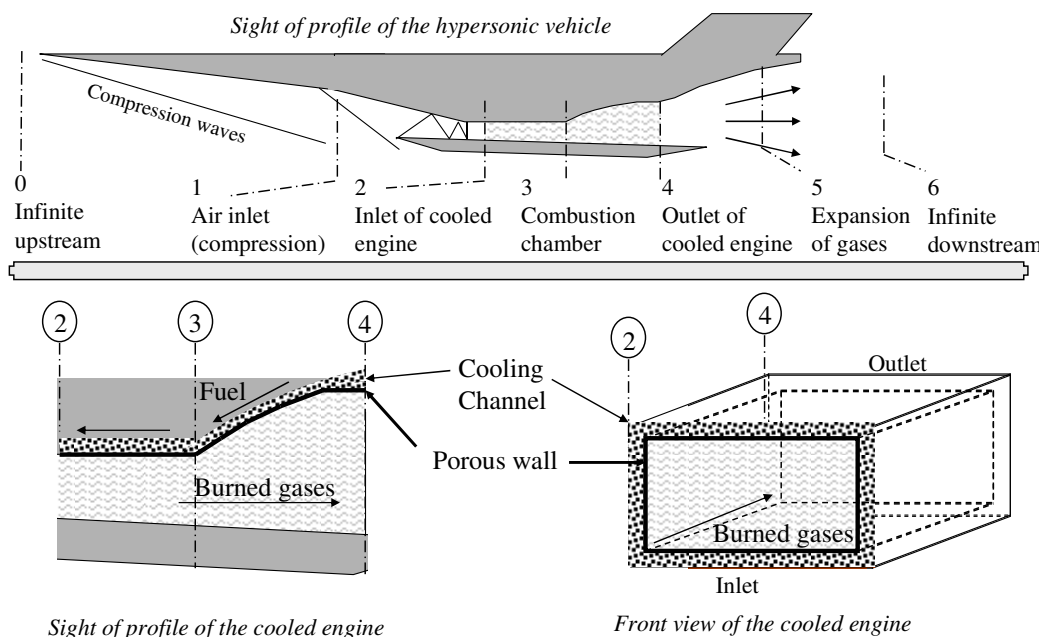


Figure 1. Overall schematic representation of the hypersonic vehicle with its cooled engine.

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 measurement method on the pyrolysed fluid to predict its burning capacity. This requires firstly to study the fuel pyrolysis under stationary conditions, particularly with supercritical state, and then to investigate the transient behaviour of the system. 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 understanding the pyrolysis of endothermic hydrocarbon fuel under supercritical states with complementary numerical and experimental approaches. This work should help to respond to the industrial need, which is related to mass flow rate measurement and burning capacity determination.

The principle of SCRAMJET technology, its advantages, and the interest of using hydrocarbon fuel have been fully studied in the literature (Powell et al., 2001). Compared to cryogenic hydrogen, heavy hydrocarbon fuels are safer and much simpler to use. Sicard et al. (2006) present an industrially oriented bench related to this field of research but it is not suitable to test measurement methods for the SCRAMJET control. Edwards et al. (2006) study fuel pyrolysis to identify the chemical reaction pathways, particularly involved in the coke formation. Their mass flow rate is about $0,1 \text{ g}\cdot\text{s}^{-1}$ in a 2 mm diameter reactor but the apparatus is not devoted to follow transient behaviour. Modelling is another feasible method for conducting engineering studies and for furthering research related to this topic. The pyrolysis and the combustion chemistry are never conjointly treated in the literature, so that coupled phenomena are not considered. Hence the relationship between fuel composition and SCRAMJET thrust cannot be taken into account. The need of a specific tool considering the overall vehicle, its cooling as its thrust, is thus evident to study the entire coupled phenomena involved in the SCRAMJET's cooling.

A stationary study has been first conducted before working on the transient system behaviour. This is a relatively innovating approach because pyrolysis under supercritical states is rarely conducted and because numerical simulations are used to provide information, which are not measured during the experiments. A numerical code, called RESPIRE (a French acronym for SCRAMJET Cooling with Endothermic Fuel, Transient Reactor Programming), has been specifically developed. Its purpose is mainly to understand the relationships between the phenomena involved in the process. But it should also be useful to test measurement methods for industrial need. Therefore, it has to operate on standard personal computer with a computation time not exceeding one night. RESPIRE uses a detailed n-dodecane pyrolysis mechanism (Dahm et

al., 2004). 1185 reactions and 153 species have been considered. This mechanism has been designed and validated by the French laboratory DCPR. It handles multi-species fluid flow, possibly under supercritical state, with heat and mass transfer. The aim of RESPIRE is to determine temperatures in the system to a tenth of a degree and the chemical composition at a mole fraction of 1 %.

In order to validate the RESPIRE numerical code, an experimental test bench has been designed and realised. It is also used for improving the comprehension of the process. This bench allows for studying fuel pyrolysis under stationary and transient conditions, particularly under supercritical state. Maximum operating parameters are about 1800 K, 8 MPa and $0,6 \text{ g.s}^{-1}$ inside the chemical reactor. It is notably composed of a fuel tank, a pump, a furnace, a Gas Chromatograph and a Mass Spectrometer. Coupling experimental and numerical approaches is hoped to improve knowledge about pyrolysis in order to identify one or two specific parameters to provide a future measurement method for the engine's control. The test bench is briefly described in a previous paper (Gascoin et al., 2006a) and some experimental results are proposed to illustrate the complexity of supercritical mixture composition after pyrolysis of fuel. This last is the n-dodecane. It was chosen for its representativity of aeronautic kerosene, its purity and its detailed pyrolysis mechanism available for the numerical study.

The purpose of this paper is firstly to give a brief overview of the RESPIRE code and a full description of the test bench. Secondly, experimental results are proposed and studied in the light of numerical information obtain thanks to the RESPIRE simulations. A feedback is obtained thanks to experimental data to give a supplementary validation of the modelling. In this study, it will be emphasised how pyrolysis conditions, obtained with the test bench, will allow us evaluating measurement methods for industrial applications.

2. RESPIRE : MODELLING AND VALIDATION

RESPIRE considers a complete hypersonic vehicle with active cooling. It allows for studying under transient conditions, the coupling between the pyrolysis inside the cooling channel and the combustion inside the engine, so as to the thermal consequences on the engine and the thrust of the vehicle. **All the governing equations are given in details in previous work (Gascoin 2006b).** The cooling channel can be studied alone to simulate a chemical reactor. The related equations will be briefly presented. They are written in transient state and the resolving method is a finite differences one. Partial derivative equations are discretized in space with centred explicit scheme and then solved in time with explicit scheme.

An example of chemical reactor considered by RESPIRE is given by the figure 2. If necessary, the pin fins are not taken into account (especially for the consideration of the flow). Because RESPIRE is a 1-D code, all variables are

constant on a cross-section of the fluid or of the material. The fluid is considered to be homogeneous on each slice along the flow. It is treated as an average single phase flow but possibly multi-species. The spatial step is of the order of $5 \cdot 10^{-3}$ m and the time step is chosen in behalf of the flow velocity expected in the channel so as to keep a particle inside a given spatial step between two time steps. The fluid has a negligible role in radiative heat transfer because it is transparent in the present conditions (similar to gas characteristic). The radiation is considered between the two faces of the channel. An average temperature is computed in the wall thickness, considering radiative, convective and conductive heat fluxes. The two faces temperatures of each wall are then deduced for the reactor made of two walls linked by numerous pin fins. The fluid is treated as an average single phase flow but possibly multi-species. The x coordinate is chosen in the direction of the fluid flow.

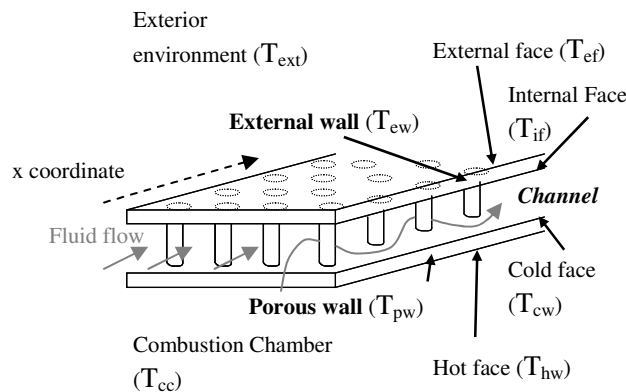


Figure 2. Example of chemical reactor geometry with adopted notations.

The velocity of the fluid v_f is determined by the momentum equation (Equation 1) and its enthalpy H_f by the energy equation (Equation 2). These equations are given here without the effusion term even if effusion through the walls can be investigated thanks to the Darcy Law. The initial conditions of the equations depend on the computed test case and its conditions (simulation of the experimental test bench or of the overall vehicle). The conditions are given by the user of the code thanks to a text file. The boundary conditions are inlet temperature, pressure and mass flow rate for the flow and external temperature or heat flux for the channel.

$$\frac{\partial(\rho_f \cdot v_f)}{\partial t} + \frac{\partial(\rho_f \cdot v_f^2)}{\partial x} = -\frac{\partial P_{sf}}{\partial x} + \frac{\partial \tau}{\partial x} \quad (1)$$

with ρ_f the fluid density, t the time, x the abscissa, P_{sf} the static pressure.

$\frac{\partial \tau}{\partial x} = -\frac{C_f}{2} \times \rho \cdot V_f^2 \times \frac{4}{D_H}$ are the frictions where D_H is the hydraulic diameter and C_f the friction coefficient.

$$\begin{aligned} \frac{\partial(\rho_f \cdot H_f)}{\partial t} + \frac{\partial(\rho_f \cdot V_f \cdot H_f)}{\partial x} = & (1 - \beta_c \cdot T_{sf}) \frac{\partial P_{sf}}{\partial t} + \frac{\partial}{\partial x} (-j_q + V_f \cdot \tau) + \rho \cdot \sum_{species} h_{i,0} \cdot w_i \\ & + \frac{1}{h_{can}} h_{cw-f} (T_{cw} - T_f) + \frac{1}{h_{can}} h_{if-f} (T_{if} - T_f) \end{aligned} \quad (2)$$

with $\beta_c = 1/\rho \times \partial \rho / \partial T|_p$ the thermal expansion coefficient, $j_q = -\lambda_f \cdot grad(T_f)$ with λ_f the thermal conductivity, $h_{i,0}$ the standard enthalpy of species, h_{can} the channel height, h_{cw-f} and h_{if-f} the convective exchange coefficients, T_{cw} and T_{if} the reactor walls temperatures in contact with the fluid.

The RESPIRE code could treat several fluid type but the main one is n-dodecane, for which a full pyrolysis mechanism (Dahm et al., 2004) is used (1185 reactions and 153 species, designed by the French laboratory DCPR). This model is the minimum one which is able to successfully predict the thermal decomposition. Most of the radical species, which have minimal concentrations in the mixture, play a determining role in the production and consumption of all other species. All compounds must be considered in order to predict their combustion. Mixtures have never been found to be at thermodynamic state because of residence times allowed for the pyrolysis, lower than 20 s. Chemical composition cannot be given by data tables depending on fluid temperature or pressure because the pyrolysis is fully controlled by the working conditions. This acts to consider detailed chemistry mechanism in relationship to thermal and hydraulic calculations. Notably, Ward et al. (2004) worked on pyrolysis in a chemical reactor under a supercritical state. They only consider a reduced mechanism which does not lend itself well to study either the cooling management or the relationship between the composition and the combustion of the fuel. The net production rates (w_i) of species i are determined using the validated pyrolysis mechanism for n-dodecane. The transport equation (Equation 3) is solved for each chemical species inside the cooling channel:

$$\frac{\partial(\rho_f \cdot Y_i)}{\partial t} + \frac{\partial(\rho_f \cdot V_f \cdot Y_i)}{\partial x} = \rho_f w_i - \frac{1}{h_{can}} \rho_{fy} \cdot V_{fy} \cdot Y_i \quad (3)$$

with Y_i the mass fractions of the i species, ρ_{fj} the fluid density through the walls and v_{fj} its velocity.

Dynamic viscosity and thermal conductivity are computed using the method of Guo et al. (2001). The method uses the Peng Robinson Equation of State. CHEMKIN polynomials are used to calculate the heat capacity of each species. An equation of state ($P/\rho = Z.R.T$) is used to determine the density considering the compressibility factor: $Z = Z^{+(0)} + \omega.Z^{+(1)}$ with $\omega = (0.2901 - Z_c)/0.0879$ the Pitzer acentric factor. The Lee-Kesler tables are needed for $Z^{+(0)}$, $Z^{+(1)}$ and to correct the heat capacity following the temperature and the pressure. Pressure of fluid is determined by use of Bulk Modulus $\beta = \partial P / (\partial \rho / \rho)$ with $\beta = \rho.c^2$.

A full validation of thermal, hydraulic and chemical aspects has been conducted under transient and stationary conditions with analytical, numerical and experimental cases. A previous work (Gascoin et al., 2006a) furnish a chemical validation under stationary conditions as a validation of the transient thermal and hydraulic behaviour of RESPIRE. Good agreement is found on temperature, compared to the CFD software CFD-ACE, which has been validated and tested by Dufour and Bouchez (2002). Thermal and hydraulic time evolutions are reasonable and quantitative results are adequate for a 1-D model, used as predimensioning tool. Computed chemical compositions are found to be of the same order as validation data (1 % molar fraction discrepancies). Calculations of fluid properties under various conditions, particularly in supercritical state, have been presented and validated in previous work (Daniau et al., 2004). Considering real pyrolysed mixture properties, and not the one of a perfect pure fluid, can decrease fluid temperature at the cooling channel outlet of about 20 %. This is due to the heat capacity which varies until a factor 2. It corresponds to a completely different fluid composition and combustion. This justifies the consideration of the modified properties. Transient conduction through channel walls has been investigated using steady state and transient heat flux conditions (Gascoin et al. 2005a). Concerning stationary state, heat flux deviation lower than 2 % is observed on wall temperature if analytical data are used as references. The transient heat flux shows a slight time shift of wall temperature, probably because of the use of average wall temperature to determine the face temperatures. The method used to compute the chemical fluid composition has been validated. Further validations of fluid temperature have been presented in previous work (Gascoin et al., 2005b).

3. FUEL PYROLYSIS EXPERIMENTAL TEST BENCH

The aim of the experimental bench is to provide a detailed comprehension of fuel

pyrolysis in conditions near the one identified for the engine. It should furnish validation data for the RESPIRE code and it should allow to test several measurement methods to be suitable for on-board and real-time industrial use. The conception of the experimental apparatus has been based on the engine's working. 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. First calculations of dimensioning have been performed to define the study parameters, such as the furnace length, the temperature profile along the furnace, the inner diameter of the chemical reactor, the mass flow rate. The simplified test bench is represented by the figure 3.

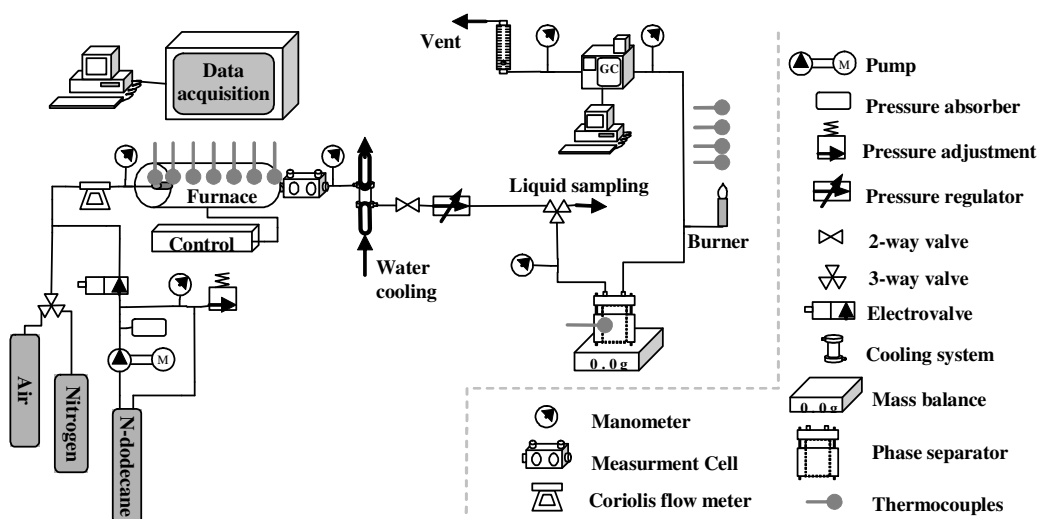


Figure 3. Simplified sketch of the fuel pyrolysis test bench.

The n-dodecane fuel is injected in the chemical reactor thanks to a pump (LEWA, FCMk1) limited to a maximum working pressure of 10 MPa and to a maximum mass flow rate of $0,6 \text{ g}\cdot\text{s}^{-1}$ with the fuel at ambient conditions. Temporal variations of mass flow rate can be studied to investigate transient behaviour of the system. The chemical reactors used for the present study are made in stainless steel 316 L. Some tests have been conducted with low-carbon steel and with Titanium. Thus the maximum operating temperature is limited at about 1200 K for the stainless steel. The furnace (CARBOLITE, STF16-450B), in which is inserted the reactor, can be heated at a maximum temperature of roughly 1850 K. Various transient temperature profiles can be realised to study transient phenomena behaviour. Pressure is regulated through an automatic valve controlled to vary the operating pressure in transient conditions. A Coriolis mass flowmeter (MICROMOTION, Elite CMF010M) is available at the reactor inlet to

measure transient mass flow rate and density. After the regulation pressure valve, pressure is near the atmospheric one and pyrolysed mixture is gathered in a dedicated phase separator laying on a mass balance. This one allows us to obtain density of liquid phase. The gas phase is evacuated thanks to a burner. Gas and liquid sampling are possible.

All these equipments, working under the conditions identified above, allow taking into account the phenomena involved in the SCRAMJET cooling. A specific instrumentation has been settled to characterise phenomena and furnish suitable data for our purpose. A Gas Chromatograph (VARIAN, Star 3800), equipped with 10 sampling loops of 5 ml, is used to analyse the gas samples at ambient conditions. The Thermal Conductivity Detector is used to quantify hydrogen whereas the Flame Ionisation Detector is dedicated to hydrocarbons, calibrated for species from CH_4 to C_3H_8 . For hydrocarbons, liquids at ambient conditions, a coupling Gas Chromatograph - Mass Spectrometre (AGILENT, 6850 - 5973) is utilised. The pyrolysis products compositions are studied in behalf of study parameters. These ones are obtained thanks to about forty simultaneous measures (temperature, pressure and mass flow rate). A specific cell, made in stainless steel 316L, has been designed to test measurement methods for industrial need and to observe the pyrolysed fluid at the furnace outlet. It is equipped by diamond windows and it is instrumented in pressure and temperature.

To conduct steady-state experiments, the furnace temperature, the mass flow rate and the pressure are fixed. After stabilisation, gas and liquid samples are collected. Furnace temperature is then increased to another desired step temperature to conduct steady-state analysis. The compositions of pyrolysis products are then available for various temperatures at given fixed conditions of pressure and flow rate. The n-dodecane is used for the present study (VWR, Rectapur, purity of 99 %).

4. EXPERIMENTAL PYROLYSIS RESULTS AND SUPPLEMENTARY NUMERICAL EXPLANATION

4.1. Characterisation of the test bench

Operating conditions presented in this paper are in the range of 1 MPa to 6 MPa, of 620 K to 1220 K, of $0,05 \text{ g}\cdot\text{s}^{-1}$ to $0,1 \text{ g}\cdot\text{s}^{-1}$; for an internal reactor diameter of $4,5\cdot 10^{-3}$ m. Residence time is not experimentally available but it can be obtain by means of RESPIRE simulations (Figure 4). The fluid temperature first increases in the first third of the furnace, then it is approximately constant before decreasing in the last third. This is due to the furnace temperature profile, which is maximum at the centre and which decreases at the border. For a global residence time of about 100 s, the time allocated to the pure n-dodecane heating is about 75 s and

the one corresponding to its downstream cooling is 15 s. This cooling is due to the furnace temperature profile and will be explained in the following section. The pyrolysis appears during a residence time equal to 10 % of the global one inside the chemical reactor. This is a characteristic time for the chemical process, which cannot be measured experimentally. This clearly underlines the necessity to simulate each experiment to obtain such important data. Despite residence times higher than in the SCRAMJET's cooling channel, calculations at thermodynamic equilibrium, with the HSC commercial software, have demonstrated that this equilibrium is not obtained inside the chemical reactor. This point proves the need of chemical kinetic to study such reactive flow.

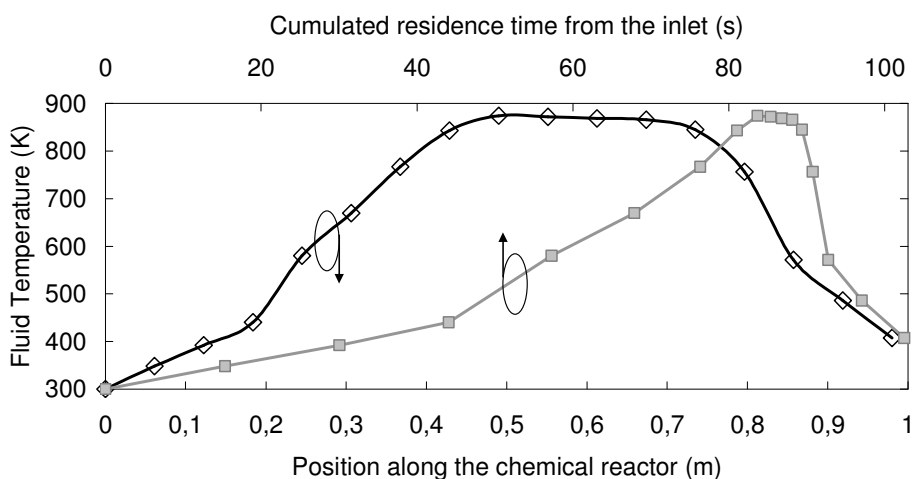


Figure 4. RESPIRE calculations of fluid temperature ($0,05 \text{ g}\cdot\text{s}^{-1}$, 5 MPa , $4,5\cdot 10^{-3} \text{ m}$ diameter).

An example of furnace temperature profile is given along the axis (Figure 5, left). This one is not exactly centred but it is shifted to the outlet because of the fluid flow inside the chemical reactor. The thermal gradients at the inlet and outlet do not have consequences on the pyrolysis process as n-dodecane does not pyrolyse under 700 K to 800 K . The most important part for the pyrolysis is the central one, where the maximum temperature is measured. In order to characterize stationary experimental tests, this maximum temperature measured inside the furnace is supposed to be the maximum one reached by the fluid. This has been confirmed thanks to RESPIRE calculations (Figure 5). Maximum temperature discrepancies between the fluid and the furnace, for all the various tested conditions, are about 50 K , *i.e.* less than 5% of temperature (Figure 5, left). Furthermore, the maximum fluid temperature corresponds to the maximum pyrolysis rate for the n-dodecane (Figure 5, right). Few variations are noticed on the chemical composition after the maximum reached fluid temperature. This allows for taking the maximum furnace temperature as a characterisation

parameter of the pyrolysis, as it is representative of the pyrolysis products analysed experimentally.

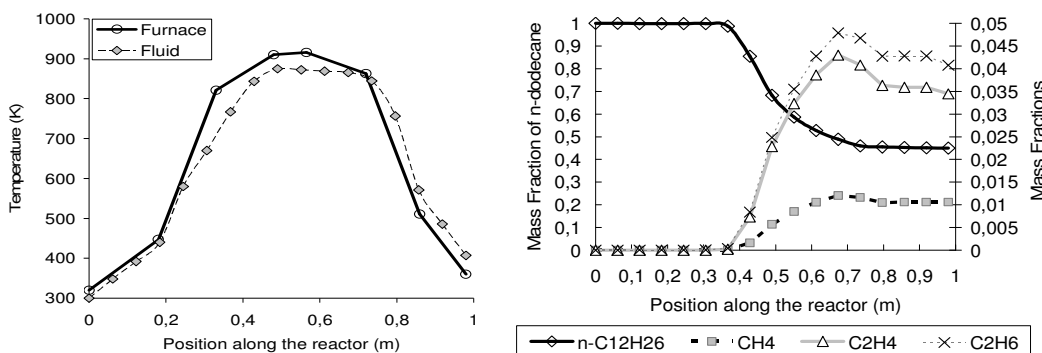


Figure 5. RESPIRE simulation of a given test case ($0,05 \text{ g}\cdot\text{s}^{-1}$, 5 MPa, 4,5 mm reactor diameter) using experimental furnace temperature as boundary conditions : fluid temperature (left), pyrolysis products composition (right).

Nevertheless, it has been determined, by use of 2-D calculations with CFD-ACE software, that thermal radial gradients inside the chemical reactor can be reached 40 K for a turbulent fluid flow. For low Reynolds number flow, hydraulic 2-D effects have been observed inside the chemical reactor and thermal gradients are thus waited. These gradients play an important role on the temperature distribution inside the fluid and thus on its pyrolysis. This point cannot be studied neither numerically nor experimentally because these tools are roughly 1-D. But using turbulent fluid flow or single phase flow may decrease the effect of these gradients. This point is not due to radial gradient inside the furnace. Five horizontal thermocouples and five vertical ones measure the temperature for three positions along the furnace in the tube (45 mm diameter) surrounding the chemical reactor. A radial gradient of maximum 2 degree has been found. This is supposed to be negligible in regard of axial gradients (several hundredth of degree).

As the n-dodecane pyrolysis starts at a temperature around 700 K to 800 K, depending on residence time and pressure ; a working pressure higher than 1,8 MPa corresponds, for pure n-dodecane, to a transition from the liquid phase to the supercritical state around 658 K. For lower pressure, a coexistence of liquid and gas phases appears. This could conduct to a stratification of phases for flows with low Reynolds numbers. It is interesting to obtain supercritical pyrolysis because the fluid can be treated as a single phase flow, even in laminar flow because no stratification appears. This is particularly interesting for RESPIRE, as it considers constant values in a cross section of the reactor, and also for the process because it is more convenient to study. Thanks to the dedicated observing cell, located at the

furnace outlet, the pyrolysed dodecane has been studied. Near the critical point of pyrolysed mixture, fluid becomes green and then very dark. We have even observed conditions with opalescent fluid ("mirror" effect) for which we can see ourselves in the fluid. This is due to optical fluid properties modification near the critical point. Our observations are consistent with the one of Oag et al. (2004).

4.2. Experimental results: understanding, validation and exploitation

Experimental results of pyrolysis are given (Figure 6) for the following test conditions : 1 MPa, $0,05 \text{ g}\cdot\text{s}^{-1}$, $4,5\cdot 10^{-3} \text{ m}$ stainless steel reactor diameter. The conversion rate passes from 20 % to 95 % in a temperature range of about 200 K. Pyrolysis of n-dodecane (Figure 6, left) produces intermediate hydrocarbons with 7 to 10 carbon atoms. This should be accompanied by a production of lighter hydrocarbons, gaseous under ambient conditions, but this is not experimentally confirmed (Figure 6, right). No gaseous products are detected before 900 K, whereas pyrolysis starts around 700 K. It is attributed to low production rate of such species at moderate temperature. This conducts to have low gaseous pressure which disables the gas phase analysis because sufficient pressure is needed to bring chemical products to the Gas Chromatograph. This point is not dramatic as it corresponds to a gaseous products mass fraction lower than few percents. The experimental test bench aims at studying working conditions with high gasification. The gasification is defined at ambient condition as the ratio between gaseous products mass and pyrolysis products mass.

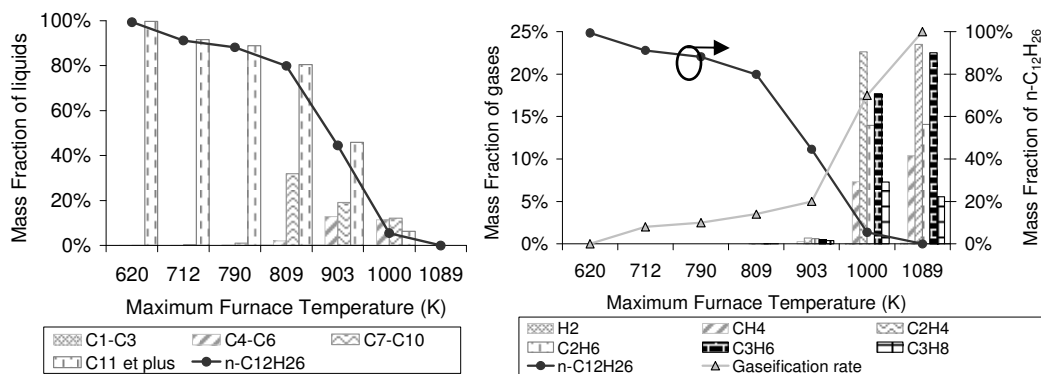


Figure 6. Experimental mass fractions of pyrolysis compounds : liquid (left) and gaseous (right) phase.

A relationship between the gasification rate and the Hydrogen/Carbon ratio appears. H/C ratio greater than 0,19 are representative of pyrolysis products which are gaseous at ambient conditions. Thus, information about this ratio could give further information about the production of light species. Despite the fact that coking appears at temperature around 900 K, it can be noticed that no

acetylene is found in the gaseous pyrolysis products (Figure 6, right). This is confirmed by the numerical simulations. To illustrate the coking activity during pyrolysis, a typical stainless steel reactor, with an internal diameter of $4,5 \cdot 10^{-3}$ m, is completely jammed by coke after five hours at 900 K with $0,05 \text{ g}\cdot\text{s}^{-1}$. The coke formation has been macroscopically studied and characterised but it is not fully presented in this paper. Some witnesses of the coke deposit are presently under study and it could be possible to estimate the coking activity during the experimental test. This would help to take it into account in the simulation, while at the present day a coke deposit rate of $100 \mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ is tabulated (based on various data of the literature). We have previously identified that H/C ratio gives information about pyrolysis. It is equal to 0,18 for pure n-dodecane and it increases as the process temperature increases. This ratio is characteristic of compounds. It is equal to 0,166 for alkenes and it varies between 0,34 for methane to 0,166 for heavy hydrocarbons. It could be an interesting tool to predict carbon deposit since the coke formation should be accompanied by a higher H/C ratio at the reactor outlet.

It is interesting to observe the quantity of gaseous products, thus the gasification rate, increasing with temperature process (Figure 6, right). This is due to the formation of always lighter species at higher temperature. A relationship between gasification and pyrolysis rate has been outlined during the experimental tests but this may depend on operating conditions as gliding may occur between gas phase and liquid phase inside the process, after the furnace outlet. This relationship could be interesting for the ground industrial process as it could give information about pyrolysis rate without chemical analysis.

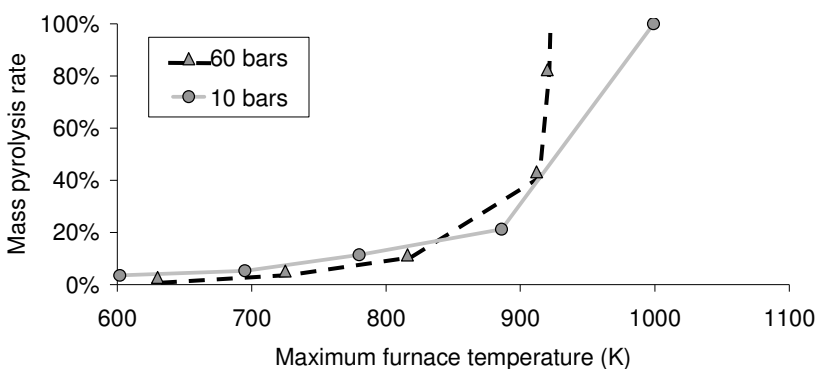


Figure 7. Influence of subcritical and supercritical conditions on experimental pyrolysis rate.

A parametric study has been conducted on various process parameters, such as temperature, pressure, mass flow rate, reactor diameter and chemical nature of reactor materials. This has permitted, thanks to design of experiments, to show the first importance of temperature and residence time on pyrolysis rate.

Parameters effects are not easy to analyse because their fluctuations are accompanied by various other ones. For example, an increase in mass flow rate raises the convective exchange between the fluid and the reactor but it decreases the residence time. Finally, the pyrolysis rate decreases. The pressure effect is easier to understand but two phenomena are thus involved (Figure 7). A pressure increase corresponds to a residence time increase through the one of density, for a given mass flow rate. And it is accompanied by a higher collision number between molecules, which favours the chemical reactions too. Finally, it is difficult to know which contribution increases the pyrolysis rate. Nevertheless, it has been observed that pressure has an influence mainly in the subcritical domain. Pyrolysis under supercritical state show results almost independent from pressure.

To give better characterisation of experiments, a mass balance has been performed for the experimental test cases, on liquid and gas phase and for hydrogen and carbon mass. Discrepancies are lower than 1 %, which is sufficient for our purpose. This allows for studying effusion through porous reactor walls for future experiments. Indeed, the injected mass flow rate for the SCRAMJET engine is expected to be slightly lower than the one pumped from the tank because of film cooling through porous walls. This point needs to be studied because it influences the combustion and thrust. Experimental results have also served to validate the RESPIRE code (Figure 8). The main differences are obtained for lighter hydrocarbons, which concentration is numerically higher. This can be attributed to the code, which does not consider thermal and hydraulic gradient in a cross section. Consequently, due to uncertainties on experimental temperature measurement, discrepancies are totally acceptable as a 200 K temperature gradient can correspond to a variation of pyrolysis rate of 100 %. Numerous conducted validations have proved RESPIRE to give sufficiently good results for our purpose through the entire range of pyrolysis rate [0 % to 100 %].

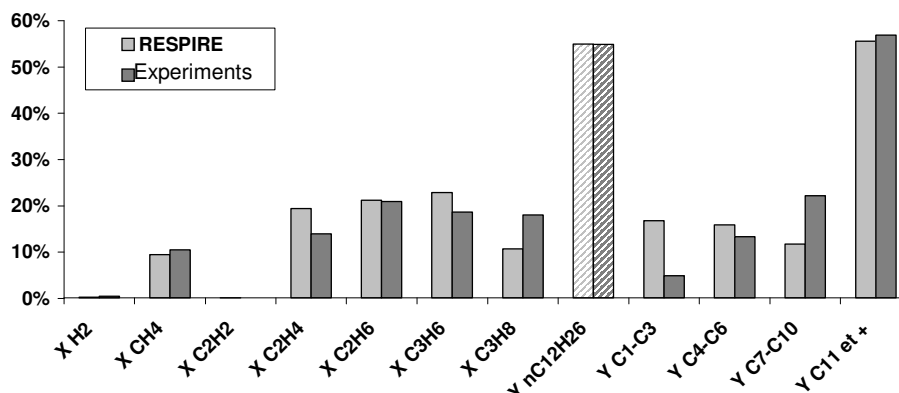


Figure 8. Gaseous Molar Fraction in the gas phase and Compounds Mass Fractions in the pyrolysis products : Experimental analysis for a given test case (773 K, 0,05 g.s⁻¹, 5 MPa, 4,5 mm reactor diameter).

5. CONCLUSIONS

A one-dimensional transient model has been programmed in order to simulate the SCRAMJET active cooling and to determine the mixture composition at the cooling channel outlet. A complete detailed mechanism with 1185 reactions and 153 species has been implemented. Equations have been presented and the RESPIRE code is quantitatively validated. RESPIRE is suitable to simulate the experiment conducted thanks to the dedicated test bench.

A specific test bench was designed and built for the purpose of COMPARER program. It is suitable to study the stationary and transient behaviour of hydrocarbon pyrolysis, possibly at supercritical state, under extreme temperature and pressure conditions (8 MPa, 1850 K, 0,6 g.s⁻¹). Chemical composition of pyrolysis products have been investigated experimentally thanks to a Gas Chromatograph and a Mass Spectrometer. Various operating parameters (temperature, pressure, mass flow rate) were tested. A parametric study has shown the prior importance of temperature and residence time on the pyrolysis. Pressure effect appears to be negligible under supercritical state, whereas it can play a role at subcritical conditions. Some relationships have been identified between gasification rate, pyrolysis rate, Hydrogen/Carbon ratio and coke deposit.

The experimental and numerical tools allow taking into account the relationships between coupled phenomena, such as fluid mechanics, heat transfer, chemical kinetics. They consider a hydrocarbon fuel, without dilution, in a reacting flow with a varying temperature profile, which is far from an ideal Perfectly Stirred Reactor configuration. The RESPIRE code demonstrates an important capacity to give information about unmeasured experimental data, such as the time dedicated to pyrolysis and the fluid temperature inside the process. As a feedback, experimental results have been used to complete the validation set of the code. Both numerical and experimental tools have shown an interesting complementarities and adequacy with the need for the COMPARER project. The dedicated experimental test bench can provide further validation data on chemical aspects and on the dynamic response of inlet time variations. The RESPIRE code can be used for other fluids and/or in other operating conditions very useful for the scientific community.

NOTATION

c	Sound velocity, m.s ⁻¹
C_f	Friction coefficient
D_H	Hydraulic diameter, m
h	Convective heat transfer coefficient, W.m ⁻² .K ⁻¹
H	Total enthalpy, J.kg ⁻¹

h_{can}	Height of the channel, m
$h_{i,0}$	Static enthalpy at 298 K of i species, J.kg ⁻¹
j_q	Conduction flux density, W.m ⁻²
P	Pressure, Pa
r	Gases constant, J.kg ⁻¹ .K ⁻¹
T	Temperature, K
t	Time, s
V	Velocity, m.s ⁻¹
Y	Mass fractions
x	Abscissa along the channel, m
Z	Compressibility factor
Z_c	Critical compressibility factor

Greek Letters

β	Thermal expansion coefficient
β_c	Thermal compressibility coefficient
λ	Thermal conductivity, W.m ⁻¹ .K ⁻¹
ρ	Density, kg.m ⁻³
τ	Friction constraint, Pa.m ⁻¹
ω	Pitzer acentric factor
w_i	Net production rate of species i

Superscripts

+	reduced coordinates (i.e. divided by the critical value)
(0)	First tabled value
(1)	Second tabled value

Subscripts

0	Standard conditions at 298 K
CC	Combustion Chamber
cw	cold face (of the porous wall)
ef	external face (of the external wall)
ew	external wall
ext	external environment
f	fluid
hw	hot face (of the porous wall)
i	species
if	internal face(of the external wall)
pw	porous wall

s static
y Orthogonal direction to x abscissa

Abbreviations

SCRamjet Supersonic Combustion Ramjet

CFD Computational Fluid Dynamics

H/C ratio Hydrogen/Carbon ratio

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