



## Real-time method for the identification and quantification of hydrocarbon pyrolysis products: Part II. Application to transient pyrolysis and validation by numerical simulation

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### ABSTRACT

A real-time quantification infra red method has been developed with a gas cell to determine the composition of hydrocarbon pyrolysis products. The aim is to chemically characterise the fuel decomposition in case of regenerative cooling. The method can be extended to a large variety of applications. A transient analysis of the method behaviour is conducted to estimate its capacity to be applied to unsteady conditions (one measure per second), which can be encountered in cooling activity and unsteady processes. A numerical tool called RESPIRE (French acronym for Supersonic Combustion Ramjet Cooling with Endothermic Fuel, Transient Reactor Programming) is used to help in understanding the complex phenomena involved in such a chemical reactor. The validation of transient behaviour with respect to the computations shows negligible time delay (lower than few seconds with gasification rate higher than 60 wt.%) due to residence time in the experimental setup. The quantification accuracy is confirmed to be around 2 mol%. The agreement obtained on gas cell measurements is found to be correct over 10–20 wt.% of gasification rate and very satisfactory over 60 wt.% but this depends on the species. An extension of the method has been developed with a dedicated online cell to be specifically applied to supercritical and multiphase flows. The quantification of the gas phase in the pyrolysis mixture in case of biphasic flow is proposed and validated with an uncertainty around 3 wt.%. The coke formation is monitored as a function of time and its quantification is even tested with 50% of uncertainty after a numerical calibration with respect to simulation.

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### 1. Introduction

The hypersonic flight is expected to be achieved with Supersonic Combustion Ramjet engine [1–4]. Due to the large heat load applied on the structure (elevated total temperature in case of high speed [5,6] and combustion heat release [7]), the regenerative cooling technique could be implemented to use the fuel as a coolant but also to voluntarily decompose it. Some of the resulting pyrolysis products (among hydrogen, ethylene, methane, etc [8]) can present sufficiently low auto-ignition delays for supersonic combustion conditions (auto-ignition delays should be 10% of the residence time, that is to say 0.1 ms [9]). The COMPARER project (CONtrol and Measure of PArameters in a REacting stReam) has been settled in 2003 to enable studying the regenerative cooling technique. To control such a technology, the combustion of

the hydrocarbon pyrolysis products should be assessed and this requires estimating the main components and their respective concentrations [10]. For this purpose, a specific Infra Red method has been developed and validated under steady-state conditions [11]. Compared with gas chromatograph, it shows an accuracy of about 2 mol% on the quantification of main gaseous products (detection limit of 4 mol%) such as methane, ethylene, ethane, propylene and propane.

The aim of this second part of paper is to apply the method to transient cases to test its adaptability to conditions which are much more difficult to analyse. Due to its nature, the GC/MS apparatus is not suitable for transient analysis and the only way to validate the FTIR data is to use numerical simulation. For this purpose, the numerical code called RESPIRE (French acronym for SCRamjet Cooling with Endothermic Fuel, Transient Reactor Programming) uses experimental pressure, furnace temperatures and mass flow rate measurements as boundary conditions for an exact simulation of the pyrolysis process [7,12]. This tool has been extensively validated since 2004 under various operating conditions, for several types

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### Nomenclature

GC	Gas chromatograph
MS	Mass spectrometer
HPLC	High performance liquid chromatograph
FTIR	Fourier transform infra red
CC	Combustion chamber
CVI	Chemical vapor infiltration
CVD	Chemical vapor deposition
ppm	Part per million

of fluids, stationary and transient regimes [7].

#### 1.1. Transient analysis of pyrolysis products formation

Very few studies are currently available on transient pyrolysis as it was already mentioned by Phuoc et al. [13] 20 years ago. Most of the “transient” studies are mainly numerically oriented in the sense that they aim at providing a kinetic mechanism which of course refers to the time [14]. Sprecher and Retcofsky [15] study the formation of free radicals whose lifetime is much lower than 1 ms (highly transient conditions) but they do it after freezing the pyrolysis mixture (steady state conditions). Bauer [16] used this technique earlier with pyrolysed hydrocarbon fuels through shock-tube experiments. Lédé and coworkers [17] have conducted a kind of “transient” study but in fact they vary the pyrolysis time through successive experiments and analyse the products after the test and not during the test. Lacroix et al. [18] did the same for the formation of pyrocarbon. Consequently, no specific device is used but only common HPLC or MS apparatus. The work of Feron et al. [19] must be noticed because they used an FTIR spectrometer in situ to identify and quantify hydrocarbon and chlorous compounds directly inside the experiment. Nevertheless, they conducted the work under steady-state conditions to obtain stable reactor operation.

#### 1.2. Reactive flow simulation

Due to the absence of experimental work related to transient estimation of pyrolysis and associated analytical techniques, the numerical simulation is an interesting tool for this study. The only transient studies related to pyrolysis are numerical ones because they are often coupled with combustion of products [20,21]. Such computations are also found for catalysis [22] or CVI [23]. Despite their interest, they do not imply experimental validation in same unsteady conditions but at best under steady ones. It is even possible to find a work under “unsteady” conditions but which is in fact represented by stationary stages [24]. This approach is questionable since the transient phenomena are not a succession of stationary steps.

Several models of heat and mass transfer for fuel pyrolysis can be found. For active cooling applications, they consider different fuels and test configurations but few are related to transient analysis. They focus mainly on heat transfer, with limited consideration of the chemistry [25–29]. Most of the studies are related to transient computations with detailed chemistry are related to combustion (with [30] or without pyrolysis [31,32]) and very few are really dedicated to pyrolysis [33,34].

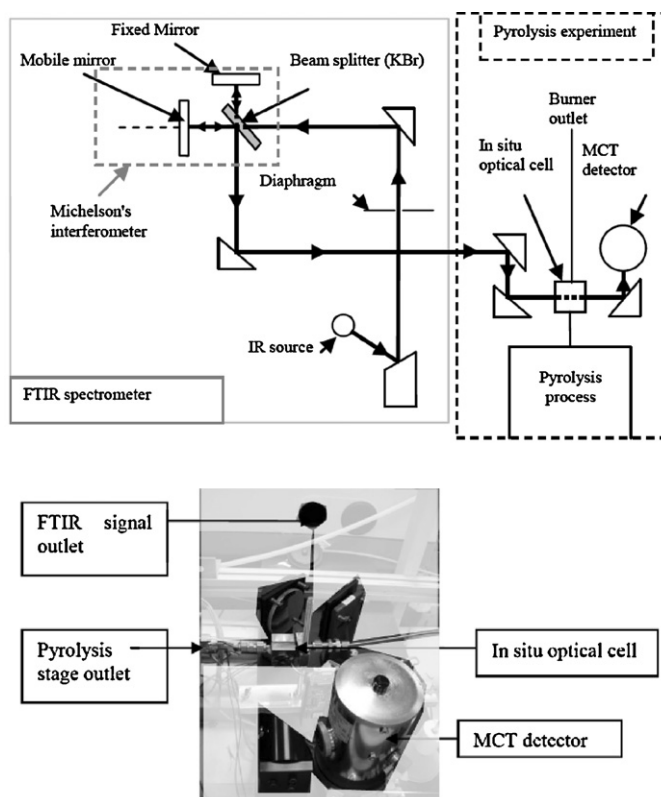


Fig. 1. Path of the infra red signal from the FTIR source to the MCT detector (a) and related photograph with the in situ cell (b).

## 2. The COMPARER test bench and the RESPIRE numerical code

### 2.1. Experimental apparatus

The COMPARER test bench has been fully described in [11]. It is representative of the SCRamjet engine. The fuel is heated and pyrolysed in the reactor by the oven, which represents the thermal effect of the combustion chamber. The test rig enables reaching a pyrolysis rate of 100% for pressures up to 80 bar, temperatures up to at least 1200 K and mass flow rates lower than  $0.6 \text{ g s}^{-1}$ . No fuel dilution is considered, which is sufficiently rare in pyrolysis studies to be mentioned. The bench has been predimensioned by the RESPIRE and NANCY tools [35] notably to get the same axial profiles in the reactor as in the cooling channel in terms of heat capacity, decomposition and Reynolds number but also to reach a similar outlet pyrolysis rate.

The pyrolysis products formed during experiments with isothermal plateaus have been monitored with respect to a large gas cell (volume of  $100 \text{ cm}^3$ , optical path length of 100 mm), which is placed approximately one meter after the outlet of the furnace (inner diameter of the line varies from 0.9 mm to 1.8 mm). This cell is kept at constant temperature of 373 K and its absolute pressure is regulated by a controlled vacuum pump at 50 mbar. The optical windows are in  $\text{BaF}_2$  and a DTGS detector is used with this cell.

In addition to this large gas cell presented in a companion paper [11], another smaller one has been used with an MCT (Mercury Cadmium Telluride) detector cooled by liquid dinitrogen (outlet of the FTIR spectrometer) to increase the sensitivity and consequently the acquisition frequency (from one measure every 15 s to one per second). The cell (geometrical path length of 2 mm) is placed directly at the furnace outlet to obtain data on hot flows (depending on the unwanted natural cooling after the furnace). A scheme (Fig. 1a)

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