The International Conference on Flight vehicles, Aerothermodynamics and Re-entry Missions and Engineering (FAR), *30 September- 3 October 2019, Monopoli, Italy.*

SOLID CARBON PRODUCED DURING THE SIMULATION OF RE-ENTRY IN THE TITAN ATMOSPHERE BY MEANS OF AN ARC-DRIVEN FLOW FACILITY

Antonio Esposito[1] *- Marcello Lappa*[2] *- Gennaro Zuppardi*[1]

Christophe Allouis[3] *– Barbara Apicella*[3] *– Mario Commodo*[3] *- Patrizia Minutolo*[3] *- Carmela Russo*[3]

1 Department of Industrial Engineering – Aerospace Branch –University of Naples “Federico II” Via Claudio 21, 80125 Naples Italy- antespos@unina.it

2 Department of Mechanical and Aerospace Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow, G1 1XJ, UK - marcello.lappa@strath.ac.uk

3 Institute for Combustion Research – National Research Council, Piazzale Tecchio 80 – 80125 Naples Italy allouis@irc.cnr.it

ABSTRACT

Spacecraft entry into Titan’s atmosphere has been investigated using a dedicated (Small Planetary Entry Simulator) facility (SPES). While in earlier works much attention was paid to the joint numerical-experimental simulation of typical entry physical parameters (namely, heat flux and total enthalpy); in the present analysis we focus on some unexpected results recently obtained at the University of Naples, in collaboration with CNR, in the framework of a new test campaign dedicated to various planetary atmospheres (including Titan itself). Such findings concern the presence of a carbon-like substance on the surface of the measuring probes used for the experiments, which seem to align with the results yielded by other authors with other strategies (an inductive plasma torch). We have confirmed the carbonaceous nature of such particulate matter via various diagnostic techniques such as SEM, Raman, FT-IR, UV-visible absorption and fluorescence spectroscopy, GC-MS and TGA. The present work is devoted to the presentation of such results together with a critical discussion of the novelty relating to the present experimental approach (arc plasma versus inductive torch) and an analysis of the chemical-physical differences pertaining to the carbon obtained with the two different methods.

Index Terms— entry simulation, solid carbon

1. INTRODUCTION

Titan, the main satellite of Saturn, is the only satellite in the solar system with a dense atmosphere (surface pressure of 1.5 bar). Below 1000 km, the two major compounds are nitrogen (~95%) and methane (~2% in the stratosphere) with a temperature of approximately 90 K. This world has attracted much interest over the years due to its unusual chemistry, which is thought to contain all the necessary ingredients for the emergence of life. For this reason, it has been observed by remote sensing for many years, both from interplanetary probes (Pioneer and Voyager's flybys) and from the Earth. The Voyager 1 (1980), Voyager 2 (1981), Cassini (2004 - 2017) and Huygens (2005) spacecraft have uncovered physicochemical processes unique in the solar system occurring both in the atmosphere and surface [1].

The atmosphere and its complex chemical reactions may be regarded as a conundrum. Its interaction with solar UV photons and cosmic energetic particles initiates chemical reactions which yield gaseous hydrocarbons and nitriles and, through polymerisation processes, solid aerosol particles which grow by coagulation and settle down to the ground [2]. This process results in the production of solid aerosols responsible for the orange haze surrounding Titan. These substances (known as tholins) are the most complex extraterrestrial organic material detected in the Solar System [3]. New missions are being designed to shed new light on these fascinating mechanisms. Though the atmosphere of Titan and its ability to produce aerosols in nominal conditions (i.e. at its average temperature of 90 K) has extensively been investigated due to the important implications about astrobiology and the “emergence of life”, however, the ability of its atmosphere to produce solid phases at the very high temperatures which are attained during the re-entry of a spacecraft has not been investigated to a comparable extent.

The atmospheric entry of a spacecraft is a critical phase for the success of a planet exploration, and an efficient thermal protection system (TPS) is required to protect the probe against the energy surface flux. The existing studies on this subject have essentially concentrated on the gas dissociation processes which occur when a probe enters the atmosphere of Titan at very high temperature [4]. These studies are required to properly predict the temperature at the probe surface (in order to design relevant protection systems).

Surprisingly, few studies have been conducted on the formation of solid particles in such processes. To the best of our knowledge only Vacher et al. [5] have addressed this subject. These authors found solid carbon deposited on the surfaces of an inductively coupled plasma torch operating with a Titan like atmosphere plasma gas. In the present work, further evidence for the existence of this phenomenon is provided on the basis of a different technique, i.e. a wind tunnel driven by an industrial arc-heated facility operating with Nitrogen as working gas (the methane necessary to simulate Titan's atmosphere composition has been added in a plenum-mixing chamber located upstream a supersonic nozzle, [4] and [6].

This hitherto not yet thoroughly explored phenomenon is of great interest due to its important implications with regard to the aforementioned protection systems (high speed solid particles may represent a significant threat for any spacecraft or probe).

2. SIMULATING ENTRY INTO TITAN'S ATMOSPHERE BY SPES

SPES (Small Planetary Entry Simulator) facility is available at the Department of industrial Engineering - Aerospace Branch of the University of Naples "Federico II". This facility (see Fig. 1) belongs to the general category of continuous, open circuit, electric arc-based, wind tunnels. Its main components are:

- an electric arc-heater (industrial plasma torch, Sulzer-Metco type 9-M), operating with pure inert gases (argon or nitrogen);
- a mixing chamber where the nitrogen plasma can be mixed with cold gases (oxygen, carbon dioxide or, methane) to simulate planetary atmospheres;
- four different conical nozzles (area ratios 4, 20, 56, 100) for operations in supersonic and hypersonic flow regime;
- a cylindrical vacuum test chamber (ultimate pressure is in the order of 50 Pa).

Typical SPES operative conditions for entry simulation applications are (order of magnitude): a total mass flow rate of 1 g/s, an average total enthalpy of 15 MJ/kg and a total pressure of 2000 Pa.

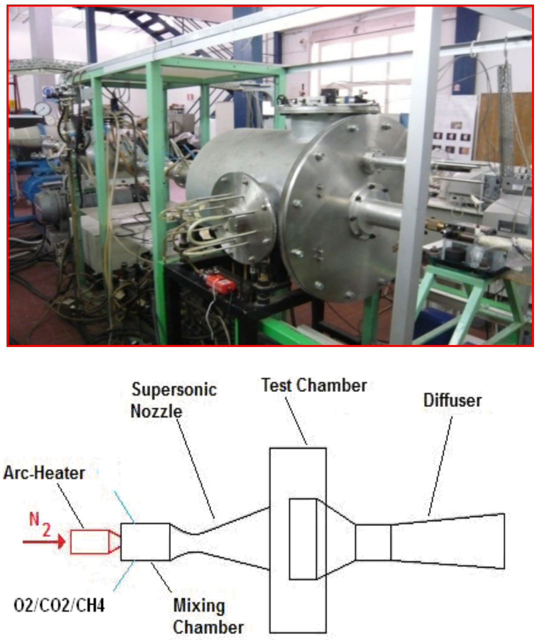


Fig. 1: SPES facility

In our experiments, the mass-averaged (or bulk) gas enthalpy has been determined at three different positions along the SPES (Refer to Fig. 1) by the *so-called energy balance method* [7]. In particular, the measured enthalpies have been calculated as average values resulting from different energy contributors at each position, as illustrated in the following:

i) The enthalpy of the gas leaving the arc-heater and entering the mixer:

$$H_{ah} = \frac{P - (m_w C\Delta T)_{ah}}{m_{g,ah}} \tag{1}$$

(evaluated by subtracting the losses due to the cooling water to the input electric power and assuming C=4186 [J/kg], the reader being referred to the List for the meaning of symbols)

ii) The enthalpy of the gas leaving the mixer and entering the nozzle:

$$H_{mc} = \frac{H_{ah} m_{ah} - (m_w C\Delta T)_{mc}}{m_{g,t}} \tag{2}$$

iii) The enthalpy of the flow at the nozzle exit:

$$H_{ne} = H_{mc} - \frac{(m_w C \Delta T)_{ne}}{m_{g,t}} \tag{3}$$

During each test the following pressures have been measured by electronic vacuum transducers:

- p_t at the mixing chamber exit
- p_{ne} at the nozzle exit
- p_{ts} at the test section
- p_{02} impact pressure at the stream centerline.

The uncertainty on the measured total enthalpy evaluation was in the range between ±10% and ±20% depending on arc power level, while the uncertainty on the measured pressures was between ±2% and ±5%.

The present analysis is articulated as follows: in Sect. 3, we provide relevant information on the experimentally determined presence of carbon on the surface of the probes used for the tests; in Sect. 4, the formation of this substance is investigated in the framework of a sophisticated multi-species numerical models considering the effective conditions established inside the SPES (Sect. 4.1) or during the re-entry of the Cassini probe (Sect. 4.2); Sect. 5 deals with the analysis of the deposited substance by means of a variegated set of complementary experimental techniques. It is shown that such carbon (which also features the presence of nanostructured particles) can display two different (more or less dense) morphologies. It has been analyzed using microscopic, spectroscopic and mass spectrometric techniques.

3. EXPERIMENTAL EVIDENCE OF CARBON DEPOSITION

3.1. Carbon Formation in SPES (DC plasma torch)

The formation of solid carbonaceous deposits occurred on two circumstances during the SPES tests:
a) on heat flux probes, made of brass, figure 2a; in this case the particulate appears in the form of black soot
b) on a total enthalpy probe, made of steel, figure 2b; in this circumstance the carbonaceous matter appears as a brown substance along the probe body, and as a black soot in the stagnation zone.


(a)


(b)

Fig. 2: Experimental Evidence of Carbon Deposition on (a) Heat Flux Probes and (b) Total Enthalpy Probe

3.2. Carbon Formation in an Induction Plasma Torch

Vacher at alii [5] used an inductively coupled plasma torch in your simulations of Titan atmosphere; carbon powder has been found on the ceramic injector and on the quartz tube, see figure 3, no deposition occurs on the part of the tube located inside the induction coil, where plasma temperature is the highest. The carbon powder revealed a high disorder degree indicating its amorphous character. The authors [5] found different particles dimensions in dependence on the different durations of formation or different temperatures, but whatever their morphology is, the samples were always found not containing nitrogen, indicating the absence of tholins.

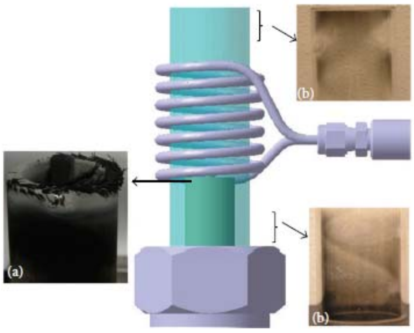


Fig. 3: Carbon deposition in Vacher's torch

4. COMPUTING CARBON DEPOSITION IN GROUND AND FLIGHT SIMULATION (OF TITAN ATMOSPHERE ENTRY)

4.1. Carbon Formation – Ground Simulation

A number of tests have been performed to simulate entry in Titan atmosphere, as for Table 1:

Table 1

m_{gas_N2} [g/s]	m_{gas_CH4} [g/s]	Hne [MJ/kg]	P_{02} [Pa]
0.4	0.1	9.3 – 24.4	3800 - 6500

Using the open software CEA from NASA [8], an extended version of the well-assessed Frozen Sonic Flow Method [4] and the experimental test data (mass-averaged enthalpies and pressures), an electronic data sheet has been implemented to calculate gas thermofluidynamic properties and chemical composition at the arc-heater outlet, mixing chamber inlet (just after mixing of cold methane and hot nitrogen plasma) and finally at nozzle outlet. The main result from this analysis is that solid carbon originates in the mixing chamber, for total enthalpy values between 10 and 15 MJ/kg.

4.2 Carbon Formation - Flight Simulation

Titan atmosphere is basically made up of 3 chemical species: Nitrogen (N_2), Methane (CH_4) and Argon (AR) whose composition is almost constant with altitude. The molar fractions are about: $X_{N2}=0.95$, $X_{CH4}=0.03$, $X_{AR}=0.02$. Due to the high number of reactions produced by high energy during a capsule entry path, atmosphere has been considered made of 18 chemical species: N_2, CH_4, CH_3, CH_2, CH, C_2, H_2, CN, NH, HCN, N, C, H, AR, N_2^+, CN^+, N^+, C^+, AR. The chemical model by Savajano et al. [9] has been used. This model is made up of 221 reactions: 205 dissociations, 11 exchanges, 5 ionizations. The numerical study has been carried out in the altitude interval 180÷470 km. The Huygens-Cassini capsule, depicted schematically in Fig.4, was a 60° half-angle sphere-cone with a diameter (D) of 2.7 m.

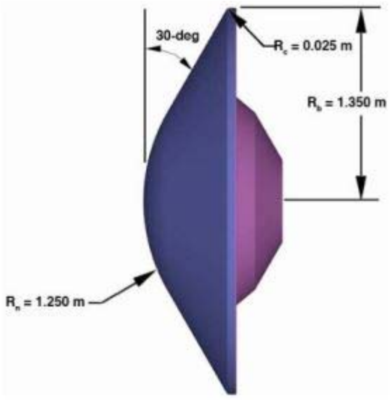
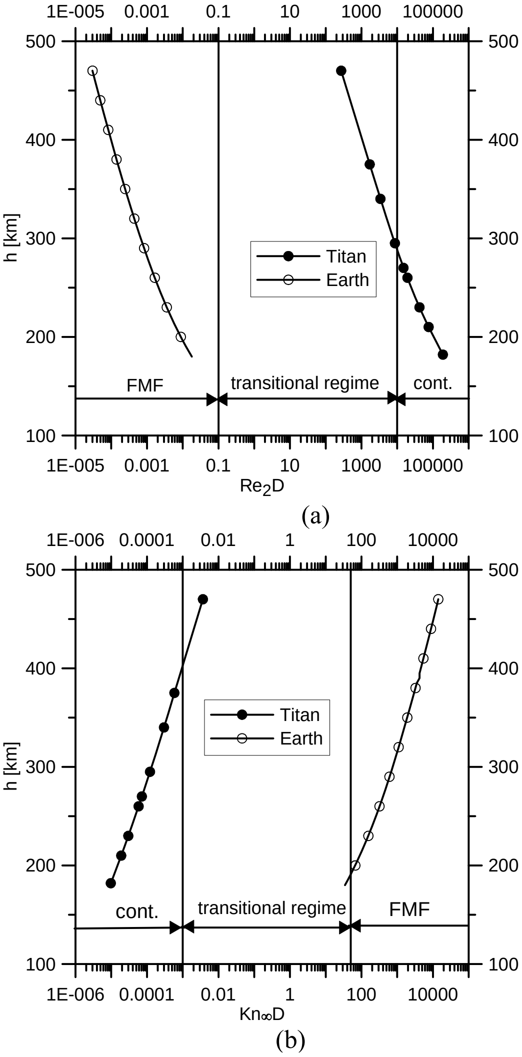


Fig. 4 - Schematic of Cassini-Hyugens capsule

The Cassini-Hyugens entry trajectory was computed by Wright et al. [10]; Figs.5(a) and 5(b), verify that the flow field around the capsule in Titan entry is in transitional (continuum low density) regime. In fact, according to: i) Vallerani [11], the transitional regime for a blunt body is defined in terms of the Reynolds number downstream a normal shock wave by $10^{-1}<Re_{2D}<10^4$, ii) Moss [12], in terms of the global Knudsen number by $10^{-3}<Kn_{\infty D}<50$.



(a)

(b)

Fig. 5 -Profiles of: Reynolds number downstream a normal shock wave (a), Knudsen number (b) as function of altitude

As the flow field is in the transitional regime, it can be solved by means of the Direct Simulation Monte Carlo (DSMC) method [13], [14], [15]; more specifically, the DS2V-4.5 64 bits [16] code has been used. This code offers the user the opportunity to simulate in a relatively straightforward way the absorption process of molecules impinging onto the surface of a body. Thereby, it is particularly suited for the simulation of the formation process of a carbon layer. In particular, DS2V-4.5 64 bits makes possible diversifying the type of molecule-surface interaction for each molecule. In the present case, the interaction with the surface of all molecules, except for carbon (C), were considered re-emitted from the surface by a diffusive re-emission at the wall temperature of 300 K, while the carbon molecule was considered absorbed by the surface, therefore eliminated from the calculation. This option greatly improves the accuracy relating to the simulation of the generation of the carbon layer on the capsule surface, whose thickness can be quantified by the flux of carbon atoms (C) impinging onto the surface.

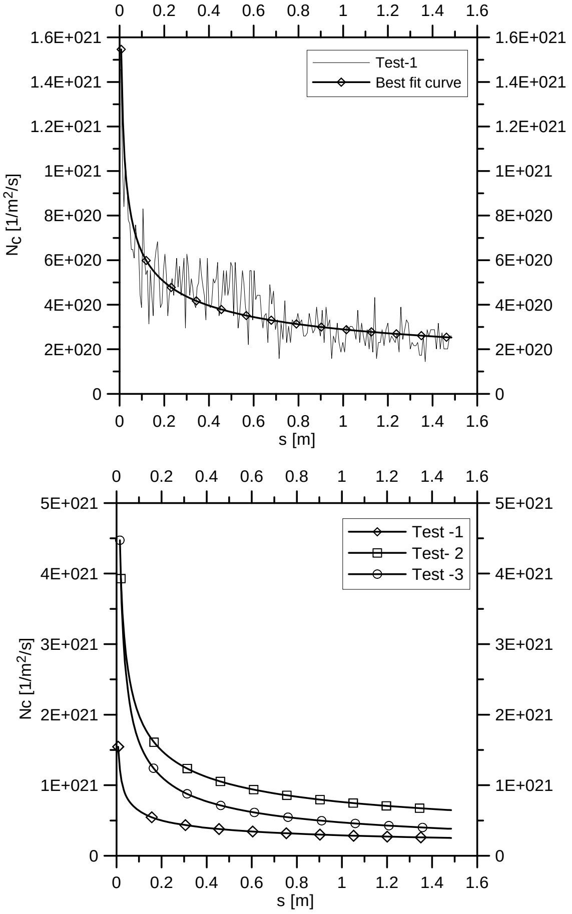
We have conducted 4 numerical tests as shown in Table 2, which reports both input data (V_∞, N_∞, T_∞) to DS2V-4.5 64 bits and total enthalpy. At these altitudes the flow total enthalpy is such that carbon atoms can be produced by dissociation of CH_4, CH_3, CH_2 etc.

Wright [10] presented the entry trajectory in terms of the flight time (t[s]). For the purpose of the present paper, the corresponding altitude was determined by means of the match of the free stream density provided by Wright and that provided the Yelle's model [17]. Temperature, gas composition etc. used in the present computations, are those from the Yelle's model.

TEST	h [km]	V_∞[m/s]	N_∞[1/m^3]	H_∞ [MJ/kg]
1	**470**	**6167**	$\mathbf{1.295\times10^{20}}$	**19.2**
2	**375**	**6049**	$\mathbf{8.117\times10^{20}}$	**18.5**
3	**340**	**5886**	$\mathbf{1.590\times10^{21}}$	**17.5**
4	**295**	**5490**	$\mathbf{3.916\times10^{21}}$	**15.3**

Table 2 -DS2V-4.5 64 bits input data and free stream enthalpy

The thickness of the carbon layer, deposited along the surface of the capsule, is closely linked to the flow of carbon atoms impinging onto the surface. Along these lines, Fig.6(a) shows the profile of the number flux (N_C) of Carbon atoms, for example, for Test 1. The profile looks pretty scattered and, as expected, it assumes the maximum value at the stagnation point (s=0 m) where the shock wave is stronger compared with that of every point along its front; correspondingly gas gets maximum reactivity. Because of the data scatter, the flux of carbon atoms (C) are compared by means of best fit curves. Computation related to Test-4 are not shown in Fig.6(b); N_C for Test-4 is negligible. Even though Test-1 is the most energized, however the formation of carbon atoms is the lowest; the generation of carbon atoms is due both to the energy level and by the density of the flow.



(b)

Fig. 6 - Profile of Carbon flux to the capsule surface for Test-1 and related best fit curve (a), comparison of the best fit curves for three tests (b)

5. CARBON EXPERIMENTAL CHARACTERISATION

An array of characterization techniques including: scanning electron microscopy (SEM), spectroscopic techniques (Raman, FT-IR, and UV-visible absorption and fluorescence), gas-chromatography-mass spectrometry (GC-MS) and Thermogravimetric analysis (TGA), was applied to the solid deposits described in Sect. 3.1, confirming its carbonaceous nature.

More in detail, the black deposit on the surface of the measuring probes was mechanically removed and preliminary analyzed by Raman spectroscopy and SEM. This material, before solvent extraction, was in the following called "whole particulate". More information on the Raman technique are reported in [18].

The brown deposit, also present on the probes, was removed dipping the probe in dichloromethane (DCM) and sonicating it in an ultrasonic bath for half an hour. The "whole particulate” was added to the sonicated DCM solution and all was then filtered with a Teflon filter (with porosity of 500 nm). All the material was thus separated into two fractions: one soluble in DCM (named DCM-soluble particulate) and one insoluble (DCM-insoluble particulate).

The Raman spectrum of the whole particulate reported in Fig. 7, has revealed the characteristic spectral lines of amorphous carbonaceous materials. These are commonly referred to as D-band (peak of disorder) and G-band (peak of graphite). The latter, in fact, is clearly visible in the Raman spectrum of graphite, whose Raman spectrum is also reported in Fig. 7 for comparison. The presence of a peak of disorder in the carbon deposit in addition to the broad bandwidth is indicative of a carbon material with a high degree of disorder. Most importantly, it is well recognized that the relative intensity of the D and G peaks, $I(\mathrm{D})/I(\mathrm{G})$ can be related to the size of graphitic domains [19]. From the measured Raman spectra we obtained an average value of $I(\mathrm{D})/I(\mathrm{G})$ of approximatively 0.85 which corresponds to a value of L_a slightly lower than 1 nm. A background in the Raman spectrum of the carbon deposit was also measured. This feature, commonly attributed to photoluminescence/fluorescence phenomena, can be ascribed to the presence of an organic matrix (organic carbon).

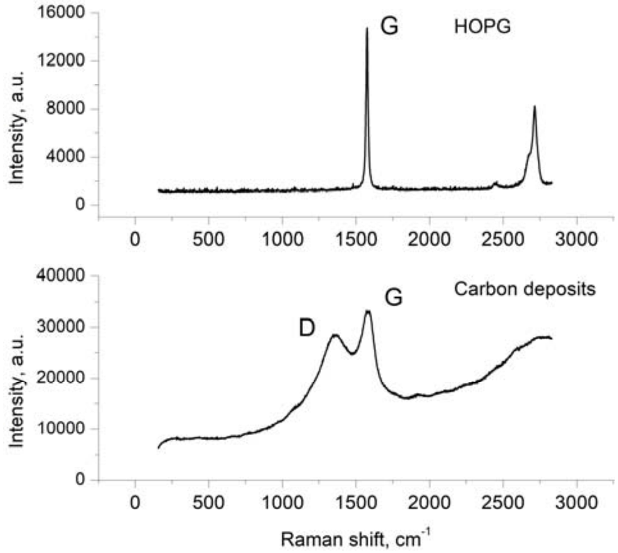


Fig. 7 Higher panel: Raman spectrum of highly oriented pyrolytic graphite (HOPG); Lower panel: Raman spectrum of whole particulate.

Interestingly, the Raman spectra of the carbon deposit resulted to be very similar to those characteristic of the carbonaceous particulate produced by hydrocarbon fuel combustion [19], therefore it is plausible to suppose that these deposits have a carbonaceous structure similar to soot.

SEM with EDX analysis applied on the whole particulate, before solvent extraction, confirmed the main presence of carbon, with traces of metals (probably polluted from arc electrodes).

The DCM-soluble particulate was analyzed by GC-MS and UV-visible spectroscopy (absorption and fluorescence). More details on the techniques are reported in [20]. The GC-MS revealed the presence of very low amount of small aromatic molecules with oxygenated and nitrogenous functionalities and the total absence of polycyclic aromatic hydrocarbons (PAH), typically formed in combustion and pyrolysis processes from hydrocarbon fuels [21]. The absorption and fluorescence spectra of DCM-soluble particulate, reported in Figs. 8 and 9, respectively, present features that can typically be ascribed to tholins, very complex substances consisting of reddish-brown polymeric material with aromatic moieties with oxygen and nitrogen heteroatoms [22], [23].

Vacher at alii [5] found carbonaceous samples deposited on the probes with amorphous character but without nitrogen, indicating the absence of tholins. Anyway, those authors analysed only the whole particulate, without solvent extraction, and without the implementation of techniques able directly detecting nitrogen functionalities. In the present work, the solvent extraction allowed isolating the tholin fraction from the amorphous carbonaceous core, enabling its detection.

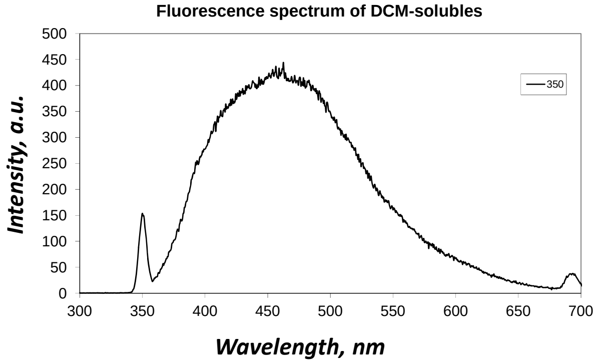


Fig. 8 Fluorescence emission spectrum (lexc=350nm) of the DCM-soluble particulate.

FT-IR spectroscopy, applied to the DCM-insoluble particulate, has provided evidence for the essentially carbonaceous nature of the substance though with high amorphous character, due to a large presence of aliphatic functionalities. The presence of oxygenated functionalities and the absence of nitrogenous functionalities is remarkable.

The TGA profile in air of the DCM-insoluble particulate presented two mass losses, indicating the heterogeneity of the sample. The main mass loss occurred at a temperature typical of carbonaceous particulate (soot) oxidation (around 600°C), whereas the second one occurred at a lower temperature (around 350°C).

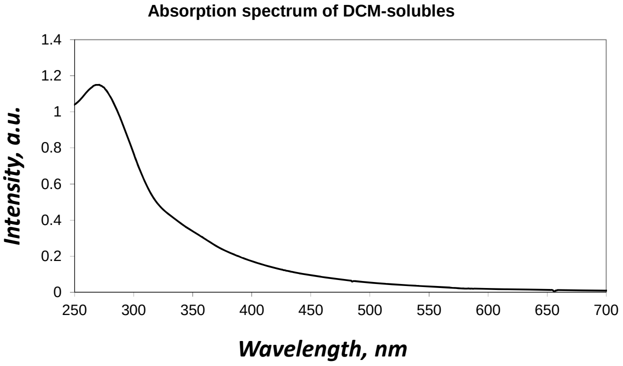


Fig. 9 Absorption spectrum of the DCM-soluble particulate.

6. CONCLUSIONS AND FUTURE DIRECTIONS

Understanding the formation of solid phases in the atmosphere of Titan is a topic of great importance from several points of view. Solid particles can be produced due to natural processes (giving rise to the so-called tholins, which so much attention have attracted over recent years owing to their remarkable implications in the field of astrobiology) or at very high temperatures when a probe or vehicle enters the atmosphere of this planet. In the latter case, the nucleation of solid particles or layers can have potentially dangerous effects, which need to be properly understood and mitigated by designing adequate protection systems.

In the present work, this problem has been tackled in the framework of a combined experimental-numerical approach implemented via a three-level analysis hierarchy. First experimental tests have been conducted using wind tunnel driven by an industrial arc-heated facility operating with Nitrogen as working gas. The formation of a solid substance has been detected and quantitatively measured. In a second stage of the study, insights into the related formation process have been obtained by using multi-species models relying on the NASA CEA code and the Direct Simulation Monte Carlo (DSMC) approach. Finally, the deposited substance has been analysed by means of a set of complementary diagnostic techniques (SEM, spectroscopy (Raman, FT-IR, UV-visible absorption and fluorescence), GC-MS and TGA). It has been shown that carbon produced by the interaction of the simulated Titan atmosphere with a solid probe at very high temperatures can be separated into two fractions by solvent extraction and filtration; it is remarkable the presence of tholins found in the fraction soluble in dicloromethane. Future studies shall be devoted to simulating the entire formation process of this substance by means of a multi-species chemical model fully integrated into a Computational Fluid-Dynamics (CFD) platform relying on the Navier-Stokes equations.

7. REFERENCES

[1] D. Dubois, N. Carrasco, M. Petrucciani, L. Vettier, S. Tigrin, P. Pernot, (2019), In situ investigation of neutrals involved in the formation of Titan tholins, *Icarus* 317, 182–196

[2] J. M. Bernard, P. Colla, A. Coustenisb, F. Raulina, (2003), Experimental simulation of Titan's atmosphere: Detection of ammonia and ethylene oxide, *Planetary and Space Science* 51 (2003) 1003 – 1011

[3] N. Carrasco, T. Gautier, E. Es-sebbar, P. Pernot, G. Cernogora (2012), Volatile products controlling Titan's tholins production, Icarus 219, 230–240

[4] A. Esposito and M. Lappa, (2019), Experimental and Theoretical Verification of the Frozen Sonic Flow Method for Mixtures of Polyatomic Gases, *AIAA Journal*, in the press.

[5] D. Vacher, S. Menecier, M. Dudeck, M. Dubois, B. Devouard, and E. Petit, (2013), Solid Carbon Produced in an Inductively Coupled Plasma Torch with a Titan Like Atmosphere, Article ID 546385, 8 pages,

[6] V. Carandente et alii, "Experimental and numerical simulation, by an arc-jet facility, of hypersonic flow in Titan's atmosphere" *Experimental Thermal and Fluid Science* 48, (2013) pp. 97 -101

[7] R. B. Pope, (1968), Measurements of enthalpy in low-density arc-heated flows, *AIAA J.*, 6(1), 103-110.

[8] G. Sanford and B.J. McBride, (1994), "Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications I. Analysis", NASA RP-1311, 1994

[9] R. Savajano, R. Sobbia, M. Gaffuri, P. Leyland, "Reduced Chemical Kinetic Model for Titan Entries", *International Journal of Chemical Engineering*, 2011(2), 1-8

[10] J. Wright, B. R. Hollis, D. Bose, L. Walpot, "Post-Flight Aerothermal Analysis of Huygens Problem", Proceedings of the 3rd International Workshop Planetary Probe, Anavyssos, Attiki, Greece, 27 June – 1 July 2005 (ESA SP-607), 2006

[11] E. Vallerani, "A review of supersonic sphere drag from the continuum to the free molecular flow regime", AGARD CPP 124, Paper 22, 1-15, 1973

[12] J.N. Moss, "Rarefied flows of planetary entry capsules", AGARD-R-808, 95-129, Special course on

"Capsule aerothermodynamics", Rhode-Saint-Genèse (Belgium), 1995

[13] G. A. Bird, *Molecular Gas Dynamics and Direct Simulation Monte Carlo* (Clarendon Press, Oxford, United Kingdom, 1998

[14] G. A. Bird, *The DSMC Method*, *Version 1.1* (Amazon, ISBS 9781492112907, Charleston, USA, 2013)

[15] C. Shen, *Rarefied Gas Dynamic: Fundamentals, Simulations and Micro Flows* (Springer-Verlag, Berlin, Germany, 2005

[16] G. A. Bird, "Visual DSMC Program for Two-Dimensional Flows, the DS2V Program User's Guide, Ver. 4.5", G.A.B. Consulting Pty Ltd, Sidney, Australia, 2008.

[17] R.V. Yelle, D. F. Strobell, E. Lellouch, D. Gautier, "Enginnering Models for Titan's Atmosphere", Proceedings of the ESA Conference on "Huygens: Science, Payload and Mission", ESA SP-1177, 1997

[18] M. Commodo, P.H. Joo, G. De Falco, A. D'Anna, O.L. Gülder, Raman Spectroscopy of Soot Sampled in High-Pressure Diffusion Flames, *Energy and Fuels* 31(9), pp. 10158-10164

[19] C. Ferrari, J. Robertson, "Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond" *Phil. Trans. R. Soc. Lond.* A (2004) 362, 2477–2512.

[20] V. Gargiulo, B. Apicella, C. Russo, F. Stanzione, A. Tregrossi, M. Millan, A. Ciajolo, (2016) "Structural Characterization of Large Polycyclic Aromatic Hydrocarbons. Part 2: Solvent-Separated Fractions of Coal Tar Pitch and Naphthalene-Derived Pitch" *Energy & Fuels*, 30(4): 2574-2583.

[21] M. Panariello; B. Apicella; M. Armenante; A. Bruno; A. Ciajolo; N. Spinelli (2008), "Analysis of polycyclic aromatic hydrocarbon sequences in a premixed laminar flame by on-line time-of-flight mass spectrometry", *Rapid Commun. Mass Spectrom.*, 22(4), 573-581.

[22] R. Hodyss et al., "Fluorescence spectra of Titan tholins: in-situ detection of astrobiologically interesting areas on Titan's surface" *Icarus* 171 (2004) 525–530

[23] N. Carrasco et al., "Chemical Characterization of Titan's Tholins: Solubility, Morphology and MolecularStructure Revisited" *J. Phys. Chem. A* **2009,** *113,* 11195–11203

LIST OF SYMBOLS

H = total enthalpy (MJ/kg)
P = electrical power (kW)
m = mass flow rate (kg/s)
p = pressure (Pa)
C = specific heat
ΔT = temperature difference
N_2 = Nitrogen
O_2 = Oxygen
CO_2 = Carbon Dioxide
CH_4 = Methane

Subscripts
ah = arc-heater
g = gas
mc = mixing chamber
ne = nozzle exit
t = total condition (beginning of expansion)
w = water
ts = test section