

Experimental analysis of direct thermal methane cracking

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The analysis of the viability of Hydrogen production without CO₂ emissions is one of the most challenging activities that have been initiated for a sustainable energy supply. As one of the tracks to fulfil such objective, direct methane cracking has been analysed experimentally to assess the scientific viability and reaction characterization in a broad temperature range, from 875 to 1700 °C. The effect of temperature, sweeping/carrier gas fraction proposed in some concepts, methane flow rate, residence time, and tube material and porosity has been analysed. The aggregation of carbon black particles to the reaction tube is the main technological show-stopper that has been identified.

1. Introduction

In last two centuries, global energy consumption has doubled every 30 years, in round numbers. Looking ahead, things seem to be very similar, mainly because of the activity of many emerging economics, particularly in Asia. Fossil fuels will continue to be the main energy source for half a century, maybe more [1]. Market and reserves limitations can affect this development, but one can remember that oil reserves have been equivalent for 30-year consumption, one year after the other. Anyway, in less than half a century the CO₂ atmospheric content can double, with a dramatic impact in the climate, and therefore in our economy and our lives.

Imaginative solution must be given to provide new ways of energy consumption with considerably reduced CO₂ emissions. This is where the so-called Hydrogen Economy appears as a potential, very nice solution; not only for refraining and reducing CO₂ emissions but for substituting fossil fuels in the very many combustion applications they are serving nowadays.

In the very long term, H₂ will have to be produced from water, using Nuclear Fusion and Renewables. However, early phases in deploying H₂ Economy will have to be based on the simplest and more direct methods for H₂ production. From this viewpoint, hydrocarbons present some favourable features, and they are already being used for that purpose (Water electrolysis is less than 5% of the total H₂ production,

and it is only justified by very low prices of electricity and the need of very pure H₂).

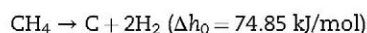
From the point of view of Greenhouse enhancement, Steam-Methane-Reforming (SMR) to produce H₂ has the main drawback of CO₂ production. In the theoretical process, 1 mol of H₂ requires 0.25 mol of CH₄ as SMR feed. The energy required to be consumed in that endothermic reaction can be obtained by burning 0.05 mol of CH₄. In other words, from 1 mol of available CH₄, 0.83 would be steam-reformed into 3.3 mol of H₂ and 0.83 mol of CO₂; and 0.17 mol of CH₄ would be burned, so producing 0.17 mol of CO₂, which means 0.3 mol of CO₂ per mol of H₂.

There is the possibility of heating the SMR unit from nuclear heat [2] or solar heat [3], and no CH₄ would have to be burned in the facility. In this case, 0.25 mol of CO₂ would be produced per mol of H₂.

CO₂ capture (separation) is already available in SMR units. Therefore, the main problem would be CO₂ confinement (the so-called sequestration). Several confinement methods have been proposed, but experimental confirmation and actual confinement reliability are far from being established. CO₂ sequestration in underground repositories would have to be placed in very low populated areas, which would be an additional economic burden to that potential solution. This point has to be taken into account in the assessment of SMR as a process to accelerate the deployment of the Hydrogen Economy in the context of Sustainable Development.

A sound alternative might be based on CH₄ decarburation [4,5] (or hydrocarbon decarburation in general, although methane reserves are the largest ones).

The decarburation reaction is



It is much less endothermic than SMR, but it also produces less energy in H₂ form (484 kJ) but it presents the fundamental advantage of not producing CO₂. Carbon atoms are easily stored, and could be used for producing special materials, as carbon fibres. Besides that, they contain a lot of energy (390 kJ/mol) that could be exploited in the future, if more CO₂ could or should be added to the atmosphere, or reliable sequestration techniques are developed.

There are several advantages in hydrocarbon decarburation as a fundamental process for paving the road to the Hydrogen Economy [4–8]. It did not receive too much attention in the first road-maps outlined to guide this development, but it deserves it, because of energy, environmental and safety reasons. If this technology is developed as can be foreseen, there will also be economic advantages, particularly if CO₂ emissions are taxed as needed to avoid climatic changes beyond acceptable values for our current life.

It is worth pointing out that methane decarburation (MDC) is more energy effective than SMR. In this one, the theoretical efficiency in H₂ production is 83%. In MDC, the efficiency goes to 84.5%, without taking into account the potential energy contained in C. The savings in CO₂ emissions and the commercial value for non-energy uses of the produced black carbon would foster their economical viability. Its main drawback is that it still is an emerging technology.

According to the decarburation reaction equilibrium, working temperatures higher than 1500 K are needed to obtain a complete decomposition, unless it is stimulated by other mechanisms, as the action of a catalyst [9–12] or the extraction of H₂ (and the extraction of C, in order to avoid recombination).

The decomposition reaction is the usual way to produce Carbon Black, a substance with a relatively small but expensive market [13]. There are some methods to carry it out [14–20]. As already said, some of them use a catalyst, which reduces the working temperature below 1000 K, but it conveys other problems, particularly catalyst deactivation (because of carbon deposition, mainly). This obliges to regenerate the catalyst, which is energy consuming (and produces CO₂ emissions in some processes). Nevertheless, the main drawback of the available methods is that they are not devised for large-scale production, and the Hydrogen Economy will need very large-scale amounts.

For laboratory research and small industrial productions, electric heating seems advisable, because it can be controlled very easily and can be applied to produce any type of temperature profile, if needed. Additionally, some methods use electric-arc discharges to produce the decomposition [20,21]. However they do not fit well with the Hydrogen Economy postulates. It is worth noting that Hydrogen and Electricity will be the main energy carriers in a context of Sustainable Development, with very specific applications on each side.

Industrial heating for future commercial MDC processes could come from solar energy, nuclear reactors or combustion. In the solar field, very high sunlight concentration factors (about 3000) are needed to reach temperatures over 1500 K [3,22–26]. There are already some designs and experimental set-ups that could be useful for long-term generation of H₂ [27]. However, if the objective is to pave the road for advancing the Hydrogen industry, we cannot wait until the maturity of ultra-high temperature solar furnaces. It is without question that they must be considered for the full development of a sustainable Hydrogen Economy, mainly based on water as H₂ source, but first stages of H₂ development should not rely on additional R&D programs of very emerging ideas.

Moreover, in MDC there is the possibility to use a fraction of the produced H₂ to keep the process going on. Hence, after the start-up for heating the chemical reactor up to the required temperature, Hydrogen would be used as fuel, so minimizing to negligible amounts the CO₂ produced. The toll paid for that would be the consumption of 15.5% of the Hydrogen produced, which would be a drawback for the process, but not a dramatic one. Depending on the price of CO₂ emissions, and the actual concern about the Greenhouse enhancement, the process could run in a CO₂-free basis or with a small amount of CO₂ emissions. In summary, MDC seems a key element to pave the road towards the H₂ World along a fast and clean track.

2. Experimental set-up

The outlined rationale led to the initiation of a research project at CIEMAT with the support of UPM and Vacuum

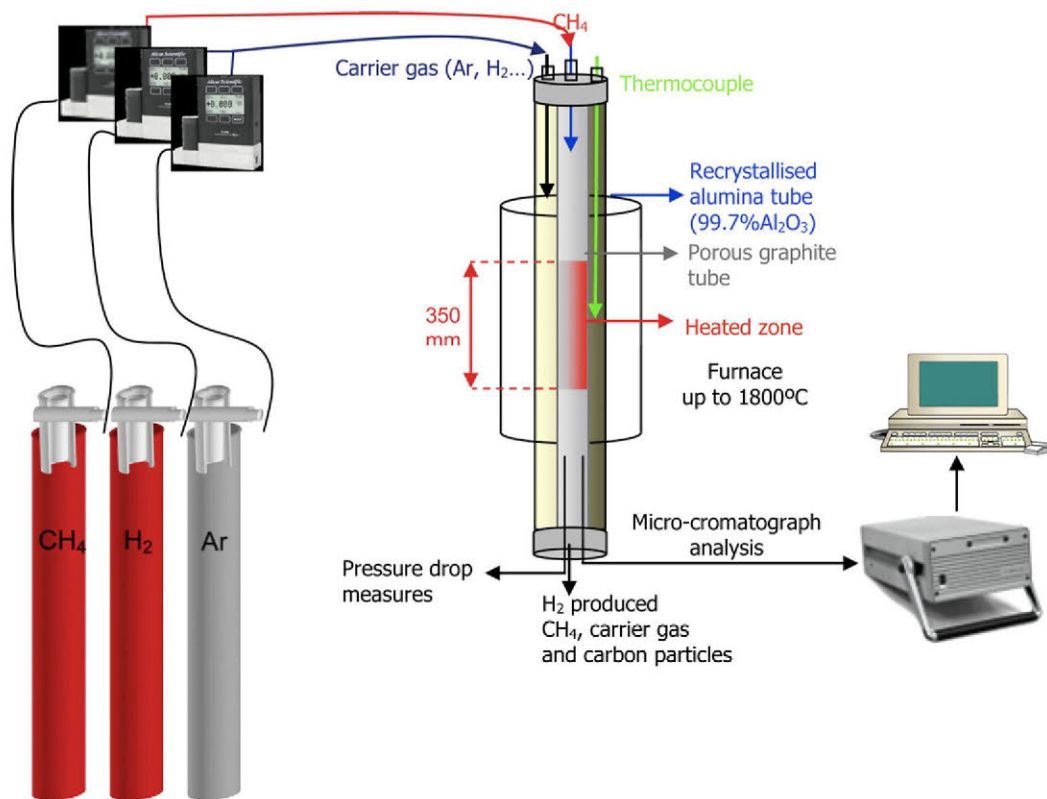


Fig. 1 – Scheme of the experimental set-up for methane cracking research.

Projects and under the supervision of Prof. Carlo Rubbia, 1984 Physics Nobel Laureate and Prof. Juan Antonio Rubio, CIEMAT Director General. The main objective of the project is to demonstrate the scientific and technical viability of methane decarbonisation by thermal cracking to produce free- CO_2 Hydrogen.

During the development of the project, two types of furnaces were used to obtain worthy data about the methane decomposition reaction that take place when a technology without catalysts based on direct methane heating is applied, as suggested by many authors [6,24,27,28]. The first furnace was able to heat a gas mixture up to $1100\text{ }^\circ\text{C}$. It was our first step towards the determination of the methane conversion to Hydrogen versus temperature, dilution gases as Argon and Hydrogen that are proposed as sweeping gases to avoid Carbon blockage, and residence time.

A second furnace able to reach $1700\text{ }^\circ\text{C}$ was commissioned in a second stage to assess the technical viability of a practical 100% methane decomposition at high temperature with a negligible dependence of the residence time. Fig. 1 shows an overview of the experimental apparatus, including the test section with the sweeping gas system integrated in a double tube structure with an alumina external tube and porous graphite as internal tube. The sweeping gas (Argon, Helium or Hydrogen) was transferred to the methane stream through the porosity of the internal test tube. Such gas flow was intended to prevent the carbon plug formation. The composition at the outlet of the furnace is obtained by micro-chromatography.

3. Experimental results

Our first experimental results are shown in Fig. 2, in which the amount of Hydrogen at the tube outlet in volume ratio percentage is depicted for three flow rates, which implies three residence times of 16, 32 and 96 s in normal conditions ($25\text{ }^\circ\text{C}$, 1 bar) and at a temperature range between 875 and $1065\text{ }^\circ\text{C}$, according to the equation:

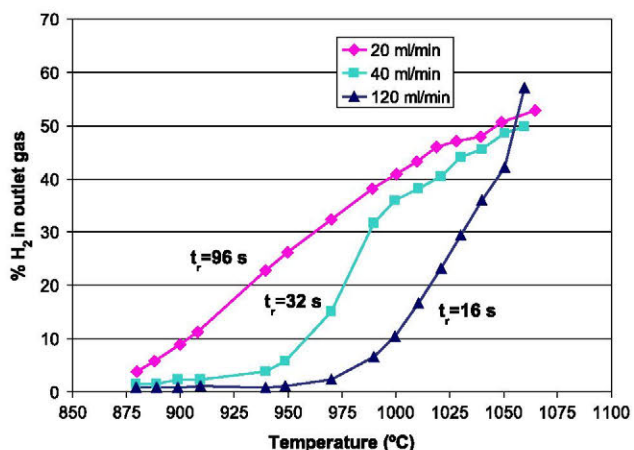


Fig. 2 – Hydrogen volumetric ratio at the outlet gas as a function of the temperature and the flow rate.

Table 1 – Operating conditions of experimental carried out in the experimental system.

Tests No.	Temperature (°C)	Porosity	CH ₄ flow rate (l/min)	Carrier gas (l/min)	Residence time (s)	Methane conversion (%)	
Gr-1	1350	Whole tube	1	He	20	0.49	74.6
Gr-2			2			0.46	47.6
Gr-3			4			0.42	40.2
Gr-4	1450	Whole tube	1	He	20	0.49	99.8
Gr-5			2			0.46	98.0
Gr-6			4			0.42	99.3
Gr-7	1450	Whole tube	4	He	80	0.12	99.8
Gr-8			8			0.11	
Gr-9	1500	Whole tube	8	He	80	0.11	89.0
Gr-10			8	He	40	0.21	92.0
Gr-11	1500 (holes)	Holes	8	He	40	0.21	94.4
Gr-12	1500	50 cm porous zone	4	He	20	1.2	93.0
Gr-13	1500	50 cm porous zone	4	He	40	0.65	99.3
Gr-14	1500	20 cm porous zone	4	He	20	1.2	94.6
Gr-15	1500	Not porous	4	–	–	7.2	99.0
Gr-16	1700	Whole tube	0.1	Ar	0.5	41.7	95.5
Gr-17			0.2			35.8	96.7
Gr-18			0.3			31.3	97.4
Gr-19			0.4			27.8	97.7
Gr-20			0.5			25	98.0
Gr-21	1700	Whole tube	0.1	H ₂	0.5	41.7	95.2
Gr-22			0.2			35.8	97.4
Gr-23			0.3			31.3	99.2
Gr-24			0.4			27.8	99.3
Gr-25			0.5			25	99.7

$$t_r = \frac{l \cdot A}{q}$$

where l is the length of the tube, A is cross section and q the volumetric flow rate. The results show how the Hydrogen production rises with temperature, reaching a conversion to Hydrogen of about a 30%, after taking into account the production of 2 mols of Hydrogen per mol of methane. The residence time becomes negligible at higher temperatures as the reaction kinetics is faster.

After the scientific feasibility has been proven, our experimental work has been focused in the evaluation of different operation conditions depending on:

- Maximum operation temperature.
- Sweeping/carrier gas fraction.
- Methane flow rate.
- Residence time.
- Type of sweeping/carrier gas.
- Tube porosity.
- Tube material.



Fig. 3 – Carbon plug specimen obtained at Gr-4 experiment.



Fig. 4 – Carbon depositions on the external surface of the graphite tube.



Fig. 5 – Horizontal furnace for SiC experiments.

The operating temperature will be the most important parameter concerning the methane conversion rate and the hydrogen generation rate. High temperatures produce high Methane to Hydrogen conversion rates.

The fraction of additional sweeping gas could be expected to have an influence in the conversion rate through the reaction products-reactants chemical balance and its dilution effect. Nevertheless, at high temperatures with the decarburation reaction far to the right, the reaction balance will be affected slightly, although it is not expected a very important effect in the methane conversion.

The main set of experiments has been done using a graphite tube with different degrees of porosity in order to assess the effectiveness of the sweeping gas to avoid carbon deposition in the tube. Most of the experiments have been done in a porous tube, except Gr-11, that was a tube with a few- μm holes, Gr-12 and Gr-13 with a tube in which the porous zone was limited to 50 cm around the hottest part, where the reaction was expected to take place, Gr-14 with a 20 cm porous zone, and Gr-15 with no porosity.

Table 1 shows the summary of the experimental work carried at different temperatures. Above 1450 °C, a conversion close to 100% is obtained, with a complete reaction for residence times above 0.20 s. At 1350 °C there is a small

dependence on the residence time and type of gas, as well as its dilution. In fact, the highest the conversion of methane into Hydrogen, the lowest the residence time effect, as the reaction kinetics become very fast.

As it can be seen in Table 1, various porous tubes were used to examine whether carbon plug could be avoided or not, and the results showed that they could not effectively prevent the carbon plug formation. In every of these experiments there was a carbon plug phenomena that limited the experiment time last. The plug, shown in Fig. 3, appears after a certain time that can vary from 30 min to 4 h depending on the operating temperature and, basically, the amount of Hydrogen formation and methane flow. A higher Hydrogen conversion, implies a higher black carbon production, and consequently, a faster carbon plug growth. Small quantities of Carbon particles are removed by the gas flow at the outlet of the tube.

Consequently, the main show-stopper in this process is the carbon plug formation that finally blocks the gas flowing through the tube reactor and makes very difficult its technological design. The challenge to avoid the formation of the carbon plug was the reason to try different materials and the analysis of the carbon formation, including its aggregation structure and hardness.

The carbon formation in the reacting tube affects its external surface as well, as can be shown in Fig. 4, which implies that carbon particles are able to diffuse through the tube wall, likely due to a low remaining porosity, compatible with the particle size of the order of nm. On the other hand, after the plug formation, heated methane is able to cross through the porosity of the wall and carbon forming the carbon black layer, in spite of the sweeping gas.

The results with graphite tubes show that carbon deposition becomes an operational problem as carbon trends to aggregate to the tube inner surface at the reaction temperature.

The testing of new materials suggested the use of Silicon Carbide (SiC) as candidate material. Four tests were made to assess if the carbon plug could be avoided with such material.

The tests were done in a horizontal furnace shown in Fig. 5, except the experiment at 1200 °C that was done in the high temperature vertical furnace of previous experiments, that was unable to increase temperature due to a malfunction of one of the three electric coils used for heating, which forced the utilisation of the vertical furnace. The effect of the flow direction was negligible.

Table 2 – Summary table of the SiC tube experiments.

Experiment #	1	2	3	4
T (°C)	1200	1300	1400	1400
Tube	SiC	SiC	SiC	SiC + Boron Nitrate layer
CH ₄ flow (l/min)	1	1.1	1	1
Ar flow (l/min)	1	0.9	1	–
Time (h)	3	3	3	3
Dissociation rate	10% methane in exit. Hydrocarbons presence. Unknown H ₂ production.	3% methane in exit. H ₂ presence 60–70%. Very Low hydrocarbons presence.	0% methane in exit (complete dissociation) H ₂ presence 93–94%	0% methane in exit (complete dissociation) H ₂ presence 93–94%
Carbon deposit	Soft carbon black	Soft dust carbon black Carbon black Hard carbon black	Soft dust carbon black Carbon black Hard carbon black	Soft dust carbon black Carbon black Hard carbon black



Fig. 6 – Soft carbon plug at 1200 °C.

The experimental campaign made analysis of the carbon plug formation and reaction efficiency in an operational temperature range from 1200 to 1400 °C, with Argon as sweeping gas. The main results for the SiC tubes are shown in Table 2. The results are comparable with previous tests in graphite tubes regarding temperature influence in the methane to hydrogen conversion ratios, which proves the negligible effect due to the tube material change.

At 1200 °C there is formation of soft carbon deposition along the tube and at the outlet (Fig. 6) that can be easily removed. A very hard carbon deposition appears in the hottest part of the tube wall when temperature is above 1300 °C. Air oxidation can regenerate the SiC tube but produce CO₂.

A test at 1400 °C, with an external layer of Carbon Nitrate to eliminate the porosity of the tube, was also done. The performance of the experiment was similar to the previous one, which implies a negligible effect of the porosity with SiC tubes.

4. Analysis of the carbon deposition

The main show-stopper for a technological application of this process is the formation of a carbon deposit in the tube wall. Such deposit starts with a carbon particle generation, whose formation has its better thermal conditions at the tube wall, that get adhered to tube, acting as a seed for a growing hard carbon structure.

In this section, a review of the available information about the carbon particles produced at different temperatures is shown.

An analysis of the characteristics of the carbon deposition has been done in function of the process temperature by the characterization of the black carbon deposition at every test performed with different tubes. In a first approximation, it is expected that the characteristics of the carbon formed do not depend on the tube material, but mainly on the temperature and the reaction kinetics that could affect the final size of the carbon particles. The first set of data has been obtained by the experiments that were done with a quartz tube, from 1000 to 1100 °C. A second set of data resume the information available up to 1700 °C, obtained with graphite and SiC tubes.

The size of the carbon particles could be related to the aggregation structure and its hardness, as well as it could be an important factor in relation with the pore size in the tube. In fact, the observed formation of carbon deposits in the outer surface of the tube is produced by the migration through the pores of particles, or methane molecules. Such problems should be solved by non-porous tubes.

Fig. 7a) shows the amorphous black carbon powder in the plug at 1000 °C. Fig. 7b) shows the electron microscopy analysis of the carbon deposit in the surface of the quartz tube, formed by a silver grey, brittle film adhered to the quartz surface. It can be seen as the carbon aggregation has a smooth structure, with a characteristic length of the carbon black in a range from 1 to 5 μm.

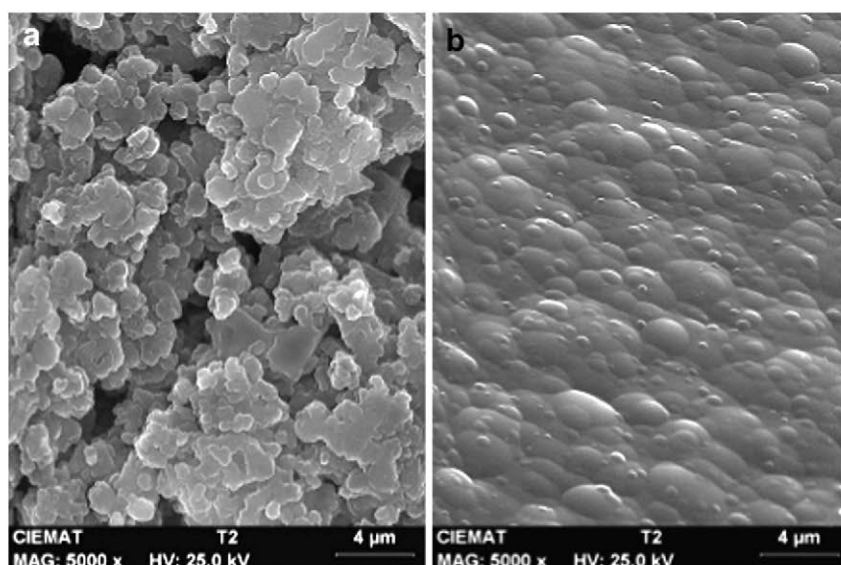


Fig. 7 – Carbon formed at 1000 °C and 60 ml/min. a) In the plug, b) in the tube.

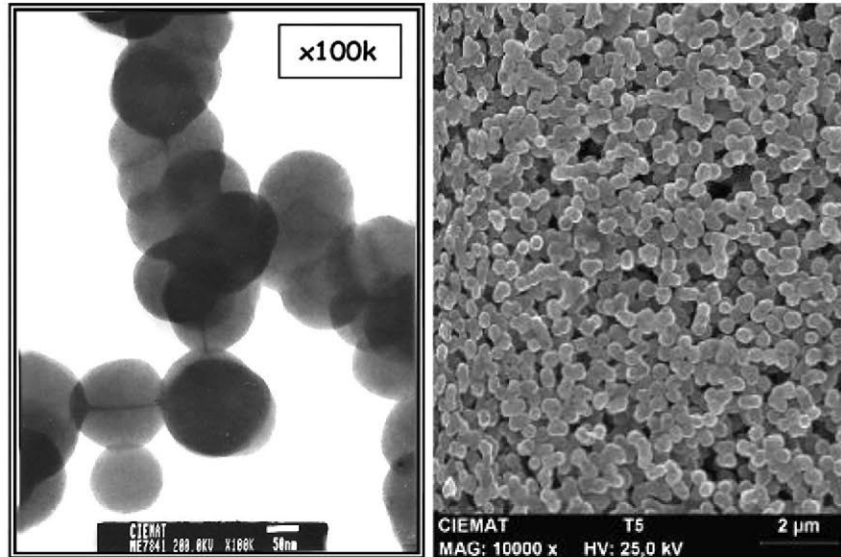


Fig. 8 – Carbon formed at 1100 °C without sweeping gas.

Fig. 8 shows the carbon formation in the centre of the tube at this temperature without sweeping gas. The tendency shows that the size of the aggregation particles is on average from 150 to 300 nm, with an amorphous morphology and a low crystallization level, as it was obtained from X-ray diffraction analysis.

In Fig. 9, we can see the black carbon particles at 1100 °C using Argon as sweeping gas with different gas/methane feeding ratios. The average size of the particles formed was between 10 and 0.5 µm. Using Argon, the average particle size was between 1 and 0.4 µm, the higher the dilution ratio, the higher the particle size. This fact can be explained as the increase in the dilution ratio reduces slightly the reaction kinetics and a lower amount of initiating carbon seed is produced. Below 1100 °C, the Hydrogen generation and the carbon formation are very low, with high residence times.

The carbon particles in the central part of the experimental tube at 1450 °C were analysed and the particle size was between 100 and 300 nm. The conversion rate was almost 100%, using Helium as carrier gas. When the Hydrogen formation is efficient appear carbon particles below 500 nm size that form a hard plug in the tube wall.

Electron spectroscopy of the carbon formed at 1500 °C shows a smooth graphitic structure, as it is shown in Fig. 10. Several tests have been done at this temperature with Helium as carrier gas, and different tube configuration regarding the porous section of the tube. The results show how that sweeping gas system is not effective to eliminate the carbon formation shown in Fig. 4, with a clear diffusion of methane or carbon particles through the pores of the tube, producing the harmful deposit in the outer surface, and producing the tube blocking as well.

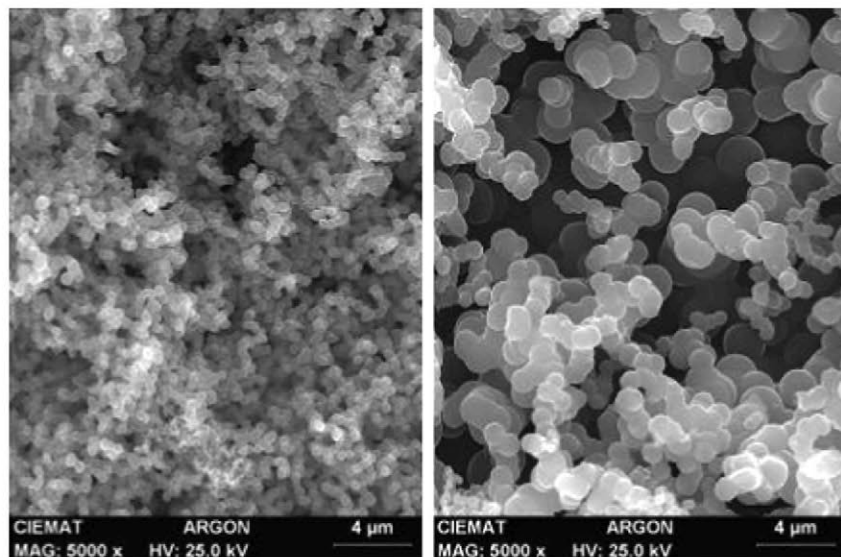


Fig. 9 – Carbon formed at 1100 °C with Argon sweeping gas with gas/CH₄ ratio from 1 to 5.

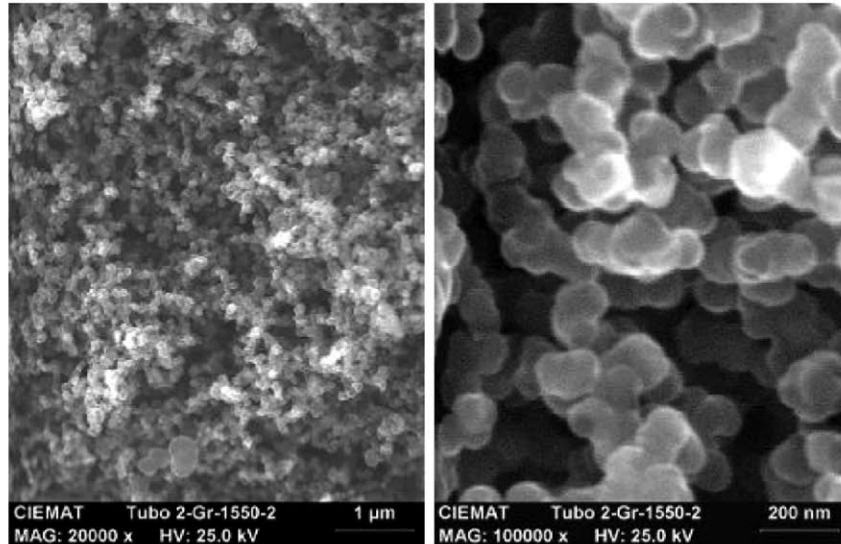


Fig. 10 – Electron microscopy of the carbon produced at 1500 °C with different augmentation.

Fig. 11 shows the cross section of the graphite tube with the carbon plug after 35 min test with a porous tube. Fig. 12 shows the carbon deposition at the outer surface of the tube after the 3 h test that was achieved with a theoretically non-porous tube, which suggests there is practical black carbon diffusion at high temperature through the tube.

At this temperature, it was proven that the sweeping gas system in a tubular reactor seems inefficient for a long-term operation, at least under reasonable pressures and at temperatures with high conversion ratio.

Fig. 13 shows the electroscopy analysis of the carbon formation that was obtained at 1700 °C, with particle sizes of the order of micrometres, which is two orders of magnitude respect to the previous experiments. Such carbon formations are very hard and a mechanical extraction is very risky for the structural integrity of the tube, at least at cold conditions. On the other hand, most of the carbon produced in the

methane conversion reaction is fixed to the tube according to our estimation.

The conclusion from the carbon analysis is that at the optimal temperatures for the chemical processes ($>1400\text{ }^{\circ}\text{C}$) there is a formation of carbon particles of the order of some 100 nm, that form a hard carbon structure deposition in the tube wall that finally leads to the tube blockage. A summary of the particles size is shown in Table 3.

The use of ceramic tubes, with a certain porosity, produces the diffusion of methane, through the pores, producing a formation of the deposit at the outer surface of the tube, when the carbon plug begins its formation. It is likely that such formation increases pressure losses in the tube and some methane flows through the porous tube.

There is no evidence of a relation between the size of the particles and the carbon aggregation hardness, which depends mainly on the temperature.

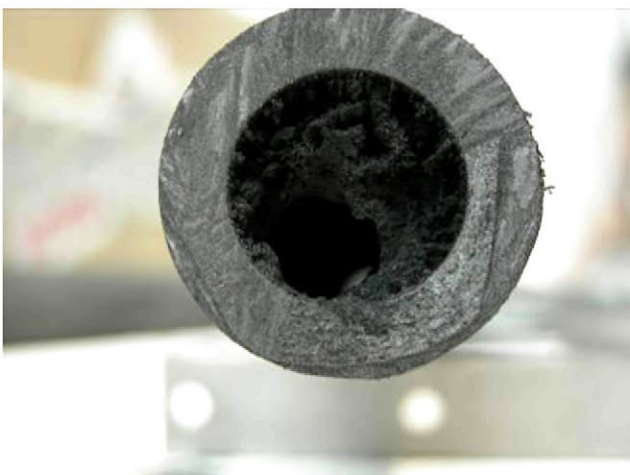


Fig. 11 – Cross section of the graphite tube after 35 min of test.



Fig. 12 – Graphite tube after 3 h tests for the experiment Gr-15, with a non-porous tube.

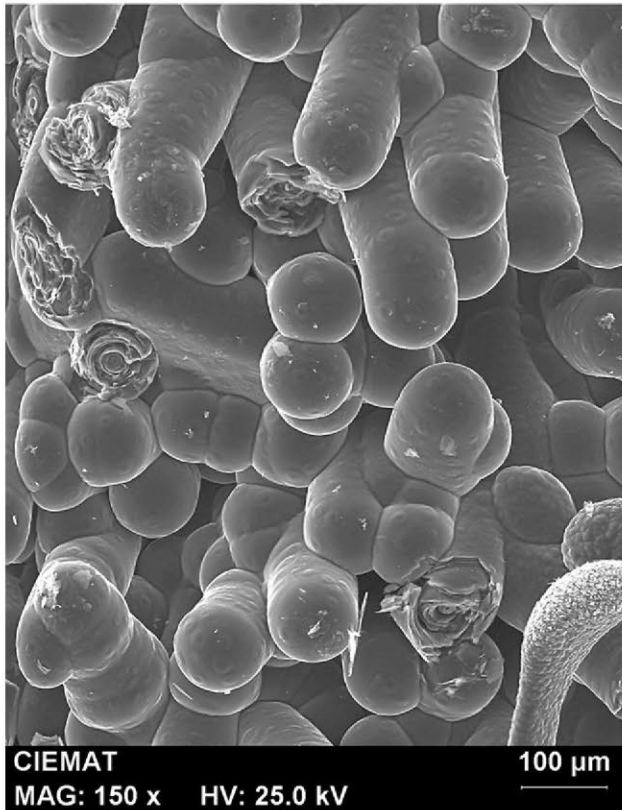


Fig. 13 – Carbon particles formed during the tests at 1700 °C.

Table 3 – Summary of carbon particle size versus temperature.

Temperature (°C)	Carbon black size at tube
1000	1–5 μm
1065	500 nm
1450	100–300 nm
1500	90–500 nm
1700	50 μm

5. Conclusion

Experimental results on methane thermolysis inside a tube reactor seem to confirm that there are two reacting regimes depending on the reactor temperature. Such reaction regimes are slightly influenced by residence time, and by the dilution effect of the sweeping gas. In general, those effects are almost negligible.

1. At a furnace temperature lower than 1200 °C, methane decomposition is not complete, and many hydrocarbons and other reaction intermediate products appear in the outgoing stream, with a sizeable fraction of H₂ and a visible cloud of carbon powder. In the case of our SiC tube test, carbon deposition is produced but easily removable by its weak agglomeration. Nevertheless, previous tests with

Quartz tubes show how during long operation tests, carbon deposition in the reactor wall could produce blockage. The low efficiency on the methane to hydrogen conversion implies that the amount of carbon produced is finally lower and the growing deposit has worst conditions for their development.

2. At temperatures higher than 1350 °C, the decomposition is practically complete, and the main component of the outgoing gas is H₂, with almost no traces of hydrocarbon gases. A cloud of carbon powder still goes out, but a huge fraction of the produced carbon appears as solid deposits firmly stick to the wall. Elimination of the deposit by simple mechanical pushing is very difficult, at least in cold conditions. That carbon deposit can be eliminated by combustion, just by blowing air into the hot oven, so producing CO₂, which is undesirable.

It is not simple to characterize the composition of the outgoing gas in the first regime, but it seems there are mixtures of hydrocarbons and free radicals produced as intermediate steps in the reaction, and in equilibrium at the temperatures reached in the experiments. Carbon particles seem to accompany those molecules, without sticking to the wall material.

On the contrary, in the second regime the thermolysis is complete, and very hot carbon aggregates stick to the wall in a similar way to a crystal growing process. The deposit grows continuously if the test lasts for long, so producing a total blocking of the inner tube, and stopping the flow of gas. At this operating regime, as carbon deposition blocks the tube, methane is forced to cross the porous wall and produces also carbon deposition in the outer surface.

The tube material has had a negligible effect in our experiments. Quartz, graphite and SiC tubes present similar results respect to residence time, Hydrogen generation and carbon plug formation.

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