

**REPORT ON THE STUDIES OF CHEMICAL
INERTNESS, REPRODUCIBILITY AND
CARBON DEPOSITION FOR COATED AND
NON-COATED AISI 347 TUBES**

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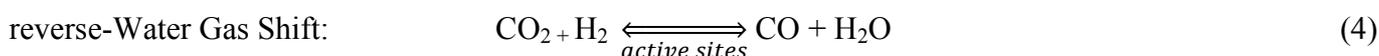
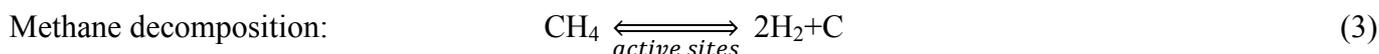
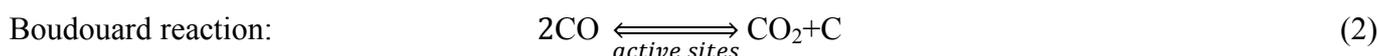
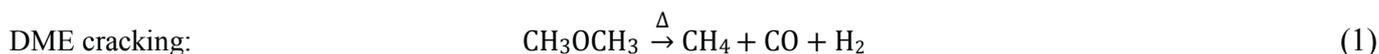
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1. SCOPE OF THE WORK

The deposition of carbon on the tubes' surface has been analysed by means of the thermal decomposition (cracking) of dimethyl ether (DME), according to Eq. (1), and the subsequent reactions of the resulting carbonaceous gaseous products to form carbon deposits, which include Boudouard reaction (Eq. 2) and methane degradation (Eq. 3). Moreover, reverse-Water Gas Shift reaction (r-WGS, Eq. 4) occurs between CO₂ and H₂, thus forming water and CO. The three latter reactions take place on active sites present on the tube surface



When carbon deposition is negligible the relative amounts of CH₄, CO and H₂ are nearly 1. Otherwise, production of H₂ increases, those of CO and CH₄ decrease, and the presence of CO₂ and water is also observed. This mainly depends on the properties of the tube surface. The formed carbon can be swept by the produced gases or deposited on the tube, which also depends on the surface properties of the material.

The DME degradation tests performed pursued two objectives: Firstly, to analyse the chemical inertness of the internal surface of the tubes (non coated and coated tubes of stainless steel 347) for the DME cracking by means of a controlled heating from 300 to 700 °C; Secondly, to quantify the carbon deposited (soot) on the internal surface of the tubes by means of degradation runs of long duration at 700 °C. This temperature was selected for the long duration runs because it is high enough to assure complete DME cracking for both (non coated and coated) tubes, thus allowing to stablish the specific differences in the deposition and accumulation of carbonaceous material on the internal surface of each tube.

Moreover, the reversibility of carbon deposition on the tube samples has been studied by means of two successive (DME degradation)-(carbon combustion) cycles, in which the combustion with air subsequent to DME degradation is used to remove completely all the carbon deposited in the previous step of DME degradation.

2. REACTION EQUIPMENT AND EXPERIMENTAL PROCEDURE

The DME degradation experiments have been carried out in automated reaction equipment (Figure 1) (*Microactivity Reference from PID Eng & Tech*) provided with a tube sample located in a heated chamber and connected on-line to a gas chromatograph (*Agilent MicroGC 490*) for analysis of degradation products. The apparatus was provided with TOHO TTM-005 controllers for the temperature and pressure and with *Bronkhorst High-Tech* mass flow controllers able to feed reactive and inert gases: (i) dimethyl ether (DME, Air Liquide, 99.99%) as reactive gas; (ii) N₂ (Air Liquide, 99.99%) as inert gas, and; (iii) purified air (Carbueros Metálicos, 99.99%) as comburent. The reactor temperature is measured by a thermocouple (K type) located in the reaction tube. There are two other temperature controllers: one for the furnace chamber and the other for the transfer line between the reactor and the gas chromatograph.

The tube sample (in AISI 347 Austenitic Steel Substrate, with 2.20 cm of internal diameter, 2.54 cm of external diameter, 45.5 cm of total length and 26 cm of effective heated length) is located within a

ceramic chamber heated by an electrical resistance that allows the controlled heating up to 800 °C. The product stream leaving the tube passes through two filters in series, the first one for retaining particles bigger than 20 μm and the second one of high efficiency for particles of more than 2 μm . A small fraction of the tube outlet stream is continuously diluted and sent by the auxiliary gas to the gas chromatograph through a thermostated line (at 200 °C) to avoid the condensation of heavy compounds.

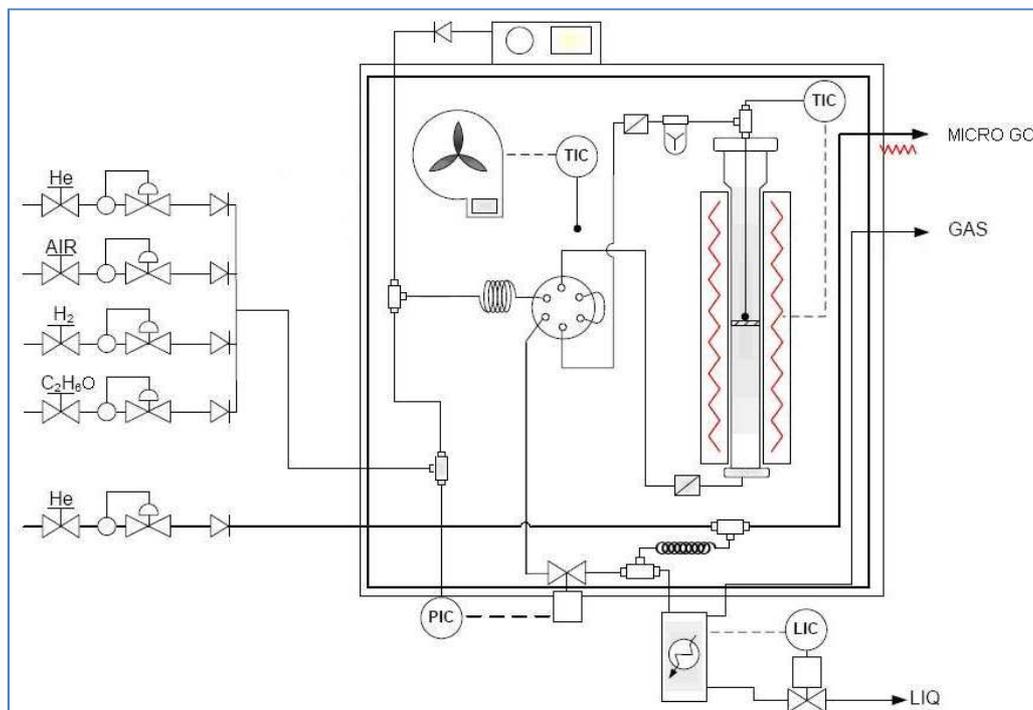


Figure 1: Scheme of the reaction equipment.

The MicroGC is equipped with 4 analytic channels: A) molecular sieve MS5 (for analysis of H_2 , N_2 , O_2 , CH_4 and CO); B) CPSIL (for C_5 - C_{11} hydrocarbons, which were not detected in this study); C) Plot Q (for CO_2 , H_2O , methanol, DME, and C_2 - C_4 hydrocarbons); and D) Stabilwax (for heavier oxygenated compounds, which were not detected in this study). The compounds were quantified and identified using calibration standards of known concentration. The conditions used in each chromatographic channel are gathered in Table 1. The total duration of each analysis is 150 s. Figures 2 and 3 depicts some examples of the chromatograms obtained during the experiments of DME degradation and during the combustion of the deposited carbon, respectively.

Table 1. Conditions used in the four analytic channels of the MicroGC 490.

Canal analítico	A (MS-5)	B (CPSIL)	C (PPQ)	D (Stabilwax)
Column temperature, °C	80	100	95	105
Injector temperature, °C	90	110	110	110
Injection time, ms	20	20	20	50
Pressure, psi	20	20	20	15

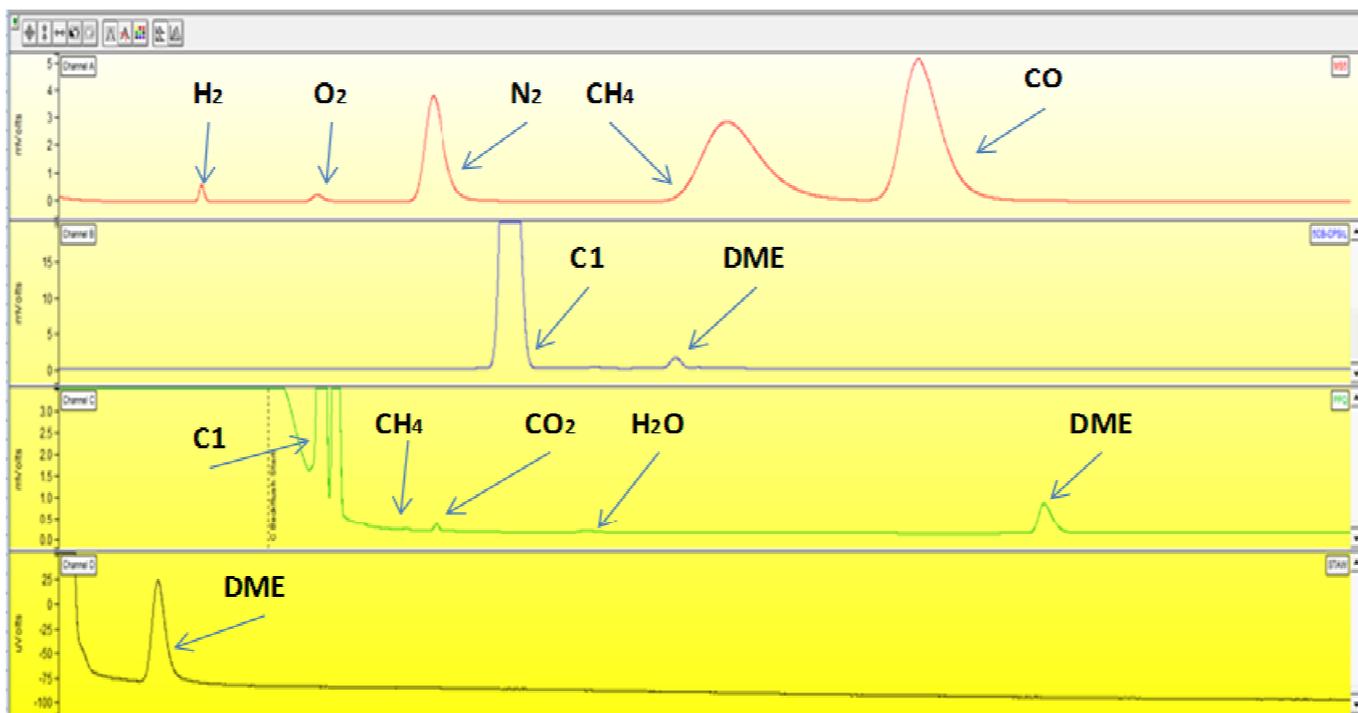


Figure 2. Example of the chromatograms obtained in the DME degradation on the tubes.

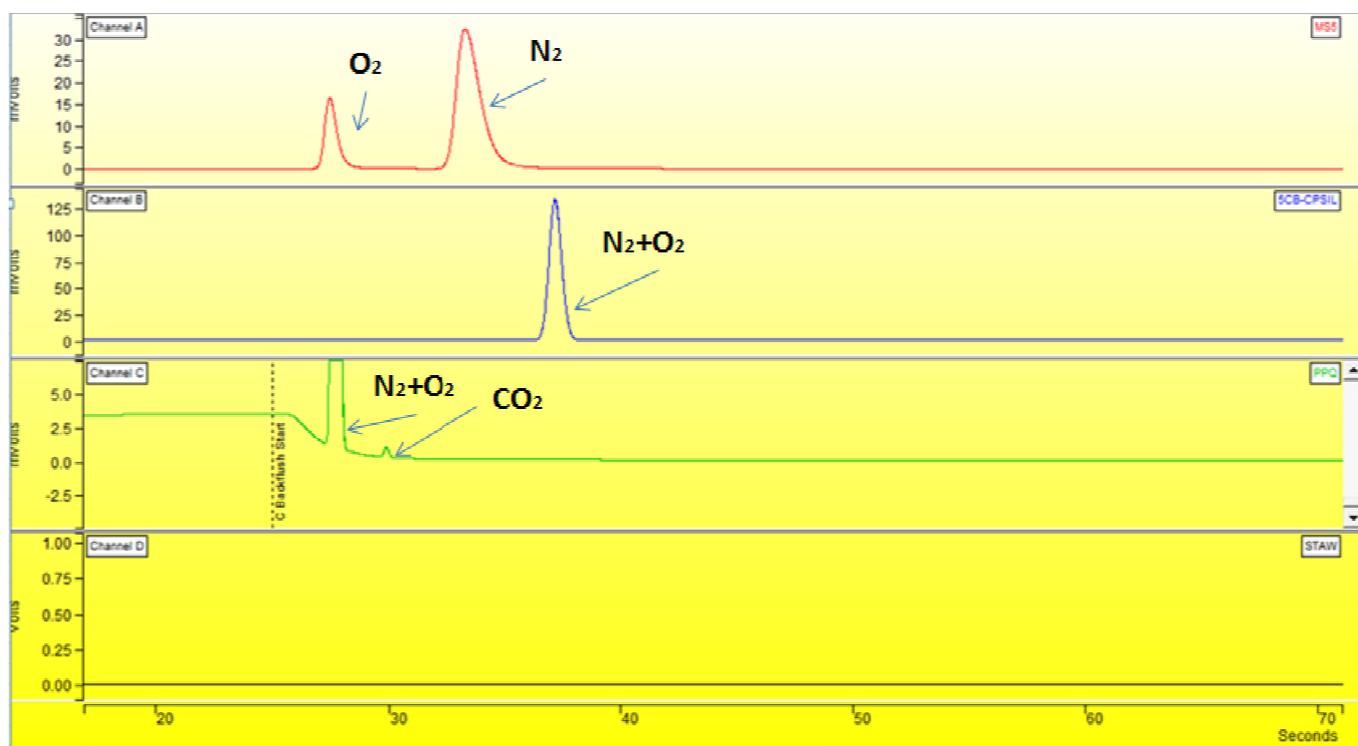


Figure 3. Example of the chromatograms obtained in the combustion of the carbon deposited in the tubes.

The experimental procedure used for the degradation-combustion cycles is as follows:

- a) *Preheating*: The tube sample was preheated with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ up to $300\text{ }^{\circ}\text{C}$ (1 bar of pressure) under a continuous flow of N_2 ($50\text{ cm}^3\text{ STD min}^{-1}$).
- b) *Carbon deposition (DME degradation)*: $40\text{ cm}^3\text{ STD min}^{-1}$ of DME was fed into the system, together with $15\text{ cm}^3\text{ STD min}^{-1}$ of N_2 as internal pattern, and the temperature was raised with a heating rate of $5\text{ }^{\circ}\text{C/min}$ up to $700\text{ }^{\circ}\text{C}$, temperature at which complete DME degradation takes place. Subsequently, this temperature was maintained constant for 20 h, thus forming a carbon deposit in the tube surface. Outlet gases were monitored by the microGC during this stage. The evolution with temperature of DME conversion by thermal cracking in the first period (between $300\text{-}700\text{ }^{\circ}\text{C}$) allows delimiting the chemical inertness of the tube surface for the decomposition of DME into H_2 , CO and CH_4 , and the products distribution at the tube outlet along the whole stage is related to the deposition of carbon on the tube surface.
- c) *Cooling*: DME flow was stopped and the sample was cooled down to $300\text{ }^{\circ}\text{C}$ under a continuous flow of N_2 of $50\text{ cm}^3\text{ STD min}^{-1}$, and this temperature was kept constant until the absence of DME was observed in the chromatograms.
- d) *Combustion*. A flow of $400\text{ cm}^3\text{ STD min}^{-1}$ of air was fed into the system for the combustion of the deposited carbon. The temperature was raised up to $700\text{ }^{\circ}\text{C}$ at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$, while the signals of CO and CO_2 were monitored by the microGC. This stage finished when these signals were not observed in the chromatogram, which assured the complete combustion of the carbon deposits. The integration of the CO and CO_2 allowed quantifying the amount of carbon deposited on the internal tube surface.
- e) *Cooling*: The tube sample was cooled under N_2 flow down to $300\text{ }^{\circ}\text{C}$.
- f) Subsequent to this first DME cracking-combustion cycle, steps b-d were repeated in order to prove the reproducibility of the internal surface of the tube for the study concerning chemical inertness and soot formation with DME molecule.
- g) *Shut down*. The sample was cooled down to room temperature under a continuous flow of N_2 of $50\text{ cm}^3\text{ STD min}^{-1}$, when the equipment was shut down and the tube sample was removed from the system.

3. RESULTS

3.1. Chemical inertness of the surfaces of both tubes

The results of DME degradation for both tubes (non-coated and coated) during the heating stage between $300\text{-}700\text{ }^{\circ}\text{C}$ are summarized in Figure 4 and Table 2. Figure 4 depicts the evolution with temperature of DME conversion in the first cycle (as delivered) and second cycle (after DME cracking and subsequent combustion) for the non-coated tube (graph a) and the coated tube (graph b). Table 2 gathers the values of temperature for attaining DME conversion of 10, 50 and 90% in the first and second degradation cycles for both tubes. The comparison of the results in the first cycle (as delivered) for both tubes (blue lines in graphs a and b) shows a similar behaviour. Nevertheless, significant differences are observed in the results corresponding to the second cycles. As observed in Figure 4a and Table 2, the surface of the non-coated tube is significantly affected by the treatment consisting in DME cracking followed by air combustion to remove the carbon deposited (steps b-d of the experimental procedure). Thus, the temperature needed for initiation of DME cracking in the second cycle is significantly lower than in the

first cycle. On the contrary, the values of DME conversion for the coated tube (Figure 4b and columns in the right of Table 2) are almost identical in the successive cycles, which gives evidence that the process of carbon deposition-removal does not affect the chemical inertness of the internal surface of this tube.

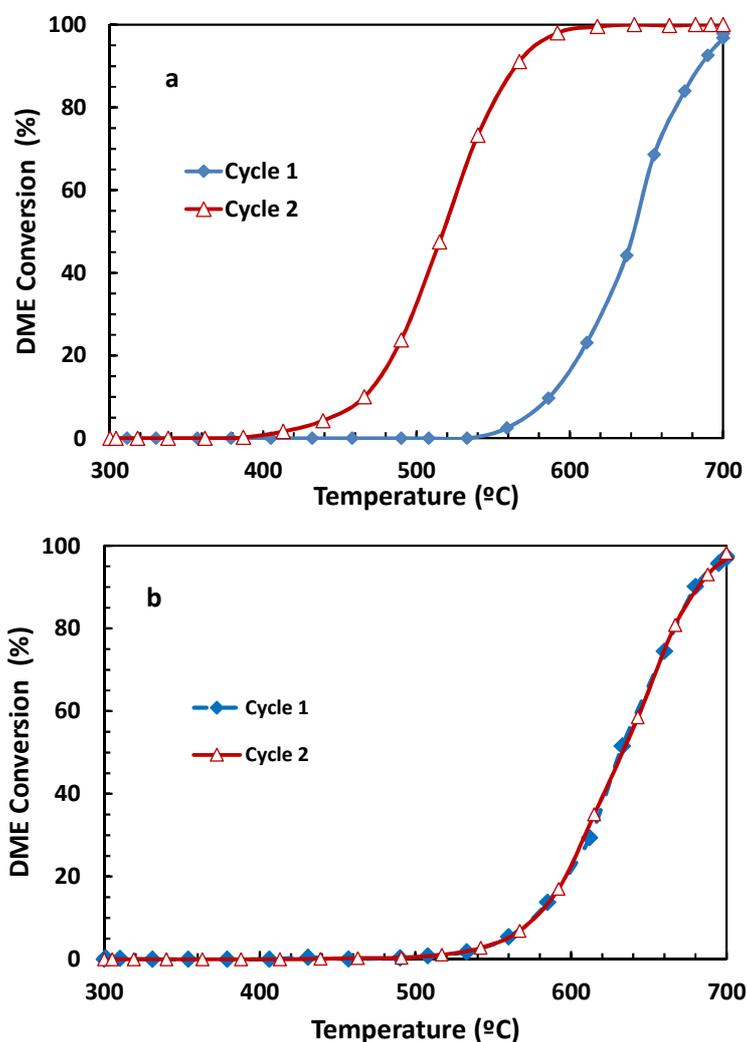


Figure 4. Evolution with temperature of DME conversion in the first cycle (as delivered) and second cycle (after DME cracking+combution) for the non-coated (a) and coated (b) AISI 347 tubes.

Table 2: Results of chemical inertness for DME thermal degradation of the non-coated and coated A347 tubes.

Internal contact Surface (cm ²) 163.28				
Volume of the tubo (cm ³) 100				
	NON-COATED		COATED	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2
T10 (°C)	587	465	574	571
T50 (°C)	641	518	631	632
T90 (°C)	685	565	680	682

3.2. DME degradation in the long duration runs

Evolution of the gaseous products at the outlet stream

The evolution of the yield of gaseous products at the outlet of the tube along the whole step of DME degradation is shown in Figure 5 (non-coated tube) and Figure 6 (coated tube). These values have been calculated as the flowrate of each gas at the tube outlet, referred to the flowrate of DME in the feed. For both tubes, the results corresponding to the first and second cycle are shown. The first period in these graphs (below 100 min) is that previously shown in section 3.1

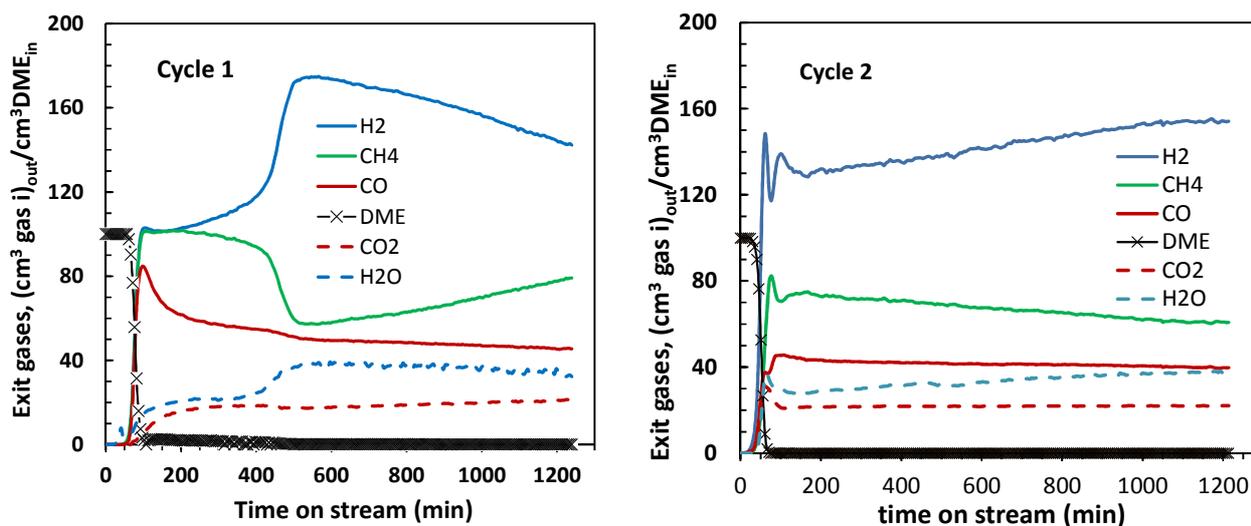


Figure 5. Evolution of the yield of products formed in the first and second cycle of DME degradation in the non-coated AISI 347 tube.

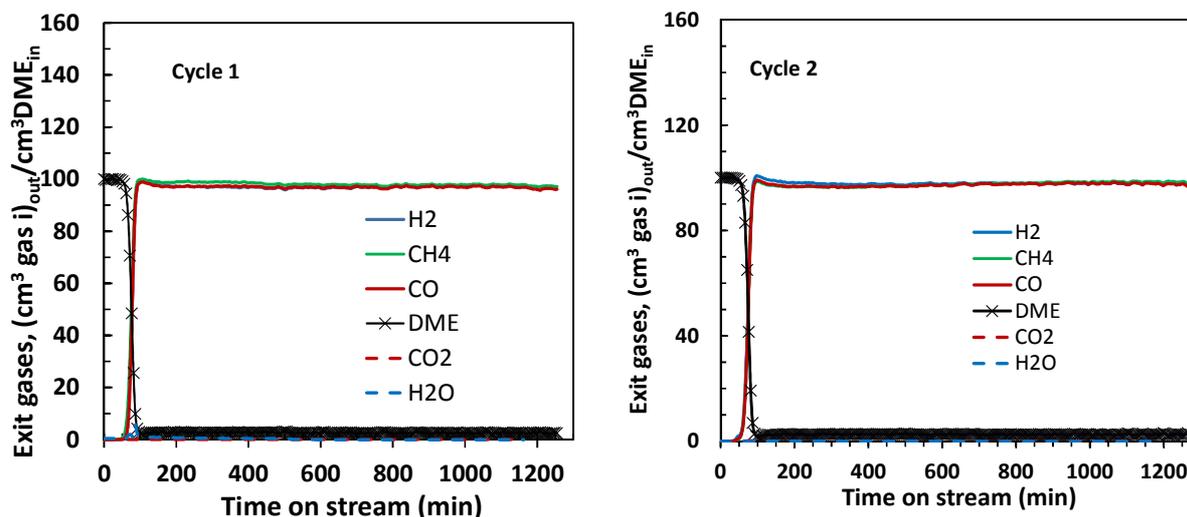


Figure 6. Evolution of the yield of products formed in the first and second cycle of DME degradation in the coated AISI 347 tube.

In the first cycle for the non-coated tube (left graph of Figure 5), above 100 min a clear difference is observed in the yield of three products resulting from DME decomposition, the yield of H₂ being significantly higher than those of CO and CH₄, and the presence of by-products CO₂ and H₂O is clearly observed. This result gives evidence of a significant formation of solid carbon. The results of the second cycle for this tube evidence even more clear difference in the yield of gaseous products since the

beginning of the long duration period at 700 °C, as a consequence of the lower chemical inertness for DME degradation and carbon formation, as commented in section 3.1

Conversely, almost equal yields of the three gaseous products are obtained along the whole DME degradation step for the coated tube, with insignificant formation of CO₂ and H₂O, which evidences a very low formation of solid carbon. Moreover, the results for the second cycle are almost identical to those of the first cycle, in agreement with the results shown in section 3.1 for this tube, which corroborates that the behaviour of the coated surface is not altered by the process of carbon degradation-removal.

Evolution of carbon deposition

The amount of solid carbon formed along the DME degradation step has been quantified from the difference between the amount of carbon in the DME fed to the tube and the amount of carbon in the gaseous stream at the tube outlet (Eq. 5). This solid carbon corresponds to both that deposited in the internal surface of the tube and that swept by the gaseous stream and subsequently retained in the filters of the equipment

$$C_{\text{formed}} = \left(t \cdot 2 \cdot Q_{\text{DME}}^{\text{in}} - 2 \int_0^t Q_{\text{DME}}^{\text{out}} dt - \int_0^t Q_{\text{CO}}^{\text{out}} dt - \int_0^t Q_{\text{CH}_4}^{\text{out}} dt - \int_0^t Q_{\text{CO}_2}^{\text{out}} dt \right) \cdot \frac{12 \cdot P}{R T_{\text{room}}} \quad (5)$$

Figure 7 shows the evolution with time of the accumulated amount of solid carbon formed during the first (blue lines) and second (red lines) DME degradation steps for the non-coated tube (graph a) and the coated tube (graph b). The results evidence a significant higher formation of solid carbon for the non-coated tube than for the coated tube, in coherence with the results in Figures 5 and 6. For the non-coated tube, carbon formation is slower at the beginning of the period at 700 °C in the first cycle of DME degradation and it is almost lineal above 400 min, whereas completely linear carbon formation is observed along the whole period of long duration at 700 °C in the second DME degradation step for this tube (Figure 7a). The amount of carbon solid formed also increases in the second cycle for the coated tube, but it remains more than twenty times lower than for the non-coated tube.

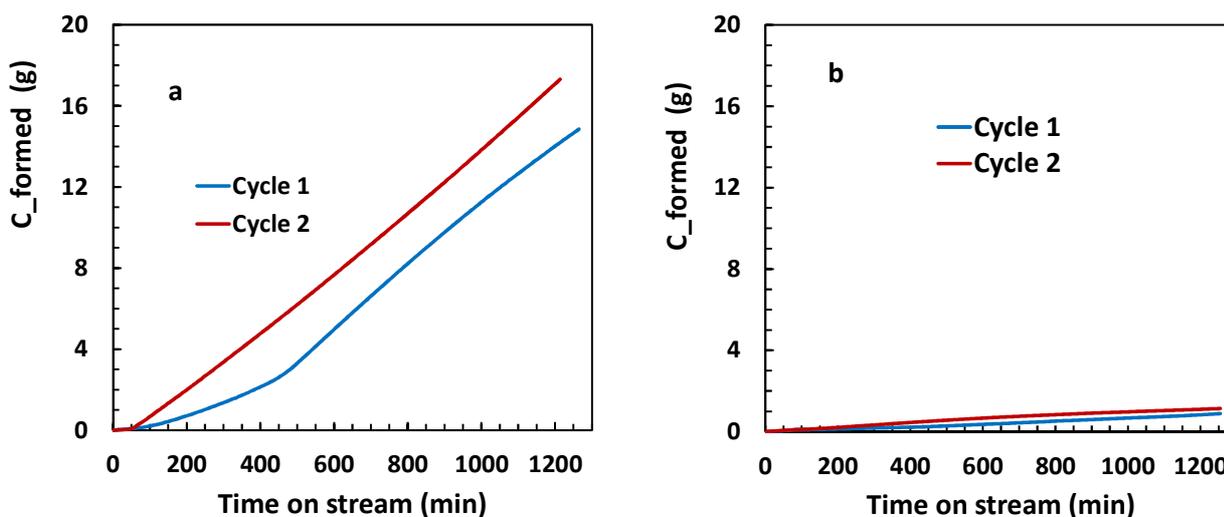


Figure 7. Evolution of the amount of solid carbon formed in first and second DME degradation steps for the non-coated (a) and coated (b) AISI 347 tubes.

3.3. Combustion of the carbon deposited in the tubes

Figure 8 depicts the evolution with time of the gaseous stream (CO and CO₂) analysed along the combustion step in the first and second cycles of DME degradation-combustion runs for the non-coated tube, and the results corresponding to the coated tube are shown in Figure 9. In this case, the differences between the results for the non-coated and the coated tube are even more noticeable than when comparing the amount of carbon solid formed in both cases. Thus, the amount of solid carbon formed for the coated tube (Figure 7b) is around one order of magnitude lower than for the non-coated tube (Figure 7b). Nevertheless, the magnitude of CO_x concentration during the combustion for the coated tube (graphs in Figure 9) is near two orders of magnitude lower than for the non-coated tube (graphs in Figure 8) and, moreover, the whole combustion takes place in less than 1h, whereas it takes around 6 h for the non coated tube.

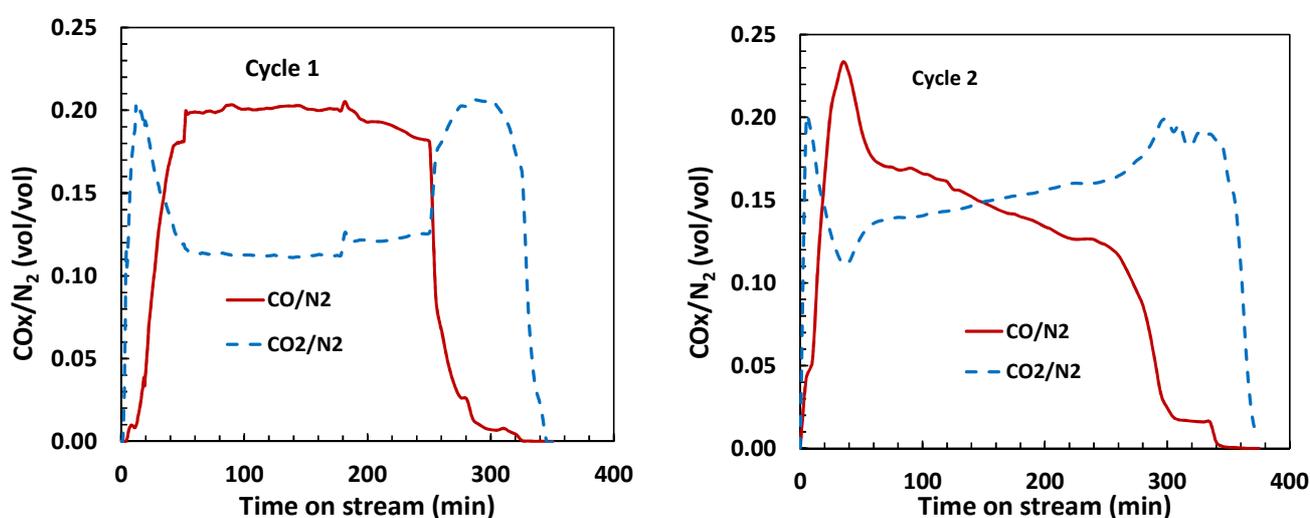


Figure 8. Evolution of the gaseous products obtained in the combustion of the carbon deposited on the non coated AISI 347 tube during the first and second DME degradation steps.

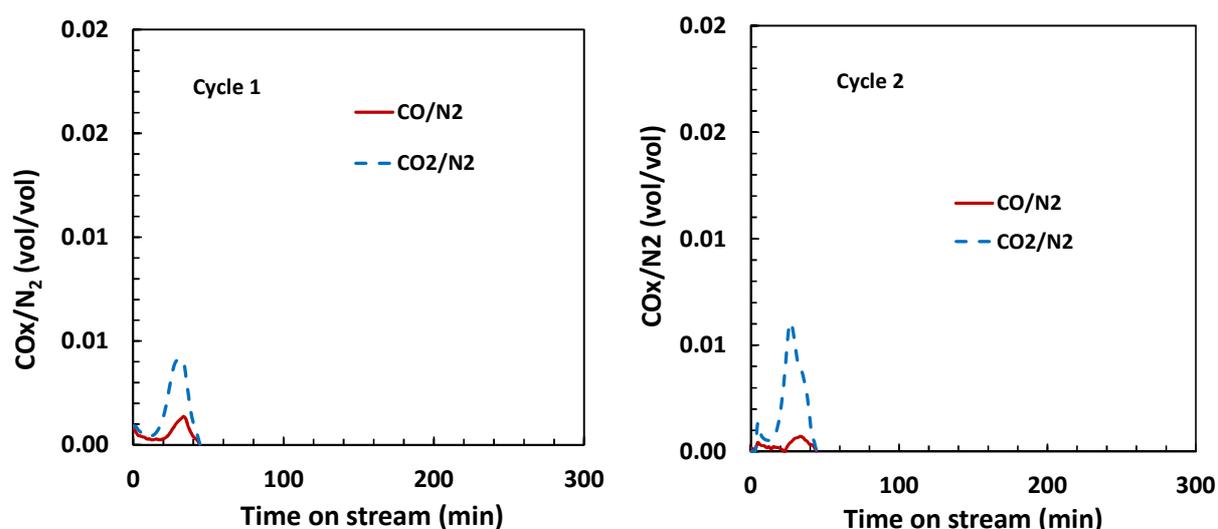


Figure 9. Evolution of the gaseous products obtained in the combustion of the carbon deposited on the coated AISI 347 tube during the first and second DME degradation steps.

The amount of carbon removed at a given time can be evaluated as follows:

$$(C_removed)_t = \left(\int_0^t Q_{CO}^{out} dt + \int_0^t Q_{CO_2}^{out} dt \right) * \frac{12 * P}{RT_{room}} \quad (6)$$

And the total amount of carbon solid deposited on the tube is calculated by integrating the curves for the total combustion time.

3.4. Overall results in the carbon deposition – combustion tests

Table 3 summarizes the results obtained for the non-coated and coated stainless steel A347 tubes in the first and second cycles of carbon deposition-removal tests. The data in Table 3 include:

- i) The total mass of DME fed in each run
- ii) The mass of DME degraded (that fed minus the accumulated amount of DME at the tube outlet)
- iii) The average percentage of DME degraded
- iv) The grams of C contained in the gaseous stream at the tube outlet (calculated from CO+CH₄+CO₂ formed)
- v) The grams of C solid formed (soot), obtained by means of Eq. (5) (final values plotted in Figure 7)
- vi) The total grams of C degraded (sum of iv and v)
- vii) The percentage of C solid formed referred to that total grams of C degraded
- viii) The grams of C deposited in the interior surface of the tube, obtained from the values of CO and CO₂ formed along the combustion step.
- ix) The percentage of C solid deposited referred to the total grams of C solid formed
- x) The percentage of C solid deposited referred to the total grams of C degraded

Table 3. Summary of the carbon deposition-combustion tests for non-coated and coated AISI 347 tubes.

		Non-coated tube		Coated tube	
		Cycle 1	Cycle 2	Cycle 1	Cycle 2
DME degradation	g DME Fed	97.5	94.7	96.9	97.5
	g DME degraded	91.2	90.9	88.9	89.6
	% DME degraded	93.6	96.0	91.7	92.0
	g C degraded	47.6	46.8	48.1	48.8
	g C gas (CO+CH₄+CO₂)	32.8	29.5	47.2	47.3
	g C solid formed	14.8	17.3	0.89	1.54
	%(gC solid formed/gC degraded)	31.2	37.0	1.85	3.16
Combustion	g C deposited	14.6	15.7	0.016	0.017
	%(gC deposited/gC formed)	98.2	90.8	1.79	1.13
	%(gC deposited/gC degraded)	30.6	33.6	0.033	0.036

This table reflects the comments in previous sections. Thus, almost equal results are obtained in the first and second cycles for the coated tube, which evidences the null effect of the DME degradation-C removal test for this sample, whereas differences are clearly observed for the non-coated tube, which has higher percentage of DME degradation in the second cycle, resulting in a higher formation of C solid (17.3 g compared to 14.8 in the first cycle).

Nevertheless, the more significant result in Table 3 is the noticeable better behaviour of the coated tube concerning the formation of solid carbon and, more importantly, the deposition of solid carbon on the surface of the tube. Thus, the percentage of carbon solid formed referred to the C degraded is around 2 % for the coated tube, compared to more than 30% for the non-coated tube. More interestingly, the percentage of C deposited referred to the C solid formed is below 2 % for the coated tube, compared to 90-98% for the non-coated tube, and the percentage of C deposited referred to the total C degraded (around 0.03%) is almost two order magnitude lower than for the non coated tube.

4. CONCLUSIONS

The ceramic coated tube has shown a significant better performance in the carbon deposition-removal tests (consisting on DME degradation-air combustion cycles), as evidenced by the following facts:

- The chemical inertness of the coated tube surface avoids the parallel reactions occurring in the active sites present on the non-coated tube
- The carbon deposition-removal cycles can be repeated without observing deterioration on the coated surface in contact with the gases
- The carbon formed on the coated tube is one order magnitude lower than on non-coated tube due to the absence of parallel reactions forming soot (Boudouard reaction and CH_4 decomposition)
- The amount of carbon deposited on the coated tube is two order magnitude lower than on the non-coated tube, and its percentage referred to carbon degraded is three order magnitude lower than on the non-coated tube

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