PREVENTION OF CARBON DEPOSITION ON THE SURFACE OF STAINLESS STEEL TUBES THROUGH CERAMIC COATING

T. Cordero-Lanzac[1], A. Arandia[1], A.G. Gayubo[1], A.T. Aguayo[1], M. Presa[2] and S. Lodha[2]

[1] Department of Chemical Engineering, University of the Basque Country (UPV/EHU), PO Box 64, 48080, Bilbao, Spain

[2] TUBACOAT S.L., Bizkaia Science and Technology Park, Ibaizabal Bidea, 702 Building, 1st floor, 48160 Derio, Spain
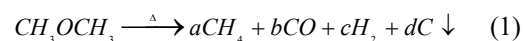
ABSTRACT

Regarding the economic and operational issues derived from the carbon deposition on the surface of stainless steel tubes in the chemical industry, the coating of the internal surface with a ceramic layer is useful for preventing the formation of deposits and extending the lifetime of the tubes. The thermal degradation of dimethyl ether (DME) at 700 ºC has been used as reaction test to compare the carbon deposition on standard and coated tubes. The results evidence an outstanding decrease in the amount of deposited carbon on the coated tubes, as well as the possibility of operating at longer times since the carbon deposits are only formed at the very beginning of the tests. The reversibility of the formation and combustion of the carbon deposits is proved for the coated tube, so that reproducible results have been attained in different cycles, which is not possible with a conventional uncoated stainless steel tube.

INTRODUCTION

The formation of carbon deposits and fouling of tubes are one of the most common operational issues regarding the operability and lifetime of materials at industrial scale [1]. Several billion dollars are spent worldwide on annual basis to upgrade/change materials apart from revenue loss on account of production halt and additional costs incurred in maintenances. Particularly, the carbon deposition from gas precursors is an undesirable and inevitable factor that takes place in most of the process of the chemical industry: ethylene production, steam reforming, hydrogenation reactions, among others [2]. From an economic point of view, stainless steel is the most frequently used material, but sometimes more expensive metals are required.

The deposition of carbon on the tube surface can be reproduced by simple chemical reactions of thermal degradation. For example, dimethyl ether (DME) is a stable chemical that thermally depredates at temperatures above 500 ºC according to the following reaction [3]:

$$CH_3OCH_3 \xrightarrow{\Delta} aCH_4 + bCO + cH_2 + dC \downarrow \quad (1)$$

The relative amounts of produced methane, carbon monoxide and hydrogen (a, b and c in Eq. (1), respectively) are nearly 1 when the carbon deposition is negligible. Otherwise, the formation of H_2 increases upon increasing the carbon formation (d). This mainly depends on the temperature. However, the formed carbon can be swept by the produced gases or deposited on the tube, which depends on the surface properties of the material.

In current situation where every dollar spent in Operation & Maintenance of plants is being monitored closely, there is a need for suppliers to come out with innovative solutions which not only help fighting fouling, erosion and corrosion but also helps in overall reduction of cost, reliable plant operations with improved energy efficiency [4].

In this work, an innovative ceramic coating layer from Tubacoat is proposed, which reduces the deposition of this carbon (fouling) and allows operating at severe conditions with a better thermal transfer, thus avoiding the need of more expensive materials and significant costs on maintenance operations.

EXPERIMENTAL

Two different tube samples were tested during the thermal degradation of DME in order to compare their performances. On the one hand, a standard stainless steel tube (named A316) and on the other hand, a coated A316 tube with the ceramic layer well-deposited on its internal surface (named A316-V907).

Ceramic silica-based coatings are specially focused to provide protection to a high number of metal substrates, resulting from a controlled fusing process of certain raw materials based on oxides like SiO2, Al2O3, Na2O, K2O, CeO2, MgO, ZnO, CaO, ZrO2, etc., designed to form a protective layer chemical bonded to the substrate.

The conventional coating process involves the preparation of the formulation by blending raw materials in a suitable formulation to meet the requirements of the coated piece, followed by a pretreatment of the workpiece to be coated (usually sandblasting as a simple step), in order to remove impurities from the metal surface followed the deposition of ceramic formulation (completely free of VOCs) on the piece. The most commonly application technologies are Spray coating, Dipping, Flow coating, Electrophoretic deposition and Powder electrostatic deposition. In this work dipping coating technology has been used as an environmental friendly industrial technique to obtain a very smooth surface finishing. Finally, a thermal treatment between 700-1000 °C is needed in order to consolidate the ceramic silica-based coatings on the metal substrate. After the sintering process, the consolidated coating develops a series of key properties for its performance as effective protection in aggressive environments. Thus, with an approximate layer of 150 μm, it forms a stable barrier of high hardness, resistant to temperature and thermal shock and inert to most chemical agents for industrial use. In addition, thanks to a surface finish with low roughness that does not require any surface refining process, it prevents the adhesion of ashes or byproducts of the process.

Experiments of carbon deposition were carried out in automated PID (Process Integral Development Eng & Tech) equipment provided with an oven that allows the controlled heating up to 800 ºC of tube samples of 2.54 cm of external diameter, 45.5 cm of total length and 26 cm of effective heated length. The apparatus was provided with TOHO TTM-005 controllers for the temperature and pressure and with mass flow controllers able to feed reactive and inert gases: (i) dimethyl ether (DME, Air Liquide, 99.99%) as reactive gas; (ii) N_2 (Air Liquide, 99.99%) as inert gas, and; (iii) purified air (Carburos Metálicos, 99.99%) as comburent. The equipment was couple in line with a gas chromatograph (microGC, Varian 4900) for analyzing the composition of the gas stream at the outlet of the system. The analyzed gases were: H_2, N_2, CO, CO_2, CH_4, H_2O and DME.

Previous experiments of DME degradation with an increasing temperature ramp (Fig. 1) demonstrate that a total degradation of DME is observed at 700 ºC for both the standard and treated tubes, with the surface properties being the only variable of the experiments. Consequently, 700 ºC was the temperature selected for the DME degradation studies of long duration.
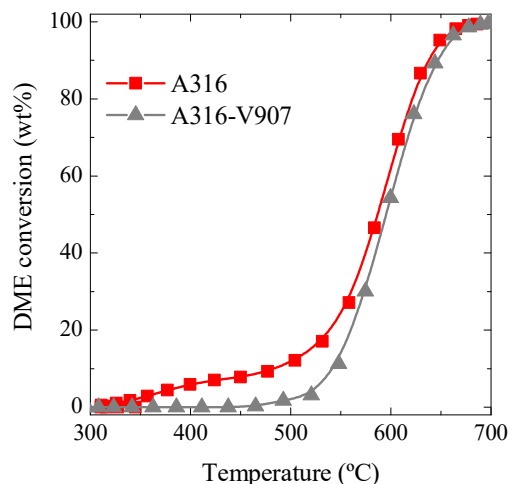

Fig.1. Evolution of DME conversion with temperature using the standard and the treated tubes

The reversibility of carbon deposition on the tube samples was studied in successive degradation-combustion cycles. The used procedure was the following:

(a) Preheating. The sample was heated up to 700 ºC (1 bar of pressure) at a heating rate of 10 ºC min^{-1} under a continuous flow of N_2 of 50 cm^3 STD min^{-1}.

(b) Carbon deposition. At 700 ºC, 25 cm^3 STD min^{-1} of DME was fed into the system during a maximum time of 20 h. Outlet gases were monitored by the microGC during this stage.

(c) Cooling. The sample was cooled down to 300 ºC under a continuous flow of N_2 of 50 cm^3 STD min^{-1} until the absence of DME was observed in the chromatograms.

(d) Combustion. A flow of 50 cm^3 STD min^{-1} of air was fed into the system. The temperature was raised up to 700 ºC at a heating rate of 5 ºC min^{-1}, while the signals of CO and CO_2 were monitored by the microGC. This is a consequence of the carbon combustion and therefore, this stage finished when these signals were not observed in the chromatograms.

(e) Shut down. The sample was cooled down to room temperature under a continuous flow of N_2 of 50 cm^3 STD min^{-1}, when the equipment was shut down and the tube sample was removed from the system.

RESULTS

Fig. 2 shows the evolution of the gas composition during the thermal degradation of DME along 20 h using the standard A316 tube (Fig. 2a) and the treated A316-V907 tube (Fig. 2b). The most interesting index is the O/C ratio, which is calculated from the amount of CO and CH_4 as CO/(CO+CH_4). Water and CO_2 are not considered because of their negligible concentration in the gas. Values of the

O/C ratio higher than 0.5 means a formation of carbon deposits as a consequence of DME degradation, since the observed carbon in the gas is lower than that expected by Eq. (1).
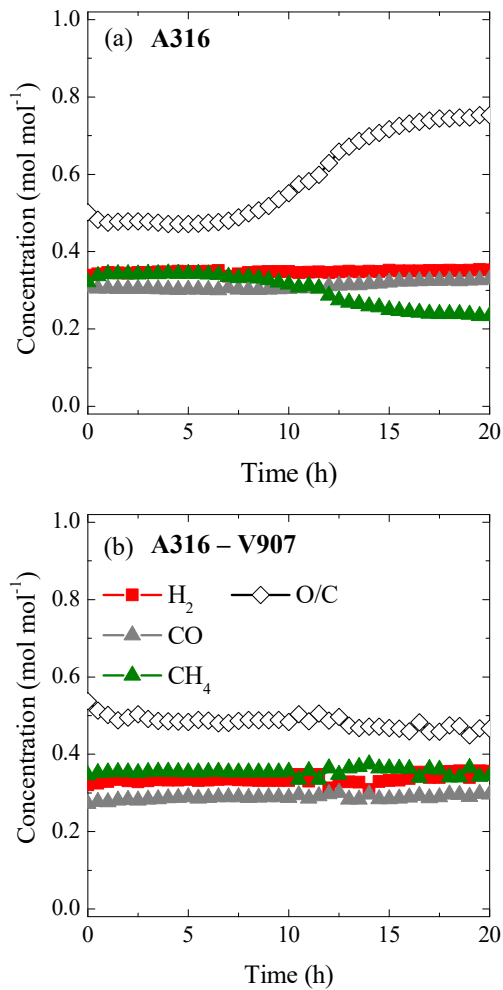

Fig. 2. Evolution with time of the gas stream composition during the DME degradation runs of 20 h using (a) the standard A316 and (b) the treated A316-V907 tube

A clear influence of the material is observed on the evolution of gas composition with time. A small degradation is displayed for the standard tube at the beginning of the reaction, but most of the carbon formation is observed from 6 h. A pronounced acceleration of the deposition rate is observed from 6 to 15 h, reaching a constant formation of carbon deposits between 15 and 20 h of experiment, with a maximum O/C ratio of 0.8. A different performance is exhibited by the coated tube, which only registers small deposition of carbon during the first 3 h of operation. Afterwards, a constant ratio of 0.5 is attained, indicating an almost null deposition of carbon from 3 to 20 h of operation.

The profiles of the gases obtained during combustion of the carbon deposited on both surfaces (CO_x fraction, almost totally constituted by CO_2) are

depicted in Fig. 3, with the area under the curve being the total amount of formed CO_2. This result is consistent with the trends observed in Fig. 2a and Fig. 2b, and confirms that a significantly higher amount of carbon is deposited on the surface of the standard tube.
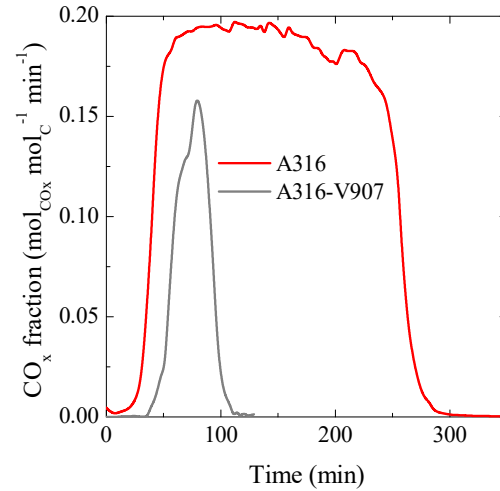

Fig. 3. Evolution of the CO_x fraction obtained in the combustion of the carbon deposited on each tube during the DME degradation runs of 20 h

The main results of the experiments are listed in Table 1. Apart from the effective internal area of the tubes (A) and the time (t), Table 1 contains different indexes related to the carbon mass balance used for monitoring the DME degradation runs: the mass of carbon fed as DME (C_{feed}), the mass of carbon in the outlet gas stream as CO and CH_4 (C_{gas}), the mass of carbon formed during each run (C_{form}, the balance between C_{feed} and C_{gas}), the mass of carbon deposited during each run (C_{dep}, calculated from the total amount of CO_2 formed), the yield of carbon deposited referred to the formed one (Y_{dep}) and the rate of carbon deposition, per unit of time and area (R_{dep}).

According to the results obtained at the same conditions, similar values of carbon are formed with both samples (C_{form}, 4.99 and 4.45 g for the standard and treated tubes, respectively). However, a pronounced decrease in the deposits (C_{dep}) is observed by the coated A316-V907 tube, which is also related to the much slower deposition rate (R_{dep}, 7.37 and 0.35 g h^{-1}m^{-2} for the standard and coated tubes, respectively). Therefore, the ceramic coating demonstrates to be effective for reducing the deposition of carbon during operation and thus, showing a very promising antifouling behaviour.

Table 1. Results of carbon deposition after 20 h of operation time for the standard and treated tubes

Sample	A316	A316-V907
A (cm^2)	163	163
t (h)	20	20

C_{feed} (g)	21.56	21.56
C_{gas} (g)	16.56	17.11
C_{form} (g)	4.99	4.45
C_{dep} (g)	2.41	0.12
Y_{dep} (wt%)	48.20	2.60
R_{dep} (g h^{-1} m^{-2})	7.37	0.35

One of the main issues of the standard tube is its catalytic performance in the formation of carbon deposits. In this sense, after the combustion of the deposits, the carbon deposition is promoted in the second experimental run (results not shown). This is also crucial for the lifetime of materials, since the possibility of making the formation and combustion of carbon deposits completely reversible could improve the performance of the desired operation. The reusability of the coated tube was also studied in five successive experimental cycles and the results of carbon deposition yield (Y_{dep}) are shown in Fig. 4. As observed, the differences between the cycles are negligible, which suggests reversibility in the formation and combustion of carbon and then indicates that the coated tubes are capable of working in successive cycles.
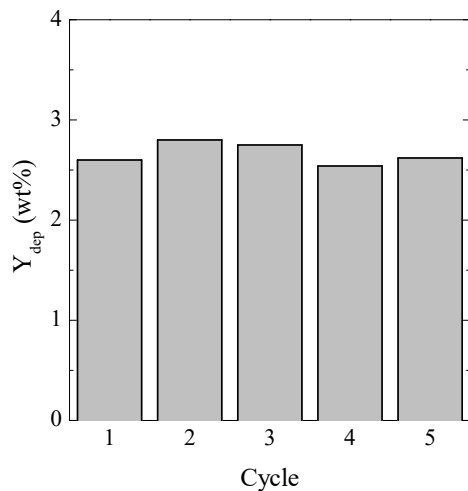

Fig. 4. Carbon deposition on the surface of the coated A316-V907 tube in successive DME degradation cycles

According to the results in Fig. 2, the deposition of carbon on the surface of coated tube is expected to occur during the first hours of operation. For this reason, experiments were carried out using three different operation times in order to study the evolution of carbon deposition with time. Fig. 5 depicts the evolution of the gas composition during the experiments for 3 (Fig. 5a), and 8 h (Fig. 5b). Moreover, Fig. 6 shows the CO_X profiles of the carbon deposit combustion in each case, together with that corresponding to the DME degradation run of 20 h. Similar results are obtained in all cases and practically any differences between the gas composition distributions are observed. A moderate

increase in the carbon production and deposition from 3 to 8 h can be estimated regarding the O/C ratio (Fig. 5b), which is slightly higher in this particular case.
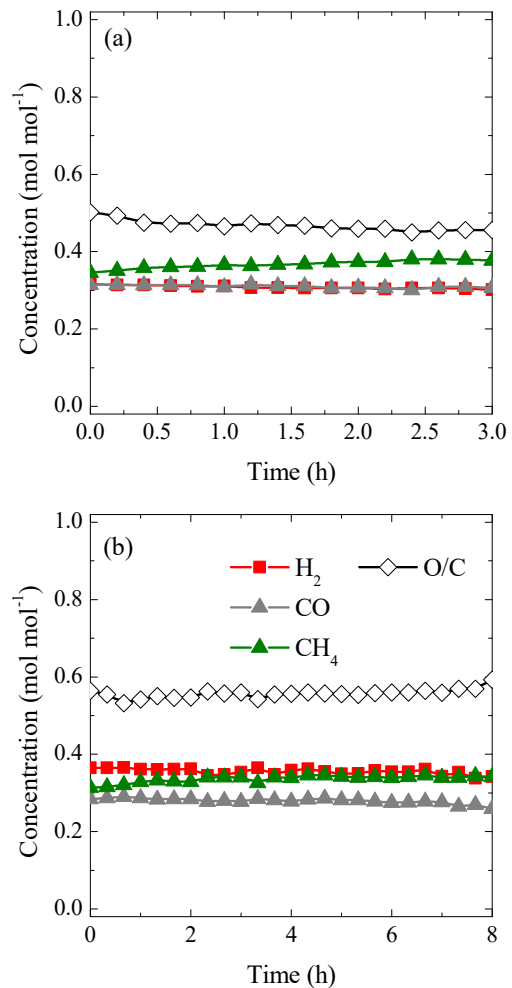

Fig. 5. Evolution with time of the gas stream composition during the DME degradation using the coated A316-V907 tube for (a) 3 and (b) 8 h

The CO_X profiles are practically overlapped for the carbon combustion at the three different operation temperatures. A small increase in the area under the curve can be seen for the experiment of 8 h respect to that of 3 h that is in agreement with the aforementioned increase in the O/C ratio.
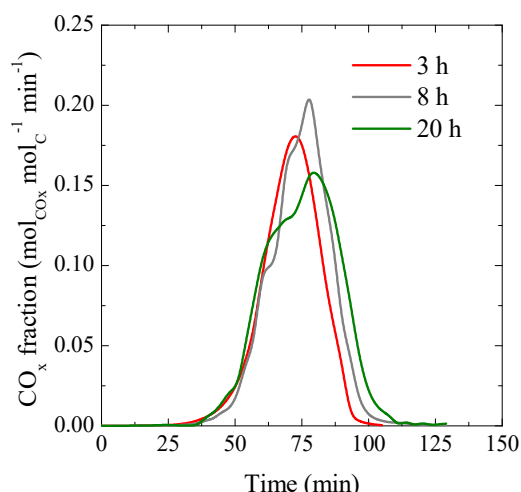
Fig. 6. Evolution of the CO_X fraction obtained in the combustion of the carbon deposited on the A316-V907 tube during DME degradation runs of different duration

The main results of these experiments with different duration are summarized in Table 2. In this case, increases in the formed carbon (C_{form}) are registered upon increasing the operation time. Nevertheless, the carbon deposition does not increase from operation times higher than 8 h (C_{dep}, 0.11 and 0.12 g for 8 and 20 h, respectively). Interestingly, the yield of carbon deposition (Y_{dep}) and the rate of carbon deposition (R_{dep}) decreases with the operation time (minima of 2.6 wt% and 0.35 g h^{-1} m^{-2} after 20 h), pointing out the good performance of this coated tube at long operation times.

Table 2. Results of carbon deposition after 3, 8 and 20 h of operation time for the coated tube

Sample	A316-V907		
A (cm^2)	163	163	163
t (h)	3	8	20
C_{feed} (g)	3.23	8.62	21.6
C_{gas} (g)	2.53	6.75	17.11
C_{form} (g)	0.70	1.88	4.45
C_{dep} (g)	0.05	0.11	0.12
Y_{dep} (wt%)	6.93	5.64	2.60
R_{dep} (g h^{-1} m^{-2})	0.99	0.81	0.35

CONCLUSION

The thermal degradation of dimethyl ether at 700 ºC has been proved to be a suitable reaction test to analyze the formation of carbon deposits on the internal surface of a standard stainless steel tube and tube coated with a ceramic layer. Carbon is similarly produced in both cases (ca. 21% of the feed) at 700 ºC, but a pronounced decrease in the carbon deposition is observed after the coating treatment. Less than 3% of the carbon is retained in the treated tube surface, whereas a value of ca. 48% is attained

for the standard stainless steel tube. Experiments of different duration reveal that the deposition of carbon in the case of the coated tube manly occurs in the first 8 h, thus drastically decreasing the deposition rate afterwards. Moreover, the coated tube shows a practically reversible formation and combustion of the carbon deposits, making it appropriate for sequenced operation cycles. Based on this, the possibilities of operating without fouling after 8 h and of reusing the tubes extend their lifetime even operating under severe carbon deposition conditions.

This technological approach provides an efficient and environmentally friendly solution that protects the components of critical degradation and maintains energy efficiency by avoiding the phenomena of contamination and corrosion. Its nature makes it especially suitable for protecting metallic substrates in high corrosion and dirt environments (refineries, petrochemical industry, cement industry and power plants, even in marine winds).

In this sense, the most important innovation is to combine in a single layer three key properties, such as resistance to temperature, resistance to corrosive/abrasive environments and antifouling properties, due to a very low roughness, which means that the coating has no influence on the flow of material that circulates inside the pipeline, as well as hindering the generation of unwanted deposits.

NOMENCLATURE

A	Effective contact area, m^2
t	Operation time, s
C_{feed}	Total carbon in the feed, g
C_{gas}	Total carbon in the gas stream, g
C_{form}	Total formed carbon, g
C_{dep}	Total deposited carbon, g
Y_{dep}	Yield of carbon deposition, g g^{-1}
R_{dep}	Rate of carbon deposition, g

Subscript

feed	in the feed
gas	in the gas stream
form	formed
dep	deposited

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