

**Chemical Inertness, Reproducibility and
Carbon Deposition for Coated and Non Coated UNS S34700 TUBES**

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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 °C has been used as reaction test to compare the carbon deposition on standard (non-coated) 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.

Key words: anti-coking, ceramic coating, stainless steel, dimethyl ether

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 coating of the internal surface with a ceramic layer is useful for preventing the formation of deposits and extending the lifetime of the tubes. [3]

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.[4] The three latter reactions take place on active sites present on the tube surface

DMEcracking:



Boudouard reaction:



Methane decomposition:



Reverse-Water Gas Shift:



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. This mainly depends on the temperature.

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.

In this work, a 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 PROCEDURE

Two different tube samples were tested during the thermal degradation of DME in order to compare their performances. On the one hand, a standard (non-coated) stainless steel tube (UNS S34700

Austenitic Steel Substrate, hereafter denoted A347) and on the other hand, a coated UNS S34700 tube with the ceramic layer well-deposited on its internal surface (named coated A347)

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 SiO_2 , Al_2O_3 , Na_2O , K_2O , CeO_2 , MgO , ZnO , CaO , ZrO_2 , 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 abrasive-blasting 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 common 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 environmentally friendly industrial technique to obtain a very smooth surface finish. 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 thickness 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)¹ equipment provided with an oven that allows the controlled heating up to 800 °C of tube samples of 2.54 cm of external diameter, 45.5 cm of total length and 26 cm of effective heated length (Figure 1). The apparatus was provided with controllers for the temperature and pressure and with mass flow controllers able to feed reactive and inert gases: (i) dimethyl ether (DME, 99.99%) as reactive gas; (ii) N_2 (99.99%) as inert gas, and; (iii) purified air 99.999% as comburent. The equipment was couple in line with a gas chromatograph (microGC, Varian 4900)² 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.

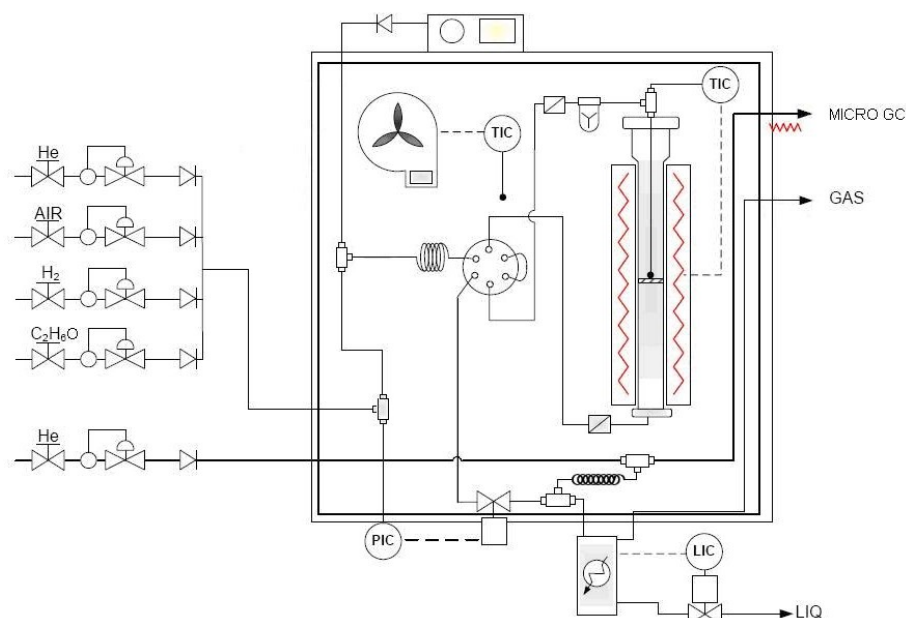


Figure 1. Scheme of the reaction equipment

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² VARIAN IBERICA, Pedro Diez 25, 28019 Madrid, Spain