Catalyzed-Assisted Manufacture of Olefins (CAMOL™): Updated for Use in Naphtha Service

Since the commercialization of the olefins plant, operators have searched for ways to be more competitive. One area always targeted includes keeping their furnaces in operation longer between decoking steps. Over the years, many anti-coking methods/technologies have become commercially available using different approaches to prevent coils from coking. One of the latest available technologies is the novel CAMOL (Catalyzed-assisted Manufacture of Olefins) Technology from BASF Qtech. As reported in the introduction of the technology to the EPC in 2008 & 2010, the CAMOL technology differs from other available anti-coking technologies in that the technology not only eliminates the catalytic (or filamentous) coke make through a physical barrier, but also gasifies the thermal (or amorphous) coke for an even greater anti-coking resistance. The proprietary manufacturing process generates a coating with almost identical thermo-mechanical properties as the base metal substrate (alloy). This allows bonding to the base metal similar to being welded with a minimum risk of spallation when going through thermal cycling. Commercially, the CAMOL Technology has been available since 2006 and is now in operation in furnaces of various designs.

BASF SE in Ludwigshafen, Germany, decided to install the technology in one of their naphtha furnaces in 2008 with a start-up in 2010. The goals of the project included:

1. Increase run length > 3 X
2. Determine impact of increased CO/CO₂ downstream

All of the coils in the furnace were replaced with CAMOL coated coils on 35/45 high temperature alloy consisting mostly of the Low Catalytic Gasifier (LCG), but included a low loading of the High Catalytic Gasifier (HCG) on the outlet coils. In addition, the fittings were also coated.

The chart below exhibits the run lengths during the first 3 years of operation.

Over the three years, it was found that modified start up procedures are required in order to reanimate the catalytic species. Three different methods were utilized:

1. Hydrogen/steam mixture;
2. Mild ethane cracking; and
3. Mild naphtha cracking.

Once the need to reduce the oxide to its active oxidation state was identified, the first experiment modified the start-up sequence to using a mild ethane for a short period of time before switching to naphtha. This proved successful, but all parties were curious to see whether better results could be obtained under a scenario which would allow the optimal reduction without the formation of any coke by using a hydrogen/steam only mixture. The results from the hydrogen showed an improvement, but also proved that mild ethane cracking would be more operationally feasible as a long term solution in more furnaces. However, in order to accommodate all furnaces in naphtha service, conditions under mild naphtha cracking needed to be defined. Through lab testing, parameters were defined and are now in the process of being implemented. Evidence of similar performance to ethane has resulted from these experiments.

A few other notable observations include:

1. The coking profile of the furnace completely changed. End of Run for this furnace was traditionally due to high outlet coil TMT’s. However, with the help of only a small quantity of the HCG catalyst on the outlets, the furnace became venturi pressure limited instead. This leads to the conclusion that only a small amount of HCG is required to gasify a significant amount of thermal coke.
2. Increased CO/CO₂ generation was immeasurable by both on-line analyzers and bag samples. Further to this observation, no upsets were observed in downstream equipment (caustic tower, acetylene converter, product quality, etc.) due to increased CO/CO₂ make from the CAMOL coated coil.
3. The coating is robust and the oxide layer is regenerable.

A sample taken from the coil after 14 months of service shows the coating in a similar condition as the “as produced” state, as shown by the SEM images below. The image on the right also shows some minor damage to the oxide layer. However, with an oxidation
procedure performed in the lab, a good quality oxide layer was reproduced. The field results also proves this phenomenon.

After overcoming the initial challenges associated with the technology, such as reactivating the catalytic species after decoking, the results are encouraging and BASF SE in Ludwigshafen will continue to move forward with the installation of a second coil in 2013. The objectives with this second coil include:

- Increasing the amount of HCG in order to meet the target run length while monitoring CO/CO₂;
- Continuing the optimization of reactivation and regeneration procedures for simplified operation
- Developing the capability to apply the technology to additional alloys (i.e. 25/35)
- Evaluating the operating limits of the technology (conversion, dilution steam ratios, etc.)

Through these activities, BASF Qtech and BASF SE expect to achieve the aggressive run length target.

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About Us

BASF Qtech offers advanced catalytic surface coatings for steam cracker furnace tubes used in the global petrochemical industry. BASF Canada Inc. and Quantiam Technologies Inc. are co-shareholders in the company.

About Quantiam Technologies Inc.

Quantiam Technologies Inc. was founded in 1998 by Dr. Steve Petrone to develop and commercialize disruptive, world-first new products based on advanced materials, catalysts, coatings and surfaces for extreme-operating environments and energy-related applications. Quantiam provides the most advanced high-performance coatings in the world for internal-surfaces of complex shapes such as tubulars. Additional information about Quantiam, its technologies, products and services is available at www.quantiam.com.

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