

AICHE PAPER NUMBER 133c

**CATALYZED-ASSISTED MANUFACTURE OF OLEFINS (CAMOL):
REALIZING NOVEL OPERATIONAL BENEFITS
FROM FURNACE COIL SURFACES**

Steve Petrone, Yan Chen and Robert Deuis

Quantiam Technologies Inc., Edmonton, AB, Canada

Les Benum and David Gent

NOVA Chemicals Corporation, Red Deer, AB, Canada

Randy Saunders and Chi Wong

NOVA Chemicals Corporation, Calgary, AB, Canada

Prepared for Presentation at the 2008 Spring National Meeting
New Orleans, Louisiana, April 6-10, 2008

AICHe and EPC shall not be responsible for statements or opinions contained in papers or printed in its publications.

CATALYZED-ASSISTED MANUFACTURE OF OLEFINS (CAMOL)*: REALIZING NOVEL OPERATIONAL BENEFITS FROM FURNACE COIL SURFACES

Steve Petrone, Yan Chen and Robert Deuis

Quantiam Technologies Inc., Edmonton, AB, Canada

Les Benum and David Gent

NOVA Chemicals Corporation, Red Deer, AB, Canada

Randy Saunders and Chi Wong

NOVA Chemicals Corporation, Calgary, AB, Canada

Abstract: NOVA Chemicals and Quantiam Technologies have undertaken a development effort of a novel materials technology aimed at realizing operational advantages with use in olefins manufacturing furnace coils previously unattainable with other methods. It is well recognized in the industry that coil internal surfaces can negatively impact furnace operational efficiency with unwanted surface catalytic processes leading to coke fouling and other well-established negative impacts on the overall cracking process. The CAMOL technology approach recognizes this potential of the coil surface significantly impacting the process, and aims to utilize these coil surfaces to provide a **positive and beneficial catalytic impact** on the process through the use of catalytic coatings with engineer-able functionality. This paper will define targeted product properties and benefits, and provide an update on laboratory and field results generated to-date. A 7-year development effort is near-completion and the product has been in commercial-scale field testing since 2005 with furnace trials underway in a broad range of feedstocks and furnace designs. Field trials are continuing through 2008 to map out the range of operational latitude provided by the technology, and to quantify operational benefits that can be achieved.

**The CAMOL technology development has been funded in part by Sustainable Development Technology Canada (SDTC) and an investment by Industry Canada - Technology Partnerships Canada (TPC).*

1.0 INTRODUCTION

From a materials perspective, the manufacture of olefins by hydrocarbon steam pyrolysis has not changed very much since originally commercialized, except to progressively operate at higher operating temperatures with overall greater cracking severity. This evolution has generally provided greater single-furnace capacities as new coil alloy materials and designs became available with tube-metal-temperatures now routinely exceeding 1100°C (2012°F). Modern world-scale plants now produce >2 billion pounds per year of ethylene with as little as 5-7 furnaces. Process containment or furnace coils have evolved in alloy composition and properties over the last 60+ years to sustain the higher temperatures and lower feedstock residence times, with a commensurate increase in unwanted or negative catalytic reactions at the coil surfaces and other carbon-based fouling mechanisms; for example, carbon or coke build-up by surface-catalyzed “filamentous” coke-make. Overall, these fouling mechanisms reduce furnace and plant efficiencies, and significantly increase furnace maintenance costs. These phenomena are well established, and efforts aimed at their mechanistic understandings to better drive technology developments towards mitigating the problem, have made some progress over the last quarter century. These have included better alloys and coil surfaces, feedstock additives and inhibitors, and coil coatings.

As example, in the 1980s and 1990s, several promising coating technologies¹⁻³ were developed and commercialized aimed at rendering the internal surfaces of furnace coils chemically inert to the pyrolysis or cracking process (i.e., shutting-down catalytic or filamentous coke-make) – a simple, clear objective, yet very difficult to attain technically given the severity of operating conditions and the state-of-the-art in coating technologies at that time. Varying degrees of success were realized and some of these coated products are currently available commercially. Overall, these coatings were able to provide some improvements in furnace run-lengths from a typical baseline of ~20-40 days, and increased through the use of inert coatings by a factor of 2-3 times but rarely exceeding ~100 days on-line. The success of some of these coatings prompted some steel producers to develop and commercialize novel alloys away from industry-standard chromia-forming austenitic stainless steels whose surfaces exhibit relatively low temperature stability under cracking conditions (<1050°C (1922°F)), and primarily move towards steels with higher temperature-stable surfaces such as alumina-formers. Several major alloy suppliers worldwide currently market such products.

In 2002, the ANK400 product was commercialized⁴, with a field-demonstrated capability of reaching 500+ day run-lengths in lighter feedstock crackers. This technology currently defines the best-achievable on a commercial scale by proper control of the coil internal surface composition and furnace operating conditions.

One materials evolution path forward, is that if, the coil surfaces that come in contact with only a fraction of the total feed-stream can provide a significant negative catalytic

impact on the cracking process, *vis-à-vis*, filamentous coke-make, and an inert coil surface is considered superior and preferred, then why could these coil surfaces not be surface engineered to provide an overall positive catalytic impact on the process? A key pre-condition for this approach to be viable demands carbon-free performance of the coil surfaces, regardless of the origin of that carbon, as either filamentous (catalytic) or gas-phase (amorphous) would accumulate on the surface catalytic sites rendering them non-functional. Once this coke-free performance is achieved over an industry-relevant range of operating conditions, other process benefits from the surface could then be potentially engineered and realized. Groups worldwide have pursued such an objective recognizing that success could provide significant operating rewards on energy and emissions reductions, and overall improvements in plant efficiencies and profitability.

The approach of the development effort reported in this Extended Abstract, **C**atalyzed-assisted **M**anufacture of **O**lefins (CAMOL), targets amongst its range of benefits, carbon-free performance for extended periods of time (years), in a broad range of feedstocks and operating conditions, and in addition, is aimed at providing an overall reduction in average operating temperature over a run-length, a lower level of steam requirement (as a surface-need only), and the potential of a positive impact on the product slate. Further, the development targets full retrofittability in existing olefins manufacturing furnaces requiring no material changes to existing furnace coils or operating procedures, except for the introduction of CAMOL catalyst coatings within the process circuit.

2.0 RESULTS AND DISCUSSION

2.1 Technology Targets and Status

Catalyst coatings have been developed that integrate catalyst formulations into commercially-viable coating systems using current industry furnace alloys and furnace coil component geometries. It was contemplated that more than one coating and catalyst formulation would be required to address the full range of feedstocks used by the industry, furnace operating conditions, and desired benefits. The coatings developed are best described as composites, consisting of metallic and ceramic constituents, and exclude expensive constituents such as precious metals. The technology targets to provide ~20 engineered chemical, physical and thermo-mechanical properties in its coatings to achieve commercial viability – a critical requirement for commercial viability generally not reached by coating technologies of the 1980s and 1990s. A summary of the CAMOL targeted properties is provided in Table 1. The coating formulations and structures, and the manufacturing technology are proprietary; upon completion of patent filings, additional details of the technology will be published.

Table 1: CAMOL Catalyst Coatings – Targeted Properties to Reach Commercial Viability

| | Targeted Property |
|----|--|
| 1 | Surface chemical composition is inert to catalytic (filamentous) formation of coke |
| 2 | Surface chemical composition and structure provides catalytic gasification of carbon at elevated cracking temperatures (>700°C (>1292°F)) - full range of carbon sources with operationally-manageable levels of CO and CO ₂ |
| 3 | Surface chemical composition and structure provides catalytic gasification of carbon at low operating temperatures (400-700°C (752-1292°F)) with specified sources of carbonaceous matter and remaining within operationally-manageable levels of CO and CO ₂ |
| 4 | Surface chemical composition and structure that does not have negative impact on pyrolysis process and product stream |
| 5 | Surface chemical composition and structure that provides a positive catalytic impact on feedstock conversion and product yields |
| 6 | Surface chemical composition that allows for significant reduction in steam-requirements for process |
| 7 | Coating system capable of in-situ repair/regeneration of outermost surface layer |
| 8 | Thermal stability of coating system to exceed operating temperature range of current furnace technologies at Tube-Metal-Temperature (>1100°C (>2012°F)) |
| 9 | Thermal Shock Resistance – Coefficients of Thermal Expansion (CTEs) matched to allow for emergency power outages and other process upsets |
| 10 | Hot Erosion resistance |
| 11 | Carburization resistance provided through a surface barrier |
| 12 | Carburization resistance provided through intrinsic enhancement |
| 13 | Oxidation resistance provided through a surface barrier |
| 14 | Oxidation resistance provided through intrinsic enhancement |
| 15 | Corrosion resistance to feedstock halogen contaminants |
| 16 | Corrosion resistance to feedstock Group-I metals contaminants |
| 17 | Corrosion resistance to feedstock and added sulfur levels (H ₂ S, DMS, DMDS, etc.) |
| 18 | Metal dusting resistance |
| 19 | Creep resistance |
| 20 | Coating System bond strength exceeding UTS of base alloy (~60-70 ksi) |
| 21 | Coating System ductility to exceed elastic limit of base alloy |

Two coating systems have been successfully advanced with the properties shown above in Table-(1) with high-level summaries of key results provided below in Section 2.2 (Laboratory-scale), Section 2.3 (Pilot-scale) and Section 2.4 (Commercial-scale). These CAMOL coatings, their key catalytic properties, and the targeted feedstocks and operating temperatures, are summarized in the table below.

| Coating System | Coating Catalytic Properties | Primary Feedstocks | Targeted Maximum Temperatures* |
|------------------|---|--|--------------------------------|
| CAMOL LCG | <ul style="list-style-type: none"> • Low-level catalytic-gasification • High-level surface coverage of catalyst | <ul style="list-style-type: none"> • Ethane/Propane • Butane • Light Naphthas (?) | >1100°C (2012°F) |
| CAMOL HCG | <ul style="list-style-type: none"> • High-level catalytic-gasification • Low-level surface coverage of catalyst | <ul style="list-style-type: none"> • Butane • Naphthas | |
| To Be Determined | <ul style="list-style-type: none"> • Low-temperature catalytic gasification efficacy • Low-Medium levels surface coverage of catalyst | <ul style="list-style-type: none"> • TLE surfaces operating at lower temperatures | 400-700°C (752-1292°F) |

* temperatures are to be finalized as all testing is completed and coated products are fully optimized

The LCG coating is typically deposited in thickness ranging from 100 to 1,000 microns. An SEM micrograph of a metallographic cross-section of a 1,000 micron thick coating is shown in Figure 1. An SEM micrograph of the topmost surface is shown in Figure 2.

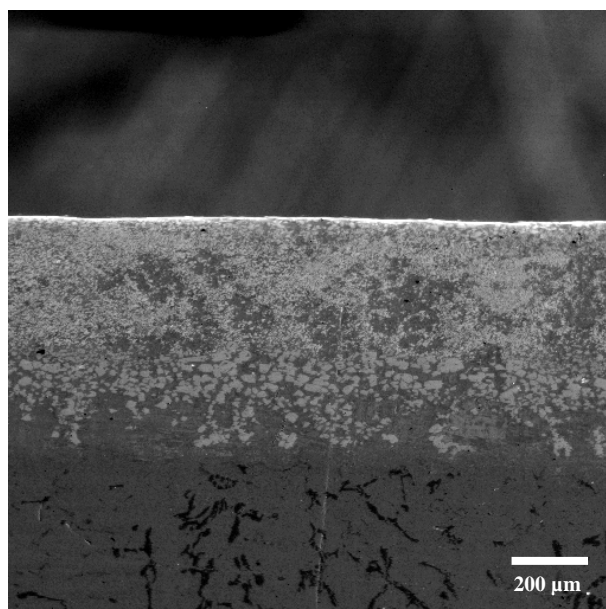


Figure 1: An SEM micrograph of a metallographic cross-section of the CAMOL Low-catalytic Gasification coating ~1,000 microns thick

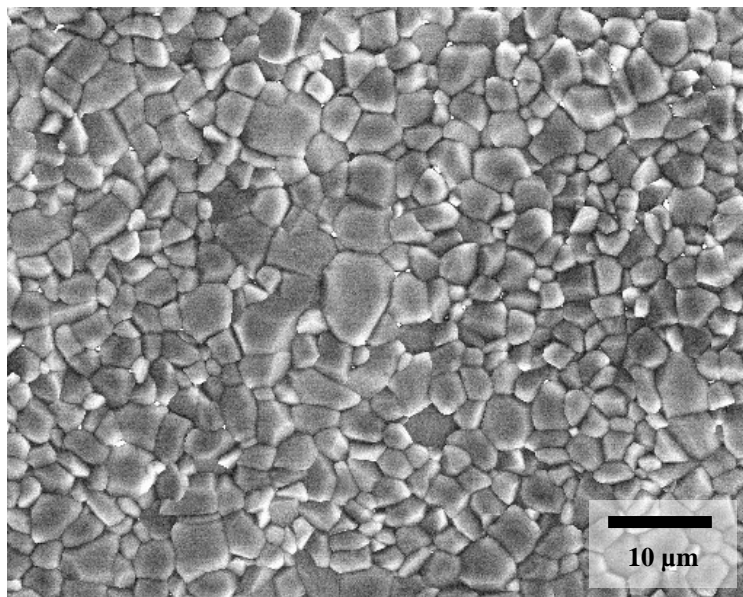


Figure 2: An SEM micrograph of the topmost surface of the CAMOL Low-catalytic Gasification (LCG) coating surface

2.2 Laboratory-scale Test Results

The experimental work undertaken to-date to develop the CAMOL technology is extensive given the scope of properties targeted to reach commercial viability. As such, it is beyond the scope of this Extended Abstract to comprehensively report on all results. A more detailed paper will be published at a later date together with longer term results as they become available. Below are reported representative laboratory-scale findings supporting some of the key targeted properties of Table-1.

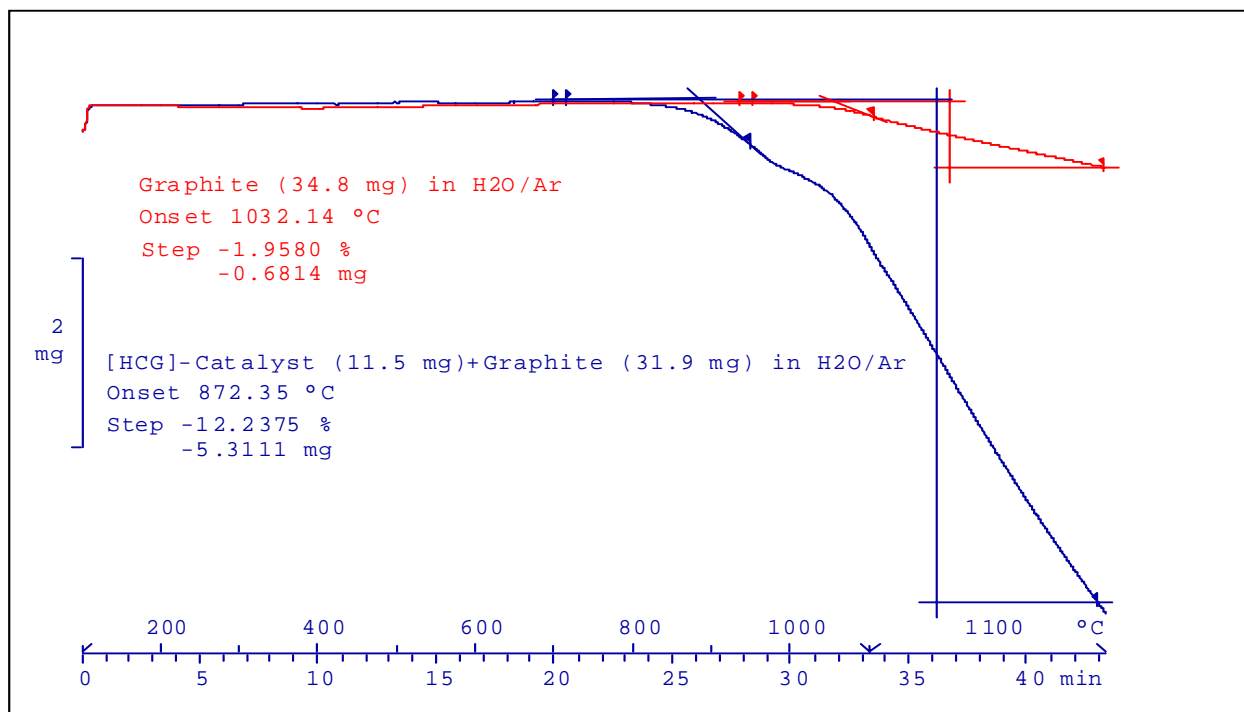
2.2.1 Gasification Screening using Thermal Gravimetric Analysis (TGA)

A Mettler-Toledo TGA unit was utilized for pre-screening of the gasification potential of candidate catalysts. Initial testing involved blending of catalysts species with graphite and undertaking a TGA run under the following atmosphere test conditions to vary overall oxidizing potential in the temperature range of 20-1150°C (68-2102°F):

- argon;
- steam/argon;
- air/argon; and
- hydrogen/argon.

This pre-screening for gasification properties involved over 700 test runs and identified a short-list of candidates that chemically exhibited attractive gasification capabilities in the operating regimes of relevance to the olefins industry. This short-list of candidates was then further reduced against their potential for incorporation into viable coating

systems satisfying the performance requirements detailed earlier in Table 1. An example of the performance of the catalyst species ultimately incorporated into the CAMOL HCG coating system is shown in Figure 3. The oxidizing potential in this test using a steam/argon atmosphere is considered very low. The temperature ramp is shown on the x-axis from 100 to 1100°C (212-2012°F). The y-axis shows measured weight loss from graphite gasification that is proportional to gasification rate. The reference run of graphite without catalyst is shown in the top profile (red) exhibiting an Onset Temperature of Gasification of ~1032°C (1890°F) with a slow gasification rate. The test run of graphite with the HCG catalyst is shown in the lower profile (blue) with a significantly lower Onset Temperature of Gasification of ~872°C (1602°F) and a higher rate of gasification.



: METTLER

METTLER TOLEDO STAR® System

Figure 3: TGA run of the catalyst species incorporated into the CAMOL HCG coating system. Time-temperature ramp is shown on the x-axis. The y-axis shows weight loss of graphite due to gasification. The test atmosphere is steam/argon providing an overall low oxidizing potential. The top profile (in red) is a reference run with graphite and no catalyst showing an Onset Temperature of Gasification of ~1032°C (1890°F). The lower profile (in blue) is graphite plus catalyst showing an Onset Temperature of Gasification of ~872°C and higher gasification rate.

2.2.2 Surface Performance under Pyrolysis Conditions

The surface performance of candidate materials and coatings was characterized in a test facility aimed at quantifying:

- coking rates;
- catalytic efficacy for carbon gasification;
- impacts on product slate; and
- impacts of decoking conditions.

Test samples are typically coated bars of higher temperature austenitic stainless steels (HK40 through to 35Cr-45Ni-Fe), each 20mm (0.79in) wide x 75mm (2.95in) long x 6.5mm (0.26in) thick, with 2 sets of coated bars arranged end-to-end and providing a surface area of up to 70% of the total reactor hot-zone internal surface area. Surface characterization of these bar samples is undertaken prior to the start of the cycle and upon completion of the test cycle using one or more of the following techniques: surface-sensitive XRD, FE-SEM/EDS, or FE-AES/XPS. This structured approach is followed to allow for a strong correlation to be developed between the characterized surface condition that is undergoing testing, and the impacts of that surface on the process and the product stream; additionally, any changes to the starting surface condition resulting from pyrolysis.

The test rig is attached directly to a GC for online quantification of the product stream. A significant database has been developed with most testing undertaken in a regime of low and near coke-free performance (some elements of the process circuit are uncoated). Under such low-coking conditions, probing of the pyrolysis process and impacts of the test materials/surfaces on potential gasification products (CO, CO₂, CH₄) has proved challenging, and often requiring that the testing be pushed into more extreme or larger-scale regimes. As examples, the use of coated bars of significant size and surface area as denoted above, rather than small coupons; or, using more severe cracking conditions, for example, for ethane cracking, conversions >85% to increase coke-formation rates. Overall, product slate analyses have compared favourably with SPYRO™ projections, and also have correlated well with both pilot-scale pyrolysis testing and commercial-scale furnace trial results. Testing has included many reference steels and materials surfaces, a broad range of candidate catalysts, and extensive optimizations of the CAMOL coatings. Feedstocks have included ethane, hexane and lighter naphtha blends, and are continually being expanded.

Based on this laboratory-scale testing and the levels of carbon gasification probed possible and quantifiable, the key catalytic properties of the CAMOL coatings and their surfaces were classified as best as feasible for a given set of test conditions for:

- onset temperature of catalytic gasification;
- relative level (rate) of gasification; and

- maximum temperature for catalytic efficacy.

Overall, the properties of the catalysts and the coating systems developed, allow the level of gasification to be a relatively engineer-able (tunable) property, that can be balanced to the gasification needs (net carbon load on the surface) of a cracking environment that is defined primarily by feedstock, temperature, and oxidizing potential.

2.2.3 Thermal Stability

Thermal stability of the coating and its ability to sustain outermost surface catalytic efficacy is a critical requirement for commercial viability. This property has been separated into two major components:

- thermal stability of the outermost surface in contact with the process stream to address surface-related properties; and
- thermal stability of the coating matrix to address near-surface and coating matrix-related properties.

As discussed later in Section 2.2.4, the stability of the outermost surface under cracking conditions has been targeted at a minimum of 100-150°C (212-302°F) greater than the industry-standard surface of chromia. The stability of the coating-matrix structure has been targeted as high as possible above operating temperatures, targeting >1100°C (>2012°F).

As longer term testing is finalized, additional field results are obtained, and the coatings are fully optimized, acceptable and safe operating regimes for each of the two coatings will be finalized. It is expected that the technology development targets will be met.

2.2.4 High Temperature Corrosion Degradation

(a) Carburization Resistance

Accelerated carburization resistance was evaluated under ultra-low oxygen levels with a carbon activity at the test surface $a_c \sim 1$, temperatures in the range of 1000-1150°C (1832-2102°F), and timeframes typically of 25-1,000 hours. These are considered aggressive conditions as many test materials are not able to sustain or generate protective surfaces under such conditions. It is noted that under these test conditions, chromia, recognized as the primary protective surface of the majority of high temperature alloys used in the industry, begins to convert to carbides at temperatures <950°C (<1742°F). It is generally believed that chromia stability under standard pyrolysis conditions is ~1050°C (~1922°F). A key target for the CAMOL coatings has been to secure thermal stability under the severe carburizing test conditions noted above, of at least 100°C (212°F), and preferably 150°C (302°F), greater than the stability of chromia.

(b) Oxidation Resistance

Accelerated oxidation testing was undertaken to secure compatibility of the CAMOL coatings and surfaces with a broad range of decoking conditions and ensuring high resistance to internal oxidation. Testing was undertaken in the temperature range of 800-1150°C (1472-2012°F) at a broad range of pressures and oxidizing potentials. The oxidizing source ranged from 100% steam through to 100% air. Results showed that the coating surfaces exhibited high compatibility under strongly oxidizing conditions. However, as the targeted properties of the outermost surface to secure optimal catalytic efficacy include surface composition, crystal structure, and morphology, it proved necessary to define start-up and decoking procedures for maximum compatibility with standard plant operating procedures. Efforts are continuing to make these procedures as broad as possible within the realm of steam-air decoking; however, there is no effort at securing compatibility with a pure-oxygen stream used by some producers.

c) Resistance to Corrosive Attack by Feedstock Contaminants

Engineering of the outermost protective surfaces was undertaken with high consideration for established and demonstrated resistance to high temperature corrosion associated with industry-published feedstock contaminants. This work is ongoing to expand the mapping of acceptable operating regimes with industry-defined feedstock contaminant levels.

2.2.5 Sulfur Resistance and Impacts on Pyrolysis Process

The robustness of catalyst efficacy under sulfur exposure is considered a critical requirement for broad-range use in commercial furnaces, especially with heavier feedstocks. In the first stage screening of candidate catalyst species that exhibited good gasification properties, the development effort utilized published literature knowledge of stability and compatibility of these candidate materials with sulfur-bearing environments at elevated temperatures. Secondly, for short-listed candidates, it undertook experimental laboratory testing as detailed below, together with field trials under a range of operating conditions.

(a) Laboratory-scale Testing in an H₂S Environment

Testing was undertaken of the catalyst species under H₂S exposure conditions of 500 ppm and 900°C (1652°F) as gas temperature. The catalysts were characterized prior to and after testing for:

- composition and stoichiometry;
- crystal structure;
- morphology; and
- catalytic efficacy.

Results showed that for the catalyst species of both the CAMOL LCG and HCG coatings, no detectable changes in the above properties were observed for the test conditions used. Further testing under more severe conditions is planned.

(b) Pilot-scale Pyrolysis Testing

Pilot-scale pyrolysis testing is reported below in Section 2.3. This testing also provided an assessment of the impact of sulfur level on the overall coking rate performance of the entire test circuit, inclusive of the pre-heat sections, the coated reactor section, and the exit collection system. The results for both ethane and butane feedstocks are shown in Figures 4 and 5, respectively. For both feedstocks, the CAMOL LCG coated reactor within the circuit showed a near-flat response with increasing sulfur levels. The greater coking rates of the reference uncoated reactor can be explained in part by greater downstream (exit) coking accumulation shown later in Section 2.3 (Figure 7).

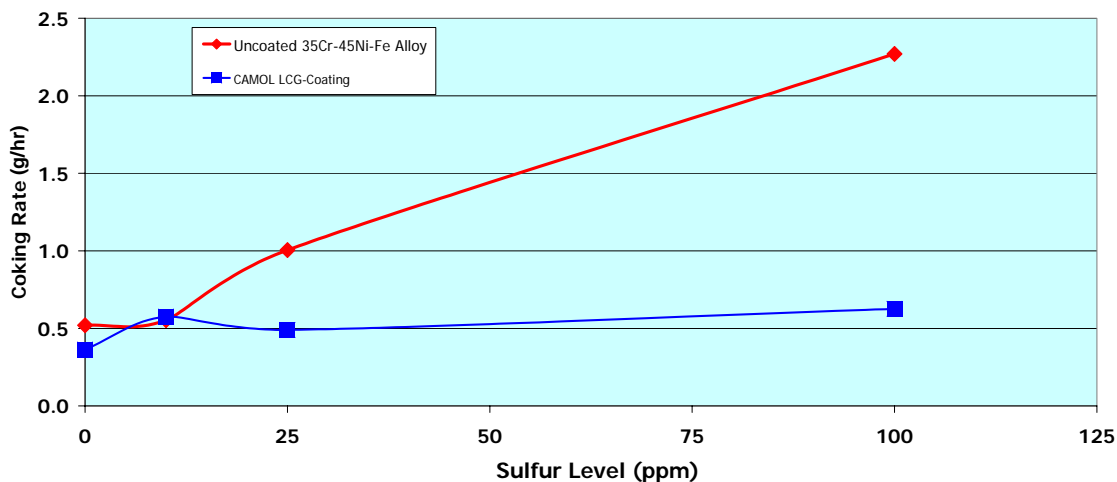


Figure 4: Overall coking-rate within the entire pilot pyrolysis test circuit as a function of sulfur level for ethane cracking, 65% conversion, 0.3:1 steam:hydrocarbon ratio.

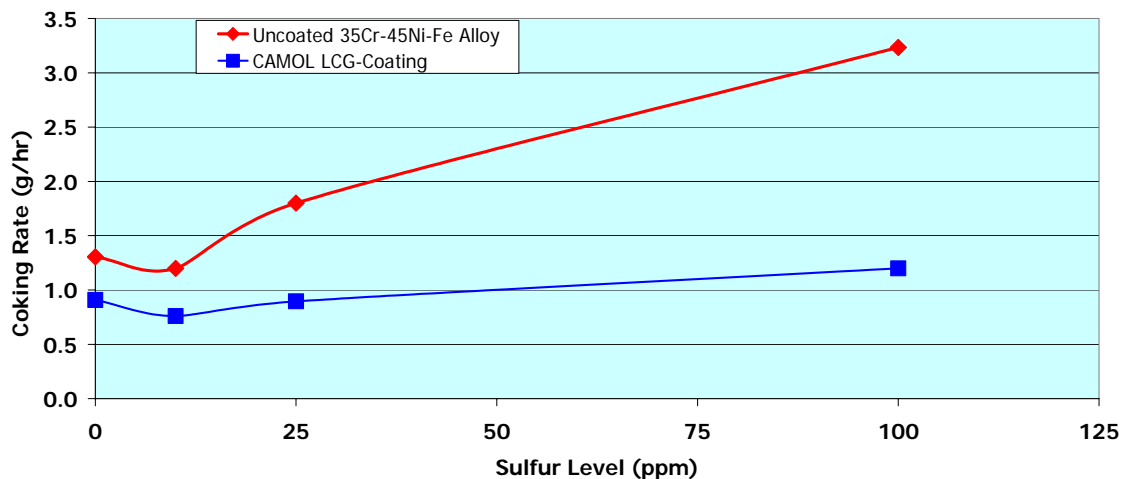


Figure 5: Overall coking-rate within entire pilot pyrolysis test circuit as a function of sulfur level for butane cracking, 95% conversion, 0.4:1 steam:hydrocarbon ratio.

(c) Commercial-scale Furnace Testing

Commercial-scale furnace trial results are reported below in Section 2.4. These trials cover a broad range of sulfur levels that are present in various forms as added sulfur and as inherent sulfur-species within the feedstocks. These results are expected to further enhance the understanding of the stability and limitations of the CAMOL coatings and surfaces, and the acceptable operating regimes for both the LCG and HCG coating systems.

(d) Initial Assessment of Sulfur-testing Results

Results to-date have shown that for the sulfur levels and temperatures tested, the CAMOL coatings exhibit good stability and robustness, and that catalytic efficacy is unaffected. Additional testing is underway with field trials, and is also planned under broader laboratory test conditions.

It is recognized that sulfur impacts on overall coking phenomena and rates are complex. Initial pilot-scale pyrolysis results suggest that whatever this complexity may be, the CAMOL LCG coating that was pilot-scale tested from 0 to 100 ppm S, has a near-flat response to increasing sulfur level, and shows a significantly lower dependence on increasing sulfur level than an uncoated reference 35Cr-45Ni-Fe alloy tube. It should be recognized that this observation is for the entire circuit in the pilot-scale test, extending well beyond the coated tube reactor section.

2.2.5 Hot Erosion Resistance

Hot erosion can play a significant role in materials degradation of alloy components in certain areas of the radiant section and the process circuit, depending on local temperature, flow characteristics and particulate loading in such regions. This material weak-link is becoming more critical as extended furnace online times of one or more years are becoming possible, and in some petrochemical plants, routine. As such, the need to remove such weak-links has become of greater commercial value and necessity.

An earlier study by Quantiam^{5,6} found that the high temperature alloys used within the Petrochemical industry in an uncoated condition, initially exhibit fair-to-good erosion resistance, but can subsequently undergo a catastrophic increase in erosion rate at a critical operating temperature after some threshold operating time. This accelerated erosion rate was ascribed primarily to internal carburization or oxidation of the near-surface which led this highly-modified region of the tube or fitting wall to exhibit an exponential increase in erosion rate. Protective coatings that impart high resistance to carburization and internal oxidation are expected to provide significant improvement to hot erosion with operating online time. CAMOL coatings, as per Table-1, are engineered with such enhancements.

It is recognized that erosion resistance is directly proportional to the hardness of a material (as well as other material properties). The CAMOL LCG coating can be deposited (if so elected) to exhibit hardness of a significant multiple of the base austenitic steel. Such election should ideally be reserved for components that do not undergo significant creep in service.

2.2.6 Thermo-Mechanical Stability

The CAMOL coatings were engineered with a high degree of thermo-mechanical robustness, for example, matching of the coefficient of thermal expansion (CTE) so as to survive unplanned or emergency furnace shut-downs in the field. Laboratory testing has been undertaken at a broad range of levels, inclusive of a thermal shock delta of $\sim 1,000^{\circ}\text{C}$ in <1 sec.

2.3 Pilot-scale Pyrolysis Test Results

The Technical Scale Pyrolysis Unit (TSPU) facility at NOVA Chemicals' Research and Technology centre in Calgary, Alberta was utilized to undertake pilot-scale pyrolysis testing of CAMOL-coated commercial-scale tube reactors and reference uncoated tubes. Two feedstocks have been tested to-date, ethane and butane, under standard operating conditions with sulfur additions as DMDS of 0 to 100 ppm with test durations of up to 100 hours.

Results for ethane cracking are shown in Figure 6 for an uncoated reference tube showing an exponential increase in pressure drop as a function of on-stream time, and the CAMOL reactor tube with a Low-catalytic Gasification (LCG) coating showing flat-line performance on pressure drop changes over the timeline of the test (~75 hours). Impacts on product slate and CO/CO₂-make were found within the range of normal steam cracking.

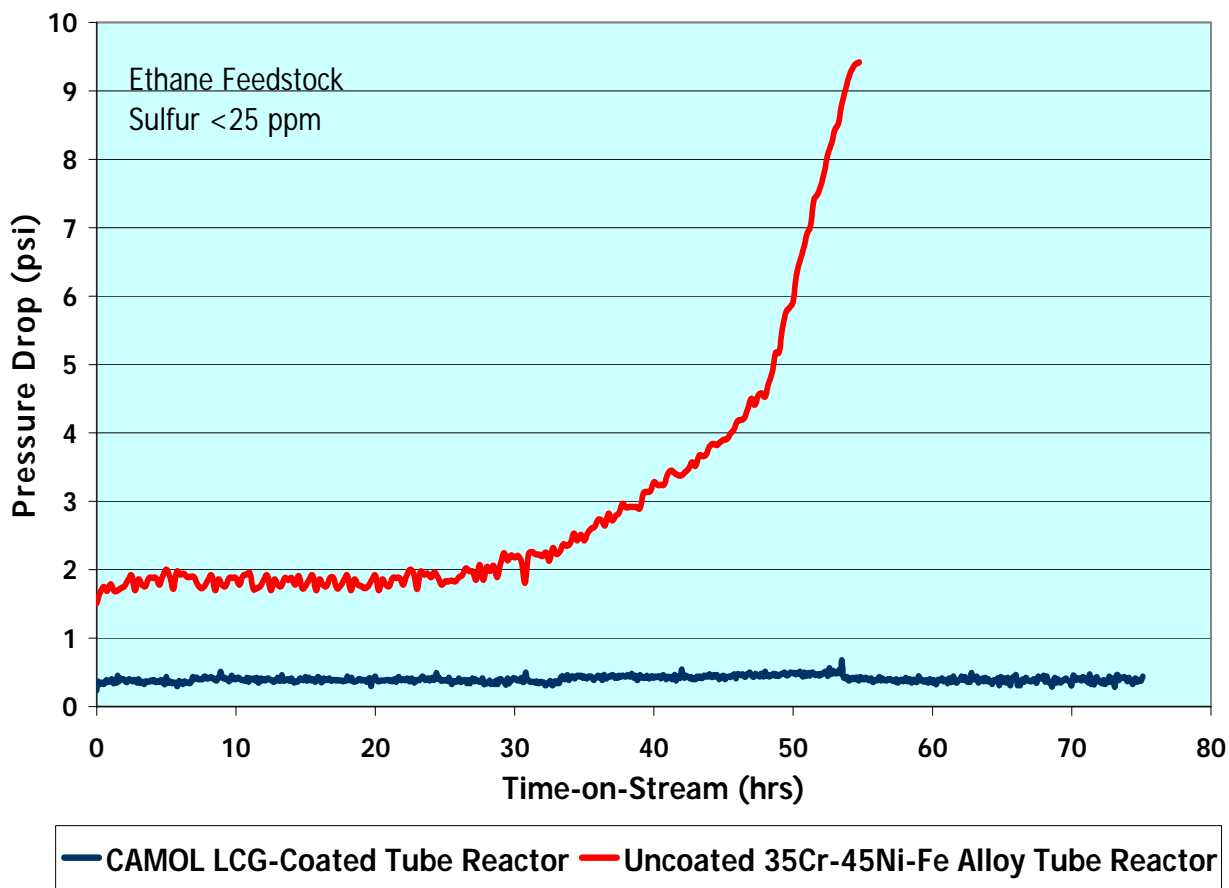


Figure 6: Pilot-scale pyrolysis testing of CAMOL Low-catalytic Gasification (LCG) coating on tube reactor

The pilot-scale test also allows an assessment of downstream coking by direct examination of the exit assembly at end-of-run. Results for ethane cracking at 65% conversion showed that the CAMOL-coated reactor (Figure 7(a) below), had a clean exit trap (free of carbonaceous-matter build-up), in comparison to the uncoated reference tube reactor (Figure 7(b)), consistent with the higher overall coking-rate measured for the entire circuit (earlier in Figure 4 for ethane cracking).



(a) Exit of CAMOL LCG-coated tube reactor

(b) Exit of Uncoated tube reactor

Figure 7: Pilot-scale assessment of downstream coking in reactor tube exit assembly: (a) CAMOL Low-catalytic Gasification coated tube reactor; and (b) Uncoated tube reactor (35Cr-45Ni-Fe).

2.4 Commercial-scale Field Trials

Commercial field trials have been a major focus for the development effort and have been separated into two groups of activities:

1. Smaller-scale Trials: Installation of coated tubes, fittings and ancillary equipment, aimed at assessing coating longevity of candidate coatings under a range of operating conditions. Efforts commenced in 2005 and coated material is removed for inspection and analysis as opportunities allow.
2. Larger-scale Trials: Installation of coated furnace coils, representing a sufficient fraction of a furnace's radiant section to enable an assessment of operating process performance.

To-date, numerous smaller-scale and three larger-scale commercial-furnace trials have been undertaken and are at different stages of completion. The specific larger-scale furnace trials, and the type and extent of coatings installed (circuit coverage), are summarized in the table below.

| | Low Catalytic Gasification (LCG) Coating | High Catalytic Gasification (HCG) Coating |
|---|---|---|
| Lighter Feedstocks (Ethane/Propane) | NOVA Chemicals Joffre, AB - Trial-(1) [2 of 4 coils, collected to one TLE] | NOVA Chemicals Trial-(2)-Joffre, AB (trial has both LCG and HCG) [2 of 4 coils, collected to one TLE] |
| Heavier Feedstocks (Butane/Naphthas) | NOVA Chemicals Trial-(3) - Corunna, ON (trial has both LCG and HCG) [4 of 6 coils, each two-coils collected to one TLE] | |

The first trial at Joffre (reported below) was installed in July 2006 and continues in operation. The other two trials were installed in March 2008 with a Q2-2008 start-up.

Overall, these trials have been aimed at supporting the development effort with timely learnings of normal-course technology scale-up, assessing performance under standard operating conditions, and as best as feasible, assessing operating latitude without risks to the facilities.

2.4.1 Lighter Feedstocks Trials

Two trials have been undertaken to assess the performance of both the LCG and HCG coatings. The first trial in the Joffre Ethylene-2 plantsite, Heater-146, involved the CAMOL LCG-Generation-(I) coating applied to two of four coils; no coating was applied to the fittings or welds. These two coils are configured such that the outlets share one TLE. The furnace started up September 1, 2006 and continues in operation.

NOVA Chemicals has developed software to allow projections of runlengths based on performance of both its furnace coils and the corresponding TLEs. The projections provide increasing confidence with furnace runtime for both the furnace coils and the TLEs. High confidence levels are generally obtained after 50-days online out to 500+ days; any projections >>1,000 days are denoted below as “Unlimited”. The results are summarized in Figure 8.

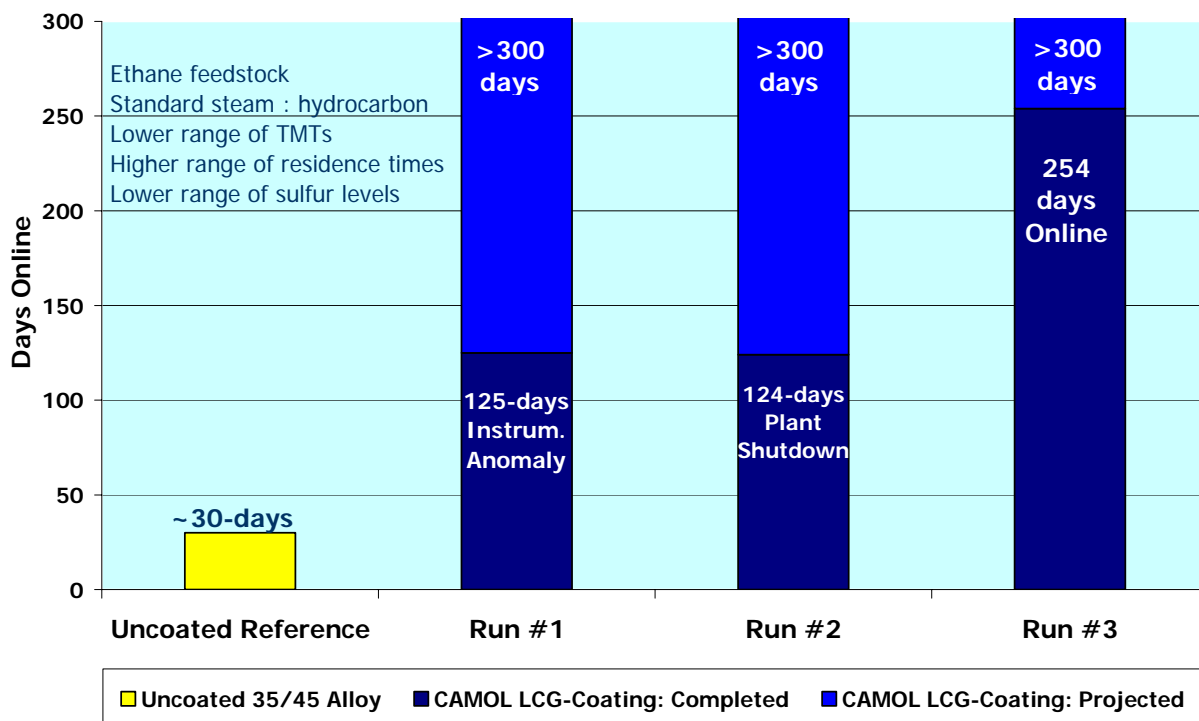


Figure 8: Initial results from Commercial Furnace Trial-(1) installed in July 2006 with a CAMOL Low-catalytic Gasification (LCG) coating in radiant section only – No TLE coverage

Run #1: A standard start-up procedure was used with no pre-sulfidation addition at start-of-run, followed by a steady-state low sulfur level during the run. The first run ran for 125 days with low coil coking rates but required a furnace shutdown due to an instrumentation anomaly. A subsequent inspection provided by a plant shutdown (after Run#2 below), showed that the anomaly was not related to the CAMOL coating. The projection for the coated coils had it not required shutdown for the instrumentation anomaly, was for >600 days.

Run #2: The second run following a standard air-steam decoke completed 124 days and was terminated for a scheduled plant maintenance shutdown. The projected runlength for this run was >300 days for the coated coils and Unlimited for the TLE.

Run #3: The third run also followed a standard decoke procedure and has completed 254 days (at March 11th) with a projection also of >300 days for the coated coils and Unlimited for the TLE.

Overall, the furnace performance exceeded expectations given it represented the first production campaign in the pilot coating manufacturing plant after scale-up of the technology out of the laboratory. The learnings were subsequently undertaken and used to optimize the LCG coating towards the current Generation-(III) product.

The second furnace trial at Joffre, AB was installed in March 2008 with LCG-Generation-(III) and HCG-Generation-(I) coatings on the tubes only. The furnace is expected to start-up in Q2-2008.

2.4.2 Heavier Feedstocks Trials

Field trials in heavier feedstocks are being undertaken at Corunna, Ontario and are advancing approximately two years behind those in lighter feedstocks. A significant portion of an SRT-3 furnace has been retubed with both the CAMOL LCG-Generation-(III) and the HCG-Generation-(I) coatings with start-up scheduled for later this year. The furnace will test a range of feedstocks from propane through to naphthas.

Additional trials are being pursued with other petrochemical producers to fully map out acceptable operating environments and regimes of the technology.

3.0 CONCLUSIONS AND FUTURE WORK

1. **Novel catalyst coatings** have been successfully developed and advanced to commercial trials, engineered to survive the extreme operating conditions of olefins furnaces, and to provide a broad range of properties and benefits inclusive of a carbon-free or a low-coking environment (achieved by extreme inertness to

filamentous coke-make, and gasification of other sources of carbon such as amorphous or gas-phase coke).

2. **Novel cost-effective coating manufacturing technology** has been developed for application of catalyst coatings to internal surfaces of tubulars and fittings, covering the broad range of dimensions and shapes used in most olefins furnaces.
3. A **non (low) coking environment** on surfaces has been successfully demonstrated at laboratory, pilot and commercial-furnace scale, providing for opportunities to bring positive catalytic impacts to the pyrolysis process (customer driven).
4. **Carbon gasification** using catalyst coatings has been successfully realized and quantified at laboratory-scale. The level of gasification is engineer-able (tunable) by the level of catalytic efficacy imparted to the surface, based primarily on catalyst composition and surface loading. This is expected to provide significant latitude in end-user defined caps on byproducts from furnace coil surface reactions, inclusive of CO and CO₂, while ensuring sufficient surface gasification capacity to meet or exceed the overall carbon load under specified cracking conditions.
5. **Laboratory-scale mapping of pyrolysis operating latitude** of process is being aggressively pursued to map out key operating regimes, inclusive of temperature and steam dilution requirements and opportunities through to the limits of low steam cracking.
6. **Field trials** commenced in 2005 aimed at validating the technology in a commercial furnace; results to-date (subject to adequate feedstock contaminants control) are good-to-excellent and correlate well with laboratory-scale results and projections. Field trials are expanding to increase furnace designs, feedstocks, and operating conditions.
7. Applicability to a **broad range of alloy compositions** is continuing, primarily within the realm of austenitic stainless steels that currently includes HK40 through to 35Cr-45Ni-Fe alloys.

Acknowledgements

The authors would like to thank the managements of NOVA Chemicals Corporation and Quantiam Technologies Inc. for permission to publish this work. The R&D project teams would like to thank the exceptional support, co-operation, and patience of the Operations groups at the NOVA Chemicals' Joffre and Corunna plantsites. Finally, the project teams would like to acknowledge and thank partial funding of this development effort by Sustainable Development Technology Canada (SDTC) and an investment by Industry Canada – Technology Partnerships Canada (TPC).

4.0 REFERENCES

1. P. S. Broutin, F. Ropital, M. F. Reyniers and G. F. Froment, *"Anticoking Coatings for High Temperature Petrochemical Reactors"*, Proceedings of the 10th Annual Ethylene Producers' Conference, New Orleans, Louisiana, March 8-12, 1998, pp. 22-46.
2. S. Petrone, R. Mandyam, A. Wysiekierski, K. Tzatzov and Y. Chen, *"A Carbon-like Coating for Improved Coking Resistance in Pyrolysis Furnaces"*, Proceedings of the 10th Annual Ethylene Producers' Conference, New Orleans, Louisiana, March 8-12, 1998, paper 17e, pp. 157-187.
3. B. Ganser, K. A. Wynns and A. Kurlekar, *"Operational Experience with Diffusion Coatings on Steam Cracker Tubes"*, Materials and Corrosion, 1999, Vol. 50, No. 12, pp. 700-705.
4. L. Benum, *"Achieving Longer Furnace Runs at NOVA Chemicals"*, Proceedings of the 14th Annual Ethylene Producers' Conference, New Orleans, Louisiana, March 2002, paper 91d.
5. R. L. Deuis, A. M. Brown and S. Petrone, *"Hot Erosion Wear and Carburization in Petrochemicals Furnaces"*, Materials and Corrosion", 2006, Vol. 57, no. 2, pp. 135-146.
6. R. L. Deuis, A. M. Brown and S. Petrone, contributors to European Federation of Corrosion Series, EFC Publication Number 47, *" Novel Approaches to the Improvement of High Temperature Corrosion Resistance"*, Woodhead Publishing, in Press for May 2008.