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CATALYZED-ASSISTED MANUFACTURE OF OLEFINS (CAMOL): YEAR-(4) UPDATE ON COMMERCIAL FURNACE INSTALLATIONS

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CATALYZED-ASSISTED MANUFACTURE OF OLEFINS (CAMOL)*: YEAR-4 UPDATE ON COMMERCIAL FURNACE INSTALLATIONS

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Abstract: The development of a novel furnace coil coating technology* has been completed that is capable of providing coke-free performance in furnace coils used for olefins manufacture. Major breakthroughs have been realized to overcome the limitations of coatings from the 20th century primarily through novel, *nano-enabled* coating processes. The new coating technology, Catalyzed-assisted Manufacture of Olefins (CAMOL), has been in commercial furnace trials since September 2006 for field-demonstration of primary performance benefits, and to map out operational latitude and limitations across a broad range of furnace designs and feedstocks. The new coatings were engineered with 21 chemical, physical and thermo-mechanical properties deemed critical in securing commercial viability. Field results, now into Year-4, have confirmed achievement of the most critical properties to ensure survivability, with optimization now completed for an optimal balance of properties for a 5-10 year coil lifetime.

The realization of non-coking coil surfaces for extreme operating conditions and a broad range of feedstocks enables additional engineerable catalytic impacts to be incorporated within the steam hydrocarbon pyrolysis process. With coating survivability and other key properties secured, CAMOL has now been incorporated into furnace coils of five commercial furnaces (4 coil designs) with major olefins producers, covering feedstocks ranging from ethane through to naphtha at various levels and types of surface catalytic activity. Planned installations and trials for 2010 and 2011 include Linde, Lummus and Technip furnaces with naphtha feedstocks ranging from low to high quality. Lighter feedstock trials are also being pursued primarily at the operating limits of furnace cracking technologies. This paper will update on field and laboratory results achieved to-date against technology targets and expectations that include:

- 1-2 year furnace run-lengths in lighter feedstocks (100-400 days in heavier feedstocks), depending on feedstock quality and operating conditions;
- high operating-temperature stability (>1130^{o}C (>2066^{o}F));
- significant reductions in average TMT operating temperature;
- significant reductions in energy requirements and GHG emissions;
- compatibility with elevated sulfur levels and feedstock contaminants;
- potential for reductions in steam dilution levels;
- potential for higher conversion levels; and/or
- neutral or positive impacts on product slate.

It is recognized that furnace and plant-specific drivers will dictate which combination of the above new materials benefits deliver the greatest economic impact to a petrochemical facility.

An update will also be presented on efforts aimed at expanding the use of the CAMOL technology, for example, to produce a high heat-transfer tube with internal tube surface area approaching external tube surface area, with the full coke-free catalyst-coating benefits of CAMOL; a Generation-II product in 2012+ targeting to provide additional benefits including a further TMT temperature reduction; and an enhanced compatibility with lower-quality heavier feedstocks.

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1.0 INTRODUCTION

The manufacture of olefins by hydrocarbon steam pyrolysis remains the primary commercial scale route for producing light olefins and now exceeds 110 million tonnes of ethylene production per year. Process evolution has provided greater single-furnace capacities as new coil alloy materials and furnace designs became available with tube-metal-temperatures (TMTs) now routinely exceeding 1100°C (2012°F). Modern world-scale plants can produce >2 billion pounds per year of ethylene with as little as 5-7 furnaces. Furnace coils have evolved in alloy composition and properties over the last 50+ years to sustain the higher severity of operation, with a commensurate increase in unwanted or <u>negative</u> catalytic reactions at the coil surfaces and other carbon-based fouling mechanisms such as amorphous or gas-phase coke accumulation. These phenomena are well established, and efforts aimed at understanding their mechanisms to better drive technology developments towards mitigation, have made some progress over the last two decades[1-5]. Materials developments have included better alloys, coil surfaces and coil coatings aimed primarily 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). Overall, efforts at improving furnace coil surfaces worldwide have led on average to furnace run-lengths in the industry at least doubling over the last decade from ~20-40 days to ~40-80 days on-line but rarely exceeding ~100 days; exceptions of >500 day run-lengths have been realized with the ANK 400 product[4,5]. Success with coatings and surfaces also 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, and primarily move towards steels with higher temperature-stable surfaces such as alumina (or mixed-alumina) formers. Several alloy suppliers currently market such products and overall these alloys have had mixed results in the field. In any event, the use of an internal inert furnace coil surface can only address the mitigation of filamentous or catalytic-coke and does very little for reducing amorphous coke build-up, which is the dominant source of coke when cracking heavier feedstocks.

The catalyst-coating technology initially reported in 2008 and now being updated in this Extended Abstract, **<u>C</u>**atalyzed-**<u>a</u>**ssisted **<u>M</u>**anufacture of **<u>Ol</u>**efins (CAMOL)[6], targets amongst its range of benefits carbon-free furnace coil performance for extended periods of time (years) for a broad range of feedstocks and operating severities. Additionally, it aims to provide an overall reduction in average operating temperature over a run-length, lower steam dilution requirements and the potential of a positive impact on the product slate. Collectively, these benefits can provide greater operating efficiencies mainly through capacity gains and energy savings. To achieve these objectives, CAMOL mitigates both major sources of coke-make, filamentous and amorphous. The product utilizes a coating matrix to secure viability in service, and the ability to generate, regenerate, and sustain an outermost surface in contact with the process stream which eliminates filamentous (catalytic) coke formation, and catalytically gasifies carbonaceous matter that would otherwise deposit and collect, with acceptable levels of CO and CO_2 byproducts. From a carbon balance perspective, as this gasification is limited to the carbon that would have otherwise collected on the internal coil surfaces, impact on total CO/CO_2 is both manageable and tunable in terms of level and relative make-up. **In effect, the coating ensures that if the furnace coil internal surface is to be catalytic, should it not provide positive catalytic impact to the cracking process by maintaining carbon-free surfaces through gasification?** It is projected that based on the current rate of innovation and adoption of furnace coil surface control and related operational improvements, operating run-lengths reaching or exceeding 1,000 days under reasonable severities are possible this decade across a broad range of furnace designs and operating conditions.

2.0 CAMOL TECHNOLOGY UPDATE

2.1 Background and Targets

Quantiam is commercially introducing catalyst-coated furnace coils that effectively integrate robust catalyst formulations into commercially viable coating systems using current industry furnace alloys and furnace coil component geometries. The coatings are best described as composites, consisting of metallic and ceramic constituents. The manufacturing technology utilizes several aspects of *nano-enabled* processing to achieve critical properties previously unattainable within the coatings industry. Overall, these coatings are engineered with 21 chemical, physical and thermo-mechanical properties to achieve commercial survivability and the targeted surface functional efficacy. These properties can be divided into two groups, with the first group aimed at securing coke-free performance, and the second group targeted to secure survivability in one of the most extreme materials-use applications worldwide.

Group A Properties: Surface properties for achieving a Low-Coking Environment and Lower-TMTs/Energy/GHG

Surface chemical composition and structure that:	
1	is inert to catalytic (filamentous) formation of coke
2	provides catalytic gasification of carbon at elevated cracking temperatures (>700^{o}C (>1292^{o}F)) - full range of carbon sources with operationally-manageable levels of CO and CO_2
3	provides catalytic gasification of carbon at low operating temperatures (400-700^{o}C (752-1292^{o}F)) with specified sources of carbonaceous matter and remaining within acceptable levels of CO and CO_2
4	has no negative impact on pyrolysis process and product stream
5	has a positive catalytic impact on conversion and product yields
6	is compatible with a significant reduction in steam dilution requirements

Group B Properties: Material Properties for Achieving Furnace Survivability, Robustness and Longevity

Coating System Capable of:	
1	in-situ repair/regeneration of outermost surface layer
2	thermal stability to exceed operating temperature range of current furnace technologies at TMTs (>1100^{o}C (>2012^{o}F))
3	thermal Shock Resistance – Coefficients of Thermal Expansion (CTEs) matched to allow for emergency power outages and other process upsets
4	hot erosion resistance
5	carburization resistance provided through a surface barrier
6	carburization resistance provided through intrinsic enhancement
7	oxidation resistance provided through a surface barrier
8	oxidation resistance provided through intrinsic enhancement
9	corrosion resistance to feedstock halogen contaminants
10	corrosion resistance to feedstock Group-I metals contaminants
11	corrosion resistance to feedstock and added sulfur levels (H_2S, DMS, DMDS)
12	creep resistance
13	metal dusting resistance
14	coating system bond strength exceeding UTS of base alloy (~60-70 ksi)
15	coating system ductility to exceed elastic limit of base alloy

Two coating systems have been extensively tested both at laboratory/pilot scale, and in commercial furnaces since 2005 (longevity testing), and subsequently optimized following five furnace trials for commercial introduction in 2010. 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 Operating Temperatures***
CAMOL **LCG**	• **Low**-level **c**atalytic-**g**asification • High-level surface coverage of catalyst	• Ethane/Propane • Butane	Catalytic, 500-1130^{o}C Inert >1150^{o}C
CAMOL **HCG**	• **High**-level **c**atalytic-**g**asification • Low-level surface coverage of catalyst	• Butane • Naphthas	Catalytic, 750-1150^{o}C

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

The LCG coating can now be deposited on the full range of tubular and fittings dimensions and geometries currently used in cracking furnaces, at thickness ranging from 50-5,000 microns with ~10% variation in radial and longitudinal uniformity on tubes. For olefins furnace trials to-date, it has been deposited in thicknesses ranging from 200 to 1,000 microns. An SEM micrograph of a metallographic cross-section of a

1,000 micron thick coating is shown in Figure 1(a). An SEM micrograph of the topmost surface is shown in Figure 1(b). Based on all laboratory and field-testing to-date, a 1,000 micron thick LCG coating is projected to exceed by a factor of at least 2, the minimum thickness required for achieving one standard furnace coil lifetime, that is, commercial introduction in 2010 will be at <500 microns with some fittings or specific locations coated to a higher thickness as deemed necessary.

(a) **(b)**

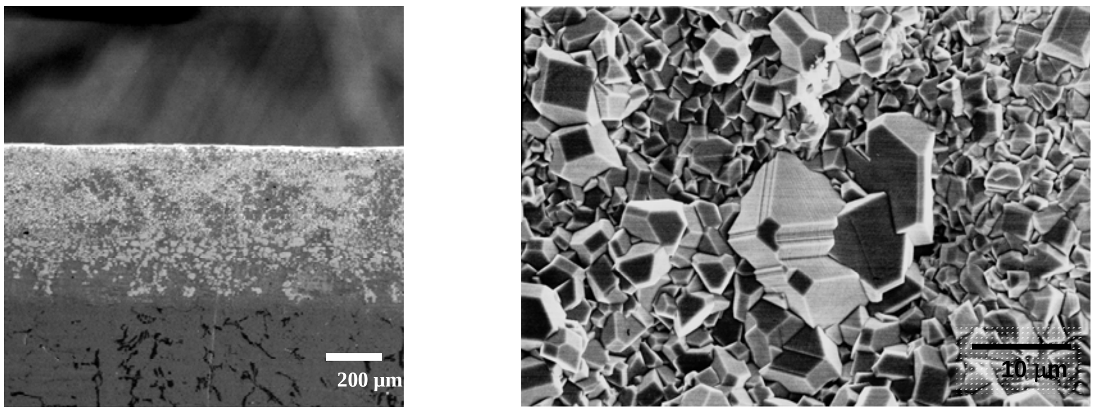

Figure 1: (a) An SEM micrograph of a metallographic cross-section of the CAMOL Low-catalytic Gasification coating ~1,000 microns thick; (b) An SEM micrograph of the topmost surface of the CAMOL Low-catalytic Gasification (LCG) coating.

It is noted that at extreme temperatures >1150^{o}C, the LCG coating loses its catalytic properties and is simply inert. This catalytic property is recoverable under normal operating temperatures.

2.2 Laboratory-scale Test Results

The laboratory and field work undertaken to develop and commercialize the CAMOL technology has been previously reported[6]. Key updates on areas of optimization that have been advanced are described below.

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; and
- thermal stability of the coating matrix to sustain the surfaces and allow for their regeneration as required.

The stability targets of the outermost CAMOL surfaces under cracking conditions were for temperatures in excess of 150^{o}C (302^{o}F) greater than the industry-standard alloy surface of chromia. CAMOL surfaces have been confirmed to have stability under standard cracking conditions of at least 1130^{o}C (2066^{o}F). It is expected that if the oxidizing potential of the feedstream is materially reduced (for example, lower steam levels), the internal surface stability of any oxidic surface species will be impacted and needs to be considered in the decision. The thermal stability of the coating-matrix structure that sustains and regenerates CAMOL surfaces as required, has been optimized to exceed 1150^{o}C (>2102^{o}F). Further improvements are projected for both the surfaces and the coating matrix.

High Temperature Corrosion Degradation: High temperature corrosion testing previously reported showed excellent resistance to carburization and oxidation, both through surface barrier protection and intrinsic protection[6]. Subsequent work has focused on field longevity testing, which to-date has confirmed compatibility with a broad range of feedstock contaminants, and within recommended furnace operating temperatures. Additional accelerated laboratory testing is planned for specific contaminants to support trials using feedstocks with unique levels of contaminants.

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. Laboratory testing of the catalysts under H_2S exposure conditions was expanded up to 1,000 ppm sulfur and 900^{o}C (1652^{o}F) process gas temperature. The catalysts were characterized both prior to and after testing for composition and stoichiometry, crystal structure, morphology, and catalytic efficacy. Results have shown that for the catalyst species of both CAMOL LCG and HCG coatings, no detectable changes in the above properties were observed for the test conditions used. Field trials have been in service since 2005 with some test feedstocks exhibiting total sulfur levels exceeding 1,000 ppm and spiking as high as 3,000 ppm. Plans are to map-out through to 5,000 ppm sulfur.

Hot Erosion Resistance: Hot erosion can play a 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 has become more important as run-lengths reach 1-2 years with future targets of 1,000+ days. The erosion resistance of a material is dependent on many properties including hardness and fracture toughness. The CAMOL LCG coating can be deposited to exhibit hardness of up to 3X that of the base austenitic steel. To-date for areas requiring such hot-erosion enhancement, the components have been coated with a Quantiam[7] hot-erosion coating.

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 was undertaken at a broad range of levels, inclusive of a thermal shock delta of ~1,000°C in <1 sec. Field results have supported that this property has been well engineered to a significant level of excess.

2.3 Pilot-scale Pyrolysis Testing

Pilot-scale pyrolysis testing results obtained under standard cracking conditions using ethane were reported previously and showed attractive flat-line response on pressure drop changes as a function of cracking time, and low propensity for downstream fouling[6]. Current testing through to 2011 is focusing on mapping the operational latitude possible under non-standard or unconventional cracking conditions enabled by the new CAMOL coating materials capabilities. The effort will focus primarily on two feedstocks:

Ethane: conversion rates of >70%; steam dilution level of <28 wt %; with and without a coke-free high internal surface area/high heat-transfer tube.

Naphtha: to be finalized once ethane testing is completed and with inputs/preferences/needs from CAMOL commercial-scale users. Current plans are focusing primarily at securing a product slate shift through catalyst species selection and catalyst surface loading.

2.4 Commercial-scale Field Trials

2.4.1 Crystallization of CAMOL's Basic Operating Benefits

Commercial-furnace trials with at least 50% of the radiant section coated with CAMOL commenced in September 2006 and progressively increased to full furnaces with subsequent trials. The original CAMOL-coated furnace coils are now in Year-4 of operation. Three additional furnaces have been installed since then in North America and Europe, covering feedstocks from ethane through to naphthas, all with conservative catalyst surface loadings aimed at securing directional information on what may be possible or achievable while ensuring low operational risks to the furnace and manageable levels of CO and CO_2.

Field trials were designed primarily to map-out the operational latitude of the CAMOL products, rather than maximizing realizable benefits for marketing purposes. This approach has proven very useful in working towards an optimized coated product prior to commercial introduction. Results to-date have confirmed that the originally engineered properties of the coatings have either been demonstrated or are on track to meet targets under standard cracking conditions. A good challenge has been in optimally exploiting the new materials properties enabled by CAMOL for commercial benefit within the economic drivers of a specific plantsite or perhaps even at the furnace level in operating regimes never before accessible. Ideally, this requires first mapping and testing at a laboratory or pilot-scale the proposed operating regime to understand potential impacts on the coatings and their surfaces. In other words, a producer has the choice of exploiting:

1. a coke-free or low-coking environment; or
2. reduction in average operating temperature (energy and GHG emissions); or
3. increased operating severity; or
4. lower level of steam dilution; or
5. an optimal combination of (1) through (4).

Maximizing any one benefit would be furnace/plant-specific, while recognizing that exploiting, for example, Benefit-(3) of higher operating severity, would likely impact what is achievable with Benefit-(1) of overall run-length. Efforts are underway to map out 2 and 3-level synergies accessible by the new CAMOL material limits.

2.4.2 Optimizing to Secure Full Range of Potential Commercial Benefits

As the primary properties and benefits of the CAMOL product continue to be crystallized and mapped towards full furnace life-cycles, through normal operation, planned shutdowns and unplanned outages, efforts have shifted to securing the full range of benefits made possible through a coke-free or low-coking environment within the radiant section. Two areas of future focus are dealing with feedstock quality, and optimal requirements on the inlet (convection section) and the outlet (TLE) of trial furnaces, specifically as to how these furnace areas may impact overall coated furnace coil performance.

Feedstock quality (contaminant) control has been a major challenge in the industry, especially with heavier feedstocks given the variability of their source and the broad range of contaminant concentrations encountered. The micrograph in Figure 2 exemplifies this challenge in a controlled laboratory coking test of a CAMOL HCG surface capable of maintaining coke-free performance over a broad range of operating conditions. The results show the achievement in the engineering of the coke-free coating surface; however, a contaminant particle that is Fe-Ni bearing was found on the surface after the test, showing a high rate of filamentous coke build-up. Past AIChE Roundtable discussions indicated that a number of producers typically filter feedstock for many of their naphtha crackers. There are a number of commercial filtering technologies available, for example by Pall Corporation[8], that generally involve both coarse and fine filtering stages, often using coalescing filter technology. An example of filter-captured contaminants in a commercial naphtha cracker are shown in Figure 3, below. It is reasonable to propose that if the surface loading on coil internal surfaces from say Fe-based contaminants is excessive, it will limit the performance achievable by any enhanced surface coil technology, be it an enhanced bulk-alloy, an enhanced surface, or a coating. In any event, it is expected that the furnace-coil performance will ultimately reflect a surface composition that is defined primarily by the contaminants.

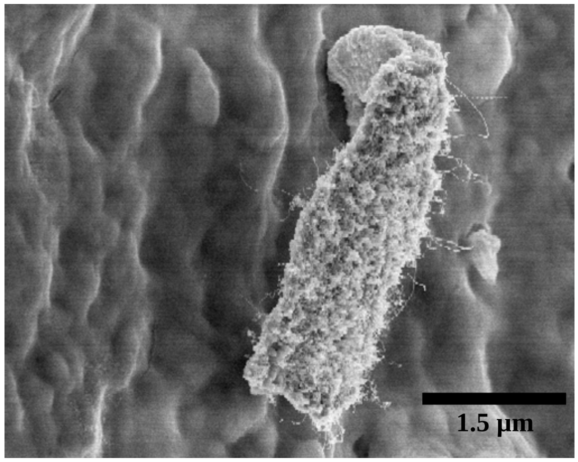

Figure 2: Surface of a CAMOL High-catalytic Gasification (HCG) coating after laboratory-scale coking test (ethane, S:H of 0.3:1, 825°C). The CAMOL outer surface in the background is coke-free, while the surface of an Fe-Ni contaminant particle shows extensive filamentous coke-build.

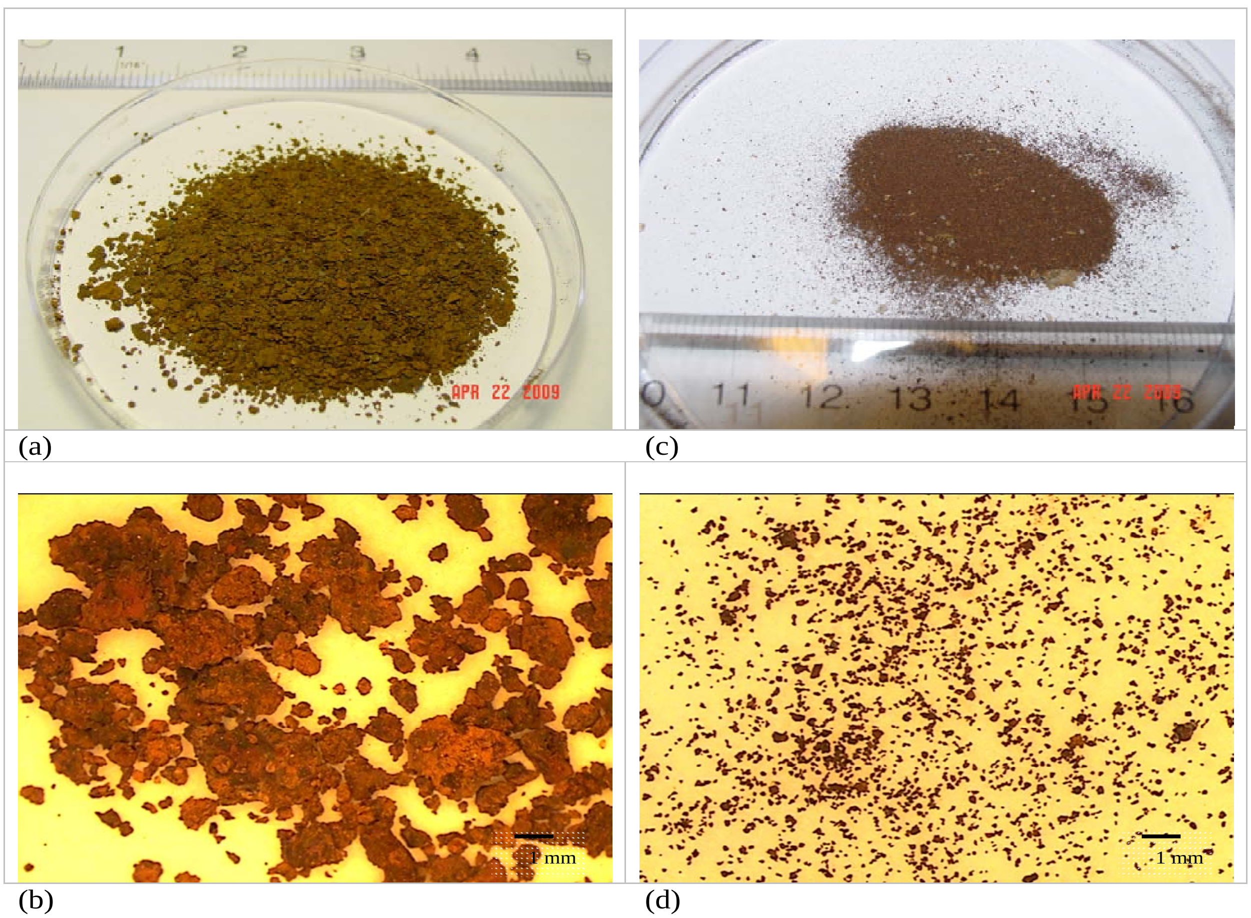

Figure 3: Naphtha feedstock contaminants trapped in a coarse filter (a) and (b), and a fine filter (c) and (d). XRD and SEM/EDS analyses show primarily Fe-based contaminant particles.

2.4.3 Focus of Future CAMOL Furnace Trials

Building on advancements made in providing a broad based low-coking environment and achieving survivability at significant operating severities, CAMOL's commercial introduction is focusing on its use in other furnace designs, and mapping achievable combinations of performance benefits as a function of critical furnace operating parameters and variables. Trials are being planned to continue to push the extremes of operating regimes on temperature, conversion/selectivity/yields, and steam dilution levels, with a preference on furnace environments with lower or controlled feedstock contaminant levels. Figure 4, below, summarizes installations completed to date by operating temperature on the y-axis as TMT-EOR (pre-CAMOL), furnace capacity, and a rudimentary classification of feedstock contaminant levels on the x-axis. It is recognized that classification of feedstock contaminant levels is very complex, and its overall impact on furnace coil performance equally so. The Fe and S levels noted at the bottom of Figure 4 are primarily for illustrative purposes only.

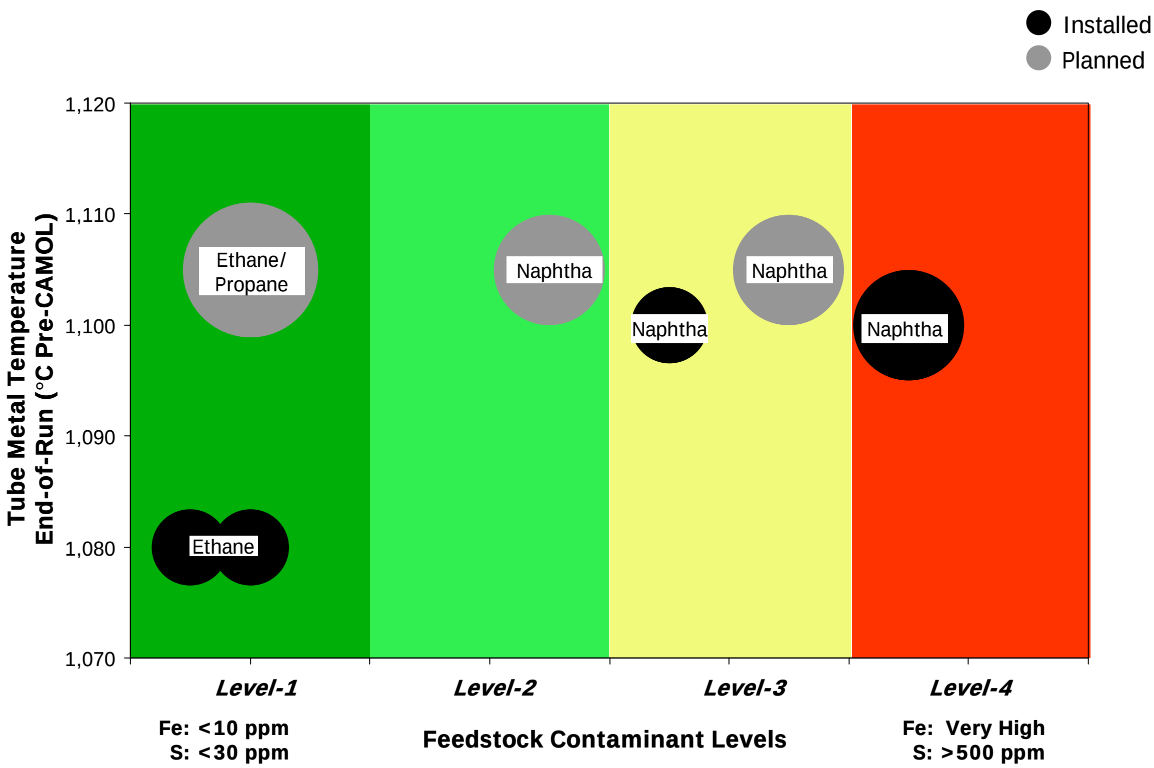

Figure 4: Existing and planned CAMOL furnace installations with level of feedstock contamination (x-axis), pre-CAMOL operating temperature (y-axis), and furnace capacity (size of bubble).

Results show that adequately addressing both of the major coking mechanisms in the radiant section, while ensuring survivability, can provide material gains in furnace performance of at least a multiple on run-lengths, and significant operating temperature reductions. Furthermore, reasonable efforts at improving feedstock quality and reducing convection-section impacts should, significantly, provide another major gain on overall coated furnace coil performance. As the CAMOL-Generation-I product moves to commercial availability incorporating learnings over the last 9 years of development, testing and trials, work is also being undertaken towards a Generation-II product with a step gain in performance benefits that assumes very attractive economic drivers for CAMOL use when coupled with feedstock contaminant improvements.

3.0 YEAR-4 OVERALL TECHNOLOGY ASSESSMENT AND FUTURE OPTIMIZATION AND DEVELOPMENT PLANS

Based on all laboratory, pilot and commercial-scale testing of CAMOL to-date, Table 1 below summarizes the key benefits crystallized or targeted in Year-4 of field trials (at March 2010), and advancing towards completion of one life-cycle. The benefits ranges in Column-(3) reflect projected achievable levels as a function of key operating variables such as feedstock quality, for example, as identified on the x-axis of Figure 4 above. As previously noted, the individual benefits are within reasonably standard operating regimes and reflect an end-user approach to maximizing an individual benefit, rather than exploiting potential synergies among benefits. It is important to recognize that significant latitude is provided by CAMOL outside of normal operating conditions; however, it should be noted that, for example, if one operates in a higher severity mode outside of standard conversion or steam dilution, it is reasonable to expect that there may be an impact on run-length due to the higher coking regime enabled. Under such new operating conditions, it is important to ensure that the coated product was imparted with adequate catalytic efficacy to manage the incremental carbon load at the surface to offset the end-user's intent to operate in more extreme regimes. This is achievable, but needs to be incorporated at the coating stage as a tunable property, much like the base composition of the tube is preselected for the range of operating temperature that it will ultimately see. Efforts are underway to understand 2 and 3-level interactions and potential synergies among benefits.

Finally, Column-(4) of Table 1 looks forward 3-4 years based on crystallized and projected successes with Generation-I of the product, and summarizes current targets for a Generation-II product This assumes success with ongoing developments and optimization of the CAMOL coating technology, together with reasonable control on feedstock contaminant quality and impacts from the convection section of the furnace.

Table 1: CAMOL Technology Status in Year-4 of Commercial Furnace Trials (at March 2010) – Crystallized and Projected Achievable Benefits

1	2	3		4	
CAMOL at March 2010	***Industry Reference***	**CAMOL Gen-I Benefits Crystallized and/or Targets***		**CAMOL Gen-II Targets***	
		Lighter Feedstocks	**Heavier Feedstocks**	**Lighter Feedstocks**	**Heavier Feedstocks**
Commercial Availability		**2010**		**Under Dev't**	
Furnace Run-length	*10-90 days online*	1-2 years	100-400 days	1000+ days	200-500 days
Temperature Reduction (TMT/SOR/EOR)		20-60^{o}C	20-60^{o}C	40-100^{o}C	40-100^{o}C
Steam Reduction	*Use 30-50 wt% steam*	10-25%	10-25%	15-40%	15-40%
Energy (and GHG) Reductions	*Use 20-40 GJ/Tonne EE*	3-12%	3-12%	5-20%	5-20%
Furnace Coil Lifetime	*3-7 years*	4-7 years	4-7 years	6-12 years	6-12 years
Maximum Operating Temperature (TMT)	*Use 1050-1120^{o}C*	1130^{o}C	1130^{o}C	1150^{o}C	1150^{o}C
***In-situ* Surface Repair/Regeneration**		LCG: >5 regenerations; HCG: 3 regenerations + >3 LCG regenerations		▪ passivation of non-CAMOL parts of circuit ▪ recovery from a major feed contamination event	
High Heat Transfer Tube with CAMOL Coating		N/A	N/A	Surface Area of ID >= OD + increase in turbulence	

* Level achieved dependent on furnace design, operating conditions, feedstock quality and fraction of circuit retrofitted with CAMOL.

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