Catalyzed-assisted Manufacture of Olefins (CAMOL): Year-4 Update on Furnace Installations

Steve Petrone, Robert L. Deuis, Fuwing Kong and Peter Unwin

Quantiam Technologies Inc.
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CAMOL

(Catalyzed-assisted Manufacture of Olefins)

1. Quantiam Experience in HT Coatings
2. What is CAMOL & Why Developed?
3. Performance Achieved and Targeted
4. Questions from the Marketplace

Quantiam

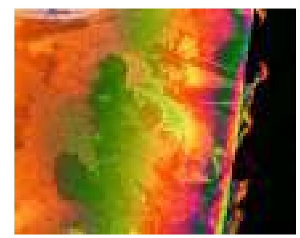
is an advanced nanomaterials company

that develops and commercializes disruptive new products

based on advanced materials, catalysts, coatings and

surfaces for extreme-operating environments

Disruptive Coated Products for Extreme Environments

	Key attributes	Status	
CAMOL Coatings	• Low-coking requiring fewer de-coke cycles • Lower operating temperature providing lower energy consumption and GHGs • Increase in throughput with reduced steam dilution levels & higher conversion	• Ready for commercialization	
HT Wear Coatings	• Provide a previously unattainable ceramic level of hardness and wear resistance, with the ductility and fracture toughness of metals (to 1100°C) • Extended longevity of parts and enhanced productivity	• Ready for commercialization	
Corrosion Coatings	• Advanced corrosion protection of industrial complex shapes; • Synergy with wear protection	• R&D with prototypes and field trials in late 2009	
Defence Materials	• High temperature (>1200°C) coatings for weapon systems (resistance to hot erosion, hot corrosion and ablation)	• Phase I prototyping underway • Phase II trial mfg to begin in 24 months	

CAMOL's 21 Engineered Properties for Viability & Functionality

Surface Properties to achieve low-coking 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)
3. provides catalytic gasification of carbon at low operating temperatures (400-700^{o}C)
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 dilution steam-requirements

CAMOL's 21 Engineered Properties for Viability & Functionality

Material Properties to Achieve Survivability, Robustness and Longevity

Coating matrix capable of:

7. in-situ repair/regeneration of outermost surface layer
8. thermal stability to exceed operating temperature range of current furnace technologies at TMTs (>1100^{o}C)
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_2S, 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

What is CAMOL and Why Developed?

CAMOL is: <u>**C**</u>atalyzed-<u>**a**</u>ssisted <u>**M**</u>anufacture of <u>**Ol**</u>efins

to shut down filamentous coke-make <u>**and**</u> gasify amorphous coke to CO/CO_2

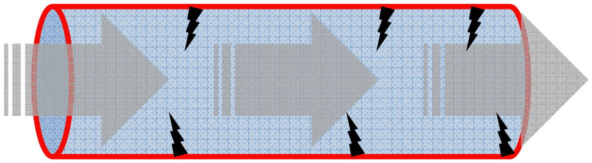
Why CAMOL? Furnace coil surface can exhibit:

1. Unwanted catalysis at coil surface with rapid filamentous coke-make; accelerates amorphous (gas-phase) coke accumulation
2. Inertness to filamentous coke-make (alloys, coatings, surfaces, additives) - 20^{th} Century Technology
3. Coke-free performance through inertness to filamentous coke-make <u>and</u> gasification of amorphous coke - 21^{st} Century Technology
   - Once achieved with robustness and survivability at operating severities, other properties then engineerable

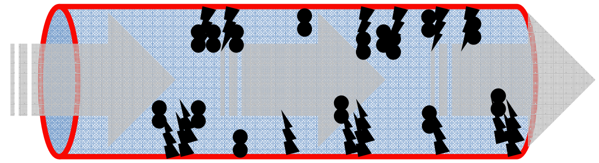
CAMOL is inert to filamentous coke and gasifies amorphous coke

Feedstock with steam
Filamentous coke
Amorphous coke
Gasified amorphous coke
CAMOL internal coating

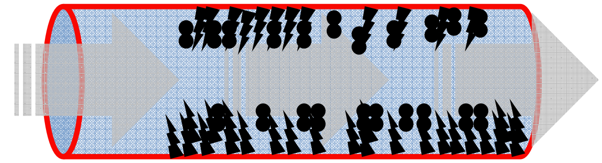
Typical coke formation in an untreated tube during steam cracking



T_1
Filamentous coke is created on the walls of a cracking furnace tube through bad, unwanted catalysis. The catalysis is a result of nickel and iron in the furnace tube's base steel.

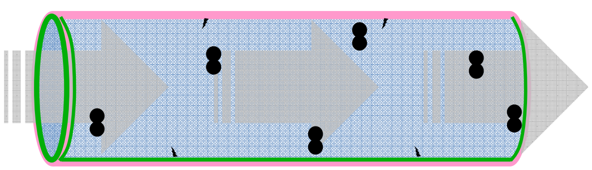


T_2
Filamentous coke-make continues building in hair-like structures. Amorphous coke, created by gas-phase cracking reactions collecting on the filamentous coke at a high rate.

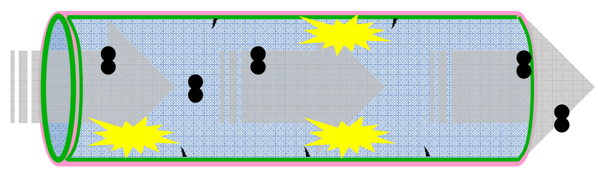


T_3
Filamentous and amorphous coke-make continue. Increases in tube pressure drops impacting feed rates and the coke acts as a thermal insulator, reducing the efficiency of heat transfer to the feed stream. Frequent de-coking is required to remove the carbon build-up.

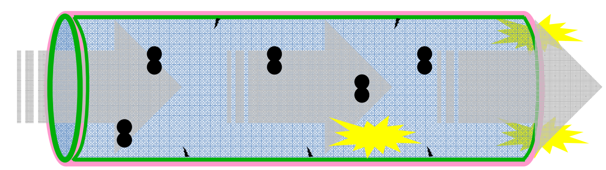
Typical coke formation in a CAMOL treated tube during steam cracking



T_1
CAMOL creates inertness to filamentous coke-make virtually shutting down this source of coke.



T_2
While amorphous coke is still created in a CAMOL coated tube, CAMOL gasifies amorphous coke to tuneable CO and CO_2 which exits the furnace.



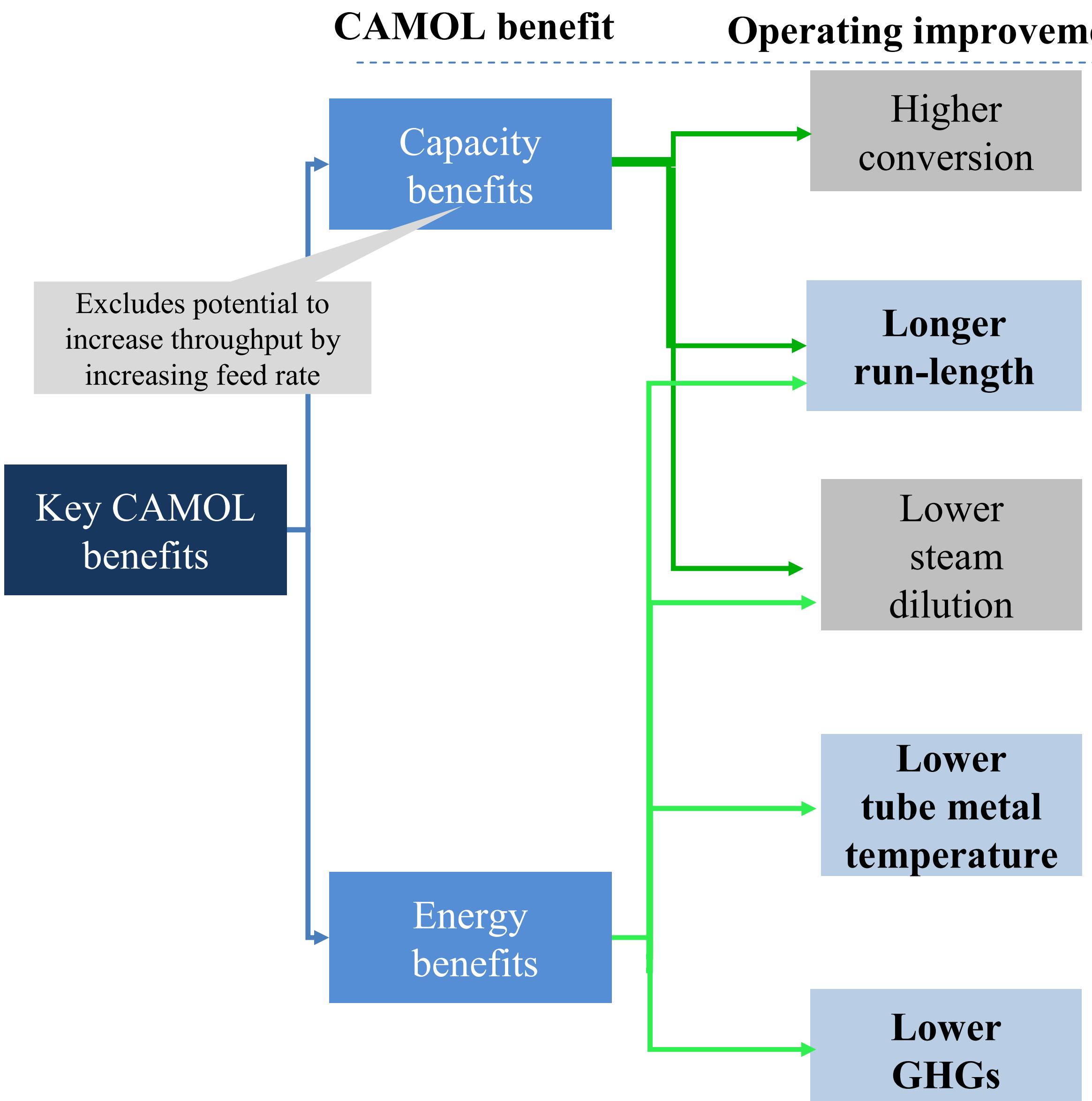
T_3
CAMOL's low-coking environment allows producers to run facilities at higher efficiency as a result of capacity gains (longer run-length, higher conversion, lower steam dilution) and energy savings (reduced de-coking frequency, lower tube metal temperature, lower steam dilution, lower GHGs).

CAMOL works by making coated furnace tubes inert to filamentous coke-make while gasifying amorphous coke

… an uncoated furnace tube cokes at significant rates

CAMOL is inert to filamentous coke-make…
… and CAMOL gasifies amorphous coke

In the field CAMOL has delivered significant capacity and energy benefits; some targets remain



Impact

- Low coking environment enables operating regimes at higher conversion

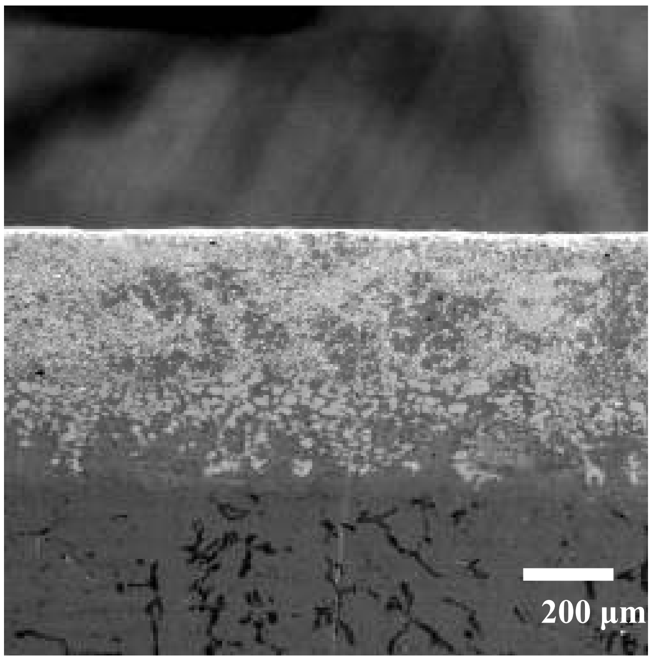
- Inertness to filamentous coke
- Gasification of amorphous carbon to CO/CO_2 (tunable)

- Outer coating surfaces stable down to significant reductions in oxidizing potential (relative to chromia) enabling lower steam dilution

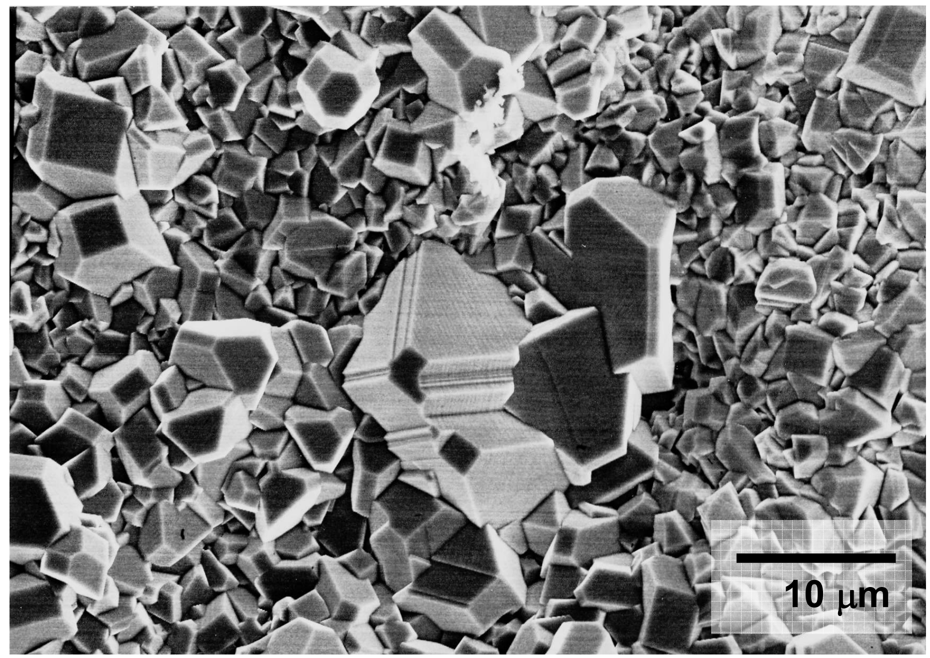
- Elimination of coke thermal barrier (and +ve catalytic impact) results in a 20-60^{o}C reduction with low catalyst surface-loading

- The CAMOL energy benefits permit less energy consumption in and thus lower GHG emissions

Micrographs of CAMOL
Low-Catalytic Gasification ("LCG") Coating

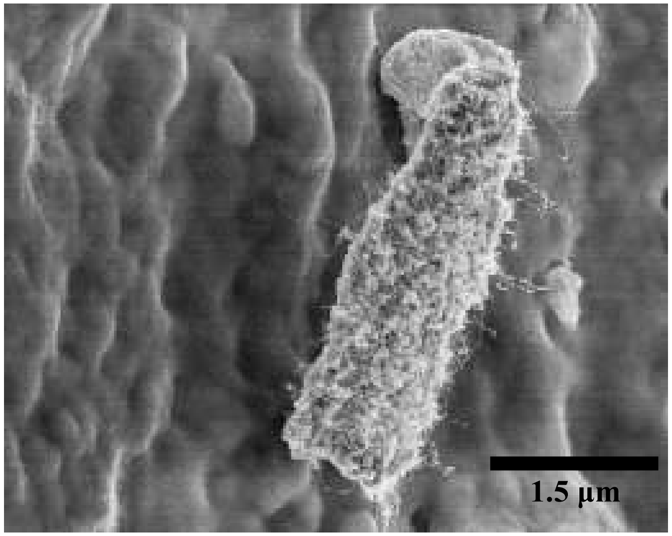


An SEM micrograph of a metallographic cross-section of the CAMOL Low-catalytic Gasification (LCG) coating ~1,000 microns thick



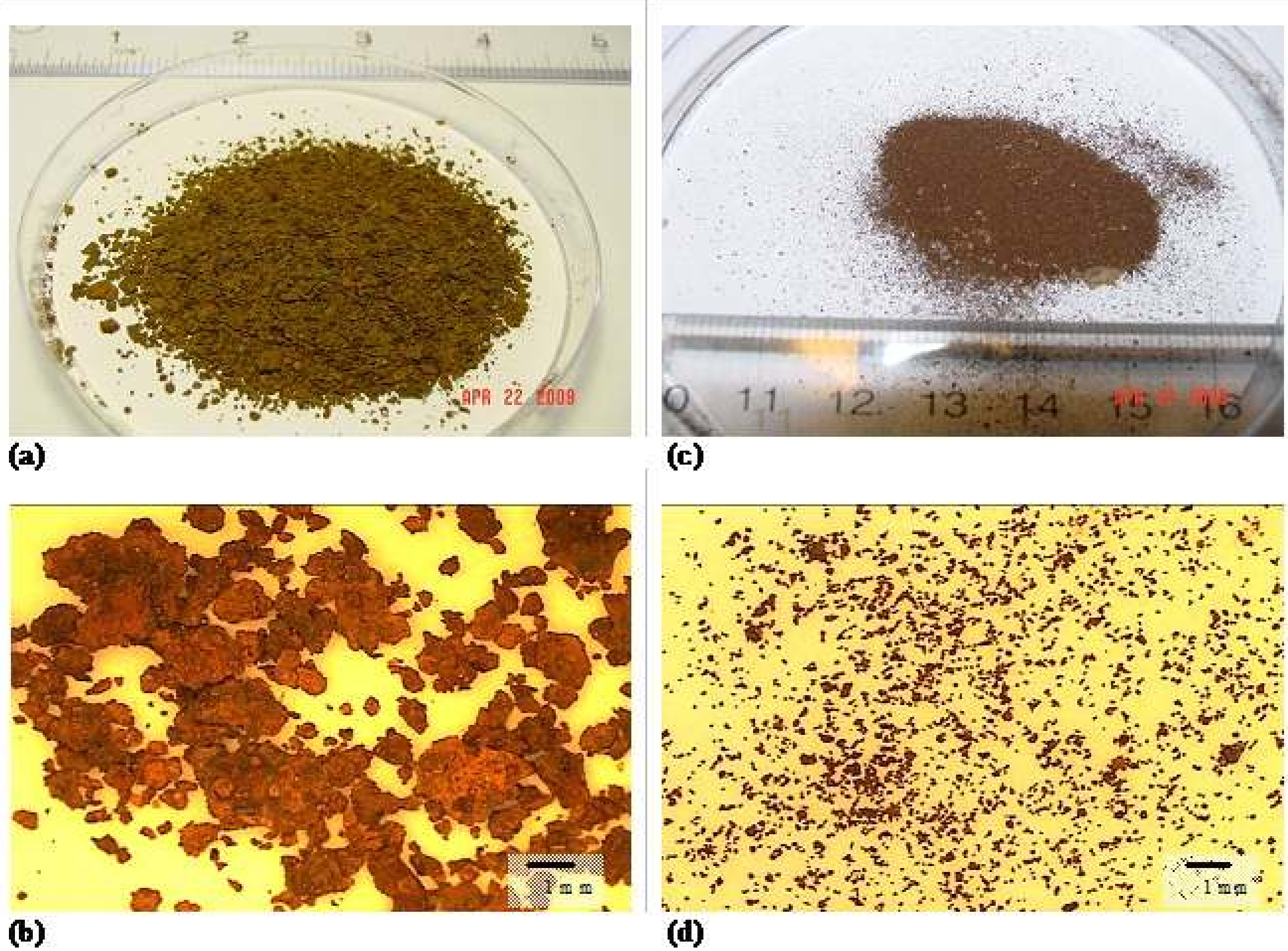
An SEM micrograph of the topmost surface of the CAMOL Low-catalytic Gasification (LCG) coating

CAMOL High-catalytic Gasification (HCG) Coating Surface after Coking Test



Surface of a CAMOL High-catalytic Gasification (HCG) coating after laboratory-scale coking test (ethane, S:H of 0.3:1, 825^{o}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

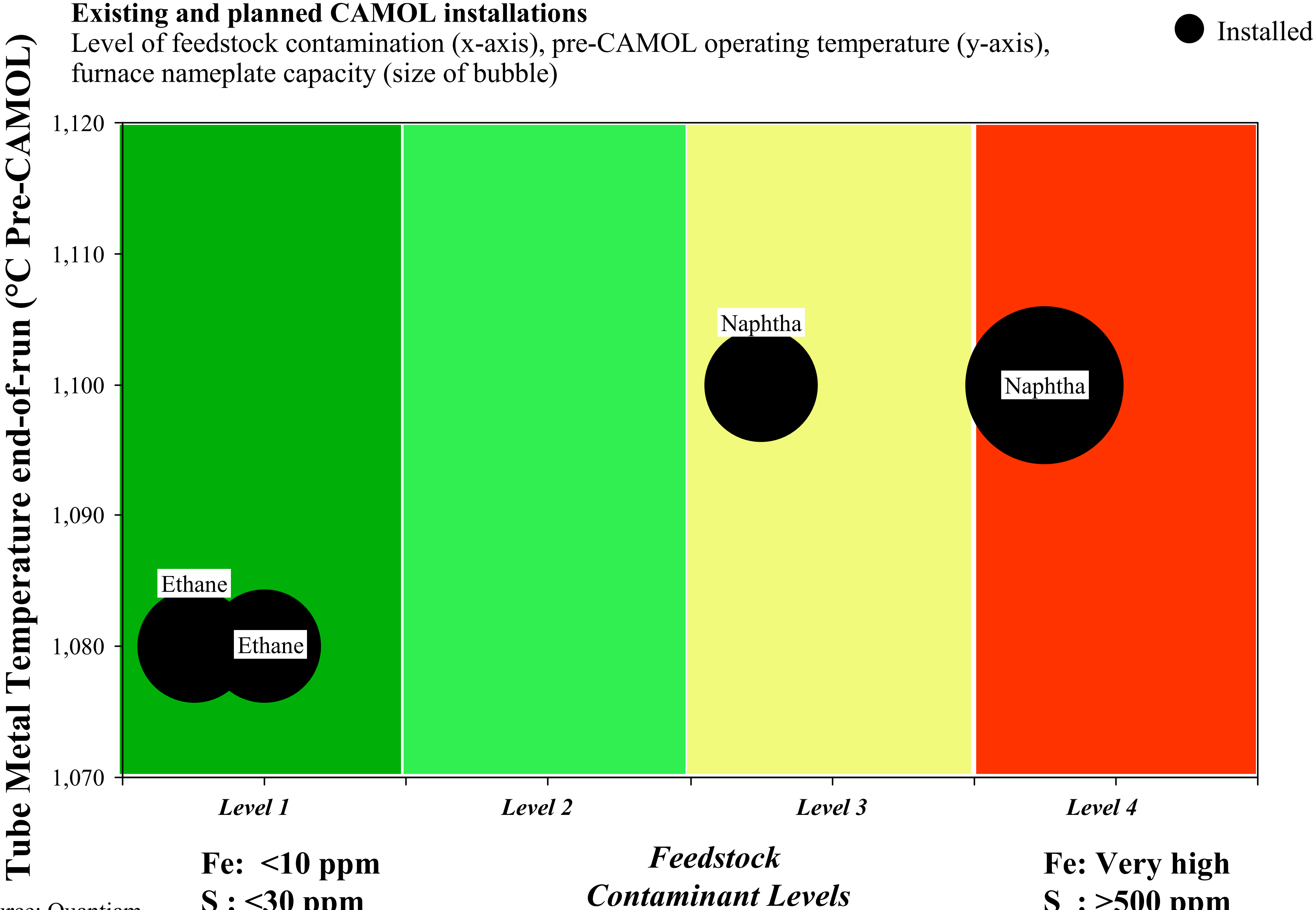
Naphtha Feedstock Fe-based Contaminants



Naphtha feedstock contaminants collected 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

Over last 4 yrs CAMOL installed in 4 furnaces in NA and EU; 3 add'l furnaces planned in the near term

Existing and planned CAMOL installations
Level of feedstock contamination (x-axis), pre-CAMOL operating temperature (y-axis), furnace nameplate capacity (size of bubble)



Source: Quantiam

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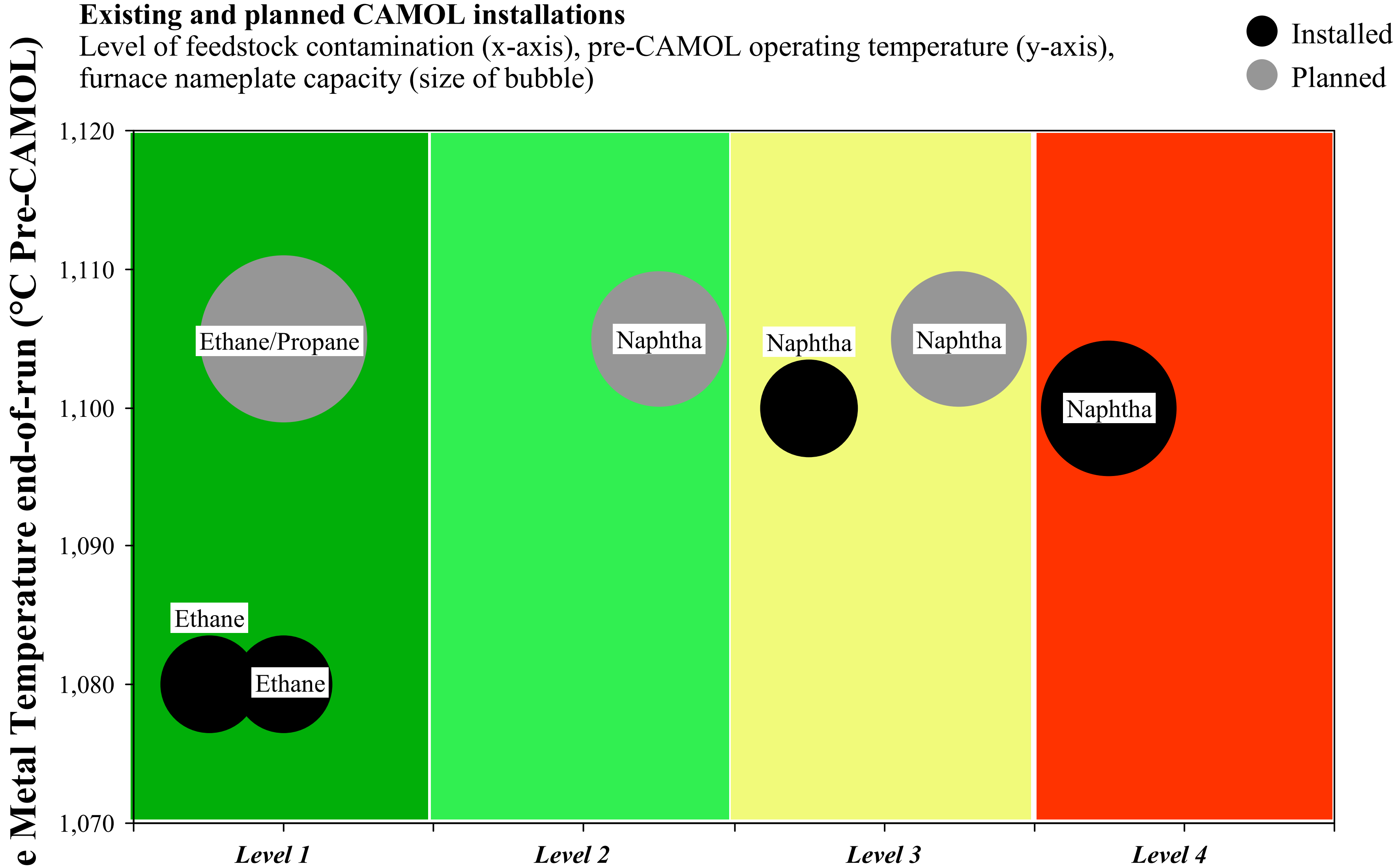

Fe: <10 ppm
S : <30 ppm

Feedstock Contaminant Levels

Fe: Very high
S : >500 ppm

Source: Quantiam

CAMOL has achieved significant results to date approaching 1 life-cycle; further enhancements planned for Gen-II

1	2				
CAMOL at March 2010	***Industry Reference***				
Commercial Availability					
Furnace Run-length	*10-90 days online*				
Temperature Reduction (TMT/SOR/EOR)					
Steam Reduction	*Use 30-50 wt% steam*				
Energy (and GHG) Reductions	*Use 20-40 GJ/Tonne EE*				
Furnace Coil Lifetime	*3-7 years*				
Maximum Operating Temperature (TMT)	*Use 1050-1120^{o}C*				
***In-situ* Surface Repair/Regeneration**					
High Heat Transfer Tube with CAMOL Coating					

CAMOL has achieved significant results to date approaching 1 life-cycle; further enhancements planned for Gen-II

1	2	3			
CAMOL at March 2010	***Industry Reference***	**CAMOL Gen-I Benefits Crystallized and/or Targets***			
		Lighter Feedstocks	**Heavier Feedstocks**		
Commercial Availability		**2010**			
Furnace Run-length	*10-90 days online*	1-2 years	100-400 days		
Temperature Reduction (TMT/SOR/EOR)		20-60°C	20-60°C		
Steam Reduction	*Use 30-50 wt% steam*	10-25%	10-25%		
Energy (and GHG) Reductions	*Use 20-40 GJ/Tonne EE*	3-12%	3-12%		
Furnace Coil Lifetime	*3-7 years*	4-7 years	4-7 years		
Maximum Operating Temperature (TMT)	*Use 1050-1120°C*	1130°C	1130°C		
***In-situ* Surface Repair/Regeneration**		LCG: >5 regenerations; HCG: 3 regenerations + >3 LCG regenerations			
High Heat Transfer Tube with CAMOL Coating		N/A	N/A		

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

CAMOL has achieved significant results to date approaching 1 life-cycle; further enhancements planned for Gen-II

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°C	20-60°C	40-100°C	40-100°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°C*	1130°C	1130°C	1150°C	1150°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.

Q&A from the Marketplace… "OK….but"

Q: OK, so CAMOL provides non-coking surfaces, serious increases in run-lengths, real temperature reductions, and other significant benefits, but can it take 2-3 tons of Fe-based contaminants over a coil lifetime and keep on ticking?

A: Realistically, no alloy, coating or surface can manage such a high contaminant load and provide a beneficial coil surface; nothing foreseeable is forthcoming for such large-scale contamination; field-enabled "inert-surface recovery" is projected; consider controlling or improving quality of feedstock and contaminants levels.

Q&A from the marketplace…. "OK….but"

Q: OK, so if CAMOL gasifies amorphous coke to CO/CO2, is there an increase of these levels in the product stream?

A: In an ethane, low-contamination environment, eliminating filamentous coke-make materially reduces furnace CO/CO2 levels; gasification of amorphous coke produces no material changes to these lower levels.

In a naphtha high-Fe environment, we have not detected any material change in levels.

In a naphtha lower-Fe environment, changes are comfortably within acceptable operating ranges.

Recall: CAMOL designed to simply gasify that which would have otherwise collected on coil surface, nothing more.

Conclusions and Future Work

1. Major strides made in mitigation of both filamentous and amorphous coking, and enhancement in overall coil performance across broad range of operating severities; approaching 1 life-cycle.
2. Initially securing low-coking, lower TMTs and lower Energy/GHGs; expanding to then optimize on steam dilution and conversion/product slate benefits.
3. Expanding trials to provide CAMOL across broad range of furnace/coil designs, feedstocks, and contaminant levels.
4. Targeting to provide CAMOL coatings in the smallest fraction of a circuit to achieve benefits – lowest cost, maximum benefits.
5. New trials being structured to maximize sharing of performance results to the benefit of the industry, while protecting commercial sensitivities of customers.

Thank-you for your kind attention!

quantiam technologies inc.

… an uncoated furnace tube cokes at significant rates

CAMOL is inert to filamentous coke-make…
… <u>and</u> CAMOL gasifies amorphous coke