Final Technical Report

Catalyst-Assisted Manufacture of Olefins from Natural Gas liquids: Prototype Development and Full-Scale Testing

US-DoE Award Number: DE-EE0005754

Project Period: October 1, 2012 to April 30, 2014

Principal Investigators:
Dr. Majid Keyvani, 281-452-8166
majid.keyvani@lyondellbasell.com
Craig Ostroff, 732-205-6022
craig.ostroff@basf.com

Recipient Organization: Lyondell Chemical Company
1221 McKinney Street
Houston, TX 77010

Other Organizations: BASF Qtech Inc.
100 Milverton Drive, 5th Floor
Mississauga ONT L5R 4H1

Quantiam Technologies Inc.
1651-94 St.
Edmonton, AB T6N 1E6

Acknowledgement: This report is based upon work supported by the U.S. Department of Energy under Award No. DE-EE000574.

Document Availability: Reports are available free via the U.S. Department of Energy (DOE) Information Bridge Website: http://www.osti.gov/bridge

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and Informational Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Tel: (865) 576-8401
FAX: (865) 576-5728
E-mail: reports@osti.gov
Website: http://www.osti.gov/contract.html

TABLE OF CONTENTS

1.0 List of Acronyms

TMT	Tube Metal Temperature
COT	Coil Out Temperature
LBI	LyondellBasell Industries (Prime Recipient)
LPO	LaPorte, TX location of LyondellBasell
QTI	Quantiam Technologies Inc.
BQ	Basf Qtech Inc. (Sub-Recipient)
BC	BASF Corporation, U.S. entity BASF Group
BCI	BASF Canada Inc., Canadian entity of BASF Group
BASF SE	European entity of BASF Group
NA	North America
GHG	Green House Gas(es)
TLE	Transfer Line (Heat) Exchanger
REO	Rare Earth Oxide(s)
HTA	High Temperature Alloy
ID	Inner diameter of a furnace tube
GC	Gas Chromatograph
HC	Hydrocarbons (feed such as ethane, propane or naphtha)
CAMOL	Catalytic Assisted Manufacture of Olefins technology, CAMOL™
SOR	Start of Run
EOR	End of Run
BP-1	Budget Period 1, the first of three planned years of the Project
SOPO	Statement of Project Objectives
DoE	US Department of Energy
KMC	Kubota Materials Canada Inc.
G1/G1E	Earliest versions of Generation 1 and Generation-1Enhanced CAMOL
G2/Gen-2	Generation-2 CAMOL developed for the Project
NGL	Natural Gas Liquids

2.0 List of Figures

3.0 List of Tables

4.0 Executive Summary

The original proposed program had three phases each lasting approximately one year and having its own set of specific objectives. The three phases were:

- Development of next generation catalyst coating and manufacturing technology (Budget Period 1)
- Trial manufacture and installation of catalyst coated prototype furnace coils
- Field demonstration in ethane steam cracker

Phase 1 (Budget Period 1), extended to 14 months and was mostly completed successfully. Some final developments were not completed until late 2014. The Project Team formulated a robust, thermo-mechanically stable catalytic coating that prevented catalytic coke formation and catalyzed the removal of gas-phase coke deposits. The team also further advanced their proven platform catalyst coating technology (Generation-1 Technology") to meet the full range of engineered coating system properties that meet Project objectives (Generation-2 coating matrix and catalytic surface) inclusive of achieving inter-diffused metallurgical bonding with a high level of matching of Coefficient of Thermal Expansion (CTE) to the selected metallurgy and prime manufacturing yields that exceed 90%. By optimizing catalyst loading, composition and coating properties on the internal tube surface area, the coating properties were tested against the projected field demonstration operating conditions and demonstrated the catalytic coating functionality and survivability in simulated "Field Demonstration Furnace" operating conditions. Specifically, the thermo-mechanical robustness of the coating's outermost oxide surface and its thermal stability met or exceeded the Project Furnace's temperature operating range, both within and at 25 °C greater than standard and severe cracking conditions as determined by laboratory scale aging for 250 hours. The team achieved a minimum of 2 times increase in internal surface area over uncoated tubular components and fittings, a 50% increase in catalyst content, a 30-50% increase in coating mass and verified weldability of coated components targeting residual elongation, after all coating-related heat treatments, of at least 5%, as determined using ASTM test procedure. What was not achieved by the end of BP-1 is highlighted by the coating and management of induction-bent fittings.

The Project Team developed a Design of Experiment study (a statistical methodology in research and development) and investigated the effect of temperature, residence time and feed dilution on the coking rate. The uncoated tube and CAMOL tube were tested side by side under the ethane cracking operation similar to a commercial furnace. The team demonstrated superior performance of coated tubes over uncoated tubes based on comparative coking rates (tube weight gain) under Project-defined operating conditions and Lyondell success metrics for its pilot-scale testing of that warranted advancing to commercial-scale furnace testing based on its historical database correlating test results with field results. Current Lyondell protocol requires 15-20% reduction in coking rate of coated tube over the uncoated tube. Furthermore, the team demonstrated performance sustainability of the coated tube over several coking-decoking cycles to simulate commercial furnace operation (targeting at least 8 decoking cycles). A performance degradation of less than 10% is desired per cycle.

5.0 Introduction

CAMOL is a disruptive technology with no commercialized in-kind competition, designed to delay, for extended periods of time, the formation of coke inside the furnace tubes during olefin (ethylene, propylene, butenes) production in the endothermic pyrolysis process, commonly known as Steam Cracking. CAMOL is a catalytically active coating that becomes an integrated phase in the HTA steel that make up the tubes, furnace coils and fittings in a steam cracker furnace.

Coke, or solid carbon buildup, forms inside the tubes, primarily in two ways: 1) filamentous, or catalytic coke forms when the HC feed sees the Ni on the tube surface; 2) amorphous, or pyrolytic coke forms in the gas phase as a byproduct of the primary reaction to form olefins. This coke forms and settles on the catalytic coke. Any type of coke is both insulating and disruptive to fluid flow, so it demands greater thermal energy input to maintain conversion, and it reduces mass flow or throughput.

CAMOL forms an oxide surface that is Mn based, instead of the traditional Cr-based oxides formed in standard tubes. The Mn-oxides serve as an inert surface, blocking off the Ni, and as a catalytic gasifier of the amorphous coke. In NA, where shale gas has driven growth in ethylene production from ethane, it is common to decoke every 30 days, requiring 2-3 days of non-production. With CAMOL the operator can extend the period between decokes to >300 days, and enjoy the consequential energy savings and reduced CO_2 output along with the incremental production.

CAMOL also reduces the required TMT of the furnace tubes by about 40-70ºC from SOR to EOR, which requires less firing of the external burners in the furnaces, saving fuel gas.

Ethylene production is the single largest use of energy by the chemical industry, consuming an estimated 450 trillion BTU in the U.S. CAMOL seeks to reduce the energy (and costs) consumed by creating novel coated furnace tubes offering a combination of improved energy and operational reliability. Based upon R&D to-date, energy reductions of 15 – 25% in the radiant section of the plant are expected, corresponding to a 6 – 10% reduction in overall plant energy consumption. Implementation of this technology in U.S. ethane-based ethylene plants would result in annual energy savings of 20 – 35 trillion BTU, equivalent to the energy used to power 370,000 households. Application of this technology has the potential to reduce GHG emissions in the U.S. by 2 million tons annually, equivalent to removing nearly 350,000 cars from the road. Extension of this technology to plants using non-ethane feedstocks and to those outside the U.S. has the potential to yield significantly greater reductions in energy consumption and GHG emissions.

Table 1: Estimate of the Impact of a Successful Implementation of CAMOL Gen 2 on Energy Consumption and GHG Emissions in the United States.

Data Inputs	2010	2014	Sources
US ethylene production from steam crackers, Billion lbs/yr.	52.3	56.8	CMAI; HIS Chemical
Energy consumption per ton or ethylene produced, GJ/mT	19	19	T.Ren et.al. Energy 31 (2006) 425-451
Energy consumption per lb or ethylene produced, BTU/lb	8,169	8,169	calculated from above
Energy consumed to produce ethylene in US, Trillion BTU/yr	427	464	calculated from above
Energy consumed to crack ethane, Trillion BTU/yr.	256	324	calculated from above
Pounds CO2 produced/ MM Btu natgas	117	117	http://www.eia.gov/tools/faqs/faq.cfm?id=74&t=11
Lbs CO2 produced / Gal gasoline (10% ethanol)	17.68	17.68	http://www.eia.gov/tools/faqs/faq.cfm?id=307&t=10
Average car mileage per year in US	12,000	12,000	http://www.epa.gov/otaq/consumer/420f08024.pdf
Average MPG per car in US	21.4	21.4	http://www.epa.gov/otaq/consumer/420f08024.pdf
Average gasoline consumption per car per year in US, gallons	561	561	calculated from above
Estimated Energy Saving and GHG Emission Reductions	**2010**	**2014**	**assuming 6% lower energy overall**
Estimated US Energy Savings	15.3	19.4	Trillion BTU/yr.
Estimated US GHG Emission Reductions	1.80	2.27	Billion pounds/yr
Equivalent Reductions in US Gasoline Consumption	102	129	Million gallons gasoline
Equivalent Reductions in US Automobiles	181,157	229,393	calculated from above

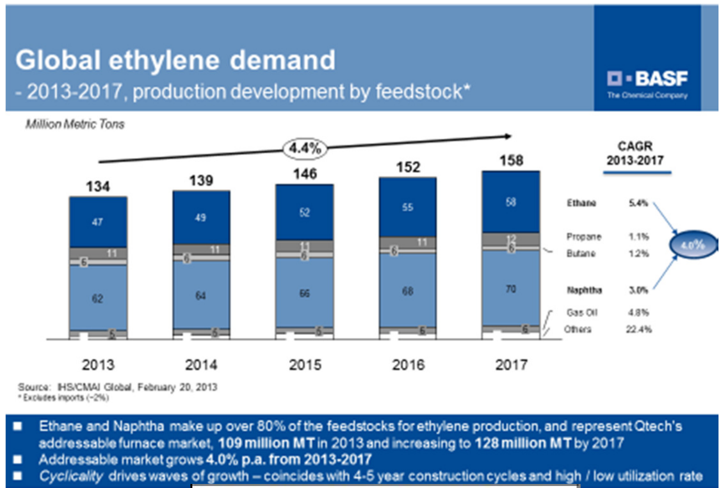

Figure 1: Global Ethylene Demand

This technology has been successfully demonstrated in Europe for the steam cracking of naphtha liquids but not on a full commercial scale for the steam cracking of ethane. Combined with the growth of domestic shale gas production, this technology has the potential to increase the competitiveness of the U.S. chemical industry since ethylene is a basic building block used in numerous downstream processes. The DOE grant cofounded and accelerated development of the technology, allowing it to be ready for commercial implementation in three years.

The overall objective of the Project is to develop and successfully manufacture prototype catalyst-coated furnace coils (tubes and fittings) and demonstrate energy savings in the commercial steam cracking of ethane to ethylene at conditions never before seen in NA, nor by the original Gen-1 CAMOL technology. This required an all-new Gen-2 formulation and process to manufacture.

If successful, Gen-2 CAMOL can be made available to all of NA at a rate of 4-6 furnace coils/year today, and expandable to 15-20 with construction of a larger, dedicated facility. The design of such production is replicable, globally, for all markets.

6.0 Background

Prior to CAMOL's introduction, a number of anti-coking technologies were introduced since 1990, and today 1-2 specific technologies dominate the landscape, supplied by the HTA providers. Since BQ is not a steel supplier, we need to adapt to the existing supply chain which brings multiple challenges.

The market leader is Kubota Materials, with home offices in Japan, and foundries in Japan, Canada (largest) and Saudi Arabia. A premium KMC product, MERT, reduces coke formation by creating turbulent flow with a powder metallurgical bead welded along the ID of the tubes. The turbulence allows for greater heat transfer from OD to ID to fluids, and results in lower TMT and slower coke formation. MERT has been commercialized over the last 10 years.

Prior to CAMOL we know of no coating product that has survived use > 6 months. At time of writing, we have a Gen-1 CAMOL coil running at BASF SE since January 2010. Samples have been cut out at 14, 48, 60 and 65 months, verifying that the technology is still present in the tubes. That furnace is naphtha fed. This Project was focused on US, shale-gas driven, ethane fed furnaces.

Specific Objectives of the Project were:

1. Develop catalytic coatings capable of providing a 10-fold increase in operating run lengths without decoking under standard ethane cracking conditions (65-68% ethane conversion).

2. Demonstrate a 2-3 fold increase in standard operating run lengths under severe cracking conditions (>68% ethane conversion) in a commercial steam cracker, together with energy and emissions reductions commensurate with this more severe operating regime.

3. Achieve 15% energy and GHG emissions reductions in the furnace radiant section and 6% overall reduction per unit of ethylene produced from the steam cracking of ethane.

The Project was divided into 3 projected phases or Budget Periods. At a high level these periods were divided into 1) development of Gen-2 CAMOL and a process to produce a prototype for trial, 2) production of the prototype for trial by LBI, and 3) operation and report-out of findings. Each was originally forecasted as 1 year in duration.

BP-1 was extended to 14 months, during which DoE funding for the period ran out. Before BP-2 was negotiated, LBI informed DoE and BQ that the Project was terminated.

In order to achieve the objectives above, BQ and our partner and co-owner, QTI, approached the challenge by addressing the greatest weaknesses of the original, Gen-1 technology, as they may become evident in the high severity operation of LBI.

Specifically, we designed experiments to enable modification of the CAMOL and HTA chemistries that would provide:

- Greater concentration of catalytic components in the CAMOL phase
- Greater maximum mass of CAMOL that can be integrated into HTA
- Greater surface area to drive down TMT in higher severity operation
- Greater durability of the oxide layer when exposed to thermal shock
- A process to apply CAMOL to induction-bent fittings
- Reduced loss of HTA elongation post CAMOL processing to facilitate welding/fabrication

Primary researchers were employed by QTI, under contract with BQ. Made up of chemists, metallurgists, powder metallurgists and surface scientists with collectively over 100 years of experience in high temperature coatings, each brought unique expertise in one or another aspect of the challenge to be met.

7.0 Results and Discussion

During the DoE co-funded 14 month BP-1, ending April 2014, BQ succeeded in developing a CAMOL Gen-2 catalyst coating and manufacturing technology to apply it to the Project's furnace tubes but not to other components. Induction-bent fittings were not resolved until Q2 2015.

Below for BP-1 is a summary of the major Objectives and the corresponding results realized by April 2014, as previously reported to the US-DoE in detail.

Task 1.0 Catalyst Coating Optimization for Energy and Emissions Reductions:
In BP-1, we targeted a Gen-2 catalyst coating system to maximize energy and associated GHG emissions reduction using ethane as the feedstock. Specifically, we:

(a) identified coating properties (at micro-level, the internal tube surface area and surface morphology, and at the macro-level, the overall internal geometry/profile);
(b) catalyst composition; and
(c) catalyst loading and optimal mapping throughout coils

These collectively had the potential to produce the greatest energy savings and ensure compatibility with composition and properties of Project base alloy(s).

<u>Autopsies of Gen-1 Field Samples:</u>

- Autopsy of 14-month sampling of G1-naphtha **<u>completed</u>**.
- Autopsy of 1 full life-cycle G1 – Ethane, Medium Severity – **<u>completed</u>** to level needed by Project.
- Autopsy on 6-month flexi-cracker samples – higher severity, **<u>completed</u>** to level needed for Project.

Results from the G1 autopsies provided major insights into the CAMOL coating properties that are over-engineered, adequately-engineered, and under-engineered in field furnace operating severities trialed to-date, and as a function of location within a cracking furnace circuit. These learnings have been used to:

a) Focus the development and advancement effort of key coating properties requiring enhancement or optimization to meet the higher cracking severity of the Project; and
b) Assist in optimally mapping requisite coating properties within the cracking circuit (primarily the furnace coils).

Consistent with TRL 5, BQ tested metal coupons coated with catalytic coatings using a laboratory scale cracking unit to simulate a steam cracking furnace with a focus on identifying the coating properties including catalyst composition produced the greatest energy savings. The unit includes front end feedstock preconditioning, steam generation and blending, all fed to a bench scale reactor within a tube furnace, exiting to an online Gas Chromatograph (GC) and vapor traps for gas capture and analysis.

Sub-Task 1.1: Define Coating Properties and Limitations to Achieve Functionality and Survivability in Field Demonstration (LPO) Furnace ("Project Furnace"): Based on knowledge and field-trial experience with existing Gen-1 catalyst technology, BQ adjusted critical coating material compositions and properties to provide target improvements in functionality and survivability in the Project Furnace. These properties included, in addition to previously published properties,

a) Physical and catalytic resistance to feed stream (feedstock and steam) contaminants, pending analysis of LPO's feed stream, followed by accelerated laboratory scale corrosion testing, if warranted. It is projected that at least one and perhaps two of the highest feedstock contaminants identified specific to the LPO furnace is considered to pose potential corrosive concerns for the coating system (other than Fe and S). This will be evaluated under accelerated laboratory testing conditions.
b) Resistance to sulfur levels (naturally-occurring plus operator additions) of 2x normal concentration typically found in the Project Furnace feed stream, without material degradation of the catalyst coating.
c) Compatibility with oxygen levels (as oxygen from air) during decoking cycles. To effectively remove carbon (coke) without material degradation of catalyst coating, we re-exposed the coating outermost surface to oxygen and, regenerated the outermost surface.
d) Compatibility with oxygen levels (as steam) during Standard Cracking Conditions (25-30% steam dilution and 63-66% conversion) and Severe Cracking Conditions (25-30% steam dilution and $\geq$ 68% conversion). Catalyst coating requires threshold levels of oxygen provided by steam to achieve carbon gasification; this threshold level must always be met at operating temperatures and catalyst loading levels (As a guideline, 65%-67% conversion requires at least 25 wt.% steam at the lowest possible catalytic gasification levels of the Generation-1 technology; the threshold oxygen (steam) level requirements for the Project's Next-generation technology is to be identified base on finalized catalyst composition and surface loading, and is expected to be no less than 20 wt.% and no more than 30 wt.%.
e) Compatibility with Project Furnace's ability to activate and reactivate coating outermost surface for maximum catalytic gasification functionality.
f) Compatibility with Project Furnace's ability to generate/regenerate outermost surface of coating system.

Sub-Task 1.2: Optimize Coil Location of Installed Catalytic Gasification Functionality Level: We "mapped" catalytic gasification functionality within furnace coils required by the coking profile of the Project Furnace operated within Standard Cracking Conditions, targeting to provide a minimum 50% and a desirable 100% over-engineering in the threshold level of catalytic gasification installed as is required to meet overall coil catalyzed gasification needs. The process of "mapping" the coil involves matching up placement of different catalyst formulations and loadings with the known coking profile of an uncoated coil. This is usually done first with an accurate temperature profile of the coil, an example of which is provided in Figure 2.

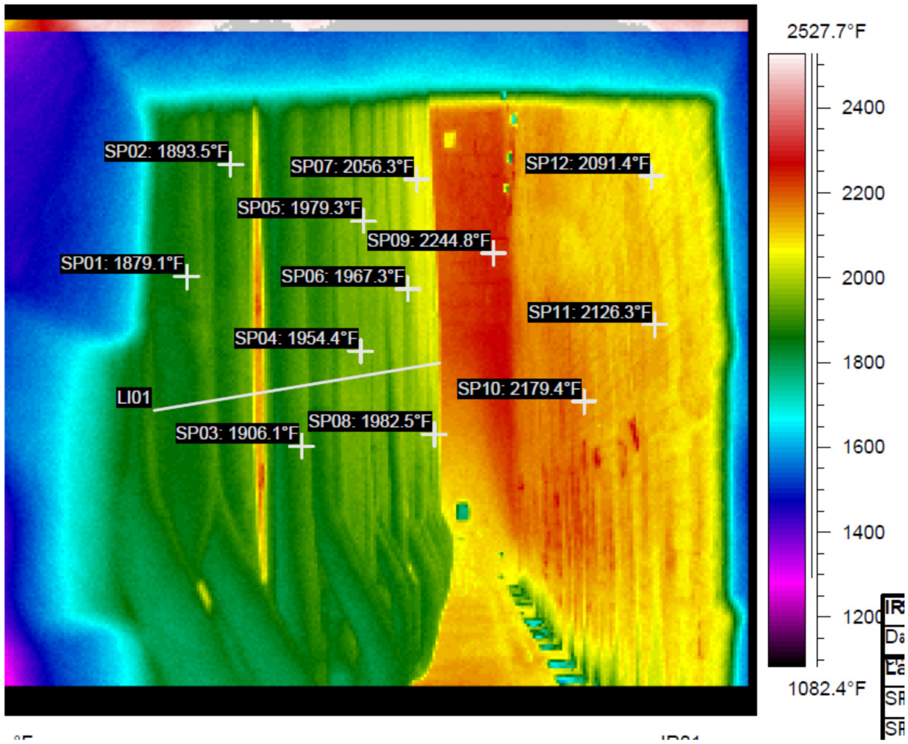

Figure 2

Sub-Task 1.3: Development of Coating System Properties: Advancement of the coating system's (matrix and outermost surface) chemical, physical and thermo-mechanical properties necessary to achieve survivability of one standard coil lifetime in Project Furnace (4 to 5 years) to focus on optimized/enhanced:

a) thermo-mechanical robustness of the coating's outermost oxide surface that meets or exceeds emergency and planned shutdowns (thermal shock).
b) thermal stability that meets or exceeds the Project Furnace's temperature operating range, both within and at 25°C greater than Standard and Severe Cracking Conditions as determined by laboratory scale aging for 250 hours.

During BP-1, feasibility studies of both (a) and (b) were successfully completed. Following an extensive state-of-the-art review, an initial experimental design for REO additions to the coating formulation was developed and executed (Phase-1). Based on positive results in Q3-2013 with a broad experimental design, a second more focused experimental design (Phase-2) was undertaken that proved successful in narrowing REO additions most compatible with the coating microstructure and its properties. It was critical that as thermo-mechanical robustness of the surface oxide is successfully increased, there are no negative impacts on either physical or chemical properties of the coating system, including of its coking performance. Key advancements from this work are summarized below:

Sub-task 1.3.1: Coating Surface Oxide Robustness Enhancement/Optimization

a) Experimental work was undertaken for enhancing oxide scale thermo-mechanical robustness based on REO additions.
b) Advanced assessment of coated coupons of Phase-1 with REO-coating additions through microstructural and surface analyses was completed.
c) Advanced engineering and trial manufacture of lab-scale powder formulations and trial coating of coupons.

d) Completed Phase-1 study – introduction of REO element/oxide into the CAMOL™ coating formulation via the mechanical alloying manufacturing route. Phase-1 results have been summarized. Five candidates REO species were evaluated – "A", "B", "C", "D" and "E". Two REO addition levels were studied: 0.05 and 0.50 weight percent. Two REO species were selected for further research, namely "D" and "E".

e) Completed Phase-2 study building on Phase-1 results but focusing on "D" and "E" additions.

f) Phase-3 study was undertaken in parallel and focused on the introduction of specified compounds "D" and "E" to form an "interim" or "sacrificial" post-consolidated surface coating which then undergoes a medium temperature surface generation step of the coating matrix. These "interim" or "sacrificial" surface coatings were characterized after the surface generation treatment was completed. A range of REO dopant levels were studied: 0.02, 0.05 and 0.20 mole percent. This Phase-3 work was successfully completed as reported.

g) Conducted thermal shock study of CAMOL – REO doped and surface generated coatings. Commenced the associated characterization studies. Initial results were favorable in terms of the location within the coating matrix for the REO additions, and their subsequent participation in oxide growth kinetics and its effect in improving overall thermo-mechanical robustness.

h) The two short listed REO species from Phases-1 and 2 underwent further study using higher addition levels and different introduction methods to ensure a finalized optimal level for both enhancement of oxide robustness, and compatibility with surface/coking performance.

i) Short-listed Gen-2 coated sample coupons and bars were prepared and tested for lab-scale pyrolysis assessment for impacts of REOs segregating to the outermost surface and their impacts on coking resistance/performance.

Work on the second feasibility study noted (Subtask 1.3.2) focusing on optimization of the coating matrix formulation (replacing a key G1 element with an alternative to better manage major furnace upsets) was successfully completed. Although results showed promise, a decision was made to not continue with this enhancement as it was deemed to not be achievable on the Project timeline to transfer to BP-2 for Trial Manufacturing.

The Project met its BP-1 objective of completing the two feasibility studies and selecting for further advancement, the enhancement capable of having greatest impact on the coating technology's robustness for higher severity operation with completion achieve-able by the end of BP-1.

Task 2.0: Base Alloy Metallurgy Optimization/Enhancement: Selected, specified, and secured an alloy from KMC for all needed Project Furnace coil components. Process for selection and requirements included:

a) Specifying alloy(s) and the fabrication of coil components in a manner that meets the operational specifications of LBI and is compatible with the manufacturing limitations of the base components by a Project-approved supplier.
b) Controlling of all micro-alloying levels that can potentially impact interdiffusion of coating constituents with base alloy matrix.
c) Reducing the level of interstitial elements that can have a negative impact on the coating process and coating properties (including C, O, S, N and P).

d) Manufacturing coil base components for the Project for optimal compatibility with coating and post-welding of such parts.

Below is a summary of advancements made on Task 2.

Steel Properties for Weldability and Experimental Heats (production batches)

a) Kubota cast three experimental heats to enable closure on bulk alloy optimization of carbide formers by year-end for improving alloy ductility (weldability).
b) Tensiles from castings in (a) were obtained and processed under simulated CAMOL^{TM} heat treatments. Results are shown in Fig. 3. Results for the experimental heats showed that with the optimized steel chemistries for this specific physical property, elongation levels as high as 7.0% were achievable, far exceeding targets.
c) Confirmatory heats were cast in February to confirm results using a "final-optimization" of the alloy chemistry.

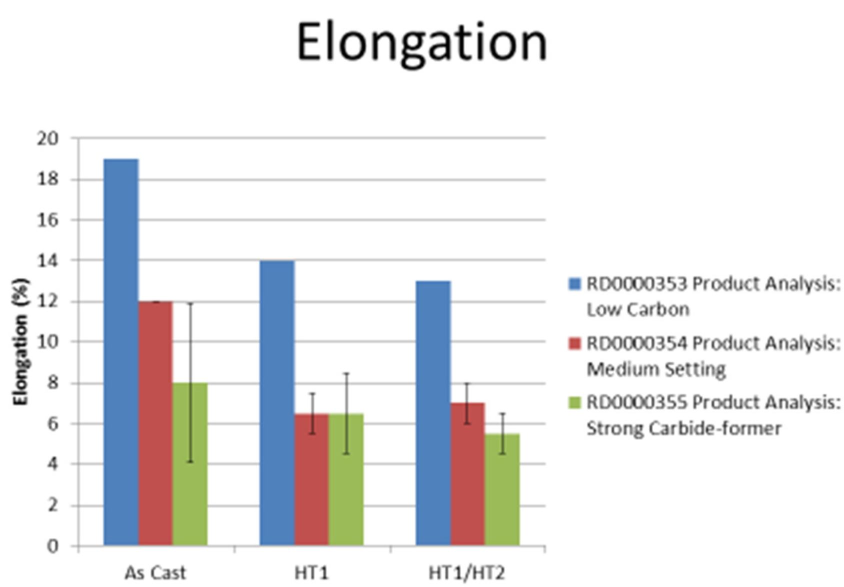

Fig. 3

Induction-bent Fittings from Centrifugally-cast Tubes

Induction-bent fittings are formed from centrifugally-cast tubes of the same metallurgy as coil tubes, and that are then bent-to-shape using induction heating to achieve a final shape of a "crank" (an "S-shaped bend") or a "sweep" (a return-bend with a large radius of curvature). The key issue on coatability of such parts is whether they can be coated prior to – the preferred path forward (and survive bending stresses), else post bending. A KHR45A centrifugally cast tube produced by Kubota to be formed into a crank fitting was successfully coated at QTI but evaluation did not begin until after the end of BP-1.

Task 3.0: Coating Manufacturing Technology Advancement/Optimization: Advancements were required on two fronts: (1) the ability to apply the Project catalyst coatings to additional component shapes/geometries specific to the Lyondell LPO furnace coil design (as Sub-task 3.1); and (2) the ability to deposit, consolidate (heat treat) and generate the targeted coating microstructure and internal surface micro and macro profiles to improve heat transfer and achieve

TMT (tube metal temperature) reductions (Sub-task 3.2). Overall, for the Project's Gen-2 coatings, it was essential to tailor the tube and fitting–coating and heat treatment processes to ensure proper coating coverage, thickness, microstructure and adhesion to the base metal.

Below, by Sub-task, is a summary of advancements made on Task 3.

Sub-task 3.1: Development of Coating Application for all Complex Shaped Parts of Project Furnace

During BP-1 BQ advanced a proven platform coating application process technology to meet the geometrical and dimensional requirement of furnace coil tubes but not to other components such as static cast fittings, and centrifugally cast tubes with post induction-heating forming. The advancements in coating application also included the incorporation of novel internal micro and macro surface profiles as summarized below in Sub-Task 3.2, and the ability to incorporate new catalytic compositional requirements in the coatings.

Work to coat all tubular components in the mill-produced condition of the tubes was successful. Coating application requirements for the induction-bent centrifugally-cast tubular into fittings (i.e., sweeps and cranks) was initiated as described in Task-2 above but did not progress until after BP-1. Advancement of powder processing methods to achieve the targeted coating properties and compositional modifications were successful in achieving both modification to the base coating chemistry and incorporating the REO additions.

Sub-task 3.2: Development of Specified Coating Application and Consolidation Manufacturing Technology to Increase Internal Surface Area

Experimental trials were successful in assessing and reducing to practice a broad range of internal-tube micro- and macro-level coating "geometric profiles" based on the platform Gen-1 technology. Efforts focused on macro-scale modifications where the risk and impact was expected to be greatest. The effort aims to further lower tube metal temperatures "TMTs" and energy consumption relative to the Gen-1 technology and potentially increase turbulence of the process stream. Results showed that we:

a) Achieved a minimum of a 2X increase in internal surface area over geometrical area (which is the internal surface area of uncoated tubular components and fittings). As an example for a tube, this is $A=2\pi rl$, where r is internal radius and l is length of the component. The targeted Project Furnace is 540,000 in^2. Increases were measured with contact surface profilometry, 3D Laser Scanning profilometry and BET (Brunauer, Emmet, Teller) measurements.
b) Optimized internal coating geometry, morphology and related properties that include micro-scale surface area and surface morphology, and macro-scale geometry/profile aimed at maximizing impact on boundary layer to maximize heat transfer across tube wall and reduce TMT. These advancements included:
    i. generating/controlling work piece internal surface finish to achieve micro-roughness R_a>100 micro-inches ("R_a" is a standard surface roughness measurement parameter in the industry);
    ii. achieving an as-deposited coating surface finish roughness threshold R_a of >50 micro-inches (primarily as micro-roughness), capable of generating and sustaining an outermost surface oxide with surface area approaching or exceeding 2X the geometrical area;

iii. utilize the combined surface area gain of at least 2X (from (ii) and targeting 3X overall when combined with the macro-scale surface profile of (iii), to achieve impacts on internal surface boundary layer, heat transfer, and TMT.

Sub-task 3.3: Fabrication (Welding)

Efforts in BP-1 aimed at securing a threshold level of Elongation of the coated steel post coating heat treatment cycles. We focused on:

1. Optimization of the two critical heat treatments needed for coating, both above 800ºC and affecting carbide structure and subsequent Elongation (weldability); and
2. Optimization of all alloy components involved in initial carbide formation at the foundry, and their evolution through the coating process.

The resulting alloy is designated as KMC KHR 45AMQ that provides both an acceptable match for Gen-2 chemistry and maintained elongation after CAMOL processing at levels of 6% or higher. The alloy was evaluated for the latter property by KMC vs. other available alloys and other modified compositions. The former was validated in the LBI pilot plant reactor described in Task 4.

Sub-task 3.4: Adaptation of a Non-destructive Laser Scanning System for Advanced QA/QC.

A new laser head was designed and built by the OEM supplier in the US specifically for the Project. Work focused on testing, calibration, and development of algorithms capable of supporting coating QA/QC of the Project Furnace trial tube geometries. We achieved +/-10 microns resolution.

Task 4: Lyondell pilot plant cracker testing

The steel supplier cast a tube with metallurgy defined by the Project team within the alloy family collective known as KHR45A to fit LBI's pilot plant cracker for testing by simulating plant operating conditions to quantify coking rate against severities aligned with Standard and Severe Cracking Conditions noted above. The Project team recognized the challenge of correlating controlled laboratory-scale testing with commercial-scale operation, and as such, the testing contemplated was directional and aimed primarily at identifying potential "flags" that needed to be properly addressed/optimized or understood prior to proceeding to a full-scale commercial trial.

Sub-task 4.1: Measure Baseline Performance of Uncoated Control Tube

The Project Team developed a Design of Experiment study (a statistical methodology in research and development) to investigate the effect of temperature, residence time and feed dilution on the coking rate. The control tube was uncoated and exposed to ethane cracking operation similar to a commercial furnace. The coke formation can be quantified by the weight gain on the tube. The weight gain on the tube and GC analysis of furnace outlet gas was used to measure coking rate at various furnace temperatures. Ethane conversion, defined as % of the ethane feed converted to other components is a measure of the cracking severity.

1. Completed: LBI completed all commissioning work to enable safe operation of Pilot Plant Cracking test unit with "standard" cracking residence time and feed diluent.
2. Completed: The testing with the uncoated reference reactor tube was advanced to allow evaluation of the effects of temperature, residence time, and steam to ethane ratio on the ethane conversion, and coke formation.

3. Completed: The testing with the uncoated reference reactor tube was completed and a baseline performance was established.

Subtask 4.2: Demonstrate Superior Performance of Coated Tube over Uncoated Tube in Lyondell Pilot-scale Test Unit

BQ applied the best catalyst coating candidates as noted in Task 1 and provided operational requirements (proper decoking, surface reactivation, and surface regeneration). A similar Design of Experiment study to that of Task 4.1 was performed in Task 4.2. The weight gain on the tube and GC analysis of furnace outlet gas was used for quantification at varying furnace temperatures. Conversion-Temperature performance curves were also generated for the coted tube and compare against the baseline data at 700, 800, and 900ºC.The tube samples generated in the test rig will be supported by appropriate autopsies by QTI and BASF-Qtech to allow correlation of cracking performance with coating and steel microstructures.

1. Completed: The testing with CAMOL G1 with 20% Beta catalyst began. The testing initially showed a lower coke rate but then following a process upset, showed unusually high coke deposit. It was concluded that the CAMOL G1 coating may have been damaged because of the aggressive (exothermic) decoking procedure used after the process upset leading to high coke deposit. The tube was sent back to QTI for autopsy and analysis to confirm.
2. Completed: The originally-applied decoking procedure was modified and a new decoking procedure was adopted and a longer decoking time was incorporated. The changes were implemented for a second and new CAMOL G1 tube received from QTI.
3. Completed: The new set of experiments (a total of 12 runs) showed a better coking resistance performance for CAMOL G1 tube over the control tube.
4. Completed: Testing of the CAMOL G2 tube was successfully undertaken and results were found to be favorable against Plan to proceed to BP-2. See Figure 4.
5. The testing protocol with CAMOL Gen 2 was similar to G1 and the results looked comparable if not better than CAMOL G1. The coking rate measured by the tube deposit on the tube was lower than uncoated tube in all the operating temperatures: 700 ° C, 800 ° C, and 900 ° C.

The ethane feed was used in all these runs and the ethane conversion for both uncoated and CAMOL G2 was comparable at a given furnace operating temperature.

CAMOL G2 tube was subjected to 10 cycles of cracking-decoking and after the 10 cycle no measurable loss of anti-coking activity was detected for CAMOL Gen 2. This was also shown by the pressure profile for the furnace tube for CAMOL Gen II and uncoated tube in Figure 5 below. CAMOL Gen II pressure profile looks flat compared to that of the uncoated tube which shows pressure increase influenced by changing operating parameters:

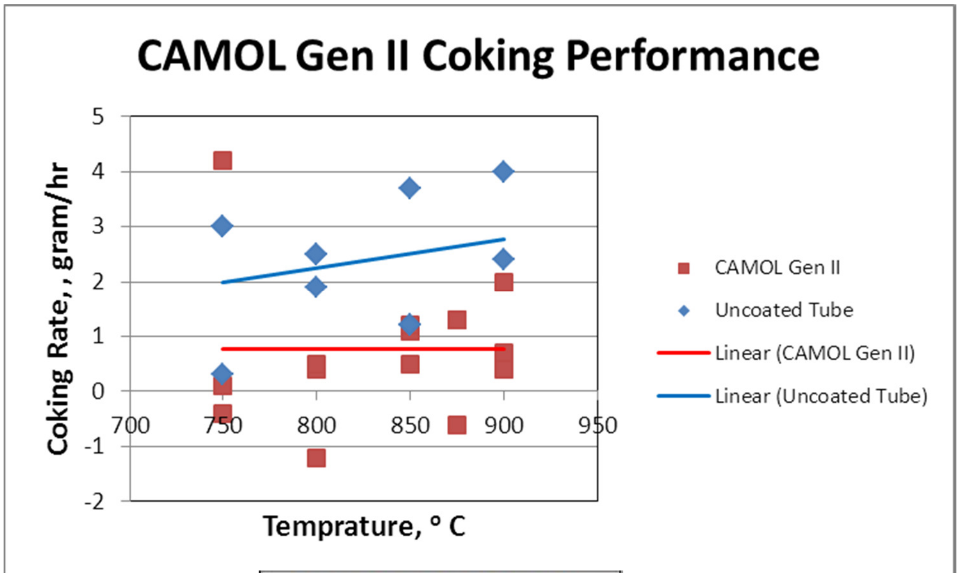

Figure 4: Gen-2 vs. Std tube

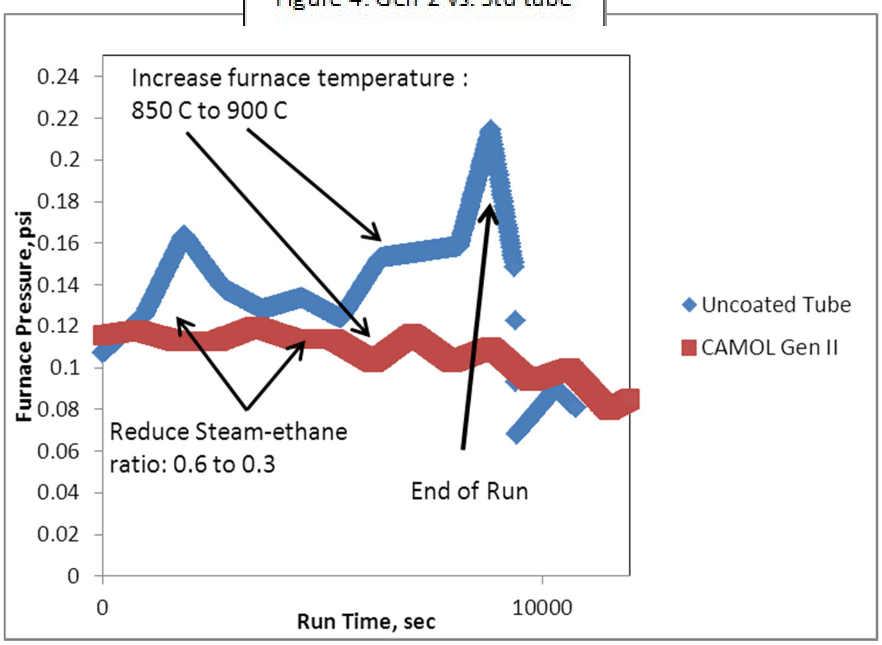

Figure 5: Gen-2 vs. Std tube

Based on these results we concluded CAMOL™ coatings had advanced towards an optimal selection of coatings, and catalyst type and catalyst loading as a function of position within furnace circuit. As BP-1 neared completion, scenario mappings were presented to the R&D and Operations Project teams in February-2014 with an assessment by scenario on:

a) impacts on coating manufacturing timeline, budget and risks to such;
b) furnace Operational risks and Benefit/Risk assessments as function of Gen-2 elements selected for installation against all information known at that time for coking and temperature profiles in the trial furnace; and
c) securing or exceeding all Project deliverables.

The Project teams had reached a final buy-in and internal approvals prior to advancing to the planned Trial Manufacturing in BP-2.

8.0 Benefits Assessment

LBI and its partner BQ, supported by the initial DoE grant, aimed to develop an innovative coating technology and a manufacturing technology, and demonstrate it in a full-scale prototype test to produce ethylene from ethane feedstock using less energy and emitting less greenhouse gases (GHG).

The principal feedstocks for this process are natural gas liquids (NGL) (ethane and propane) and petroleum liquids (naphtha and gas oils). CAMOL Gen-2 is particularly suited for high-severity cracking of ethane gas where it is expected to result in a 6-10% reduction in energy consumption per unit of ethylene produced at (68% conversion). However, CAMOL will be marketed for all steam cracking units that produce ethylene, including those that use other NGL or liquid feedstocks. At the current ethane conversion rate (68%), the impact of CAMOL technology on energy consumption is estimated 29-49 Trillion BTU/yr. in the US alone, corresponding to a reduction in CO2 emissions of 3.4-5.7 billion pounds per year. This would be equivalent to removing 350,000-580,000 cars from US roads (see table below).

Since the Project with DoE was cancelled at the end of BP-1 there is no benefit to be reported. At time of writing, these benefits have yet to be realized in a commercial trial.

9.0 Commercialization

This technology has been successfully demonstrated in Europe for the steam cracking of naphtha liquids but not on a full commercial scale for the steam cracking of ethane. Combined with the growth of domestic shale gas production, this technology has the potential to increase the competitiveness of the U.S. chemical industry since ethylene is a basic building block used in numerous downstream processes. The DOE grant co-funded and accelerated development of the technology, allowing it to be ready for commercial implementation in three years.

The overall objective of the Project is to develop and successfully manufacture prototype catalyst-coated furnace coils (tubes and fittings) and demonstrate energy savings in the commercial steam cracking of ethane to ethylene at conditions never before seen in NA, nor by the original Gen-1 CAMOL technology. This required an all-new Gen-2 formulation and process to manufacture.

If successful, Gen-2 CAMOL can be made available to all of NA at a rate of 4-6 furnace coils/year today, and expandable to 15-20 with construction of a larger, dedicated facility. The design of such production is replicable, globally, for all markets.

10.0 Accomplishments

The successful completion of BP-1 has provided the following impacts on the Project teams and their respective facilities:

1. Solid understanding through autopsies of Gen-1 samples of the strengths and weaknesses (adequate and inadequate levels of the engineered properties of the Gen-1 product in furnace trials, and what is required to be enhanced to meet Project furnace operating targets.
2. Advancement of coating system to meet Gen-2 objectives.
3. Advancement of coating manufacturing technologies to meet Project needs;
4. Advancement of lab-scale pyrolysis testing capabilities for assessing higher severity cracking.
5. Advancement of pilot-scale pyrolysis testing (Lyondell) to support Project objectives.
6. Advancement of steel base alloy metallurgy to meet coating system requirements and weldability requirements.
7. Readiness for scale-up to Trial Manufacturing of prototype coated tubes and fittings for Project furnace coils.

No patents are filed to date by BQ.

11.0 Conclusions

The Project ended prematurely, at the end of BP-1. No conclusions are drawn nor evolved from the applicability of Gen-2 CAMOL to meet the key SOPO objectives listed in 6.0. In April 2014 there were still several challenges to be met, specifically the application of induction-bent fittings.

We can conclude that changes made to base HTA metallurgy proved that CAMOL can be produced without prohibitive detrimental effect on physical properties critical to weldability. Reduction in C, Cr, with added Zr and Ti enable adaptation of the Gen-2 chemistry with higher catalytic concentration, and overall mass.

12.0 Recommendations

At the end of BP-1 no recommendations for the whole of the Project could be made. Results of the final product and trial will not be generated until 2016.