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IMPROOF: INTEGRATED MODEL GUIDED PROCESS OPTIMIZATION OF STEAM CRACKING FURNACES ON PILOT SCALE

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Abstract: The IMPROOF project will demonstrate several of the latest technological innovations in the field of fouling minimization and energy efficiency improvement at pilot and industrial scale. These include the use of new advanced high temperature alloys, in combination with novel 3D reactor technologies and coated with high emissivity coatings. In this work, the coking resistance of two different industrial reactor materials, a chromia forming Centralloy® ET 45 Micro and an alumina forming Centralloy® HT E, was compared during steam cracking of propane in a pilot plant furnace. In addition, the Centralloy® HT E reactor material was combined with the 3D SCOPE® reactor technology in order to bench mark it to bare tubes. Four out of five coking cycles were performed at the SOR industrial conditions, while during the 4th coking cycle the reactors were exposed to high-temperature EOR industrial conditions in which tube metal temperatures (TMTs) of 1050 °C were reached. While the ET 45 Micro reactor was shown to deteriorate after the 4th coking cycles, alumina forming HT E reactors proved stable with an even improved coking resistance. Applying 3D SCOPE® technology reduced the temperature gradients from the reactor wall towards the center, resulting in decreased coke formation due to lower TMTs compared to bare reactors. After exposing all the reactors to EOR conditions, Centralloy®

HTE SCOPE® had an outstanding coking performance, producing nearly 3 times lower amounts of radiant coke compared to the bare ET 45 Micro and HT E reactors. To further improve the energy efficiency of olefin furnaces a high emissivity coating will be applied to the furnace walls in future experiments. In addition to the application of a high emissivity coating applied on the external surface of the radiant coils.

Introduction

Steam cracking is considered a mature technology and the most dominant process for olefin production [1]. Nevertheless, a lot of research is still conducted towards steam cracking optimization. The growing demand of light olefins ensures maximization of the output of existing plants and novel technological developments towards reducing the energy input per ton of ethene and propene. One of the most important contributions to the total energy consumption per ton is the unavoidable decoking step. Decoking of steam cracking reactors is necessary to burn off the deposited coke on the inside reactor wall of the long tubular reactors, suspended in the furnaces, as a result of unwanted side reactions [2]. That is primarily why steam is added to the feed, also improving the selectivity towards the desired light olefins, i.e. ethylene and propylene. Typically, the outlet temperature of the tubular reactor is very high, around 820 – 890 °C. In modern cracking furnaces, the residence time is reduced to a few hundred milliseconds in order to improve the yield of desired light olefins. After the cracking temperature has been reached, the gas is quickly quenched to stop the cracking reaction in a transfer line heat exchanger to recover as much energy as possible. Approximately 8 % of the chemical industry's total primary energy is attributed to steam cracking and is therefore the most energy-consuming process of the sector [3]. In addition, the process is responsible for massive amounts of CO_2 emissions [4]. Massive amounts of economical revenue can be achieved by improving the energy efficiency of the steam cracking plant as the needed energy counts for an important part of the light olefin production in typical ethane and naphtha based plants [4]. Ethylene furnaces have to decoked regularly, typically after run lengths in the order of 30-60 days, to remove the coke that was build up in the coil. During decoking, mixture of steam-air is sent through the reactor to combust and gasify the coke, while the production of the desired products is halted for roughly 48 hours [5]. The heat-transfer efficiency of the firebox decreases by 1-2 % from start-of-running to end-of-run cracking conditions, due to the extra thermal insulation of the deposited coke layer. This efficiency decrease results in an increase of the fuel consumption of the furnace by 5 % [6].

Several technological innovations exist to reduce coke formation including the application of high-performance alloys [2, 7-16], coatings [17-19], pretreatments [20, 21], feed additives [22, 23], and 3D reactor technologies [5, 24-26]. 3D reactor designs manufactured out cutting-edge reactor alloy, combined with optimized process control and a more uniform heat transfer could increase run lengths [27], with the result of an increased lifetime of the furnaces and a reduction in CO_2 emissions. Munoz et al. [2] indicated that better performing radiant coils can reduce catalytic coking, while it was mentioned by Schietekat et al. [25] that advanced 3D coil design such as the swirl flow reactor design, and presumably other 3D reactors such as the SCOPE® design [28] (by Schmidt + Clemens GmbH + CO. KG), can mitigate coke deposition. Optimal geometries reduce the radial gradients inside the reactor by increasing mixing, and thus lowering the wall temperatures where coke formation happens. Lower wall tube temperatures will extend the run length, by lowering the coking rate exponentially, resulting in lower energy consumption for decoking on an annual basis. An incredible useful tool to optimize these geometries is advanced 3D CFD reactor simulations. And most of the time it is the only instrument available to investigate the performance of these 3D profiles.

In this work a 3D reactor design, SCOPE® [28], is, for the first time, been experimentally evaluated under industrial relevant operating conditions. In total three different reactors were studied in a pilot plant steam cracking unit: a reference material Centralloy® ET 45 Micro, a reactor manufactured from Centralloy® HT E as an advanced coil material and a reactor that combines the advanced coil material with the SCOPE® 3D reactor design. Five cracking cycles were conducted of varying durations, to investigate both the catalytic and asymptotic coking behavior. All cycles except for the fourth resemble industrial propane cracking conditions, while the conditions for cycle 4 are chosen to resemble high temperature carburization conditions that are present in industry during end-of-run conditions. At end-of-run conditions, the material undergoes aging, after which it is observed in industry that coking behavior of the material behaves different.

In the future the energy efficiency of the pilot plant will be evaluated before and after the application of a high emissivity coating on the furnace refractories. In a subsequent step a high emissivity coating will be applied on the external surface of the radiant coils to further improve the overall energy efficiency.

Figure 1: SCOPE® 3D reactor coil technology

Pilot plant

The experiments were performed on the pilot plant for steam cracking setup available at the Laboratory for Chemical Technology at the University of Ghent. A schematic representation of the setup is given in Figure 2. The setup is been described in numerous previous articles [17, 18, 22, 29-34], and therefore, only a short description of the setup is given.

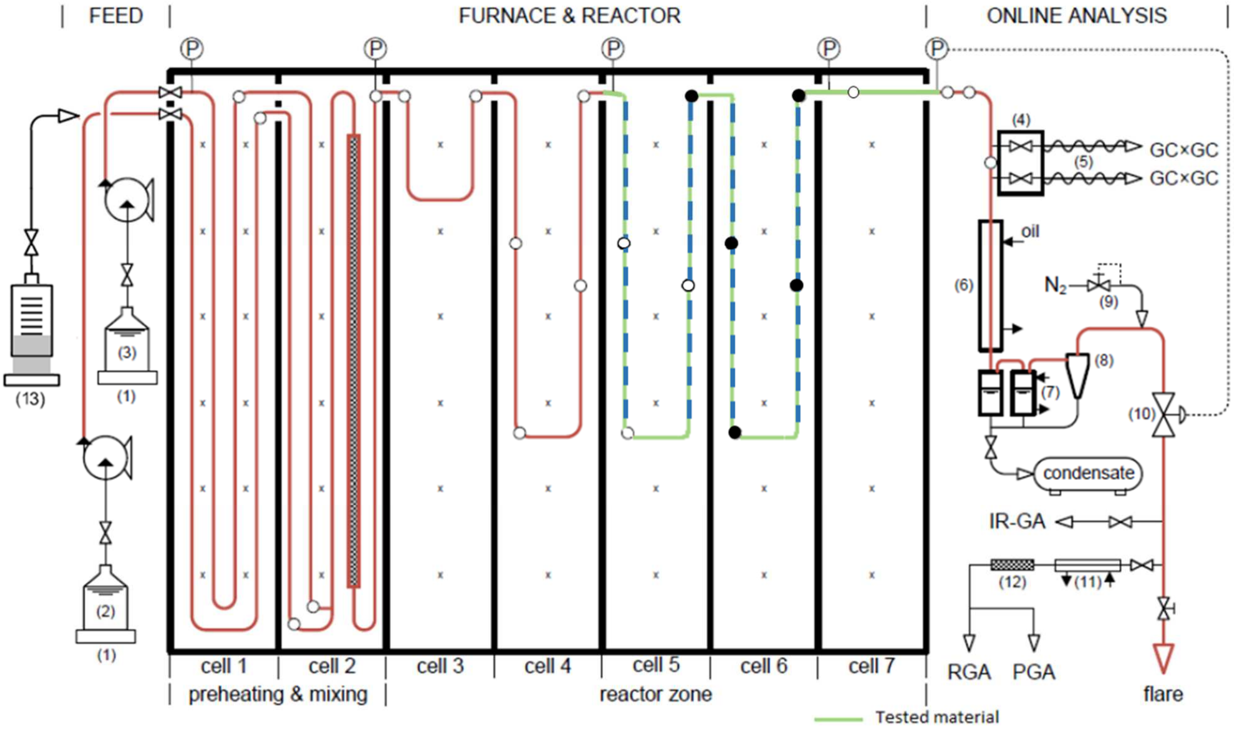

Figure 2: Schematic overview of the pilot plant setup during the experiments with the three different reactors: ET 45 Micro, HT E and HT E SCOPE® (green) (blue dashed line: SCOPE® profile), with the same inlet section in Incoloy 800HT (red). ((○): process gas temperature, (●): process gas temperature and, for the reactors with HT E material, reactor outer wall temperature, 1: electronic balance, 2: demineralized water reservoir, 3: liquid hydrocarbons reservoir, 4: heating sampling oven, 5: heated transfer lines, 6: oil cooled heated exchanger, 7: water cooled condenser, 8: cyclone, 9: thermal mass flow controller, 10: outlet pressure regulation valve, 11: water cooled heat exchanger, 12: dehydrator, 13: ISCO 500D syringe pump, (P): process gas measurements, GC×GC: two-dimensional gaschromatogry, RGA: refinery gas analyzer, PGA: permanent gas analyzer, IR-GA: infrared gas analyzer)

The setup consists out of three main parts: a feeding section, a reactor section and an analysis section.

The feeding section consists out of different vessels and bottles from which a wide variety of both gaseous and liquid hydrocarbon feedstocks can be fed towards the reactor.

The reactor section comprises the reactor and the furnace. The furnace has seven separate cells for which the temperature can be controlled individually, in order to impose a certain temperature profile. In the first two cells, the feedstock is preheated, evaporated (if necessary) and mixed with the diluent (steam), allowing homogeneous conditions at the beginning of the reactor. Steam cracking and coke deposition only occur in the last four cells, where the temperature is above 600 °C. Cell three, in this study, acts as a connection between the convection and the radiant section of the setup. The gas phase temperature is measured by means of twenty thermocouples and four pressure transducers that are mounted along the coil.

An additional five thermocouples were welded on the outer surface of the reactor, in order to measure the skin tube temperatures during operation. The three studied reactors were made out of two heat-resistant tube alloys which were welded together. Incoloy 800HT in the first two radiant cells and ET 45 Micro (reactor 1) or HT E (reactor 2 and 3) in cell 5 to 7. The first part of the reactor is almost 4.8 m long with an internal diameter of 9 mm and is placed in cells 3 and 4. During the experiments the temperature in these cells is kept below 644 °C to keep cracking and thus coking in these cells to a bare minimum. The second part is located in cell 5 and 6, bypasses cell 7 and is manufactured out of ET 45 micro or HT E (green reactor line in Figure 2). The 3D technology 'SCOPE®' is only applied in the vertical straight tubes and is marked with a blue dashed line. The internal diameter of the ET 45 Micro and HT E bare coils is 37.4 mm, while the reactor coil with the SCOPE® profile was specifically designed to have an equal cross sectional area as the bare reactors. This design resulted in an internal diameter ranging from 35 to 39.1 mm from top-to-top and valley-to-valley, respectively, and nine fins. Table 1 shows the alloy composition as it is reported by the manufacturer.

The analysis section allows on-line identification and quantification of the entire product stream, a wide boiling point mixture, containing all permanent gases, such as H_2, N_2, CO and CO_2 and hydrocarbons ranging from methane to polycyclic aromatic hydrocarbons.

Table 1: Typical composition of the Reactor Material INCOLOY® 800HT® and the Commercial Centralloy® ET 45 Micro and Centralloy® HT E [35-37]

Alloy	Composition [wt %]								
	C	Si	Mn	Cr	Fe	Ni	Al	Nb	Additions
INCOLOY® 800HT®	0.06-0.10	< 1.0	< 1.5	19.0-23.0	39.5 min	30.0-35.0	0.25-0.60	-	Ti, Al+Ti 0.85-1.20
ET 45 Micro	0.45	1.6	1.0	35	bal.	45	-	1.0	MAE, RE
HT E	0.45	-	-	30	bal.	45	4.0	0.5	MAE, RE

RE: Addition of reactive elements; MAE: Addition of micro-alloying elements

Experimental procedure

The experiments performed on the pilot plant setup consisted of several steps: pre-sulfiding (pre-S), cracking and decoking.

A total of 5 coking/decoking cycles were performed for each reactor. During the initial heating up phase, steam was fed to the reactor while the temperature of the reactor was gradually increased from 300 to 800 °C with a heating ramp of 50 °C/h. This slow heating rate is specifically chosen in order to reflect the typical heating-up process of the industrial process where thus a thin but very uniform protective oxide layer is formed. Prior to every coking step a pre-sulfiding step with DMDS was performed. When the temperature profile remains stable, sulfur is introduced to the reactor to passivate it. Before introducing the hydrocarbon feed to the reactor, the reactor is heated under steam atmosphere, until the desired temperature profile is reached. Then, the flow rate of propane and steam are set to the desired value.

Simultaneously with the introduction of the hydrocarbon feed, hexane diluted DMDS is added to the gas stream.

Three different coking durations were employed for the standard temperature profile, namely 2, 6 and 12 hours, while the end-of-run (EOR), high tube metal temperature (TMT), experiment was run for 1 hour and 40 minutes. After every coking cycle, the deposited coke was burned off with a steam-air mixture, while the CO and CO_2 formed during the combustion and gasification of the coke was continuously measured with an infrared analyzer. With the measured amounts of CO and CO_2 the total amount of burnt off coke can be calculated. To start a decoking cycle, the reactor is heated under an inert flow of helium, to preserve the coke layer. After reaching the desired temperatures (cell 3 to 7 at 800 °C), the infrared measurement is started and steam is added to the reactor together with a flow of helium. Once helium flow is stopped air is admitted to the reactor. When the measured CO_2 concentration drops below 1.0 vol%, the temperature in cells 5 to 7 are increased to 900 °C. When practically all the coke is gasified and/or combusted, the flow of steam is switched off and the decoking procedure continues with a pure air atmosphere.

All experimental runs were carried out at a constant coil outlet pressure, while maintaining a coil residence time of ~0.9 s and Reynolds numbers in the order of $4.2 – 5.4 \cdot 10^3$. During the experiment 'TMT max', the COT is set at 110 °C (bare tubes) / 160 °C (SCOPE®) higher than baseline COT. Although this is not industrially realistic, the experiment is included to mimic the high TMT values at the end-of-run conditions. Metallurgical aging of the material is hereby simulated as it is shown that at higher metal temperatures the Fe-Ni-Cr alloys carburize faster than their alumina forming alloys [16]. From the second industrial coking cycles onwards the material has been previously exposed to these harsh end-of-run conditions, i.e. the alloy experienced metallurgical aging. The order of the coking cycles is presented in Table 2. These different durations are employed to have a better distinction between catalytic and asymptotic coking rates, where the standard coking cycle of 2 hours gives an indication for the catalytic coking rate. Based on previous experiments the stage of catalytic coke formation was estimated to last approximately 3 hours [29].

Table 2: Order of the experiments with duration and COT/TMT set point

Coking cycle	**Duration [h]**	**COT [°C]**
1	6	Baseline
2	2	Baseline
3	6	Baseline
4*	1.67	Baseline + 110/ + 160**
5	12	Baseline

*Experiment TMT max, EOR condition
** HT E + SCOPE®

Tube metal temperatures

During the experiments the tube metal temperatures (TMT) were continuously measured via weld on thermocouples for the reactors involving HT E. For the ET 45 Micro reactor, no weld-on thermocouples were utilized. The TMTs were in this case measured via an infrared dual wave-length pyrometer from Sensortherm® Metis M322 and a manually inserted thermocouple type K that was touching the outer tube surface of the coil at various positions along the axial direction. These two measuring means are depicted in Figure 3.

The position that resulted in the highest TMT is reported and used for the control of the 'TMT max' experiment.

Figure 3: Picture of the setup for the temperature measurements of the outer surface of the ET45 micro reactor. (Left) Infrared temperature measurement; (right) manual thermocouple type K touching the reactor surface through an ignition hole

Results and discussion

Product yields

The goal of this study is to investigate the performance of the three different reactors on their coke mitigation abilities while maintaining the same cracking severity.

Figure 4 shows the yields of ethene and propene averaged over different analyses taken during a given experiment.

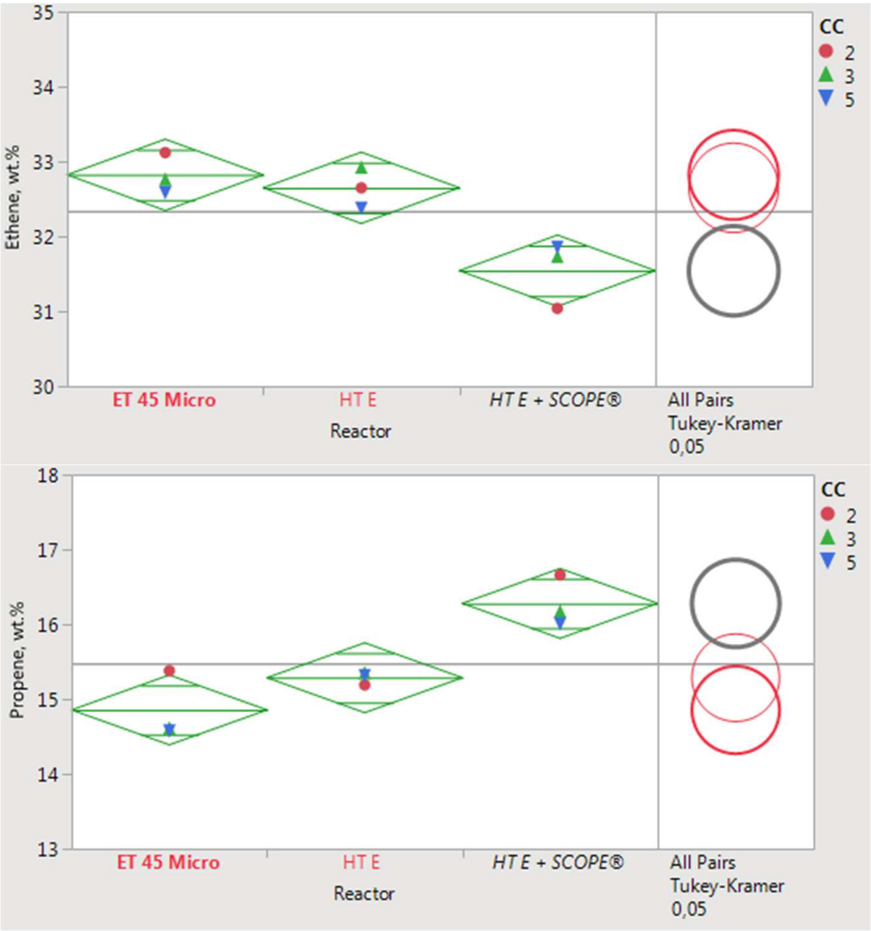

Figure 4: Ethene (top) and propene (bottom) variance per coking cycle (CC) and per reactor

The statistical analysis demonstrates that there is no significant change in ethene formation between ET 45 Micro and HT E, but HT E + SCOPE® obtains lower ethene yield. While the propene yield increased for HT E + SCOPE® in comparison with both ET 45 Micro and HT E. The former is caused by the reduced over-cracking in the near wall region due to lower tube metal temperatures.

Coke formation

A comparison of the coking rates is depicted in Figure 5.

As the coking rate of the second cycle is giving a representation of the catalytic coking rate, its values are obviously larger. This explanation can also be applied for the fourth coking cycle, although the influence of the applied extreme cracking severities will share a bigger contribution to the overall coking rate. This is due to the fact that a higher severity or cracking temperature results in higher coking rates [38, 39].

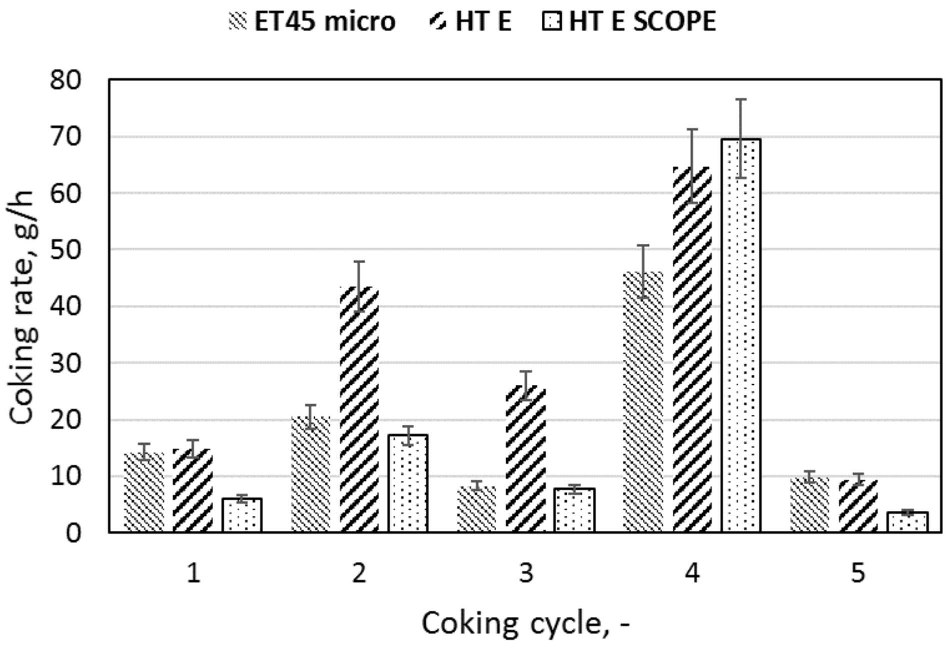

Figure 5: Coking rates as a function of the coking cycles for the three different reactors: ET 45 Micro, HT E and HT E + SCOPE®

Considering the fact that in an industrial steam cracker the coils experience maximal TMT values during the EOR of the first coking cycle, aging the alloy at the start of its lifetime. And adding the fact that the asymptotic coking rate has most influence on the overall run length [40], makes the coking rate from cycle five the most interesting value of the study. In fact, the difference between the third and fifth coking rate holds most information on how the actual reactor will perform in an actual steam cracker.

For ET 45 Micro the coking rate increased when comparing cycle 3 with cycle 5. An increase of 1.2 was observed. The increase is even larger when the observed coking rates are deconvoluted in a purely catalytic and an asymptotic contribution. This can be achieved by subtracting the amount of coke obtained during the 2 hour coking cycle (CC2) from the amount of coke measured during the third and fifth cycle and attributing the remaining coke to an asymptotic rate. The factor then becomes 3.4. The coking rate increase is attributed to the change in the oxide scale of the chromia forming alloy. ET 45 Micro is protected by a complex system of oxide layers with chromium-manganese spinel on top of a chromia layer and with a thin layer of SiO_2 at the oxide-metal interface [16], visualised in Figure 6. During cycle four, the metal was aged metallurgical to mimic extreme end-of-run conditions, for which the TMT reaches values above 1050 °C. During those harsh conditions the protective oxides tend to transform into chromium carbides. Furthermore, the growing coke layer on top of a chromia- or Cr-Mn-spinel scale incorporates significant amounts of Cr and Mn as nanoscale sized (worm-like shaped) oxides. The structure of these oxides suggests a kind of oxide intercalation into the coke. This phenomenon is corrosive since it extracts Cr and to a lesser extent Mn from the base material and by that, contributes to the depletion of oxide forming elements in the alloy.

Although the oxides are restored during decoking, the decoking is only partially reestablishing the original oxides. In other words, the oxide to carbide transformation initiates a non-reversible damage to the protecting scale resulting in a rough, ash-like oxide with an increased surface area that accelerates subsequent coking rates significantly [16]. This finding is in stark contrast with the coking rate decrease observed for the reactors manufactured out of HT E. After the high temperature EOR coking cycle, a factor 2.8 and 2.1 reduced coking rates were obtained for HT E and HT E + SCOPE®, respectively. When assigning a catalytic and asymptotic coking rate the coke reduction factors become even higher, i.e. 6.7 and 3.4 for HT E and HT E SCOPE® respectively. The protective scale formed after the heating up phase on the HT E reactors is expected to be composed out of Al_2O_3 and an oxide with a combination of Cr and Al, as it is shown in Figure 7 [16].

Due to a much better thermodynamic stability alumina scales are favorable as protection at extreme conditions typical for a steam cracking furnace provided that the kinetics ensures an unbroken and tight scale growth and that internal oxidation is suppressed. The latter is achieved by a suitable alloy composition [16].

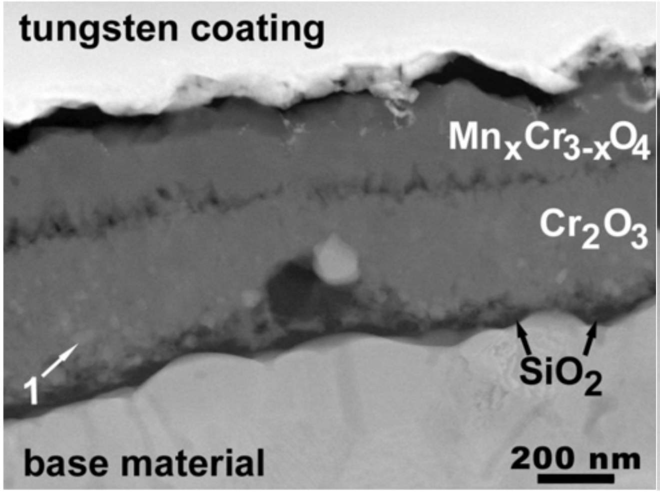

Figure 6: STEM-HAADF micrograph of the oxide scale on the ET 45 Micro material after the heating-up phase (1 : particles with Fe and Ni) [16]

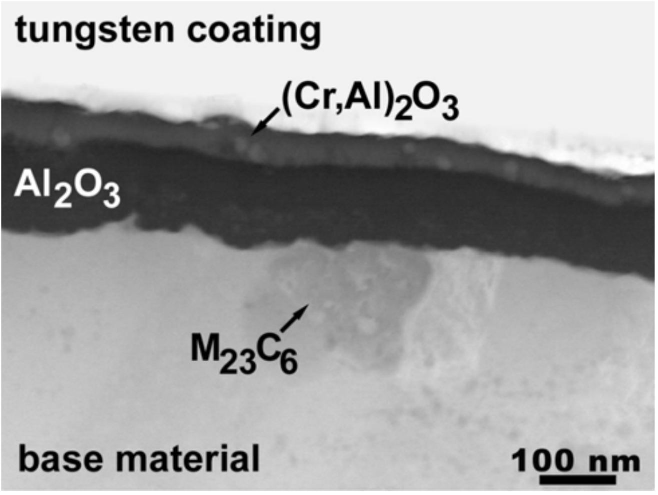

Figure 7: STEM-HAADF micrograph of the oxide that can be found on the HT E reactor surface after the heating-up phase [16]

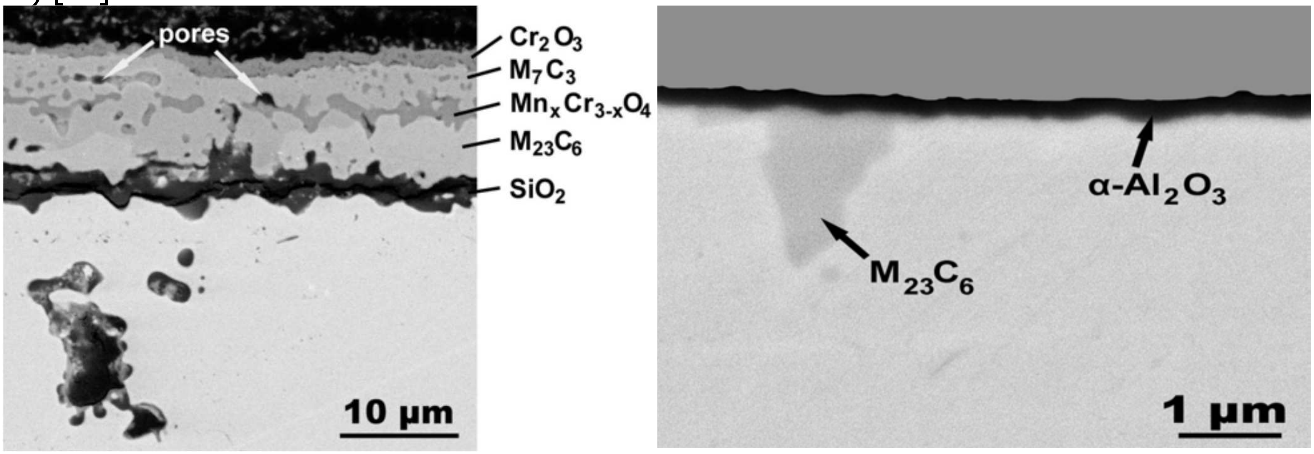

Figure 8: SEM-micro-graphs (BSE) of the reaction layers in cross section: Test conditions: 1 coking-decoking cycle with 1 h decoking; max temperature 1100 °C. (left) ET 45 Micro; (right) HT E [16]

In general, the HT E + SCOPE® reactor had an outstanding performance with regard to its coking tendency, except for cycle 4, the 'TMT max' experiment. It has to be mentioned that the COT was increased by another 50 °C in comparison with the bare reactors, to compensate for the lower tube wall temperatures.

The excellent coking performance during the standard tests can be immediately attributed to the (expected) lower radial gradients of the SCOPE® 3D profile. The profile enhances mixing, reduces the average cup temperature and thereby reducing the inner surface temperature.

Figure 9 shows the deposited coke as a function of time for the different reactors. Although HT E has a higher coking rate at the beginning, its rate drops after even one single higher temperature cycle of short duration faster and eventually drops below the coking rate of ET 45 Micro. The combination of HT E + SCOPE® shows a better coking performance than the other two tested reactors over the presented time regime.

Figure 9 further shows a better performance for the reactors manufactured out of HT E when the estimated coke deposition (based on the tests prior to the high TMT experiment) is compared with the one measured after the high temperature experiment. The coke deposition reduction is less pronounced for HT E + SCOPE®, because it is more difficult to push to higher temperatures. During the tests prior to the high temperature exposure, the α-alumina scale is not fully established, Cr,Al-oxides are still present (see also Figure 7). This mixed oxide scale changes when the material is exposed to higher temperatures, during which the α-Al_2O_3 is fully developed (Figure 8 right). The complete opposite trend can be observed for the reactor manufactured out of ET 45 Micro. The reactor performs worse in comparison with the estimated coke deposition. This can be attributed to the chromia scale that suffers deterioration during the high TMT experiment (Figure 6 versus Figure 8 left). The difference between the HT E reactor and HT E + SCOPE® can be solely explained by the reduction in tube wall temperature.

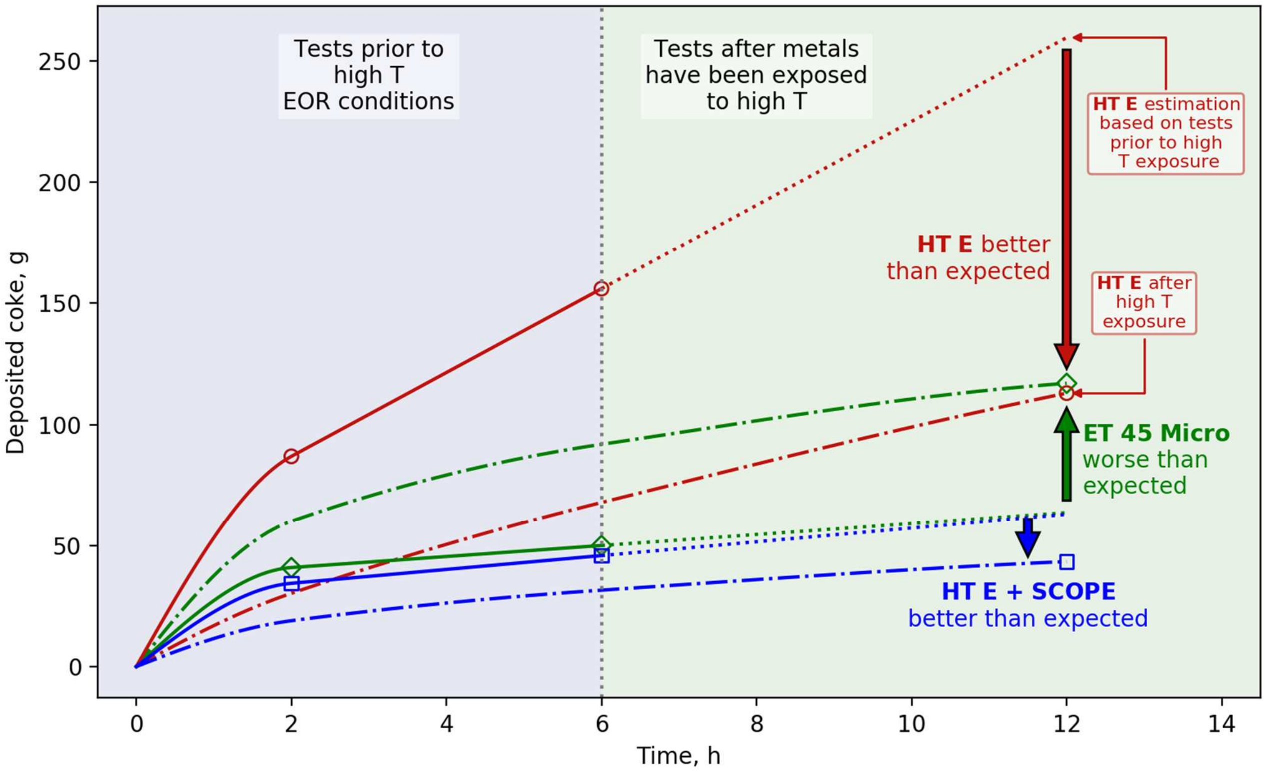

Figure 9: Deposited coke as a function of time for the three different reactors, ○ (red) HT E, ◇ (green) ET 45 Micro, and □ (blue) HT E + SCOPE®. Dotted lines are estimated values based on the tests prior to the exposure of the tubes to higher temperatures, while the dash-dotted line shows the estimated coke (based on cycle 5, the 12 h coking run) after the exposure at EOR high temperatures. Tests prior to high TMT conditions (blue haze), before 6 hours, tests after high TMT experiment (green haze), after 6 h.

Tube metal temperatures

When comparing the measured outer surface temperature during the standard experiments (Figure 10), it can be observed that the temperatures of the HT E + SCOPE® reactor are significantly lower than for the bare HT E reactor, a difference of at least 20 °C. This can be again explained by the lower radial temperature gradients of the reactor [5]. Which means that for the same inner gas phase temperature a lower metal tube temperature is required, which has, as a further consequence, that longer run lengths can be achieved because the metallurgical threshold temperature will be reached at a slower pace.

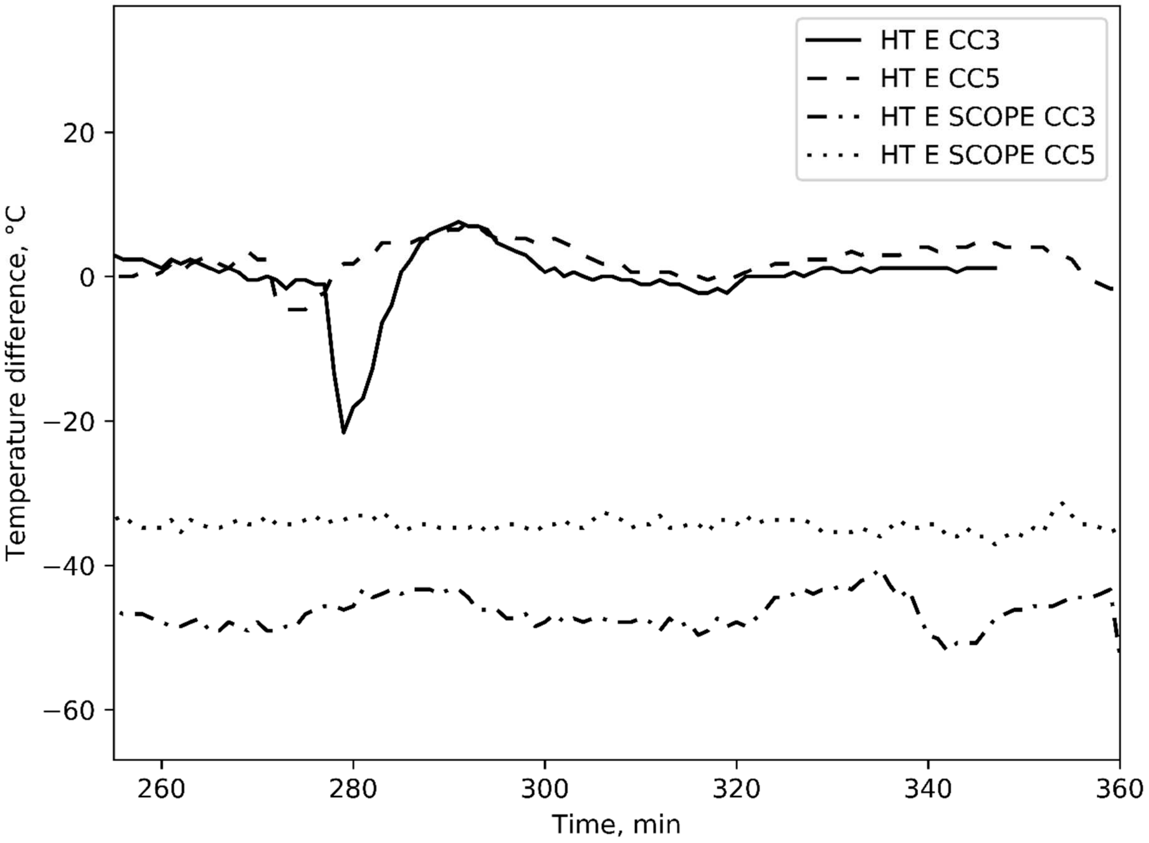

Figure 10: Relative difference of the measured tube metal temperatures during coking cycle 3 and cycle 5 for the reactors manufactured out of HT E, i.e. bare and SCOPE® (reference: average of HT E CC5)

Furnace fuel consumption

During every step of the experiments, the natural gas consumption was monitored. The natural gas serves as fuel for the furnace. It is mixed with air by the combustion controller and then distributed over the 90 wall burners. Its consumption is, therefore, a good measure for the fuel intake of the furnace and thus the energy efficiency. Because the operating conditions were kept identical for different reactors, the energy efficiency of the tested reactor can be derived. In general, roughly 10 % lower fuel consumptions were obtained for the HT E + SCOPE® reactor.

This, again, shows that due to a more uniform temperature distribution of the SCOPE® design, a better heat transport from the furnace towards the reacting gas phase is achieved. Less over- and under-cracking of the mixture can lead to the same yield output with a lower heat input.

Conclusions

Three different reactors were experimentally validated in a pilot plant setup under industrially relevant conditions for propane cracking. The first reactor is constructed from Centralloy® ET 45 Micro, a chromia forming alloy. The second and third reactor were manufactured from Centralloy® HT E, an alumina former. A 3D reactor technology, called SCOPE®, was installed in one of the Centralloy® HT E reactors. The cross sectional area of all three reactors were kept identical. Five coking cycles of different durations were imposed for all three reactors, to acquire knowledge in the catalytic and pyrolytic coking mitigation capabilities of the reactors.

ET 45 Micro shows a better catalytic coking behavior at the initial lifetime stages of the coil (before aging) than HT E. However, it appears that the asymptotic coking rate of HT E is lower than for ET 45 Micro. The transformation of the protective oxide scale to an agglomeration of carbides explains why ET 45 Micro worsens when the coil is subjected to high temperature end-of-run conditions, while the coking behavior of Centralloy® HT E even improves after aging. As the main contributor to the industrial run length is attributed to the asymptotic coking rate, it becomes clear that HT E will perform better in a typical industrial furnace.

The combination of the better performing material, Centralloy® HT E, with the 3D geometry, SCOPE®, outperforms the other two reactors regarding its coking behavior. A factor 2.7 lower coking rate after the first industrial metallurgical aging cycle can be achieved by combining alloy HT E with the 3D SCOPE® technology. The reason for lower coking rates can be attributed to the lower radial gradients inside the coil. These lower radial gradients result further in lower tube metal temperatures, meaning that the industrial plant can be operated longer because the temperature threshold of the material would be reached slower. The fuel consumption to fire the furnace was almost 10 % lower when comparing the bare HT E reactor with HT E + SCOPE®.

Lower coking rates, and lower tube metal temperatures at the start-of-run will both increase the run lengths. Add the fact that lower gas consumptions were measured for the combination, Centralloy® HT E + SCOPE®, makes a clear indication that the energy efficiency of an industrial steam cracker can be drastically increased by selecting the optimal reactor technologies.

Acknowledgment

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References

1. ExxonMobil, *The outlook for Energy: A view to 2040*. 2012.
2. Munoz Gandarillas, A.E., et al., *Coking Resistance of Specialized Coil Materials during Steam Cracking of Sulfur-Free Naphtha.* Industrial & Engineering Chemistry Research, 2014. **53**(35): p. 13644-13655.
3. Ren, T., M.K. Patel, and K. Blok, *Steam cracking and methane to olefins: Energy use, CO2 emissions and production costs.* Energy, 2008. **33**(5): p. 817-833.
4. Ren, T., M. Patel, and K. Blok, *Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes.* Energy, 2006. **31**(4): p. 425-451.
5. Schietekat, C.M., et al., *Computational Fluid Dynamics-Based Design of Finned Steam Cracking Reactors.* Aiche Journal, 2014. **60**(2): p. 794-808.
6. Zimmermann, H. and R. Walzl, *Ethylene*, in *Ullmann*. 2012, Wiley: Weinheim.
7. Petrone, S.S.A., R.C. Mandyam, and A.G. Wysiekierski, *Surface alloyed high temperature alloys*. 2000, Google Patents.
8. Verdier, G. and F. Carpentier *Consider new materials for ethylene furnace applications. An innovative metallurgy solves maintance issues*. 2011. **90**, 61-62.
9. Industries, M. *Manaurite XM: Heat resistant alloys for hydrocarbon processing*. 2012 [cited 2015; Available from: http://www.manoir-industries.com/site/ref/scripts/FR_Brochures-Petrochem_122.html.
10. Industries, M. *Manaurite XTM: Heat resistant alloys for hydrocarbon processing*. 2012 [cited 2015; Available from: http://www.manoir-industries.com/site/en/ref/Manoir-Petrochem-Brochures_75-72.html.
11. Group, S.C. *Why choose S+C? Because you know what matters in the petrochemical industry*. 2016 [cited 2018 21/02/2018]; Available from: https://www.schmidt-clemens.com/fileadmin/sc-downloads/SC_Broschuere-Petrochemie_ENG.pdf.
12. Munoz Gandarillas, A.E., et al., *Influence of the Reactor Material Composition on Coke Formation during Ethane Steam Cracking.* Industrial & Engineering Chemistry Research, 2014. **53**(15): p. 6358-6371.
13. Crynes, L.L. and B.L. Crynes, *COKE FORMATION ON POLISHED AND UNPOLISHED INCOLOY-800 COUPONS DURING PYROLYSIS OF LIGHT-HYDROCARBONS.* Industrial & Engineering Chemistry Research, 1987. **26**(10): p. 2139-2144.
14. Jakobi, D., C.K. van Moesdijk, P., and A. von Richthofen, *Tailor - Made Materials for high temperature applications: New strategies for radiant coil material development*, in *NACE Corrosion 2009*. 2009.
15. Jakobi, D., P. Karduck, and V.R.A. Freiherr, *Nickel chromium alloy*. 2011, Google Patents.
16. Jakobi, D., P. Karduck, and V.R.A. Freiherr, *The High-Temperature Corrosion Resistance of Spun-Cast Materials for Steam-Cracker Furnaces - A Comparative Study of Alumina- and Chromia-Forming Alloys*, in *NACE Corrosion 2013*. 2013.
17. Schietekat, C.M., et al., *Catalytic Coating for Reduced Coke Formation in Steam Cracking Reactors.* Industrial & Engineering Chemistry Research, 2015. **54**(39): p. 9525-9535.

18. Olahova, N., et al., *CoatAlloy ™ Barrier Coating for Reduced Coke Formation in Steam Cracking Reactors: Experimental Validation and Simulations.* Industrial & Engineering Chemistry Research, 2017.
19. Petrone, S., et al., *CATALYZED-ASSISTED MANUFACTURE OF OLEFINS (CAMOL): YEAR-(4) UPDATE ON COMMERCIAL FURNACE INSTALLATIONS.* AIChE: Texas, 2010. **Vol. 88a**.
20. Sarris, S.A., et al., *Optimization of the in Situ Pretreatment of High Temperature Ni–Cr Alloys for Ethane Steam Cracking.* Industrial & Engineering Chemistry Research, 2017. **56**(6): p. 1424-1438.
21. Zhang, Z.B. and L.F. Albright, *Pretreatments of Coils to Minimize Coke Formation in Ethylene Furnaces.* Industrial & Engineering Chemistry Research, 2010. **49**(4): p. 1991-1994.
22. Wang, J., M.F. Reyniers, and G.B. Marin, *Influence of dimethyl disulfide on coke formation during steam cracking of hydrocarbons.* Industrial & Engineering Chemistry Research, 2007. **46**(12): p. 4134-4148.
23. Olahova, N., et al., *Coking tendency of 25Cr-35Ni alloys: influence of temperature, sulfur addition and cyclic aging.* Industrial & Engineering Chemistry Research, 2018.
24. DeSaegher, J.J., T. Detemmerman, and G.F. Froment, *Three dimensional simulation of high severity internally finned cracking coils for olefins production.* Revue De L Institut Francais Du Petrole, 1996. **51**(2): p. 245-260.
25. Schietekat, C.M., et al., *Swirl flow tube reactor technology: An experimental and computational fluid dynamics study.* Chemical Engineering Journal, 2014. **238**: p. 56-65.
26. Gyorffy, M., et al. *Mert performance and technology update*. in *AIChE Spring Meeting: Ethylene Producers Conference, Tampa Bay, USA*. 2009.
27. Zhang, Y., et al., *Impact of flue gas radiative properties and burner geometry in furnace simulations.* AIChE Journal, 2015. **61**(3): p. 936-954.
28. Wolpert, P., et al., *Finned tube for the thermal cracking of hydrocarbons, and process for producing a finned tube*. 2008, Google Patents.
29. Dhuyvetter, I., et al., *The influence of dimethyl disulfide on naphtha steam cracking.* Industrial & Engineering Chemistry Research, 2001. **40**(20): p. 4353-4362.
30. Pyl, S.P., et al., *Biomass to olefins: Cracking of renewable naphtha.* Chemical Engineering Journal, 2011. **176–177**: p. 178-187.
31. Van Geem, K.M., et al., *On-line analysis of complex hydrocarbon mixtures using comprehensive two-dimensional gas chromatography.* Journal of Chromatography A, 2010. **1217**(43): p. 6623-6633.
32. Dijkmans, T., et al., *Production of bio-ethene and propene: alternatives for bulk chemicals and polymers.* Green Chemistry, 2013. **15**(11): p. 3064-3076.
33. Olahova, N., et al., *Thermal Decomposition of Sulfur Compounds and their Role in Coke Formation during Steam Cracking of Heptane.* Chemical Engineering & Technology, 2016. **39**(11): p. 2096-2106.
34. Pyl, S.P., et al., *Wood-derived olefins by steam cracking of hydrodeoxygenated tall oils.* Bioresource Technology, 2012. **126**: p. 48-55.
35. Group, S.C., *Centralloy(r) ET 45 Micro Material Data Sheet*. 2009.
36. Group, S.C., *Centralloy(r) HT E Material Data Sheet*. 2014.

37. Xu, L.Y., et al., *Failure analysis of Incoloy 800HT pipe at high temperature.* Engineering Failure Analysis, 2013. **31**: p. 375-386.
38. Van Geem, K.M., et al., *Coke Formation in the Transfer Line Exchanger during Steam Cracking of Hydrocarbons.* Industrial & Engineering Chemistry Research, 2009. **48**(23): p. 10343-10358.
39. Froment, G.F., *COKE FORMATION IN THE THERMAL-CRACKING OF HYDROCARBONS.* Reviews in Chemical Engineering, 1990. **6**(4): p. 293-328.
40. Reyniers, G.C., et al., *COKE FORMATION IN THE THERMAL-CRACKING OF HYDROCARBONS .4. MODELING OF COKE FORMATION IN NAPHTHA CRACKING.* Industrial & Engineering Chemistry Research, 1994. **33**(11): p. 2584-2590.