

# State-of-the-art of Coke Formation during Steam Cracking: Anti-Coking Surface Technologies

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**S** Supporting Information

**ABSTRACT:** Although steam cracking is a mature technology, mitigation of coke formation remains one of the main challenges in the petrochemical industry. To increase the olefin output of existing plants, coil materials that can withstand higher temperatures are desired. This work reviews material technologies that were developed and tested in the past three decades to minimize the rate of coke deposition and extend the furnace run length. The material not only determines the mechanical properties of the coil but also affects the coking rate substantially. In some cases, differences in coking rates by more than a factor 10 have been observed. SiC materials could be operated at significantly higher temperatures, and this leads



to higher olefin selectivity if one includes acetylene hydrogenation; however, the mechanical joints make it currently impossible to take advantage of their superior temperature resistance. On the industrial scale, operational improvements have been reported with advanced reactor surface technologies such as high-performance alloys and coatings during the past decade. Catalytic coatings go a step further than barrier coatings by actively removing coke that is deposited on the coils. Another trend is to add aluminum to the coil material, which forms a protective aluminum oxide layer on the reactor wall during operation and results in reduced carburization. To optimize the coking mitigation capabilities of the coils, the state-of-the-art materials and/or coatings should be combined with 3D reactor technologies, which is not always possible for all materials because of the advanced machining that is needed.

# 1. INTRODUCTION

Steam cracking is the most important petrochemical process for the production of base chemicals. Also, in the future, it is expected to be the dominating process for light olefins and aromatics production.<sup>1</sup> Simultaneously, it is the most energyconsuming process in the chemical industry and globally uses approximately 8% of the sector's total primary energy demand.<sup>2</sup> Energy cost accounts for approximately 70% of production costs in typical ethane- or naphtha-based olefin plants.<sup>3</sup> An advantage of this process over other cracking processes is that the chemistry involved leads to the formation of large amounts of unsaturated compounds. It is the principal industrial method for producing lighter alkenes, including ethylene, propylene, 1, 3-butadiene, and aromatics, such as benzene, toluene, and xylene, which are now considered commodities. They form the building blocks for a wide range of derivates used in our daily lives. Similar to electricity or cooling water, they must be produced at the lowest cost, continuously, and reliably to feed integrated downstream units. Nevertheless, the crackers are the real profit centers with margins typically of 100 to 200 \$ per ton ethylene produced for well-operated plants. The applications of olefins and aromatics are numerous, and their derivatives are traded around the world.

Commercial steam cracking of hydrocarbons is performed almost exclusively in fired tubular reactors. The hydrocarbon feed stream enters the furnace and is preheated by heat exchange in the convection section with the flue gas. Afterward, the feed is mixed with steam and further heated to initial cracking temperature (500-680 °C), depending on the feedstock. At this point, the stream enters a fired tubular reactor in which it is heated to temperatures of around 750-875 °C for about 0.1–0.5 s under a controlled inlet flow rate of the hydrocarbon feed and steam. During the short reaction time, the feed is cracked into smaller molecules such as ethylene, and heavier olefins and diolefins. Since the conversion of saturated hydrocarbons to olefins in the radiant tube is highly endothermic, high energy input rates are desired. The reaction products leaving the tube at 800-850 °C are quenched to 550-650 °C within 0.02-0.1 s to prevent degradation of the highly reactive products by secondary reactions. This quenching takes place in the transfer line exchanger by vaporization of high-pressure boiler

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feedwater. The resulting product mixture, which can vary widely in composition depending on feedstock and severity of the cracking operation, is then separated into the desired products by using a complex sequence of separation and chemicaltreatment steps.<sup>4</sup>

As the reactor tubes need to withstand the high furnace temperatures, the industrial standard is the use of special ironnickel-chrome alloys, which show excellent heat resistance. However, iron and nickel are also known to catalyze the deposition of carbonaceous deposits (coke) on the reactor wall.<sup>4</sup> This degrades the overall efficiency of the reactor, and thus, reaction conditions are selected to minimize coke formation. Coke accumulation exhibits a number of negative effects on the efficiency of the steam cracker. The formed coke layer causes a reduction of the available cross section of the tubes for the process gas, leading to a higher pressure drop over the reactor. Furthermore, coke present at the reactor tube wall implies an enhanced resistance for heat transfer.<sup>5</sup> The unit can usually only run for a few weeks before it has to be taken out of production for decoking.<sup>6</sup> Typically this will require production to be halted for 48 h, having a considerable adverse effect on the economics of the process.<sup>7</sup> In most cases, decoking requires the furnace to be isolated from the process and then a flow of steam or a steam/air mixture is passed through the furnace coils at 850-950 °C. This converts the hard solid carbon layer to carbon monoxide and carbon dioxide. Once this reaction is complete, the furnace can be returned to service.<sup>4</sup>

Numerous studies have been conducted to understand coke formation and the factors affecting it. Coke is formed via three principal mechanisms: the heterogeneous catalytic mechanism, the heterogeneous free-radical mechanism, and the homogeneous droplets condensation/tar deposition mechanism.<sup>8</sup>

In light of the negative effects of coke formation on the economics and energy efficiency of the process, many efforts have been made toward the development of technologies to reduce coke formation. These technologies can be divided into three groups:

- Surface technologies
- Three-dimensional (3D) reactor technologies
- Use of feed additives

The focus of this work is not on 3D reactor technologies or feed additives. For the former, many recent developments<sup>9-11</sup> have limited the negative impact of the resulting pressure drop increase, while for the latter, mostly dimethyl disulfide (DMDS) is used. The reactor material is thus one of the most important factors, maybe the most important factor, that determines coke formation. In the past few decades, step-by-step, new, and better construction materials have been developed and applied industrially. In this paper, the application of advanced reactor surface technologies such as high-performance alloys and special coatings as well as their ability to reduce coke formation are discussed. Good run length improvements for ethane cracking have been reported with different surface coatings. However, for naphtha and heavier feeds, the picture is less clear, where improved materials (aluminum and nonaluminum containing) and coatings (catalytic and noncatalytic) can be a game changer. For example, promising catalytic coating compositions need to be tuned in relation to the feed and how the reactor is operated, as will be discussed in this work. Finally, the implications are assessed by simulation because this is almost the only way to compare different technologies for a specific case as a one-to-one comparison on an industrial scale is difficult and expensive.

#### 2. REACTOR SURFACE TECHNOLOGIES

**2.1. Metallurgy Developments.** During the past decade, furnace coil suppliers have done a tremendous amount of work on finding new construction materials and techniques for producing reactors in steam cracking furnaces that can withstand more severe operating conditions.<sup>12</sup>

Modified coils can help to achieve these conditions, but coil design is limited by metallurgy. Generally, in pressure vessels, pipings, fittings, valves, and other equipment in refineries and petrochemical plants, a wide variety of iron- and nickel-based materials are used. Plain carbon steel is the most common. It loses strength and is susceptible to oxidation at 316–343  $^{\circ}\text{C}.$ On addition of Cr (0.5-9%) and Mo (0.5-1%), the working temperature can be increased to 650 °C. As these alloys have inadequate corrosion resistance at high temperature, more specialized Fe-Ni-Cr alloys are required. The aggressive environments in petrochemical and refining applications require cast and wrought heat-resistant alloys, which have high Cr and Ni content. In the 1960s and 70s, the 25Cr-35Ni alloys replaced the commonly used wrought materials. To increase the carburization resistance of the coils further, more recently, 35Cr-45Ni alloys are employed.<sup>12,13</sup> In the most recent cracking furnaces, aluminum is added to the coil's metallurgical matrix.

The evolution, up to 2011, of the materials typically used in steam cracking furnaces is listed in Figure 1.<sup>12</sup> This evolution can also be observed when comparing the publications from Jakobi et al. from 2003<sup>14</sup> and 2010,<sup>15</sup> in which the Aluminum containing material Centralloy HT E is added in the latter, more recent, article.

To reduce coking and enhance carburization resistance of tube materials, a recent generation of alloys are enriched with aluminum. To be completely accurate, Manoir proposed the first alloy containing aluminum in 1981, Manaurite XA.<sup>16</sup> Because of mechanical and production issues, the manufacture of this alloy was stopped. The amounts of Al are limited to prevent the possible formation of low-melting point compounds. In a sufficient amount, it also decreases the creep-resistance properties. To restore those creep properties, carbide formers such as tantalum can be added.<sup>12</sup> Adding aluminum to the alloy can further result in internal oxidation at the inner tube surface, as was observed for 40XO after 1 year of service.<sup>17</sup> This internal oxidation is also visible in HT A. However, in the improved Al-containing alloy, HT E from Schmidt + Clemens, this is eliminated.<sup>18</sup> In fact, in 2010, Jakobi et al. published the improvements performed in the "HT-alloys" family.<sup>15</sup> The optimization is located in a refinement of the diffusivity of oxide-forming elements in the matrix, causing the initially formed oxide layer to be stabilized with respect to catalytic coke formation and to high-temperature corrosion.

In petrochemical and refining industries, radiant coils must be selected in light of the following considerations:<sup>4,12,13,19–21</sup>

- Operating temperatures: Ethylene furnaces usually consist of a multipass configuration-type of coils. Because of endothermic cracking reactions and more coke deposition in the last passes, the outlet tubes of the radiant coils operate at a higher temperature. Coke acts as a thermal barrier, and the tube skin temperature needs to be increased to keep the same conversion despite the coke thickness.
- Mechanical properties: The mechanical properties of a material are used for a first screening by the material engineer. However, it is difficult to improve all material properties simultaneously, and typically compromises

Review



Figure 1. Historical summary of the evolution, up to 2011, of steam cracking coil alloys. Reprinted with permission from 12. Copyright (2011) Verdier.

need to be found. For example, while a 25/35 material has superior creep properties, its carburization resistance is affected due to its lower Cr content as compared to 35/45. Starting from the 60s, centrifugally cast alloys are used to substitute the wrought materials due to their higher creep strength.

- Tube service life: The service life of ethylene furnace coils is influenced by numerous factors, including furnace operating conditions, decoking practices, and alloy selection. In many cases, coil service life is limited and shortened by carburization of the inner tube surface, favored by the gasphase environment inside a cracking coil and localized tube wall thinning. The alloy composition also has a substantial influence on coking characteristics. Tube service life is economically important in plant operations. Furnace capital costs represent ca. 20% of the total cost of an ethylene plant. About one-third of this is for radiant coils. With current metallurgy, a 5-year service life in the hottest section and a 7-year service life of the inlet section of a furnace are typical. Doubling the service life is one of the important cost savings that producers try torealize.
- Carburization resistance: Because carbon diffusion is thermally activated, at high temperatures, carbon from the coke diffuses into the metal of the tubes. The mechanical properties, mostly creep- and thermal-shock-resistance properties, are altered to the point that the tube material becomes very brittle. The tube can then fail at the first thermal shock. Because of the mentioned issues, radiant coil outlet materials have evolved from what was originally a 25Cr/35Ni material to a higher Cr-content alloy, typically 35Cr/45Ni material. Frequent and/or aggressive decoking practices appear to accelerate this carburization. Even higher Cr contents in 42Cr/48Ni materials, for example, makes diffusion through the bulk matrix very slow, and therefore, the kinetics of carburization are slowed down. Additionally, an increased content of Cr allows the continuous formation of a protective oxide layer and serves a low coking surface.<sup>22</sup>
- Fabricability: There are many outstanding materials with highly desirable mechanical properties and corrosion

resistance; however, their manufacturing is still limited. There are few applications where welding or bending or some other forming operation is not required to construct a useable piece of equipment. Also, there are some materials which have excellent properties that can be fabricated as produced, but because of "aging", they cannot be modified or repaired after exposure to operating conditions. Therefore, materials must be selected on the basis of their maintainability as well as their original fabricability. In general, the wrought heat-resistant alloys have greater fabricability than the cast materials, but because of their lower strength in comparison with centrifugally casted materials, they are rarely in use in the radiant section of steam crackers (except for finned tubes in the Kellog MS-furnaces).

- **Cost:** Economics enter into every business decision. However, the material selection should not be based only on the initial cost of the material. Its life-cycle cost or cost effectiveness should govern instead. It usually is much more cost-effective to specify a material that will provide an extended life, particularly in areas that are difficult to repair or in components that would cause major shutdowns in case of failure. In these situations, the original cost of the material can be insignificant compared to the loss of production caused by the use of a lower cost, but less effective, material.
- Availability: Prior to the original specification of a material, consideration should be given to its future availability for repairs or replacement in the form or forms that it will be used. In those cases where it might not be available, alternative replacement materials should be identified.

One of the most extensive comparisons has been done by Muñoz et al.<sup>8</sup> for ethane steam cracking under industrially relevant operating conditions using nine commercially available materials. Both Al-enhanced alloys and alloys that do not contain aluminum were compared with silicon carbide. The main characteristics and surface composition of these materials are presented in Table S1.

As can be seen from Figure 2, the Al-enhanced alloys showed a better resistance to coke formation than those without aluminum in their formulation. Good protection against coking



**Figure 2.** Comparison of the initial and asymptotic coking rates for non-Al containing alloys (i,iii) and Al-enhanced alloys (ii,iv) during ethane steam cracking in the electro balance setup. The error bars correspond to the standard deviation ( $\sigma$ ) of the experiments of each material. Reprinted with permission from ref 8. Copyright (2014) American Chemical Society.

| Table 1. Composition <sup>24</sup> of the Tested Alloys [wt %] by Jakobi et al. <sup>23</sup> |      |     |     |    |      |     |    |                         |
|---|------|-----|-----|----|------|-----|----|-------------------------|
| alloy   | С    | Si  | Mn  | Cr | Fe   | Nb  | Ni | other                   |
| HT E  | 0.45 | -   | -   | 30 | bal. | 0.5 | 45 | + additions, Al (2.5–6) |
| ET 45 Micro   | 0.45 | 1.6 | 1.0 | 35 | bal. | 1.0 | 45 | + additions             |

was achieved on these materials when a layer of manganese chromite developed during preoxidation.<sup>8</sup> Note that no sulfur was added and that in all cases the temperature remained substantially below the temperatures at which carburization of Ni, Cr alloys becomes important. This is clearly a limitation in the experiments, implying that the results cannot be one-to-one translated to a real cracking furnace.

In general, the behavior of heat-resistant alloys for radiant coils in steam crackers depends on many different material and process parameters. In a comparative study, Jakobi et al.<sup>23</sup> tested samples from radiant coils under thermal and chemical conditions which are very similar to the conditions at the reactor outlet of a steam cracking coil, where the process gas temperature is at its highest value and the thickness of the coke layer deposited on the inner surface is at its maximum level. The composition of the tested alloys is listed in Table 1.

The cyclic corrosion test consists of a sequence of alternating cracking, in a mixture of steam and hydrocarbons, and subsequent decoking, with a steam—air mixture. The sample temperature is raised during the cracking cycle up to 1100 °C, to induce a highly aggressive atmosphere and to compare the corrosion- and coking-resistance of high-temperature alloys forming a chromia or alumina scale. Chromia-forming alloys have a limited resistance against carburization and also against coking when the sample temperature exceeds the range of 930 °C. The protective chromium oxide layer becomes unstable and transforms to chromium carbide. The alumina-forming HT-alloy shows excellent protection against oxidation and carburization. If the sample temperature exceeds 900 to 950 °C, the transient alumina transforms into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which remains thermodynamically

stable even under severe cracking conditions. The main limitation of this work is the absence of a real cracking environment and the fact that no coking rates can be measured, which are an indication of the run length.

Several FeNiCrAl-alloys that form a protective alumina  $(Al_2O_3)$  scale have been developed, and they are praised for their excellent corrosion properties. The alloys exhibit a maximum working temperature that greatly exceeds any chromia-forming alloy.<sup>25</sup> For example the alumina-forming technology (AFT) from Kubota represents a new generation of cracking coils that, if pretreated properly, have a uniform aluminum oxide layer on the inner surface. The uniform alumina scale results in an excellent carburization resistance and can reduce catalytic coke formation.<sup>26</sup>

Another example of alumina-forming alloys, Sandvik APMT, shows also excellent properties when it comes to prevent coke formation and carburization.<sup>27</sup> APMT has a good corrosion resistance in most atmospheres due to the formation of a dense alumina scale (see Figure 3).

This scale is an effective barrier against diffusion of carbon and oxygen from the gas phase into the metal matrix, as well as for blocking the catalytically active alloying elements, like Fe, inside the alloy from reaching the oxide surface. Laboratory experiments, as well as field trials, indicate that APMT results in lower coking rates in comparison with conventional chromia-forming alloys. According to the results from test installations, tube metal temperatures (TMT) measured on the APMT tubes are  $\sim 10-30$  °C lower than that of the cast 35Cr-45Ni tubes after the same time on-stream when ethane is used as feedstock. When naphtha was used as feedstock, the difference was even bigger,



Figure 3. Cross section of alumina scale of APMT, formed in air after 3000 h at 1200 °C. Reprinted with permission from ref 27. Copyright (2007) Lundberg.

~20–60 °C after the same time on-stream. Because of the higher porosity of coke when cracking naphtha, the thermal conductivity is smaller, and hence, the difference in TMT when cracking naphtha is larger than when cracking ethane. In both cases the coil outlet temperature (COT) was measured to be slightly higher in the APMT tubes. This difference in TMT is a strong indication that the coke layer formed inside the APMT tubes is much thinner than the one formed in the reference tubes over time. The reason for the differences in heat transfer efficiency is attributed to the lower coking rate of APMT.<sup>27</sup>

The Al-containing alloy, HT E, has been installed for over 14 years, and a 10 year field performance review is described by Jakobi et al.<sup>28</sup> The HT E material is supplied to more than 120 steam cracking furnaces covering a broad range of different feeds, different geometrical designs and material combinations. Jakobi et al. concluded that when employing an Al-containing material, the ethylene plant operator has two choices:

- Maintaining the existing operational parameters and hereby obtaining increased furnace run lengths, because less coke is deposited with the application of the alloy. For a comparison test program between two ethane furnaces, executed over a period of nine months, a run length prolongation of 2.6 for identical operating conditions was seen.
- Changing the existing operational parameters and either aiming for a higher conversion/higher cracking severity or aiming for an increased throughput. This is, again, possible due to the lower coke formation. For naphtha cracking furnaces (Lummus SRT III), an average increase of 4.3% of the feed flow rate is reported while keeping the run length unchanged.

Additional benefits include the following: the furnace maintenance costs can be reduced as the alloy has a greater tolerance to operational transients (unscheduled shut-downs) and temperature excursions, while a reduction in CO formation is also observed. The time demand to reach full cracking conditions after start-up/decoking could be shortened up to 50%, thus gaining precious production time.

As the potential benefits from an upgrade of the steam cracker coils are influenced by a number of inter-related factors, it is important to mention that the upgrade should be tailor-made. When the end-of-run (EOR) threshold for a certain plant is, for example, TLX/TLE based, there is no advantage to install a different radiant section. Or when longer run lengths are desired, the (unchanged) inlet passes might become a bottleneck as more coke will build up in these locations as well.

Figure 4 and Figure 5 show an HT E tube section that was removed from a steam cracking coil after 18 months of



**Figure 4.** SEM image of the top surface view of HT E after 18 months of operation; original machining marks are still visible. Reprinted with permission from ref 28. Copyright (2014) Jakobi.



**Figure 5.** SEM image of the cross section of HT E after 18 months of operations; no carburization visible; oxide thickness 2  $\mu$ m. Reprinted with permission from ref 28. Copyright (2014) Jakobi.

| material         | tensile strength [MPa] | [W/(mK)] | thermal expansion $[1/K \times 10^6]$ | temperature limit $[^{\circ}C]$ and reason | thermal shock resistance |
|------------------|------------------------|----------|---------------------------------------|--|--------------------------|
| $Si_3N_4$        | 416.7                  | 32       | 2.8                                   | 1900/melting                               | 11.9                     |
| SiO <sub>2</sub> | 54.4                   | 1.37     | 0.45                                  | 1750/melting                               | 1.9                      |
| $Al_2O_3$        | 454.9                  | 35.3     | 5.37                                  | 2050-2072/melting                          | 5.9                      |
| SiC              | 250                    | 114      | 2.66                                  | 2545/decompose                             | 21.8                     |

Table 2. Materials Properties for Potential Ceramic Furnace Coils. Recreated with Permission from Ref 32. Copyright (2014)Mako



Figure 6. SiC tube to SiC tube joint. All joints are helium leak tight. (Left) Two lap joints and two sleeve joints. (Right) Two additional lap joints. Reprinted with permission from ref 32. Copyright (2014) Mako.

operation. In Figure 4, the original machining marks are still visible, indicating that the surface did not undergo any detrimental changes. Figure 5 on the other hand shows that the alloy is highly resistant to carburization due to the protective alumina scale. Furthermore, the alloy shows no catalytic active sites.

Manaurite XAl4 is the Al-containing alloy that is offered by Manoir Industries. Like the previously mentioned alloys, it forms an  $Al_2O_3$  oxide layer on its surface during the initial heat up stages and is claimed to have improved carburization and coking resistance. The alloy develops a uniform, autoprotective and self-healing oxide layer with very high thermal stability that is highly suitable for steam cracking conditions.<sup>29</sup> At the moment of writing, no publically available plant trial data is available including XAl4.

**2.2. Ceramic Materials.** In ethane pyrolysis furnaces, the maximum ethane conversion is limited to 60 and 70%. The reasons for this are due to undesirable catalyzed reactions on the metal surface and to metallurgical limits on the tube skin temperature. The surface reactions accelerate with increasing temperature, increasing the amount of undesirable byproducts such as coke, CO, and  $CO_2$ .<sup>30</sup> These materials cause carburization and corrosion in the tube metal that reduce service life. Therefore, metal furnace tubes require replacement approximately every 6 years.<sup>31</sup> Coke deposition also results in increased local tube temperatures which further aggravates the alloy degradation process. Increasing ethane conversion with low byproduct formation would enable ethane producers to increase their ethane cracker capacity substantially with minimal, if any, downstream modifications.<sup>30</sup>

Use of advanced ceramics, such as silicon carbide (SiC) or a multiphase ceramic containing some silicon carbide is well-known.

It would allow chemicals to be processed at significantly higher temperatures than traditional metal-alloy coils, improving the energy efficiency and yield of the petrochemical process.<sup>31</sup> Table 2 compares properties at room temperature for several candidate ceramics: silicon nitride (Si<sub>3</sub>N<sub>4</sub>), fused quartz (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), and silicon carbide (SiC) that are helium leak tight, meaning they are completely hermetic and can be manufactured in production lengths of at least 1.8 m long and with diameters from 0.006–0.102 m or larger.<sup>32</sup>

SiC has been selected over other ceramics for steam cracking because it has a high heat resistance, high strength, and can withstand temperatures as high as 1400  $^{\circ}$ C; its conductivity is high; and it has a low surface activity toward byproduct formation (i.e., coke). SiC ceramic tubes, which last 2 to 3 times longer than metal-alloy tubes, have been developed to limit coil replacement. Due to their relative inertness compared to metals such as nickel and iron, they have been demonstrated to have very low levels of coke deposition. SiC reduces catalytic coke formation associated with use of coils created from these metals.<sup>32</sup>

However, producing ceramic tubes long enough to be used in steam cracking furnaces has been a challenge. Furthermore, these tubes are very short compared with convectional coils.<sup>30</sup> Commercial vendors produce SiC ceramic tubes not longer than 4.5 to 6 m, while the minimum length of furnace coils is 9 to 12 m.<sup>32</sup> FM Technologies, Inc. (FMT)<sup>32</sup> has been able to join pairs of SiC ceramic tubes to create longer furnace coils using various methods, including high-energy pulsed electron beam technology, polymer and microwave joining technology.<sup>32</sup>

At present, the joining technology for SiC to SiC (see Figure 6) and SiC to metal joint is helium leak tight (completely hermetic)

and oxidation resistant, with service temperatures from 1150 to 1400  $^{\circ}\mathrm{C}$  for SiC to SiC and 900 to 1000  $^{\circ}\mathrm{C}$  for SiC to metal.  $^{32}$ 

Such high operating temperatures increase the conversion by up to 10%, shorten residence time and reduce catalytic coke formation associated with the use of metal coils.<sup>33</sup> Recently, a new U-shaped loop of 15 to 24 m long with side weldable metal ends suitable for ethylene application was introduced. Figure 7 illustrates the concept of the U-shaped ethylene coil.



**Figure 7.** A demonstration unit of the U-shaped ethylene coil. Reprinted with permission from ref 32. Copyright (2014) Mako.

To evaluate the potential of the ceramic materials and their application in industrial steam cracking units, reactor simulations were carried out using the commercial software package COILSIM1D.<sup>34</sup> The simulations were performed at various coil outlet temperatures ranging from 800 to 1100 °C and with ethane as a gas feed. The upper values of this temperature range are higher than the usual range of operation of steam crackers, for which COILSIM1D has been extensively validated (COT: 663–961 °C). However, given the limited availability of experimental data for such high temperature for ethane pyrolysis,<sup>35</sup> and considering the fact that COILSIM1D is based on firstprinciples, the simulation should be able to provide a reasonable representation of the behavior that could be expected under these severe conditions. Similar simulations have been performed at elevated temperatures by Van Goethem et al.<sup>36</sup> with the software tool SPYRO, for which similar trends were

observed. At higher temperatures, the decomposition of ethylene starts to become important. This decomposition is initiated by the disproportionation of ethylene to a  $C_2H_5$  (ethyl) and a  $C_2H_3$  (vinyl) via hydrogen abstraction. Further decomposition of the latter radical explains the increased formation of acetylene, while reactions with the former radical explain the increase in propene, 1- and 2-butene, and 1,3-butadiene.<sup>37,38</sup> An overview of the simulated mass fractions of the main hydrocarbon species obtained during steam cracking of ethane is given in Table 3. As expected, a higher coil outlet temperature leads to higher conversion. Similarly, the yields of hydrogen, methane, acetylene, 1,3-butadiene, and aromatics increase. However, the yields of the desired products (i.e., light olefins), in particular ethylene, decrease for temperatures beyond 1000 °C.

Considering that conversion is a key parameter when it comes to distribution of product yields, simulations were also carried out for a constant ethane conversion of 85%. A summary of the simulated yields of the most important species formed during steam cracking of ethane is presented in Table 4. It can be observed that to achieve the desired conversion while keeping a lower coil outlet temperature, longer residence times are required. The higher residence times lead to increased yields of aromatics, such as benzene, styrene, and naphthalene. Especially, the amount of benzene is increased in comparison with the lower COT. The simulations reveal that higher temperatures, beyond 1000 °C, again lead to decreased yields of ethylene, although the conversion is kept constant. However, the yield of acetylene increases; therefore, with a larger acetylene converter, it is possible to boost olefin production even further.

IFP and Gaz de France<sup>30</sup> have developed a high-temperature furnace technology, called "ethane booster", which enables a process temperature of 1000 °C or more to be attained. The ethane booster can be installed between a conventional furnace and its transfer line heat exchanger.<sup>30</sup>

The resulting pyrolysis furnace design comprises several channels, each separated by a ceramic (silicon carbide wall), through which the feed passes while being heated indirectly by a gas-fired system. The heating system includes ceramic single ended radiant tubes arranged in series. Pyrolysis reactions are carried out throughout the length of the furnace. With this novel technology, an ethane conversion of 95% or more can be obtained together with high ethylene selectivity and low byproduct formation.<sup>30</sup>

Towfighi et al.<sup>39</sup> tested different sizes of ceramic materials as inert materials at various reactor temperatures. A laboratoryscale packed bed reactor has been used to investigate the effects of these inert materials on naphtha steam cracking. The results show that the yields of lighter products, such as hydrogen, methane, ethylene, and propylene increased over packed inert materials. Figure 8 shows that ethylene yields in a packed bed reactor are higher than in an empty tube over a wide range of severities. A different result was achieved with the C<sub>5</sub><sup>+</sup> products as shown in Figure 9. The lower concentration of C<sub>5</sub><sup>+</sup> products in packed bed reactors leads to the assumption that the packing material in the reactor improves the conversion of feed to lower hydrocarbon molecules in naphtha steam cracking reactions.

It is suggested that in an empty tube, the gas is mainly heated by contact with the walls, and the heat is transferred from the wall to the gas by convection. On the other hand, in a packed bed reactor, the packing material acts as a heat sink to absorb the radiative heat from the reactor wall and then transfers that heat into the cracked gas by a convective mechanism. The absorbed radiative heat of the ceramic particle is transferred to the gas -

| Table 3. Simulated Yields | [wt %] for Selected | Hydrocarbon Specie | s at Different Coil | Outlet Temperatures | [°C] during Steam |
|---------------------------|---------------------|--------------------|---------------------|---------------------|-------------------|
| Cracking of Ethane        |                     |                    |                     |                     |                   |

| COT [°C]                          | 80       | 00 85    | 900        | 950   | 1000  | 1050  | 1100  |
|-----------------------------------|----------|----------|------------|-------|-------|-------|-------|
| residence time [s]                | 0.1      | .54 0.14 | 41 0.132   | 0.126 | 0.121 | 0.118 | 0.116 |
| conversion [%]                    | 23       | 3.2 47.  | 7 68.6     | 83.3  | 92.6  | 97.9  | 99.7  |
| COP [bar a]                       | 2        | .2 2.2   | 2 2.2      | 2.2   | 2.2   | 2.2   | 2.2   |
| dilution $[kg_{H_2O} kg_{C_2H}]$  | [-1] 0.1 | 33 0.3   | 3 0.33     | 0.33  | 0.33  | 0.33  | 0.33  |
| CIT [°C]                          | 63       | 30 63    | 0 630      | 630   | 630   | 630   | 630   |
|                                   |          |          | yields [wt | :%]   |       |       |       |
| H <sub>2</sub>                    | 1.48     | 2.99     | 4.25       | 5.07  | 5.57  | 5.90  | 6.21  |
| $CH_4$                            | 0.48     | 1.88     | 4.42       | 7.64  | 10.86 | 13.72 | 15.43 |
| $C_2H_2$                          | 0.02     | 0.14     | 0.56       | 1.50  | 3.13  | 5.44  | 7.84  |
| $C_2H_4$                          | 20.33    | 40.02    | 54.75      | 62.49 | 64.14 | 61.44 | 56.28 |
| $C_2H_6$                          | 76.79    | 52.32    | 31.44      | 16.66 | 7.38  | 2.14  | 0.28  |
| $C_3H_6$                          | 0.14     | 0.57     | 1.03       | 1.28  | 1.41  | 1.49  | 1.42  |
| $C_3H_8$                          | 0.03     | 0.10     | 0.17       | 0.15  | 0.08  | 0.02  | 0.00  |
| 1,3-C <sub>4</sub> H <sub>6</sub> | 0.11     | 0.66     | 1.77       | 2.94  | 3.68  | 3.93  | 4.15  |
| benzene                           | 0.00     | 0.04     | 0.24       | 0.87  | 2.05  | 3.71  | 5.58  |
| toluene                           | 0.00     | 0.00     | 0.00       | 0.02  | 0.04  | 0.05  | 0.04  |
| styrene                           | 0.00     | 0.00     | 0.00       | 0.13  | 0.35  | 0.73  | 1.27  |
| naphthalene                       | 0.00     | 0.00     | 0.00       | 0.03  | 0.10  | 0.25  | 0.50  |
| ethylbenzene                      | 0.00     | 0.00     | 0.00       | 0.00  | 0.00  | 0.01  | 0.01  |
|                                   |          |          |            |       |       |       |       |

Table 4. Simulated Yields [wt %] for Selected Hydrocarbon Species at Different Coil Outlet Temperatures [°C] and a Constant Conversion during Steam Cracking of Ethane

| COT [°C]                           | 850      | 900   | 950         | 1000  | 1050  | 1100  |
|------------------------------------|----------|-------|-------------|-------|-------|-------|
| residence time [s]                 | 7.672    | 0.764 | 0.146       | 0.040 | 0.013 | 0.005 |
| COP [bar a]                        | 2.2      | 2.2   | 2.2         | 2.2   | 2.2   | 2.2   |
| dilution $[kg_{H_2O} kg_{C_2H_6}]$ | -1] 0.33 | 0.33  | 0.33        | 0.33  | 0.33  | 0.33  |
| CIT [°C]                           | 630      | 630   | 630         | 630   | 630   | 630   |
| conversion [%]                     |          |       |             | 85    |       |       |
|                                    |          | yi    | elds [wt %] |       |       |       |
| H <sub>2</sub>                     | 4.48     | 4.99  | 5.20        | 5.14  | 5.11  | 5.06  |
| $CH_4$                             | 19.14    | 10.85 | 8.06        | 7.76  | 8.10  | 8.58  |
| $C_2H_2$                           | 0.33     | 0.89  | 1.59        | 2.40  | 3.20  | 3.81  |
| $C_2H_4$                           | 43.52    | 58.32 | 63.06       | 63.76 | 63.21 | 62.31 |
| $C_2H_6$                           | 15.01    | 15.01 | 15.02       | 15.02 | 15.02 | 15.01 |
| $C_3H_6$                           | 1.20     | 1.35  | 1.26        | 1.37  | 1.70  | 2.22  |
| $C_3H_8$                           | 0.13     | 0.14  | 0.14        | 0.16  | 0.18  | 0.21  |
| 1,3-C <sub>4</sub> H <sub>6</sub>  | 2.08     | 3.06  | 3.11        | 2.84  | 2.43  | 1.98  |
| benzene                            | 7.38     | 2.72  | 1.10        | 0.51  | 0.22  | 0.09  |
| toluene                            | 0.05     | 0.05  | 0.03        | 0.01  | 0.01  | 0.00  |
| styrene                            | 1.91     | 0.57  | 0.17        | 0.06  | 0.02  | 0.01  |
| naphthalene                        | 1.50     | 0.24  | 0.04        | 0.01  | 0.00  | 0.00  |
| ethylbenzene                       | 0.04     | 0.01  | 0.00        | 0.00  | 0.00  | 0.00  |
|                                    |          |       |             |       |       |       |

surrounding the particle.<sup>39</sup> All the experiments, with and without packing, where performed with identical residence times.

Browne et al.<sup>40</sup> investigated the effect of variations in temperature, charge flow rate, and the charge dilution ratio on the rate of coke formation during steam cracking of *n*-hexane. For this purpose, a micro pilot with a quartz tubular reactor has been built to study the influence of the process conditions and the metallurgy. Coking and decoking cycles were carried out on a number of nickel, refractory steel, and silicon carbide samples placed in the reactor in order to determine how the thermal aging of the samples affects their coking characteristics. Table S2 gives the weight of coke deposited on each sample as a function of the temperature and flow rates. For nickel, the maximum coke yields occur at relatively low temperatures 600-800 °C and low flow rates. With the refractory steel and silicon carbide samples,

the largest coke deposits occur at the highest temperatures (i.e., 950 °C). Lower flow rates would also seem to favor the formation of coke for these materials.<sup>40</sup>

Table 5 and Table 6 give a comparison of the initial and asymptotic coking rate for respectively 60% of conversion at 700 °C with a hexane flow rate of 15 mL  $h^{-1}$  and for a 95% conversion at 850  $^{\circ}$ C with a hexane flow rate of 18 mL h<sup>-1</sup>. These results emphasize the influence of the degree of conversion of *n*-hexane and of the temperature on the coking rates. At lower conversion and for a low temperature (700  $^{\circ}$ C), the difference in the asymptotic coking rates between the refractory steel and silicon carbide becomes more evident. In other words, under less severe reaction conditions, the difference in the catalytic activity of these materials is more pronounced. At high conversion and temperature (850 °C), the



**Figure 8.** Yields of ethylene in steam cracking of naphtha in an empty tube and in a ceramic packed bed reactor. Reprinted with permission from ref 39. Copyright (2002) American Chemical Society.



**Figure 9.** Yields of  $C_5^+$  in steam cracking of naphtha in an empty tube and in a ceramic packed bed reactor. Reprinted with permission from ref 39. Copyright (2002) American Chemical Society.

Table 5. Coking Rates at 60% Conversion at 700 °C for a Water:Hexane Flow Rate (ml/h) of 15:5. Adapted with Permission from Ref 40. Copyright (1998) Wiley

|                  | coking rate $(10^{-3} \text{ g/m}^2/\text{s})$ |            |  |  |
|------------------|--|------------|--|--|
|                  | initial  | asymptotic |  |  |
| Ni               | 2322.22  | 37.78      |  |  |
| refractory steel | 73.61  | 0.06       |  |  |
| SiC              | 0.06   | 0.19       |  |  |

Table 6. Coking Rates at 95% Conversion at 850  $^{\circ}$ C for a Water:Hexane Flow Rate (ml/h) of 18:6. Adapted with Permission from Ref 40. Copyright (1998) Wiley

|                  | coking rate $(10^{-3} \text{ g/m}^2/\text{s})$ |            |  |  |  |
|------------------|--|------------|--|--|--|
|                  | initial  | asymptotic |  |  |  |
| Ni               | 1930.56  | 23.61      |  |  |  |
| refractory steel | 52.22  | 0.42       |  |  |  |
| SiC              | 0.40   | 0.39       |  |  |  |

asymptotic rate of coke deposition is practically the same for the silicon carbide and the refractory steel, but the initial coking rates are quite different.<sup>40</sup>

Coking-decoking cycles had no apparent effect on the coking rate of the silicon carbide sample; that is, the rates of coke formation remained constant for the sample despite 15 coking-decoking cycles at temperatures ranging from 750 to 950  $^{\circ}$ C.<sup>40</sup>

Stone and Webster<sup>4f</sup> investigated the use of several advanced ceramic materials for steam cracking of ethane in a bench scale unit. Both ceramic and quartz material have shown significant

anticoking properties. Unlike alloy tubes, a ceramic cracking tube has no catalytic sites, and in principle, no catalytic coke can be formed. However, the presence of certain acid sites can catalyze coke formation.

Although the ceramic materials have clear advantages over metal alloys, their industrial-use cases are limited if not nonexistant today. This is due to the brittle nature of ceramic materials, which means that during thermocyclic exposures (crackingdecoking cycles) they are more prone to ruptures. Even though FMT proposed joints for connecting ceramic SiC tubes together and joints connecting SiC tubes to metals, the major advantage of ceramic materials (high temperature resistance) is reduced as those joints operate under lower temperatures than classical cracking tubes (1150  $^{\circ}$ C and 900–1000  $^{\circ}$ C, respectively).

**2.3. Coatings.** To reduce coke deposition rates, anticoking coatings on the reactor walls have been studied. In recent years, several companies have tested coated coils that result in a drastic reduction of coke formation. In all cases, rather thin coatings have been formed on the inner surfaces of high-alloy steels. Success with coatings also prompted some steel producers to develop and commercialize novel alloys away from industry-standard chromia-forming austenitic stainless steel, whose surface exhibit relatively low-temperature stability under cracking conditions. They primarily moved toward steels with higher-temperature stable surfaces such as alumina or mixed-alumina formers.<sup>20</sup>

Figure 10 describes the effects of different coatings on coke formation. A so-called barrier coating passivates the catalytically active sites of the reactor alloy, eliminating catalytic coke formation. However, the noncatalytic coke formation, often termed pyrolytic coke, is not prevented. In contrast, catalytic coatings convert deposited coke to carbon oxides and hydrogen, by reaction with steam, through gasification reactions.<sup>42</sup>

Phillips Petroleum Company improved the radiant heat transfer efficiency by applying a ceramic coating to the radiant section of a pyrolysis furnace. As a consequence, a thin film of the coating on the refractory surface increased its emissivity. The uncoated refractory material has an emissivity of around 0.65 at furnacerelevant temperatures, which means that 65% of the incident radiation is absorbed while the remainder is reflected back to the furnace. By applying the ceramic coating, the emissivity of the refractory material was increased to 0.92, resulting in a significant increase in furnace efficiency as seen from a lower stack temperature and a reduced fuel consumption while the furnace throughput could be increased by 9%. Additionally, the distribution of the heat to the coils was seen to be more uniform. The increase in furnace throughput leveled off at 6% after 6 months as issues with the adherence of the coating to the refractory wall meant that some parts of the refractory surface lost its coating over time.<sup>4</sup>

2.3.1. CoatAlloy. Westaim Surface Engineered Products, Inc., Kellogg Brown and Root, Inc. and Union Texas Petrochemicals Corporation have collaborated on evaluating a new generation of coated tubes and fittings in commercial furnaces, called CoatAlloy.<sup>44</sup> The coating developed by Bergeron et al.<sup>44</sup> is applied via chemical vapor deposition (CVD) and is further designed to have the following characteristics:

- Low coking rate
- Improved carburization resistance
- High temperature stability
- A service life equal to or better than the base alloy
- No spalling or cracking during thermal cycling or moderate flexing

Review



Figure 10. Effect of different coating types on coke formation; from left to right: bare tube, barrier coating, and catalytic. Reprinted with permission from ref 42. Copyright (2014) Schietekat.



Figure 11. CoatAlloy coated tube before service. Reprinted with permission from ref 44. Copyright (1999) Bergeron.



50 microns

Figure 12. CoatAlloy coated tube after 1 year of service. Reprinted with permission from ref 44. Copyright (1999) Bergeron.

- No negative impact on weldability
- No negative impact on the creep properties of the base alloy
- Improved resistance to abrasion and hot erosion

From the end of February 1999, the coating from Bergeron et al. has been installed and tested by at least 10 major ethylene producers with operating experiences from 1 month to almost 3 years. The coating has proven to significantly reduce coke buildup in ethylene pyrolysis furnaces, which enables an increase in the production through higher conversion and longer run lengths.<sup>44</sup> Extensive metallurgical testing has proved strong carburization resistance due to the formation of a stable and continuous oxide layer that reduces carbon deposition and prevents

the diffusion of carbon into the furnace tubes. Figure 11 shows a sample of a coated tube before it was placed in service. The first layer is the unaltered base tube. On top of the base alloy, the diffusion barrier is located, which isolates the enrichment pool from nickel and iron in the base. The Enrichment Pool is the source of atoms that generate and regenerate the Engineered Surface, the actual anticoking surface.<sup>44</sup>

Figure 12 shows a typical sample from the middle section of a coated tube after 1 year of service. The protective oxide layer covers the entire surface and there is no evidence of any chromium carbides nor carburization.<sup>44</sup>

The barrier coating has also proven to reduce coking with a variety of feedstocks. The indications show that the same benefit demonstrated in commercial ethane crackers should also be



Figure 13. SEM image of AlcroPlex Diffusion Coating on HP 40 base material (A: Al/Si diffusion layer, B: Al/Si diffusion layer–transition zone to barrier layer, C: Cr/Si barrier layer, D: base material (HP 40 Nb mod. Microalloyed)). Reprinted with permission from ref 51. Copyright (2002) Wiley.

possible with heavier feedstocks.<sup>45</sup> CoatAlloy-1100 and Coat-Alloy-1060 are Surface Engineered Products' second generation of anticoking coatings and represent a major improvement over the original coating. Improved coating performance was accomplished by creating a more stable Enrichment Pool and Diffusion Barrier. This results in a slower rate of diffusion of elements into the base alloy and to the surface of the coating. These new products have significantly longer coating life in ethylene pyrolysis furnaces. For example, the estimated lifetime of CoatAlloy-1100 is approximately 10 times that of one of the original CoatAlloy coatings at any given operating temperature.<sup>45</sup>

Recently an improved version of the technology for gas-based ethylene cracker coils has been developed and is currently owned by Manoir Industries. The new version of the anticoking coating technology claims not only to significantly enhance run lengths of coils, as the previous version did, but also to address high-temperature thermal stability—a critical goal for many ethylene producers. This new version is currently in testing phase at 3 major ethylene producers.<sup>46</sup>

The process forms high quality diffusion coatings of multiple materials and/or alloys for extreme chemical environments in upward of 1200  $^{\circ}$ C.<sup>47</sup> The advancement is an engineered coating system that provides the necessary surface characteristics to mitigate catalytic coke formation.

Tube inner surface coatings resist carburization, which brings about changes in creep strength, ductility, and toughness. They are self-healing and have sufficient hardness and toughness to resist erosion by coke particles. They also withstand the thermal shock and cycling, inherent during the decoking procedure.<sup>48</sup>

More recent experimental tests were conducted at a pilot plant steam cracker to compare the coking tendency of the improved and to be a commercialized coating with a reference 25/35 Cr–Ni base alloy. The comparison was made under ethane steam cracking, while the influence of process conditions, coil outlet temperature, presulfiding, continuous addition of sulfur, and aging was evaluated. The surface of both tested reactors (coated and uncoated) were studied by means of SEM and EDX analysis. All the findings show that the coating is capable of reducing coke formation and maintains its anticoking activity over multiple cracking-decoking cycles, while reducing the CO and CO<sub>2</sub> yields.<sup>49</sup>

2.3.2. AlcroPlex. An additional type of coating, which is similar to CoatAlloy and forms a protective alumina scale, is AlcroPlex from Alon Surface Technologies designed by Ganser et al.<sup>50</sup> The coating is a two-layer diffusion coating. The first layer is a chrome-silicon barrier layer. The second layer is a silicon–aluminum layer that is used to reduce catalytic coke formation.<sup>50</sup> It is applied via a complex chemical vapor deposition technology that results in a high-temperature metallurgically stable coating, that further ages into a metastable surface. Once the coating is aged in service, chromium migrates to the surface through the aluminum-rich layer and establishes the foundation for the coating by Ganser et al. (Figure 13).<sup>51</sup>

While the coating proved to be working well in some furnaces, the coating showed an inadequate uniformity, and during high temperature operation, the aluminum just continued to diffuse into the base material until it was no longer useful. Given the bad experience, several new coatings were developed for which AlcroPlex gave the best results.

- After 14 months of operation in an ethane cracking furnace, the coating resulted in several performance improvements of the furnace. Increase of furnace run length from 30 days (uncoated) to up to 60 days (coated)
- Reduction in carbon monoxide production
- Easier decoking (reduction in time)
- No carburization visible

Metallurgical analysis also shows good results for the coating (Figure 14 and Figure 15). There is no carburization visible, and the diffusion coating is essentially unchanged after operation.

Thermogravimetrical tests were also performed with a coated HP 40 material during ethane and naphtha steam cracking. Prior to the cracking experiments, the samples underwent a standard activation procedure (SAP):

- Heat treatment of the coupons in a special furnace in a 10:1-mixture of nitrogen and air at 970 °C for 5 h ("preoxidation")
- Cooling the coupons to 850 °C in nitrogen atmosphere
- Treatment in hydrogen atmosphere for 1 h ("prereduction")
- Performance of 10 coking/decoking cycles (15 min pyrolysis of *n*-hexane, 5 min decoking with air; "activation phase")



Figure 14. AlcroPlex coating "as-processed". Reprinted with permission from ref 50. Copyright (1999) Wiley.



**Figure 15.** AlcroPlex coating after 1 year of service (hottest section). Reprinted with permission from ref 50. Copyright (1999) Wiley.

The results can be found in Table 7 and Table 8. The coating not only decreased the coking rate by about 80% for naphtha and 90% for ethane but also the carbon monoxide formation decreased to practically zero (within the measurement error of the tests). Despite the application of an artificial aging procedure (cyclic coking/decoking cycles), the positive effect of the Ganser et al. coating is still visible.

However, based on what currently has been discussed in the open literature, this technology is currently not being commercialized and, thus, most likely, suffers from some disadvantages that were not discussed in the above-mentioned papers. 2.3.3. Catalyzed-Assisted Manufacture of Olefins (CAMOL). The objective of novel catalytic coating technologies such as CAMOL is to realize coke-free operation. Major breakthroughs have been realized to overcome the limitations of coatings from the 20th century primarily through novel, nanoenabled coating processes. In particular, adhesion to metal surfaces is difficult in combination with thermal shocks. The coating technology, designed by Petrone et al.,<sup>52</sup> has been in commercial furnace trials since September 2006.<sup>52</sup>

These advanced catalytic coatings are applied on the internal surfaces of steam cracker furnace tubes and fittings, enabling the so-called catalytically assisted manufacture of olefins from petrochemical feedstock. The coatings are designed to improve operational profitability of petrochemical furnaces by reducing carbon formation, thus increasing online production time and reducing energy requirements and  $CO_2$  emissions.

The coatings from Petrone et al. are best described as composites, consisting of metallic and ceramic constituents. Overall, these coatings are engineered with 21 chemical, physical, and thermo-mechanical properties to achieve commercial survivability and the targeted surface functional efficacy.<sup>53</sup> The coating is composed of  $Mn_rO_{y}$  MnCr<sub>2</sub>O<sub>4</sub>, or combinations thereof in a first region, where x and y are integers between 1 and 7. In a second region,  $X_6W_6(Si_z, C_{1-z})$  is present wherein X is Ni or a mixture of Ni and one or more transition metals and z ranges from 0 to 1. The first region provides the barrier for catalytic coke formation, whereas the second region shows the catalytic sites for coke gasification. This gasification region may include  $CaWO_4$ , or a barium-yttrium-tungsten oxide  $(Ba_3Y_2WO_9)$ .<sup>54</sup> There are two coating formulations to meet the needs of different crackers, feedstocks, and operating conditions. Both the lowcatalytic gasifier (LCG) and high-catalytic gasifier (HCG) coatings are inert to filamentous (catalytic) coke production and provide catalytic gasification of carbon at low operating temperatures (400-700 °C) with specified sources of carbonaceous matter while remaining within acceptable levels of CO and CO<sub>2</sub>. The LCG coating can be used in lower coking environments such as conventional ethane-propane furnaces, while the HCG coating targets operating environments with higher coke production found when cracking heavier feedstocks such as naphtha.<sup>53</sup>

The technology differs from other available anticoking technologies, apart from YieldUp (see section 2.3.4), in that,

Table 7. Coke Formation during Cracking of Naphtha on Two Different Coupons (Average of 3) before and after the Standard Activation Procedure (SAP) as a Function of the Number of Coking/Decoking Cycles. Adapted with Permission from Ref 51. Copyright (2002) Wiley

| coke formation (mg/h)                            | befc        | before SAP   |             | after SAP    |             |              |  |
|--|-------------|--------------|-------------|--------------|-------------|--------------|--|
| material   | first value | second value | first value | second value | third value | fourth value |  |
| HP 40 base                                       | 0.21        | 0.48         | 1.16        | 1.70         | 2.61        | 3.53         |  |
| HP 40 AlcroPlex                                  | 0.23        | 0.34         | 0.70        | 0.56         | 0.46        | 0.62         |  |
| % coke HP 40 AlcroPlex (regarding to HP 40 base) | 110         | 71           | 60          | 33           | 18          | 18           |  |

Table 8. Coke Formation during Cracking of Ethane on Two Different Coupons (Average of 3) before and after the Standard Activation Procedure (SAP) as a Function of the Number of Coking/Decoking Cycles. Adapted with Permission from Ref 51. Copyright (2002) Wiley

| coke formation (mg/h)                            | befo        | ore SAP      |             | after SAP    |             |              |  |
|--|-------------|--------------|-------------|--------------|-------------|--------------|--|
| material   | first value | second value | first value | second value | third value | fourth value |  |
| HP 40 base                                       | 0.15        | 0.21         | 0.16        | 0.40         | 1.40        | 2.34         |  |
| HP 40 AlcroPlex                                  | 0.25        | 0.31         | 0.22        | 0.13         | 0.16        | 0.23         |  |
| % coke HP 40 AlcroPlex (regarding to HP 40 base) | 167         | 148          | 138         | 33           | 11          | 10           |  |

Typical coke formation in an untreated tube during steam cracking



Figure 16. A comparison of coke formation in an untreated tube and in a CAMOL treated tube during steam cracking. Reprinted with permission from ref 55. Copyright (2012) BASF.



Figure 17. SEM images of the coil coated with the catalytic coating by Petrone et al. "as produced" and after 14 months of service. Reprinted with permission from ref 56. Copyright (2013) BASF.

the technology not only eliminates the catalytic (or filamentous) coke through a physical barrier but also gasifies the thermal (or pyrolytic) coke for an even greater anticoking resistance (see Figure 16). The proprietary manufacturing process generates a coating with almost identical thermo-mechanical properties as the base metal substrate (alloy).<sup>55</sup>

In 2008, BASF SE in Ludwigshafen, Germany, decided to install the technology in one of their naphtha furnaces with a start-up in 2010. All of the coils in the furnace were replaced with catalytically coated coils on a 35/45 high-temperature alloy consisting mostly of the low catalytic gasifier (LCG), but included a low loading of the high catalytic gasifier (HCG) on the outlet coils. Over the 3 years, it was observed that the coking profile of the cracking furnace completely changed. Only a small amount of HCG is required to gasify a significant amount of coke. A sample taken from the coil after 14 months of service shows that the coating is in a similar condition as the "as produced" state, as shown in Figure 17.<sup>56,57</sup> However, some carburization on the gas side of the coating can be observed.

BASF SE in Ludwigshafen installed a second coil in 2013. The objectives with this second coil include:  $^{56}$ 

- Increasing the amount of HCG
- Continuing the optimization of reactivation and regeneration procedures
- Developing the capability to apply the technology to additional alloys (i.e., 25/35)
- Evaluating the operating limits of the technology (conversion, dilution steam ratios, etc.)

At present, new furnaces with more active coatings are being tested because of the limited benefit of the first generation. It is anticipated that this could lead to significant longer run lengths No results are available yet.

2.3.4. GE Coatings. General Electric Global Research centers in Shanghai, China and Niskayuna, New York developed a robust, novel coating technology for the inner wall of furnace tubes that prevent the deposition of coke, called YieldUp. Wang et al.<sup>58</sup> proposed a family of ceramic catalysts having a unique chemical structure that is designed to convert coke to carbon oxides on contact, very similar to what the objective is of the CAMOL coating and in general all catalytic coatings. Thus, when coke forms during cracking, it is instantaneously gasified on contact with the wall. In comparison with barrier coating technologies, the coating by Wang et al. is effective for both catalytic and pyrolytic coking.<sup>42,59</sup>

The ceramic coating consists of a sintered product of a perovskite material and an inorganic material (cerium oxide, zinc oxide, tin oxide, zirconium oxide, bohemite, and silicon dioxide). The perovskite material is SrZr<sub>0.3</sub>Ce<sub>0.7</sub>O<sub>3</sub>, BaZr<sub>0.3</sub>Ce<sub>0.7</sub>O<sub>3</sub>, BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3</sub>, or BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3</sub>. The formed continuous, strong coatings have a good adhesion strength and thermal shock resistivity. The properties of the novel coated coils depend on the specific inorganic materials and the perovskite material used in this method, as well as on the working conditions of the coating. During sintering, the perovskite material can react with the inorganic materials. Then the sintered product, "powder", is applied on the inner surface using different methods, such as air plasma spray, sol-gel coating, solution coating, and the most preferred slurry coating. The slurry may be applied to the surface by different techniques, such as sponging, painting, centrifuging, spraying, filling, dipping, and draining. Coupons coated with slurries were heated to 400 °C in an oven and then rapidly cooled to room temperature to test the thermal shock resistance. No coating spalled off, indicating that the coatings have good thermal shock resistivity.<sup>58,60</sup> When exposed to high-temperature steam, water molecules are chemisorbed and deprotonated, resulting in the formation of highly reactive oxygen atoms that instantaneously react to form CO and CO<sub>2</sub> upon contact with coke.42

The performance of three different coating formulations was tested in a Jet Stirred Reactor (JSR) setup and compared to an uncoated reference alloy, Incoloy 800 HT. Table 9 summarizes

Table 9. Summary of Coke and Yield Data of JSR Experiments for the Comparison between YieldUp Formulations. Adapted with Permission from Ref 42. Copyright (2014) Schietekat

| coupons                           | Incoloy 800HT      | YieldUp1       | YieldUp2           | YieldUp3 |
|-----------------------------------|--------------------|----------------|--------------------|----------|
| cycles                            | coke               | gain [mg] over | 6 h of cracking    |          |
| 1st                               | 39.0               | 5.0            | 10.0               | 10.2     |
| 2nd                               | 42.5               | 6.5            | 12.0               | 11.3     |
| 3rd                               | 45.0               | 9.0            | 17.2               | 12.6     |
| species                           |                    | yield [        | wt %] <sup>a</sup> |          |
| H <sub>2</sub>                    | 4.28               | 4.37           | 4.22               | 4.21     |
| $CO_2$                            | 0.02               | 0.19           | 0.02               | 0.02     |
| $CH_4$                            | 7.06               | 7.12           | 7.18               | 7.10     |
| СО                                | 0.07               | 0.93           | 0.07               | 0.06     |
| $C_2H_6$                          | 30.66              | 29.67          | 30.56              | 30.53    |
| $C_2H_4$                          | 50.53              | 50.64          | 50.67              | 50.53    |
| $C_3H_8$                          | 0.11               | 0.11           | 0.12               | 0.11     |
| $C_3H_6$                          | 0.75               | 0.78           | 0.81               | 0.80     |
| $C_2H_2$                          | 1.28               | 1.41           | 1.41               | 1.46     |
| 1,3-C <sub>4</sub> H <sub>6</sub> | 1.11               | 1.13           | 1.03               | 1.03     |
| benzene                           | 2.42               | 2.37           | 2.34               | 2.33     |
| <sup>a</sup> Average ov           | er all cycles with | 10-11 analys   | ses per cycle.     |          |

the coke and yield data of the experiments performed during steam cracking of ethane. The YieldUp1 coating shows an increase in  $H_2$ ,  $CO_2$ , and CO yields compared with the reference alloy. The other coatings show similar yields compared to the

reference experiment.<sup>42</sup> High levels of CO and CO<sub>2</sub> are detrimental for the downstream system of a steam cracker, so is CO (typically ca. 400 ppm in the effluent) a poison for the catalyst of all hydrogenation units. The hydrogen produced in a steam cracker is used as a makeup stream in those units and contains  $CO.^{61}CO_2$  on the other hand (typical 100 ppm) and hydrogen sulfide are removed from the cracked gas by one-through (caustic wash) and regenerative solvent scrubbing (first step in the downstream section). The caustic tower is specifically designed to handle rather low amounts of CO<sub>2</sub> in the cracked gas stream. The gas is removed because it can freeze at low temperatures in fractionation equipment and it can be absorbed in ethylene, affecting its product quality.<sup>61</sup> Increased values of both CO and CO<sub>2</sub> will, thus, bring substantial additional costs. Lower amounts of ethylene are also observed for YieldUp1 in the table, which further decreases the economic benefit of applying this specific coating in an industrial steam cracker.

The coking rate is significantly reduced for all coating formulations compared to the reference alloy. For the first cycle, the coking rate is reduced by a factor of 7.8, 3.9, and 3.8 compared with the reference alloy for YieldUp1, YieldUp2, and YieldUp3, respectively. This improvement in performance was obtained by gasification of the cokes by the coating. Consequently, the effluent during cracking over YieldUp1 contained more CO and  $CO_2$  than during the reference experiment.

As can be seen from Figure 18 both initial and asymptotic coking rates are seen to increase over the number of cycles for all experiments, which is attributed to an increase in surface roughness.<sup>59</sup>

As YieldUp1 showed the lowest coking rate among all tested coating formulations, it was further investigated on a larger scale in the UGent pilot plant for steam cracking using ethane and naphtha as feedstock. These experiments allowed the coating's performance to be evaluated under typical industrial conditions in a well-controlled and monitored environment. The reactor inner surface was coated with the YieldUp1 coating and compared to a reference reactor made out of Incoloy 800 HT. The influence of several process conditions (coil-outlet-temperature, continuous sulfur addition, presulfidation, and dilution) and feedstock (both ethane and naphtha) was evaluated. The quantities of coke produced were drastically reduced as compared with an uncoated reference coil.<sup>59</sup>

The results of the experiments with ethane as feedstock are summarized in Table 10. Comparing the coated reactor (YieldUp1) to the reference Incoloy 800 HT reactor (INC), it is seen that the amount of coke deposited was reduced by a factor of 4.4 by application of the YieldUp1 coating compared to the Incoloy 800HT reactor. Consequently, the effluent contained more hydrogen, CO, and CO<sub>2</sub> than during the INC experiment as cokes are gasified to carbon oxides and hydrogen. The increase in hydrogen and carbon oxide yields by application of the YieldUp1 coating is much higher in the pilot plant experiments than in the JSR experiments due to the larger surface-to-volume ratio of the pilot plant reactor.<sup>42</sup> As mentioned before, this rather drastic increase of CO and CO<sub>2</sub> and the accompanied purification costs negate the economic benefit of having longer run lengths.

The absence of continuous addition of dimethyl disulfide (DMDS) increases the CO and  $CO_2$  yields. Hence, continuous addition of DMDS can mitigate CO and  $CO_2$  production when the coating is applied. Presulfidation of the coil with a steam/DMDS solution (PRES) shows a similar influence on yields compared to solely continuous DMDS addition in experiment YieldUp1. Presulfidation before continuous DMDS addition



Figure 18. Comparison of the initial (left) and asymptotic coking (right) rates for the Incoloy 800 HT reference (black) and the three YieldUp formulations; YieldUp1 (green), YieldUp2 (blue), and YieldUp3 (red). Reprinted with permission from ref 59. Copyright (2015) American Chemical Society.

Table 10. Summary of Cokes and Yield Data of Pilot Plant Ethane Experiments. Adapted with Permission from Ref 42. Copyright(2014) Schietekat

| experiment                                  |                  | INC       | YieldUp1 | DMDS             | PRES                   | COT    | DIL1   | DIL2   |
|---|------------------|-----------|----------|------------------|------------------------|--------|--------|--------|
| process conditio                            | ns               |           |          |                  |                        |        |        |        |
| reactor                                     |                  | Incoloy   | coated   | coated           | coated                 | coated | coated | coated |
| feed [g/h]                                  |                  | 3000      | 3000     | 3000             | 3000                   | 3000   | 3000   | 3729   |
| $H_2O$ flow rate [g/h]                      |                  | 1155      | 1155     | 1155             | 1155                   | 1155   | 578    | 718    |
| $N_2$ flow rate [g/h]                       |                  | 0         | 0        | 0                | 0                      | 0      | 898    | 0      |
| S addition [ppm of S/                       | /g HC]           | 50        | 50       | 0                | 50                     | 50     | 50     | 50     |
| $H_2O/HC$ ratio $[g/g]$                     |                  | 0.385     | 0.385    | 0.385            | 0.385                  | 0.385  | 0.193  | 0.193  |
| (H <sub>2</sub> O+N <sub>2</sub> )/HC ratio | [g/g]            | 0.385     | 0.385    | 0.385            | 0.385                  | 0.385  | 0.492  | 0.193  |
| COT [°C]                                    |                  | 856       | 855      | 856              | 856                    | 871    | 855    | 855    |
| COP [bar abs]                               |                  | 1.70      | 1.70     | 1.70             | 1.69                   | 1.70   | 1.68   | 1.70   |
| C0-C4 species                               |                  |           |          | yiel             | ds [wt %] <sup>a</sup> |        |        |        |
| H <sub>2</sub>                              | 4.20             | 4.54      | 4        | .88              | 4.52                   | 5.03   | 4.24   | 4.04   |
| CO <sub>2</sub>                             | 0.02             | 2.19      | 3        | .61              | 2.44                   | 3.39   | 1.02   | 0.98   |
| $CH_4$                                      | 3.72             | 3.48      | 3        | .65              | 3.58                   | 4.18   | 3.67   | 3.59   |
| СО  | 0.01             | 1.75      | 3        | .72              | 2.03                   | 3.31   | 1.65   | 0.99   |
| $C_2H_6$                                    | 36.10            | 36.79     | 30       | 5.13             | 35.98                  | 31.42  | 36.62  | 38.50  |
| $C_2H_4$                                    | 51.33            | 50.57     | 49       | 9.97             | 51.03                  | 53.44  | 50.55  | 49.26  |
| 1,3-C <sub>4</sub> H <sub>6</sub>           | 1.40             | 1.31      | 1        | .20              | 1.33                   | 1.51   | 1.41   | 1.38   |
|   |                  |           | coke for | rmation [g coke/ | 6 h]                   |        |        |        |
| from reactor                                | 18.5             | 4.2       |          | 1.6              | 2.4                    | 1.4    | 3.0    | 6.1    |
| in filter                                   | N.D.             | 0.2       |          | 0.5              | 0.9                    | 0.0    | 0.5    | N.D.   |
| total coke                                  | 18.5             | 4.4       |          | 2.1              | 3.3                    | 1.4    | 3.5    | 6.1    |
| <sup>a</sup> Average over 12–13 a           | inalyses per exp | periment. |          |                  |                        |        |        |        |

shows a coke tendency lower than that of continuous DMDS addition only. The increase of the coil outlet temperature (COT) shows increased yields of methane, ethylene, and 1, 3-butadiene. Surprisingly the higher COT experiment showed lower coke formation than the YieldUp1 experiment, which means that the catalytic coating converts more coke at higher temperatures as higher coke formation is to be expected at a higher COT. The higher CO and  $CO_2$  yields confirm this argument. This means that longer run lengths are possible at higher COT in an industrial cracker. The effect of dilution was evaluated in two experiments: DIL1 and DIL2. In experiment DIL1, the steam mass flow rate was halved, and nitrogen was added to compensate for the reduction of volumetric flow. As can be seen from Table 10, the reduction of steam seems mainly to affect the conversion of CO and  $CO_2$ . A coking rate similar to YieldUp1

was observed. Hence, it seems that enough water is present to convert coke to carbon oxides. In experiment DIL2, the steam dilution was also halved; however, this time, no nitrogen was added. Lower olefin, CO, and CO<sub>2</sub> yields were measured. Higher coke formation is expected due to higher hydrocarbons partial pressure and the coating converting less coke to CO and CO<sub>2</sub> due to the lower steam partial pressure.

The results of the experiments with naphtha as feedstock are summarized in Table S3. It is seen that the amount of coke deposited was reduced by a factor of 2 by application of the YieldUp1 coating compared with the Incoloy 800 HT reactor. Consequently, the effluent contained more CO and  $CO_2$  than during the INC experiment as coke is gasified.

These pilot experiments showed that the catalyst is robust and maintains anticoking activity over multiple cracking-decoking cycles.

At present, the GE YieldUp coatings are currently being tested in full scale operation. The fact that CO and  $CO_2$  formation is significantly increased plays a major role in the reason modifications to the coating were considered. The authors believe that with proper DMDS dosing and catalyst selection these values can be substantially reduced in order for the coating technology to become industrially more attractive.

**2.4. Alloy Pretreatments.** Gaseous pretreatment of highalloy steels used in the coils of the ethylene's furnace at high temperatures sometimes results in improved operation. Many pretreatments cause significant diffusion of Cr and Mn to the surface and of Fe and Ni to layers below the surface. The phenomena occurring during pretreatments and differences in resulting surface changes are still not well understood.<sup>62</sup>

Horsley and Cairns<sup>63</sup> started investigating different pretreatments for a high-alloy steel with gaseous mixtures of  $H_2/H_2O_1$  $CO_2/CO_2$ , or  $H_2/H_2O/CO/CO_2$  at 650–1000 °C for 2–4 h. To avoid carburization, wet hydrogen was used as the selective oxidizing medium. The untreated steel used contained by weight 19.9% Cr, 24.6% Ni, 0.7% Nb, 0.6% Mn, 0.56% Si, 0.04% C, and the remainder Fe. Several of their pretreatments caused a significant enrichment at the surface of Cr and Mn as oxides. After one pretreatment, a surface layer of 0.3  $\mu$ m contained about 65-70% Cr and 30-35% Mn. Fe and Ni were not detected until greater depths. These findings suggest that specific pretreatments might be developed that would result in reduced coke formation on metal surfaces. Cr and Mn oxides are more stable oxides as compared with Fe and Ni oxides. Once Cr and Mn oxides form, they essentially stop diffusing because these oxides are larger entities as compared with the metal elements. The oxides collect at and near the surfaces of the steels.<sup>63</sup>

Several gases were investigated for pretreating of Incoloy 800 coupons. Although Incoloy 800 is not employed in the radiant section of steam crackers, the results show the importance of a proper, optimized pretreatment of alloys. Comparative results were obtained for runs made at 950 °C and 4 h. All tested gases resulted in large enrichments of Cr and Mn near the surface. The results obtained from this study<sup>62</sup> suggest that the following sequence of events occurs:

- Cr concentrations at the surface increased rapidly in the initial phases of a pretreatment. At 950 °C and with pretreatments of  $H_2$ /steam, the Cr concentrations had increased to about 72% within 15 min.
- As the pretreatments continued, more Cr diffused, but substantial amounts of Mn diffused from rather considerable depths and entered the surface layer. This Cr and Mn diffused to a high degree through the initial layer of Cr oxides that had formed. At or near the surface they are oxidized and the surfaces formed had higher Mn/Cr ratios.
- Transfer of Ti in substantial amounts seems to be affected by the oxidation ability of the pretreating gas.

Zhang and Albright<sup>7</sup> tested the pretreatments on Incoloy 800 using a 50:1 molar mixture of  $H_2/H_2O$  at four temperatures from 750 to 1000 °C with a pretreatment time of 4 h. Very large changes of the metal composition occurred at and near the surface in the first hour. For the remainder of the run, the rates of metals transferred were much slower and relatively constant. Such a pretreatment decreased the amount of coke deposited on the surface. Pretreating the coupon only with CO at 850 °C for 24 h resulted in essentially no adherence of coke to the coupon. The resulting entrained coke or coke precursors would be

transferred to and through the TLE to the following scrubbing tower.  $^{7}$ 

Sarris et al.<sup>64</sup> investigated eight different pretreatments (see Figure S1) for a classical 25/35 Cr/Ni alloy. Their effect on the coking resistance of a high-temperature alloy was evaluated under ethane steam cracking conditions in a thermogravimetric setup.<sup>8</sup>

As seen in Figures S2, the treatment of the alloy by conducting a high temperature oxidation followed by a steam/air treatment shows the best coking performance. This treatment leads to a reduction by a factor 5 in comparison with the reference standard treatment.

SEM and EDX surface and cross sectional observations show that during the preoxidation at elevated temperature followed by a steam/air treatment, a homogeneous oxide layer consisting of  $MnCr_2O_4$ ,  $Cr_2O_3$ , and  $NiFe_2O_4$  is formed on the surface, optimizing the anticoking performance of the tested material.<sup>64</sup> The spinel  $MnCr_2O_4$  is proven to have great coking inhibition effects during ethane and light naphtha cracking.<sup>8,65</sup>

A preoxidation pretreatment very close to industrial operation is utilized during the experiments performed by Jakobi et al.<sup>18,23</sup> Slow heating up with steam is proposed, and it results in a very uniform oxide layer for both chromium-forming and aluminumforming alloys (Figure 19 and Figure 20). The authors further



**Figure 19.** Oxide scale on alloy ET 45 Micro (NiCrSi) after heating up under steam. Reproduced with permission from reference 18. All rights reserved. Copyright (2009) Nace International, Houston, TX.

state that the degree of cold work in the mechanical pretreatment of the inner tube wall, perpendicular to the centerline of the tube and in the rotational direction of the pull bore drill, has a significant influence on the quality of the oxide scale, built up during the initial preoxidation, and with this, on the density of catalytic active sites for coke formation.<sup>18</sup>

A joint research between NOVA Chemicals and Kubota led to a development of a technology capable to reduce both catalytic and pyrolytic coke, called ANK400.<sup>66</sup> An inert spinel layer formed from manganese chromium oxides is shown in Figure 21. The spinel is capable of reducing the coking by an order of magnitude compared to the conventional bare coils.<sup>66–68</sup>

The inert spinel layer illustrated in Figure 21 acts as a protective layer that shields the heat resistant alloy from the process gas and thus prevents carburization of the metal by the hydrocarbons present in the process gas.

Figure 22 illustrates the run length performance of three commercial furnaces after replacing the tubes with ANK 400



**Figure 20.** STEM-HAADF micrograph of the oxide scale on HT E (NiCrAl) after heating up under steam. Reproduced with permission from reference 23. All rights reserved. Copyright (2013) Nace International, Houston, TX.



Figure 21. SEM image of ANK 400 spinel surface. Reprinted with permission from ref 66. Copyright (2006) Gyorffy.



**Figure 22.** Extended run lengths due to the use of ANK 400. (The end of run criteria is indicated by the color of the column). Reprinted with permission from ref 68. Copyright (2017) Gyorffy.

coils. With the original reactors, a run length of about 33 days could be reached while the ANK 400 coils allowed to extend the run length by more than 400 days.

A lot of ethylene producers employ a sulfur pretreatment, prior to cracking, as they believe that this treatment increases run lengths and the longevity of the coils. However, most research papers indicate that sulfur promotes coke formation, rather than suppressing it. $^{64,69-73}$  Reyniers et al. $^{69}$  already showed in '95 that the main purpose of adding sulfur as a pretreatment or during cracking operations is to reduce the formation of CO and CO<sub>2</sub>. The sulfur reduces steam reforming reactions by covering the nickel active sites found on the metal surface. Very recently, Jakobi et al.<sup>74</sup> exposed the reason for this detrimental effect of sulfur on most alloys. The authors indicate that chromiumforming alloys suffer degradation due to the sulfur treatment, while aluminum-forming alloys experience no influence. Catalytic metal particles increase the growth of carbon nanotubes, where the particle is located on the tip of the whiskers. The catalytic tip comprises a molten Ni-sulfide mate. The catalytic sulfur induced tips are solely found on the chromia-forming alloys, aluminum-forming alloys seem to be unaffected by the process. Because of the liquid state of the particle, carbon diffusion is increased and therefore so is the growth of the carbon nanotube. Previous research<sup>75,76</sup> has already indicated the possibility of these liquid Ni particles. However, the research of Jakobi et al.<sup>74</sup> also indicates the formation of catalytically activated carbon nanotubes with MnO/Mn-S as a catalyst. The latter is attributed to the carbon- and sulfur-induced corrosion of the Cr-Mn-spinel/chromia layer, due to aging. The formation of both Ni- and Cr-based tips, with sulfur inclusion, is found on chromia-forming alloys.

# 3. CONCLUSIONS

The reactor material is one of the most important factors that determines the amount of coke formed on a steam cracking tube. Low-coking alloys, barrier and catalytic coatings have been investigated and in some cases commercialized. For metal surface technologies, increasing the content of Cr and Si in alloys can effectively reduce coke formation. However, the increase in Cr and Si is restricted by their negative impact on the mechanical properties. One of the most applied methods consisted of the addition of aluminum to the cracking coils (i.e., coating the surface with alumina), which is much more stable than chromia at higher temperatures. According to the latest results, Al-enhanced coils show a better resistance to coke formation for ethane cracking. A thin, but very uniform,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer is formed on top of the surface after exposure to the high-temperature aging. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer further shows a better resistance to pretreatments with sulfur in comparison with chromia-forming alloys.

Use of advanced ceramic materials would allow chemicals to be processed at significantly higher temperatures than traditional metal-alloy coils, potentially improving the energy efficiency and yield of the petrochemical process. SiC tubes reduce the amount of coke formed because of their low catalytic coking. However, producing ceramic coils long enough to be used in steam cracking furnaces is still one of the main challenges because otherwise higher olefin selectivities could be obtained.

Coking tests demonstrate that a significant reduction in coke formation can be achieved using specialty coatings. These advanced coatings are applied on the internal surfaces of steam cracker furnace coils. Two coating types exist: barrier and catalytic. The barrier coatings shield off the catalytic active sites for coke formation, while the catalytic coatings go a step further by not only eliminating catalytic coke, but also catalytically gasifying the pyrolytic coke. Both CAMOL and YieldUp are catalytic coatings, while CoatAlloy and AlcroPlex are barrier coatings. AlcroPlex is a twolayer diffusion coating, a barrier layer composed out of Cr and Si and a Si–Al layer that reduces the catalytic coke formation. CoatAlloy consists out of an Engineered Surface, for the catalytic

coke formation reduction, an Enrichment Pool, and a Diffusion Barrier that makes sure no metals are diffusing from the base metal toward the engineered surface. The CoatAlloy technology has proven in industry that it could significantly enhance run lengths and improve mechanical properties, such as thermal stability and resistance to carburization. The catalytic coating CAMOL is composed of two regions,  $Mn_xO_y$  and/or  $MnCr_2O_4$ , responsible for the elimination of catalytic coke, and CaWO<sub>4</sub> or  $Ba_3Y_2WO_9$ , responsible for the gasification of coke. YieldUp is a result of the sintered product of a perovskite material and an inorganic material. The perovskite material is  $SrZr_{0.3}Ce_{0.7}O_3$ ,  $BaZr_{0.3}Ce_{0.7}O_3$ ,  $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_3$ , or  $BaCe_{0.8}Y_{0.2}O_3$ . The activity of the YieldUp coating can be tuned by sulfur addition and catalyst preparation to circumvent the disadvantages of high CO and CO<sub>2</sub> formation.

It is clear that the discussed technologies give ethylene producers the ability to increase their production, while decreasing their energy consumption and thus reducing their ecological footprint.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b03221.

Table S1 shows the measured bulk composition of the materials tested by Muñoz et al.;<sup>8</sup> Table S2 shows the measured weight of coke from the experiments performed by Browne et al.;<sup>40</sup> Table S3 includes the summary coke and yield data of the experiments performed by Schietekat et al.;<sup>42</sup> and Figures S1 and S2 show the overview of the experimental procedure and the coking results of the experiments performed by Sarris et al.;<sup>64</sup> respectively (PDF)

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#### Notes

The authors declare no competing financial interest.

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# ABBREVIATIONS

3D = three-dimensional

AFT = alumina-forming technology

CA = continuous addition

CAMOL = catalyzed-assisted manufacture of olefins

CIP = coil inlet pressure bar abs

COP = coil outlet pressure bar abs

COT = coil outlet temperature K CVD = chemical vapor deposition  $C_{5+}$  = molecules with >5 carbon atoms DMDS = dimethyl disulfide EDX = energy-dispersive X-ray EOR = end-of-run HCG = high-catalytic gasifier IR = infrared LCG = low-catalytic gasifier MXM = manaurite XM PGA = permanent gas analyzer Pre-S = presulfidation RGA = refinery gas analyzer SEM = scanning electron microscope SRT = short residence time TLE/TLX = transfer line heat exchanger

# TMT = tube metal temperature K

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