Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 57(2) 143-153, 2015

Review

FORMATION OF COKE DEPOSITS AND COKE INHIBITION METHODS DURING STEAM CRACKING

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Received February 6, 2015, Accepted April 15, 2015

Abstract

Steam cracking belongs to the most important processes in petrochemical industry. Steam cracking is accompanied always by formation of coke deposits on inner walls of steam cracking tubes and of TLE. Coke formation significantly and negatively influences economic and energetic balance of the process. Different ways to minimize the coke deposition in steam cracking units are searched together with detailed understanding of coke formation mechanisms. The amount and character of created coke depends on operating parameters, feedstock type, on the reactor and TLE material, their surface modifications and also on addition of inhibitors. Summary of information about coke formation during steam cracking and of coke inhibition methods is given.

Key words: Steam Cracking; Coke Formation; Coke Inhibitors; Surface Modification; Cracking Coil Material.

1. Introduction

Steam cracking is a thermal process during which hydrocarbon feedstock is heated above the limit of thermal stability in the presence of steam. Overrunning this limit leads to decomposition and formation of stable low molecular hydrocarbons and solid residue. The main products are ethylene, propylene, methane, unsaturated C_4-C_5 fractions, benzene and hydrogen. Ethane, LPG, naphtha, kerosene, gas oil and vacuum gas oil (VGO) can be used as feedstock. The contact time has to be short (< 0.5 s) avoiding the unwanted secondary reactions. Most of the reactions running by steam cracking are highly endothermic. The heat transfer into the reaction mixture represents a substantial action during steam cracking process. Huge transfer surface is necessary for the intensive heat transfer, which is ensured by reactor branching into pipe sections [1-2].

Steam cracking is accompanied by secondary reactions. The main secondary process is coke formation. The coke formation in the steam cracking has negative impact on the economy of the process. Coke is deposited on inner surface of cracking pipes. Coke formed by steam cracking can cause pressure drop increase, heat transfer reduction, hot spots and corrosion by carbonization. The produced coke changes the process kinetics and has negative effect on yield of desired products [3].

The properties of coke depend on the type of feedstock. For example coke formed from naphtha or kerosene has amorphous character and is soft. Its thermal conductivity varies between 12.5 and 21, whereas the coke formed from ethane or LPG has thermal conductivity 2-3 times higher (42-50 kJ/m.h.°C). This type of coke has regular structure, what makes it harder [1]. The growth of the coke layer thickness causes increasing resistance to heat transfer, what has negative impact on heat transfer in reactor and in transfer line exchanger (TLE). Process of steam cracking can run till the pressure drop or outside pipe temperature does not reach limit values. After reaching limit values it is necessary to shut down the process and remove the coke from reactor and TLE. The process shutdown has negative effect on the economy of ethylene unit. Therefore it is needed to optimize the operation of steam cracking unit: the steam cracking time has to be the longest and the coke removing has to be the shortest.

To reduce coke formation it is necessary to understand the coking mechanism and to describe the main precursors and inhibitors. It is necessary to reduce catalytic active particles and to inhibit coke precursors, which are raised by secondary reactions during steam cracking. One of the possibilities how to inhibit coke formation is to add additives. Thiochemical compounds or organophosphorous compounds can be used as additives [1,4-11]. The metal reactor surface has catalytic effect on production of coke. Various surface modifications can be applied such as polishing, alonization, silica coating and chemical vapour deposition (CVD) for reduction of the catalytic effect [7,12-14].

2. Process configuration

Steam cracking as the most important process for production of low molecular alkenes and aromatics requires high temperatures (600 – 900°C) and tubular reactor with good resistance to high temperatures. The process consists of two major parts – the cracking furnaces and the separation section. Feedstock is preheated at temperatures from 600°C to 650°C in a convection section of the furnace and enters the reaction section, where the temperature varies between 780°C and 900°C, in dependence on used feedstock. The feed is cracked in tubular reactor coils suspended in a fired rectangular furnace. Radiation burners in the sidewalls or long flame burners in the bottom of the furnace provide the heat required for the endothermic reactions. To avoid product loss by the secondary reactions, the products are rapidly cooled in TLE. Outlet temperature of TLE is set in ranges from 350°C to 450°C depending on the feedstock. TLE is composed of multi-tube heat exchanger for recovery of waste heat. Cooling by TLE is important from economic reason, because of preventing the loss of valuable products such as ethylene, butadiene and using the heat from produced gases. TLE are generally constructed from low alloyed steel like 15 Mo3 (98 wt.% Fe, 0.17 wt.% C, 0.20 wt.% Si, 0.60 wt.% Mn, 0,03 wt.% P, 0.30 wt.% Mo) [1,15]. The second main part of steam cracking process is formed by separation section where the valuable products are recovered and purified.

3. Coke formation mechanisms

The coke formation in thermal cracking is a complex process. Laboratory and industrial studies revealed three main mechanisms of coke formation in pyrolysis reactor and in TLE [16]:

1. Catalytic coking mechanism
2. Radical coking mechanism
3. Polyaromatic condensation

3.1 Catalytic coking mechanism

It is known, that catalytic activity of the reactor surface enhances coke formation. Highest catalytic active metals are ferromagnetic compounds. Active sites are formed, which react with hydrocarbons mainly aromatics. Filamentous coke is formed on nickel and iron particles by catalytic process. This process is most intensive in starting phase of thermal cracking, because of the high density of active sites on the reactor surface. In this mechanism the hydrocarbon molecule is chemisorbed on the metal particles on the reactor surface and is converted to coke. Accumulation of coke around the metal particle generates the pressure, which can dislocate this metal particle. The metal particle is then lifted from the surface and carbon crystallizes at the end of the particle. The precipitation of carbon can give rise to structure deficiencies in the carbon lattice, thereby creating reactive carbon centres along the filamentous skin. Hydrocarbon radicals and molecules from the gas phase are incorporated at these reactive sites. Result of this process is formation of lateral filaments and complexly is forming a porous layer of interwoven filaments [16-18].

Mechanism of filamentous coke creation is still discussed. Fundamentals are that filamentous coke is formed by series of surface reactions leading to decomposition of hydrocarbon compounds. Others reactive compounds are reacting on this carbon structure and forming filament [17-18].

3.2 Radical coking mechanism

The coke deposited on surface of reactor reacts with free radicals in gas phase by free radical mechanism. Hydrogen, methyl, and ethyl radicals are the most active species but all unsaturated molecules in gas phase are potentially reactants. Long aliphatic side-chain of this molecule is subjected to decomposition. The remaining part of the molecule creates in few steps the ring structure. This ring hydrocarbon is rapidly dehydrogenated to aromatic s structure. In this way, the aromatic structure continues to grow further and the free radical site at the coke surface is regenerated by further hydrogen abstraction. As a consequence, the concentration of the active sites on the coke surface becomes a function of the gas phase composition [16,19].

This mechanism explains the formation of coke layer containing carbon atoms with hybriddization sp^2. The amount of hydrogen in this coke layers is very low in agreement with industrial studies. The cross-linking of aromatic layers forms coke deposits, which is very problematic to drill out, because these layers are extremely hard. This mechanism is most important one on the coke formation.

3.3 Polyaromatic condensation

This mechanism includes formation of polynuclear aromatic in gas phase. Aromatics are the most important intermediates. Some aromatic structures are formed by trimerisation or other reactions involving acetylene. Consequently this aromatics dehydrogenate and condense, form drops of tar or coke particles. These coke particles and tar drops are integrated to coke layer on reactor walls. Little amount is drifted by gaseous phase. Dehydrogenation reactions are running during integration of coke particles and tar drops in coke layer. Hydrogen is entrained by gaseous phase what results in following thickening of coke layer. This mechanism is important in cracking of heavier types of feedstock (heavy naphtha, atmospheric gas oil and vacuum gas oil). Polyaromatic condensation mechanism practically does not occur at temperature lower than 700°C [16,20-21].

4. Effect of feed composition

It is known, that feedstock character has effect on coke formation. Shutdown of pyrolysis unit after 60-80 days of run with naphtha as feedstock is necessary due to excessive temperature of cracking pipes. However, shutdown of furnace with ethane feedstock is needed after longer time and for reason of over limit pressure drop [1,15]. Company Pyrotec examined influence of feedstock type on coke formation in radiation part of cracking pipes. Significant difference between using naphtha and ethane as feedstock was proved. Comparison of the cracking rate of naphtha and ethane in conventional vertical pipe reactors proved, that in case of naphtha cracking the temperature profile on the outer wall of reactor grows faster and steeper than in case of ethane used as feedstock [22].

Towfighi *et al.* [4] explain this observation by different coke thermal conductivity for ethane and naphtha. Coke formed during steam cracking of ethane has the value of thermal conductivity 2-3 times higher than coke formed during steam cracking of naphtha or gasoil. That means that reactor temperature during naphtha steam cracking increases much faster than using ethane as feedstock. Coke formed during ethane steam cracking has lower thermal resistance what causes lower reactor temperature increase for the same coke thickness like for the coke formed during steam cracking of naphtha

The rate of coke formation depends on feedstock character, mainly on structure, molecular weight, content of different hydrocarbon types (PIONA) and portion of sulphur compounds, which are known as coking inhibitors. The coke formation during dienes steam cracking is much faster than during alkenes steam cracking and this is faster than on alkanes steam cracking. The coke formation rate from 1,3-butadiene is 5-6 times higher than for steam cracking of ethane [23]. Based on the experimental data on stem cracking of hydrocarbons, tendency of various compounds to form coke in pyrolysis furnaces increases in the following order [22]:

Methane < ethane < ethylene < propylene < benzene < ethylbenzene, xylene < styrene < alkenes C4 < cyclopentadiene < methylnaphthalene < anthracene < methylanthracene < acetylene.

Aromatics are important type of coke precursor. Structure of aromatics is similar to structure of coke. More branched aromatics are reactive, mainly by high temperature, which is in pyrolysis reactors [22,24-25]. Relative coking formation rate in cracking reactor and in TLE for different feedstock is referred in Table 1.

Table 1. Relative coke formation rate in cracking reactor and in TLE [25]

Feedstock	Relative coke formation rate in cracking reactor	Relative coke formation rate in TLE
Alkanes	0.20-0.80	0.14-0.50
Alkenes	0.73-1.03	0.35-0.80
Butadiene	1.68	1.35
Acetylene	>5.00	3.00
Cycloalkanes	1.20	1.45
Aromates	1.50	0.33
Polyaromates	>8	12.00-30.00

Correlation between molecular weight and the rate of coke formation is known. The rate of coke formation rises with growing of molecular weight. Coke formation rate of atmospheric gas oil is 2-4 times higher than by using naphtha as feedstock under steam cracking condition [25].

In dependence on molecule structure two types of coke formation mechanism are described in study [26]:

- Aromatic structures formation from unsaturated hydrocarbons, which have less than six carbon atoms
- Rearrangement and dehydrogenation of hydrocarbon structures, which have six and more carbon atoms and hydrogen deficit m $C_nH_{2(n+1-m)}$ is more than 1.

The first type of mechanism is important for aromatic structure formation from alkanes, monocyclic cycloalkanes and low alkenes. The second one is important for cycloalkanes and cyclodienes.

4.1 Alkanes

It is highly unlikely for alkanes with more than two carbons that they are involved to coke formation in TLE, because their conversion at pyrolysis conditions is high. This fact confirms that coke formed in TLE is originated only from pyrolysis products. Ethane is more reactive than methane. Coke formation from ethane is caused by degradation products [26-27].

There is no effect of chain length on coke formation from one particular carbon atom in the molecule, when hydrocarbon has more than five carbon atoms. Coke formation from individual carbon atoms grows in order: primary < secondary < tertiary. This rule applies for reactor and TLE [26].

4.2 Cycloalkanes

Coke formation rate for cyclic hydrocarbons with one or two rings is about 50 % higher than for alkanes. There is no large differences between 5 and 6 carbon rings and between alkylated and unsubstitutes cycloalkanes. Carbon in α-position relative to the ring has higher rate constant value than the same carbon in alkane, whereas carbons on the distant position from the ring have similar rate constant value as carbons in alkanes [26].

Decaline and decahydroanthracene are single polycyclic hydrocarbons used in study [26]. Coke formation from cycloalkanes with two rings was similar as coke formation of cycloalkanes with one ring, but molecules with more rings had a higher tendency to coke formation.

4.3 Alkenes

Coke formation from unsaturated hydrocarbons was more intensive than from saturated mainly in first half of reactor. This fact was significant with increasing reactivity of unsaturated hydrocarbons. Ethylene formed the least coke from studied alkenes and coke was evenly distributed over length of the reactor. Acetylene, which is considered the strongest coke precursor, formed 2.5 times more coke in first half of the reactor than in second [25]. Also cyclopentadiene belongs to the strongest coke precursors.

Ethylene, the main steam cracking product, has the smallest tendency to coke formation from all unsaturated hydrocarbons. In spite that ethylene is one of the main coke creators due to its high concentration in reactor system. Propene has similar character as ethene. Differences in coke formation were observed in TLE due to presence of alyl radicals. These alyl radicals are precursors for heavier products formation. The part of propene forms coke directly, whereas the rest of propene is splitted and then forms coke [26].

4.4 Alkines

The coke formation rate for acetylene on surface free of metals is 10 times higher than for ethylene. The coke formation for alkines in reactor was higher than in TLE. Catalytic activity of steel surface of reactor has the effect on coke formation rate mainly for acetylene and propine. Coke formation from acetylene despite high coking rate is not so significant due to its low concentration in reactor system [26].

4.5 Aromatics

The tendencies to coke formation of 18 aromatic hydrocarbons were observed mainly because they are part of the feedstock and of steam cracking products. Benzene after methane and ethane was the weakest coke precursor. Polycyclic structures as acenaphthylene, anthracene, and chrysene had high coke potential in pyrolysis reactor and TLE [27-28].

The coke formation rate for all observed aromatics increased with increasing of carbon number in chain of substituted alkyl part. This fact is evident mainly for benzene and naphthalene derivatives, for anthracene derivatives was insignificant. Coke formation potential grows by increasing of number of aromatic cycles. Methylanthracene, acenaphthylene and chrysene are the strongest coke formation precursors from all hydrocarbons. These aromatics form highly stable radicals [28].

5. Effect of reactor material

Effect of reactor surface composition on coke formation is examined for many types of alloys and quartz [9,12,14,16,21,29-30]. Main catalytic processes run on nickel and iron particles. These particles catalyse dehydrogenation reactions of hydrocarbons at higher temperature. Experimental studies proved that the rate of coke formation was first high and decreased gradually to constant value. High initial rate of coke formation was caused by catalytic effect of metal surface [1,9,14,16,21,30]. Formed coke layer reduces quantity of catalytic active centres. Effect of reactor surface is unimportant in using quartz reactor [4,31].

In the past, stainless steel with high carbon content was used as the reactor material. Later it was enriched with various metals to reduce coke formation. In present, alloys with low carbon content such as HK 40, HP 45, Incoloy 600 and Incoloy 800HT are used as construction materials [1,9-10,29,32]. Key considerations in selecting appropriate metallurgy for pyrolysis furnaces are:

- Oxidation
- Carburization
- Creep strength
- High temperature ductility
- Cost

Parameters of reactor surface have effect on coke formation, because physical and chemical properties of surface influence course of radical and surface reactions during pyrolysis of hydrocarbons. Formation of stable, solid and protective oxidation layer is necessary to minimize carburization and oxidation processes of reactor surface. To achieve required layer of oxides minimum required content of Cr in alloy represents 25 % [4]. Higher mass content of Cr forms more stable layer of oxides, but stability of alloy is lower. The presence of Cr, Ni and Si in alloy is effective against carburization and it secures protective and regenerable layer of oxides on surface, which is formed by oxosilylene, chromium oxide, alumina, magnesium oxide and other. Layer of these oxides on reactor surface decreases mass of coke formed by catalytic mechanism by decreasing of diffusion rate of carbon and his solubility in alloy [33-34]. Rank of oxides stability is following:

$Al_2O_3>TiO>TiO_2>SiO_2>Cr_2O_3>SiO>Mn_2O_3>Mn_3O_4>FeO>Fe_2O_3>NiO>CrO_3$

These oxides are stable at higher temperature, for example: Cr_2O_3 up to 1050°C, SiO_2 up to 1100°C and Al_2O_3 up to 1150°C. According to Parks [32] the material Alloy 28/48 W and Alloy 35/45 have excellent operating properties and maximal effectiveness at present. Presence of components W and Nb in these materials improves carburization resistance. Synergistic addition of W, Nb, Ti and Zr markedly increases carburization resistance.

In most furnaces traditional Fe-Cr-Ni alloys are still used. Their ability to reduce coking and resist carburization has been attributed to the formation of protective oxide layer, typically chromium (Cr_2O_3) on the furnace [21].

The addition of aluminium to Fe-Cr-Ni alloys can be highly beneficial for reducing coke formation and carburization. Aluminium forms alumina (Al_2O_3) on the surface when exposed to an oxidizing atmosphere. Alumina is much more stable than chromia at temperatures higher than 930°C [21].

Effect of HP 40 on coke formation is described by Zychlinski *et al.* [13]. Alloy HP 40 and alloy coating with technology AlcroPlex were compared in this study. AlcroPlex is a CVD technology. High temperature metallurgically stable coating is created on reactor surface by this technology. First step of this technology is a coating (CVD) on the surface of reactor using chromium. Next step is a coating using aluminium. Chromium migrates to the surface through the aluminium rich layer during steam cracking. This modification reduces the coke formation by 80% with naphtha and by 90% with ethane as feedstocks. These results were achieved even after repeatedly simulating material aging.

Study of Rahimi *et al.* [35] compares the rate of coke formation on Incoloy 600 and stainless steel. More formed coke was detected on stainless steel in all experiments in comparison with Incoloy 600. The rates of coke formation were different what depended on elemental surface composition. These differences were explained by higher content of Ni in Incoloy 800 alloy than in stainless steel. Particles of Fe, Cr and Ti in stainless steel catalysed formation of filamentous coke.

The effect of the reactor material composition on coke formation has been studied for ethane and naphtha cracking under industrially relevant conditions [16]. The reduction of coke formation is observed on specialized alloys compared to Fe-Cr-Ni heat resistant steels. Thin layer of alumina on the reactor surface provided the highest resistant to coking. This fact was demonstrated with scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The decrease in coking rate translates in a run length increase of 50 % for typical naphtha furnace equipped with reactors made out of an Al-enhanced alloy instead of typically applied heat resistant steel.

An experimental study [21] of the coking tendency during ethane steam cracking of two material groups was carried out in quartz electrobalance setup under industrially relevant ethane steam cracking conditions. SEM and EDAX of coked and uncoked coupons revealed that the composition of the oxide layer in contact with the cracked gas, formed after the initial preoxidation or decoking, has an important influence on the amount of coke deposited. As a group, the Al-enhanced alloys showed a better resistance to coke formation than those without aluminium in their formulation.

6. Coke reduction

6.1 Coke reduction by addition of inhibitors

Additives are added to the feedstock to reduce formation of coke or to change its character. In present, thiochemical compounds are used commercially and organophosphorous compounds and alkali metal compounds are in process of research.

6.1.1 Thiochemical compounds

Thiochemical compounds are used in commercial hydrocarbon steam cracking units. They have an impact mainly on rate of coke formation and on decrease of carbon monoxide yield [5,7,10,34].

Addition of thiochemical compound to feedstock can reduce the mass of coke in two ways:

- Reaction of thiochemical compounds with metal surface forming of metal sulphides (passivation of reactor surface)
- Reaction of sulphur with free radicals in gas phase.

Three ways of thiochemical compounds application are used: application of compound on inner side of the reactor, continual addition in feedstock and combination of both [1]. In present, dimethyl disulphide is used as inhibitor of coke and carbon oxide formation in industrial ethylene units [5]. Inhibition effect of dimethyl sulphide, diethyl disulphide, methyl mercaptane, ethyl mercaptane, butyl mercaptane and carbon disulphide on coke formation is a research subject of several investigators [36].

The temperature of dimethyl disulphide decomposition ranges between 400°C and 500°C and is lower that temperature for decomposition of hydrocarbon feedstock (about 600°C). Some thiochemicals are more stable and they need more energy to their decomposition. For example the temperature of complete decomposition of benzothiophene is about 675°C and for thiophene is this temperature about 800°C. For the same concentration of sulphur in feedstock, the rate of coke formation on already deposited coke layer asymptotic coking rate decreases in the given order [4]:

Dimethyl disulphide > ethyl merkaptane > dimethyl sulphide > carbon sulphur > benzotiophene > thiophene.

Bajus [37] summarized the order of thiochemical additives which influence asymptotic coking rate:

Sulphur > dibenzyl sulphide > diethyl sulphide > tiophene > dibutyl ditiophosphorite Zn > dibenzyl disulphide.

Different mass of thiochemical compound is needed to get the same value of sulphur concentration in feedstock in dependence on the feedstock type and reactor surface area. Conditions in industrial units are setup to addition 100-200 mg S/kg for steam cracking of ethane, propane and butane. For example for DMDS is this value 480-968 mg S/m^2 [25].

Rahimi *et al.* [35] observed an increase of coke formation rate at the increase of hydrogen sulphide addition. Cracking energy for bond HS-S is 381 kJ/mol what is less than energy needed for cracking C-H bond in propane and butane. HS· radical causes acceleration of radical reactions and speeds up coke formation. This conclusions were given for stainless steel reactor. However, the rate of coke formation decreases after increasing concentration of sulphur in form of H_2S at a fixed temperature for Incoloy alloy. This decrease of coke formation rate is caused by a higher Ni content in Incoloy alloy. Nickel catalyses cracking of hydrogen sulphide in gaseous phase at temperature 850-875 °C and simultaneously reacts to high stable NiS.

Decreasing of carbon monoxide formation by 80% was observed in study of Rahimi *et al.* [35] at using 50 mg H_2S /kg LPG feedstock. The coke formation rate was reduced by 25% more while using the DMDS addition than using hydrogen sulphide addition. This fact is explained by different structure of molecules.

Dimethyl disulphide

DMDS is used in ethylene furnaces to reduce coke formation. When gaseous hydrocarbon feedstock is used, it is necessary to apply a huge portion of DMDS to cover reactor surface before launching of furnace and continual addition to the feedstock follows. In the case of primary naphtha as feedstock it is necessary to use only presulfidization. Thiochemical compounds present in naphtha should reduce the rate of coke formation and monoxide production [5,9,11].

Effect of thiochemical compounds on coke formation in hydrocarbon steam cracking is not fully explained. This fact is confirmed by different even contradictory conclusions of many various research publications. Influence of thiochemical compounds on coke formation is complicated and depends not only on method of application but well as on type and mass of used thiochemical compounds and composition of reactor surface [2,7,11].

Certain similarities were found when compared inhibitory effects of DMDS and H_2S on rate of coke formation and production of carbon monoxide. The rate of catalytic coke formation using DMDS is lower as using H_2S. Energy needed for dissociation of S-S and C-C bonds in DMDS and HS-S bond in H_2S is lower as energy needed for cleavage C-C and C-H bonds in propane and butane. Therefore cleavage reaction of thiochemical additives acts as initiator for radical reactions in steam cracking and increases the rate of LPG feedstock cracking [11,35].

6.1.2 Organophosphorous compounds

Organophosphorous compounds are added to feedstock, but they are not used to surface modification. The effect of organophosphorous compounds on rate and character of coke formation was studied in following studies. Ghosh and Kunzru [38] and Vaish and Kunzru [39] investigated the influence of triethyl phosphite and triphenyl phosphite on the coke formation during naphtha cracking at 815-835°C. Addition of these compounds (50-1000 mg P/kg) reduces the coke formation without affecting the product yields. Das *et al*. [40] and Chowhury and Kunzru [41] investigated the influence of benzyl diethyl phosphite (100-500 mg P/kg) and triphenyl phosphine sulphide (50-100mg P/kg) on the pyrolysis of naphtha in the temperature range of 800-830 °C. Reduction in coke formation as well as CO production was observed. Kisalus [42-43] reported that triphenyl phosphine (25-100 mg/kg) and triphenyl phosphine oxide (25-100 mg/kg) could supress the coke formation during hexane cracking without affecting the conversion of hexane at temperature of 780-840 °C. Tong [44-45] reported the influence of phosphoric triamide (200-500 mg/kg) on the steam cracking of hexane at 770-790°C and the influence of phosphonate/triphosphonate compounds on the steam cracking of heptane at 780°C. Reduction of coke formation was observed. Wang *et al.* [8] investigated the influence of three P-containing compounds: hexamethyl phosphoric triamide (HMPA), tripiperidinophosphine oxide *(TPyPO) and dioctyl phenylphosphonate (DOPP) on the conversion of hexane during* thermal cracking at temperature of 850-900°C. The increasing of hexane conversion was observed.

The effect of triphenyl phosphine oxide (TPPO) in the rate of coke formation and morphology of formed coke at the surface of some coupons with different kinds of metals during thermal cracking of naphtha was investigated. Using stainless steel 304 and iron as a coupon, the rate of coke formation reduce to an optimum concentration for inhibitor in feedstock due to the formation of a metal-phosphorus complex which passivates metal activity for coke formation, but about the stainless steel 304 coated with nickel and chromium with CVD method, it was found that the rate of coke formation increases as the increasing of concentration of inhibitor due to the increasing of the rate of dissolution and diffusion of surface carbon atoms through the metal particles [46].

6.2 Coke reduction by modification of reactor and TLE surface

6.2.1 Surface polishing

Polishing of rector surface changes value of intensity of radiation at the surface of the heat transfer by radiation. The radiation intensity affecting heat transfer changes form value 0.1 (polished surface) to 0.9 (rough or coked surface). This difference between polished and unpolished surface can reduce needed furnace temperature by 50-100°C [4]. The reduction of surface temperature subsequently reduces coke formation.

Temperature is only one from parameters, which can clarify the reduction of coke formation by polishing. Mechanical polishing reduces overall roughness and the number of surface failures, which were generated by armatures and reactor production [44]. This argument was proved under laboratory conditions, when the roughness was decreased from 71 rms to 6 rms. Active metal particles, which are on the reactor surface, are with this mechanical operation eliminated. Experimental values proved significant reduction of formed coke during cracking of different feedstock. Ratio of the mass of coke formed on unpolished and polished surface was from 5.6 for isobutane to 28.1 for ethane [29].

Decrease of temperature is not only one of the positive effects of polishing. Another positive is reduction of number of catalytic active particles on reactor surface. Experimental data confirmed significant decrease of formed coke weight during steam cracking of different feedstock.

6.2.2 Surface alonization

Alonization of reactor surface is technology, which decrease the coke formation using the layer of Al_2O_3 on surface. This layer has no catalytic active particles, which could cause the coke formation via catalytic mechanism. This layer has a high temperature resistance and thus prevents material carburization.

Albright and Yu [48] studied effect of alonization on coke formation. This study gives valuable information on coke morphology formed on alloy steel. Using SEM and EDAX formation of filamentous coke was not observed on alonized surface and Fe, Ni and Cr particles were not detected in coke for many coke precursors in pilot plant.

The results form industry using of alonized surface of Incoloy 802 and unalonized surface of Incoloy 802 in ethylene unit in Gulf Canada Ltd. indicated that alonized layer will last on reactor surface for 3.5 years [49]. Following informations were obtained:

- No weight loss of alonized surface during 3.5 years
- Roughness of alonized surface without changes after alonization
- According to EDAX the amount of Al (42-87 wt.%) in reactor surface
- High percentage of Cr, Al, Nb and Si on alonized reactor surface
- Thickness loss by 20 % of unalonized surface
- More carburizing on unalonized surface

Two factors prove that alonized reactors operate at lower temperature then unalonized reactors:

- Less formed coke on alonized surface cause lower temperature level
- Thermal conductivity of coke on the alonized surface is higher.

6.2.3 Silica coating

Brown [50] observed that silica coating decreases coke formation rate in cracking pipes. Silica coating is applied on alloy by decomposition alkoxysilans in carrier gas. Alkoxysilan (tetraethyl orthosilicate) is injected (1 wt.%) to preheated steam. This mixture proceeds into the reactor at temperature from 600°C to 850°C. Silica coating has amorphous character with thickness 1μm or less.

Metallurgical testing of silica coating alloys proves minimal destructive effect to primary reactor surface. This silica coating protects alloy surface from oxidation reactions during high temperature cracking reactions. Protection against carburization is significant too [7,51-52].

Measurement of coke formation was done on coated and uncoated surfaces of alloys HK 45, Incoloy 800 and quartz in laboratory scale [53]. Study proved that coke formation ratio on HK 40 alloy was 4 to 6 times higher than on HK 40 alloy with silica coating. These experiments showed that reduction of coke formation on reactor surface coated with silica at used reaction conditions was significant.

The influence of the combination of two Si-containing additives, BTMS and TEOS, with DMDS on coke formation during steam cracking has been evaluated both on laboratory scale and in a pilot plant unit. The combination of Si pretreatment + presulfidization + continuous addition of 2 mg/kg DMDS results in a decrease in the rate of coke formation up to 40 % when hexane is cracked in the lab-scale unit. Under similar conditions in the pilot plant the coke formation in decreased by 70 %, while the CO production decreases by more than 90 % [7].

7. Conclusion

The coke formation as highly undesirable process in steam cracking is a complex process which depends on feedstock type, metal composition of reactor surface, addition of inhibitors in feedstock and reaction conditions (residence time, conversion, temperature profile and partial pressure of hydrocarbons). The coke formation occurs via three mechanisms: catalytic coking mechanism, radical coking mechanism and polyaromatic condensation. Catalytic coking mechanism can be controlled by material of reactor and transfer line exchanger (TLE). The rate of coke formation by this mechanism can be affected by content of metal particles (Cr, Ni, Co) in reactor surface or by formation of coatings with Si and/or Al compounds. Radical coking mechanism can be controlled by addition of organophosphorous or sulphur containing compound or steam/feedstock ratio.

Symbols

LPG	*Liquefied Petroleum Gas*
VGO	*Vacuum Gas Oil*
TLE	*Transfer Line Exchanger*
CVD	*Chemical Vapour Deposition*
PIONA	*Paraffin, Isoparaffin, Olefins, Naphthenes and Aromatics*
SEM	*Scanning Electron Microscope*
EDAX	*Energy Dispersive X-ray Analysis*
DMDS	*Dimethyl Disulphide*
HMPA	*Hexametyl Phosphoric Triamide*
TPyPO	*Tripiperidinophosphine Oxide*
DOPP	*Dioctyl Phenylphosphonate*
TPPO	*Triphenyl Phosphine Oxide*
rms	*root mean squared*

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