

UNRAVELING THE IMPACT OF TEMPERATURE AND FEEDSTOCK COMPOSITION ON COKE FORMATION IN STEAM CRACKING REACTORS

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ABSTRACT

The production of olefins by steam cracking reactors faces significant challenges due to coke formation, which has a detrimental effect on their performance and productivity. To tackle this issue, it is crucial to enhance our understanding of fouling phenomena and their relationship with feedstock composition and process conditions. While it is widely believed that aromatics contribute to increased coke formation, our research challenges this assumption by conducting steam cracking reactions using a naphtha feedstock spiked with various aromatic compounds. It is found that the addition of single-ring aromatics of up to 6 wt.% in the feed results in a reduction in the total coke formation rate in the steam cracker tubes and the transfer line heat exchanger (TLE). Conversely, a 2 wt.% spiking with a double-ring aromatic exhibit a minor increase in coking rate. In turn, adding a 1.2 wt.% naphthene-diaromatic shows a notable increase in the coke formation rate. However, temperature plays a pivotal role in coke formation as well, as higher temperatures are found to promote feedstock conversion and secondary reactions which contribute to coke deposition. The deposition of coke significantly increases by more than 70% in transfer line heat exchanger for two types of feedstocks—one spiked with 3 wt.% single-ring aromatic and the other with naphthene-diaromatic—due to a 20°C rise in temperature. In our study, we utilize the "Fouling Assessment Setup (FAST)", an experimental unit that makes it possible to assess fouling in the cracker tubes and the TLE in a single experimental run. By employing a refinery gas analyzer (RGA) and a comprehensive gas chromatograph coupled with a flame ionization detector (GC×GC-FID), we also gather real-time information on the composition of the reactor effluent. In summary, our study underscores the significance of the full comprehension of the underlying mechanisms of coke formation in steam cracking reactors.

INTRODUCTION

Steam cracking plays a crucial role in the (petro) chemical industry as it is the main production process for light olefins. Nevertheless, this process

yields byproducts that ultimately result in the formation of a coke layer on the internal surface of steam cracker tubes [1-4]. Although coke is mostly produced in small amounts, typically less than 0.1% by weight, the continuous buildup of these carbonaceous residues on the cracker tube walls and in the transfer line exchanger (TLE) finally leads to the shutdown of the steam cracking furnace to remove the carbon deposits from the reactor tube walls. These repetitive shutdowns negatively affect the economic efficiency of the steam cracker process [5, 6].

Extensive research, encompassing both theoretical and experimental approaches, has been conducted to understand the mechanisms of coke formation. Previous studies have identified three primary mechanisms: catalytic heterogeneous, non-catalytic heterogeneous, and non-catalytic homogeneous. The catalytic heterogeneous mechanism occurs mainly in the early stages of cracking when the reactor material's catalytic sites are still exposed and not yet covered by coke [1, 2]. In contrast, the non-catalytic heterogeneous mechanism in the radiant section depends heavily on feedstock properties. This stage involves the gradual encapsulation of the reactor surface with carbonaceous coke, resulting from reactions between gas-phase coke precursors and partially dehydrogenated filaments on the tube surface. Over time, this mechanism becomes more dominant as the catalytic sites become increasingly covered by coke [3]. The third mechanism, entirely dependent on feedstock properties, involves the condensation of high boiling point components in the product, leading to the accumulation of polyaromatic hydrocarbons (PAHs). These PAHs form the primary structural components of coke in lower temperature sections, such as the TLE. Consequently, a higher presence of polyaromatic hydrocarbons (PAHs) in the reactor effluent leads to increased fouling in the TLE section of a steam cracker [4].

Extensive research has already been done to gain a more comprehensive understanding of the conditions that provoke and affect coke formation. Among the various contributing factors, the composition of the feedstock and the operating

temperature emerged as pivotal influencers on the coke formation [6-11].

Elevating the temperature in the cracker tubes exhibits a pronounced impact on the formation of a coke layer on the inner walls of the tube. This observation can be attributed to the increased formation of by-products through secondary reactions. These by-products promote the formation of coke thereby diminishing the operational run-length of the furnace [12]. On the other hand, it is widely accepted that certain hydrocarbons, such as aromatics, present in steam cracker feedstocks, serve as precursors for coke formation during the cracking process [8, 13-16].

To challenge this hypothesis, the presented research investigates how the presence of aromatic compounds in the feedstock and the operation at increased temperature affect the formation of coke. To accomplish this, coke formation during steam cracking reactions is measured in a series of experiments carried out using a bench-scale setup that mimics the operating conditions in the cracker tubes and the TLE of an industrial steam cracker. In these experiments a reference naphtha spiked with different percentages of single-ring aromatic compounds (3%, 6%, and 9 wt.%), a double-ring aromatic compound (2 wt.%), and a naphthendiaromatic compound (1.2 wt.%), is cracked.

Moreover, additional experiments are conducted at elevated temperatures using two feedstocks, one spiked with single-ring aromatics (3wt.%) and one spiked with a naphthendiaromatic (1.2 wt%). When cracking these feedstocks the temperature in the reaction section (radiant) of the bench-scale setup is increased by 20°C. The aim of the research is thus to assess the relative influence on coke formation of temperature on the one hand, and feedstock composition on the other hand.

The experimental study makes use of the Fouling Assessment SeTup (FAST). By the use of two distinct methods, FAST facilitates the independent assessment of fouling in the cracker tubes and the TLE in a single experimental run. One method is conducted offline and involves the combustion of coke formed in a specific section of FAST, while measuring the resulting CO/CO₂ emissions using an infrared (IR) spectrometer. The second method is an online measurement in the radiant section. A coupon is suspended inside the radiant section of the tubular reactor, and its gradual increase in weight due to coke deposition is monitored using a magnetic suspension balance (MSB). The latter approach enables the calculation of both the catalytic and the asymptotic coking rates in the radiant section. The catalytic coking rate corresponds to the coking rate at the beginning of the cracking run when the catalytic activity of the material is dominant. In contrast, the asymptotic coking rate refers to the coking rate at the end of the

cracking run, where the surface of the material is covered by coke and the catalytic activity of the material is insignificant. At this stage, the effect of the feedstock composition on the coking rate becomes dominant. For further information, reference is made to the work of Muñoz Gandarillas et al. [17]. Furthermore, a precise analysis of the composition of the reactor effluents is made. High-temperature effluent samples, that is cracked feedstock samples, are taken and injected in a Refinery Gas Analyzer (RGA) and a comprehensive two-dimensional gas chromatograph with a flame ionization detector (GC×GC-FID).

FOULING ASSESSMENT SETUP (FAST)

FAST is an experimental apparatus specially designed to evaluate the propensity towards fouling in the cracker tubes and the TLE of steam crackers for a wide range of feedstocks. As seen in Fig. 1, the setup can be subdivided in four distinct sections: feed section, convection section, reaction section, and analysis section. The reaction section corresponds to the radiant section and the transfer line exchanger (TLE). Each of these sections is clearly labeled on the simplified schematic in Fig. 1.

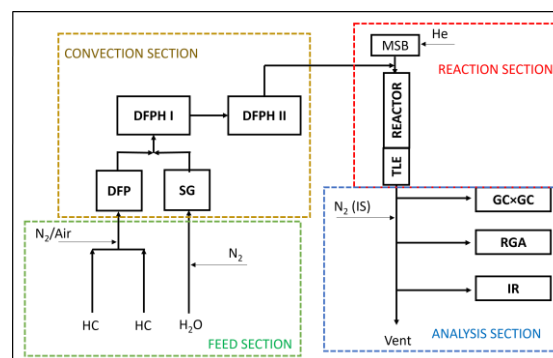


Fig. 1. Simplified schematic of FAST used to assess the coking formation in reactor tubes and TLE during steam cracking.

Feed section

Hydrocarbons (HC), water, nitrogen, and air are fed to the setup. Nitrogen is introduced separately into the outlet of the TLE and serves as the primary internal standard (IS) to determine product yields in the effluent [18, 19]. Helium is directly fed to the inlet of the reactor through a separate line. It protects the Magnetic Suspension Balance (MSB) against deterioration due to the composition of the flow coming from the convection section [17].

Convection section

The convection section comprises four distinct zones. They correspond to the Steam Generator (SG), the Dry Feed Preheater (DFP), the Dilute Feed Preheater I (DFPH I), and the Dilute Feed Preheater II (DFPH II). In an industrial steam cracker, these heat exchangers are heated by the hot flue gases

leaving the radiant section. In the DFP (150°C), the undiluted hydrocarbon feed is preheated. Water is supplied to the SG (200°C) where it is evaporated. Downstream of the DFP, the preheated hydrocarbon stream is diluted with steam. The mixture finally flows through DFPH I (260°C) and DFPH II (400°C). Here the diluted feed reaches temperatures corresponding to the feed temperature of the reactor tubes in the radiant section of an industrial steam cracker.

Reaction section

The diluted feed, consisting of hydrocarbons and steam, exits the convection section and is introduced into the Incoloy 800HT reactor tube from the top side. The reactor tube has a length of 0.6 m and an internal diameter of 10 mm. The reactor tube is divided into four zones, each having a length of 0.15 m. The first three zones (Reaction Zone 1 to 3) are considered to mimic the conditions in the cracker tubes in the radiant section of an industrial cracker where steam cracking of the feedstock takes place. The temperature of the outer tube wall in these sections is strictly controlled by using electrically heated furnaces. In contrast, the last tube section is to mimic the conditions in the TLE of an industrial steam cracker. Here the tube wall temperature is controlled by a combination of an electrically heated furnace and the introduction of air through a coil that is spirally wrapped around the tube.

As mentioned, the assessment of coke mass deposition using FAST relies on two distinct measurements: online and offline. In the online approach, a coupon made of 35/45 Cr-Ni alloy (10×4×1 mm) is suspended in Reaction Zone 3 of the reactor. The coupon is suspended using a Platinum wire with a 0.5 mm diameter, which is connected to the MSB. Consequently, the MSB continuously measures the incremental weight of the coupon, due to fouling with coke. This allows to calculate both the initial (or catalytic) and the asymptotic coking rate

For the offline coke measurement, the total weight of coke deposited on the reactor wall during the experiment is burned through a post-cracking decoking of the reactor tube. Decoking is done in two steps. In the first step, Reaction Zone 1 to 3 are kept at low temperatures, allowing to burn off the coke on the tube wall in TLE only. In the second step, the radiant coke is burned off. The calculation of the total deposits in step 1 and step 2 follows the methodology outlined in the "Online and offline coke measurement" paragraph.

Analysis section

The analysis section of the experimental setup facilitates the determination of the composition of reactor effluents during cracking, spanning a broad

range of boiling points. More specifically, the quantification of N₂, H₂, CO, CO₂, and a spectrum of hydrocarbons ranging from methane to polycyclic aromatic hydrocarbons (PAHs) in the reactor effluent can be quantified. The lower boiling point hydrocarbon products (C₁ to C₄), as well as N₂, H₂, CO, and CO₂, are separated and detected using a Refinery Gas Analyzer (RGA) in conjunction with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). Additionally, all hydrocarbons ranging from methane to PAHs are subject to online analysis via comprehensive two-dimensional gas chromatography (GC×GC) before being detected with a FID. The quantification procedure is based on the internal standard methodology as described in more detail in [18-20].

Online and offline coke measurement

In the offline method, the total amount of coke deposited in a specific section (radiant or TLE) during the complete experimental runtime, is burned off. With the use of a dedicated IR spectrometer, measurements quantify the volumetric concentrations of carbon monoxide (CO) and carbon dioxide (CO₂) in the combustion gases over time. The measured values can then be correlated to the total amount of coke formed in one section during one experiment using the following formula:

$$m_c = MM_c \sum_{i=0}^N \frac{\dot{Q}_t}{360} * \frac{(y_{CO,i} + y_{CO_2,i}) * p_i}{R * T_i} \quad (1)$$

where MM_c represents the molecular mass of pure coke, \dot{Q}_t stands for the volumetric flowrate of combustion gases, R denotes the gas constant, y represents the volumetric fraction, p signifies pressure, and T indicates the temperature value.

During one experimental run, the deposition of coke is also continuously monitored through online weighing of a coupon placed at the designated position (Reaction Zone 3), facilitated by the use of the MSB. Subsequently, the acquired data of deposited coke mass data is modeled using Eq. (2), where parameters A , B , C , and D are optimized to minimize the total sum of squares between the model and the experimental data.

$$m_t = A t + B \left(1 - \frac{1}{2} (e^{-Ct} + e^{-Dt}) \right) \quad (2)$$

In Eq. (2), the so-called fitted mass curve, m_t represents the mass of coke on the coupon surface at time t . The corresponding variation in mass over time, that is the coking rate, can be calculated by taking the derivative of Eq. (2) and dividing by the coupon's surface area. The coking mass, the fitted

coking curve and the coking rate for one experiment are illustrated in Fig. 2.

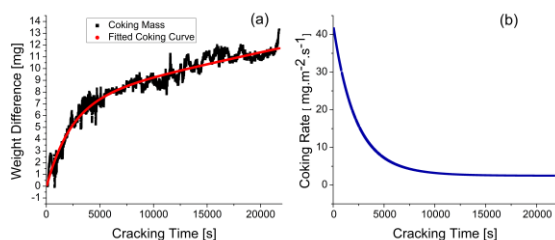


Fig. 2. (a): Filtered and fitted coking curve for the sample spiked with 3 wt.% single-ring aromatics at 950°C; (b): corresponding coking rate obtaining by differentiating the fitted coking curve.

OPERATING PROCEDURES AND CONDITIONS

The tube wall temperatures for two operational temperature conditions in different sections of FAST during the cracking of a feed, are provided in Table 1. The tube (or coil) outlet pressure (COP) is set at 1.8 bar. The latter is controlled by a back-pressure regulator (BPR).

Table 1. Summary of the temperature profile in the radiant and TLE sections of FAST.

Reaction Zone 1 [°C]	Reaction Zone 2 [°C]	Reaction Zone 3 [°C]	TLE [°C]
600/620	660/680	950/970	400

During the 6-hours cracking phase of an experiment, hydrocarbons are supplied to the Dry Feed Preheater (DFP) at a flow rate of 140 g/h, while demineralized water containing 60 ppmwt. of dimethyl disulfide (DMDS) is fed into the Steam Generator (SG) at a flow rate of 49 g/h. The steam generated in the SG is mixed with the hydrocarbon flow downstream of the DFP and upstream of the DFPH I. To achieve a temperature close to the steam cracking temperature, the mixture passes through DFPH I and DFPH II in series. Finally, the mixture is fed to the topside of the reactor tube through a high-temperature transfer line (HTTL).

EFFECT OF FEEDSTOCK COMPOSITION ON COKE FORMATION

In contrast to the catalytic coking rate, which is influenced by surface conditions, like aging and roughness, the asymptotic coking, considered the most crucial factor to evaluate fouling tendencies in industrial steam crackers, primarily depends on the composition of the feedstock. [21]. In this study, it is assumed that the asymptotic fouling regime where the coking rate stabilizes and remains relatively constant, is reached during the last hour of the experiment that lasts 6 hours in total (Table 2). In general, the experiments with different feedstocks learn that adding up to 6 wt.% of single-ring

aromatics like benzene and toluene, results in a minor decrease of the asymptotic coking rate. This contradicts the commonly held belief that aromatics are the main building blocks for coke [22]. However, the addition of double-ring aromatics and cyclic ring molecules like naphthene-diaromatics results in a notable increase of the asymptotic coking rate. Increases up to 23% are measured. This increase must be attributed to the pronounced activity of higher boiling point aromatics, resulting in an increased fouling in a cracking environment.

The offline assessment of coke buildup in both the radiant and the TLE section is conducted using a post-cracking decoking procedure, as explained. To calculate the average fouling rate in each section, the total quantity of coke deposits is divided by the duration of the cracking experiment, which is 6 hours, and is provided in Table 2. Based on the findings from offline coking measurements, it can be concluded that the introduction of benzene and toluene as spiking components does not result in an increased fouling level in the TLE section. When compared to the spiked single-ring aromatic (3 wt.%) sample, the spiked naphthene-diaromatic (1.2 wt.%) sample exhibits a higher rate (15%) of coke deposition in TLE section. This observed increase in fouling can be attributed to the increased production of PAHs in the reactor section (1.83 vs 1.23 wt. %), signifying that the condensation of heavier hydrocarbons is the principal mechanism driving fouling in the TLE section [23, 24].

For the offline coke measurements in the radiant section, a notable rise in the rate of coke formation is observed when shifting from the spiked single-ring aromatics to the spiked double-ring aromatic and spiked naphthene-diaromatic feedstock. This observation is most pronounced when a spiked naphthene-diaromatic (1.2 wt.%) sample is added. The observed coking rate increases with 45% as compared to the coking rate when a spiked single-ring aromatic sample (3 wt.%) is added. This corroborates the findings derived from the online coke measurements.

Table 2. Online and offline coke measurement during steam cracking at 950°C with different feedstocks.

	Online Coke Measure ment	Offline Coke Measurement	
	Asympto tic Coking Rate ($\text{mg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)	Radiant Coking Rate ($\times 10^3$ mg/s)	TLE Coking Rate ($\times 10^3$ mg/s)
Spiked single-ring aromatic (3 wt. %)	1.25	14.71	6.02
Spiked single-ring aromatic (6 wt. %)	1.21	12.78	5.65
Spiked single-ring aromatic (9 wt. %)	1.19	12.81	5.79
Spiked double- ring aromatic (2 wt. %)	1.37	15.42	6.35
Spiked naphthene - diaromatic (1.2 wt. %)	1.79	21.28	6.92

EFFECT OF TEMPERATURE ON COKE FORMATION

When the coking rates (offline measurements) at two different operational temperatures (950°C and 970°C) are compared (Table 3), it becomes apparent that the increase in temperature has a significant impact on the formation of coke in the TLE section. The deposition of coke shows a substantial increase of more than 70% for two feedstocks of spiked single-ring aromatic (3 wt.%) and spiked naphthene-diaromatic sample, owing to the 20°C temperature elevation. It is intrinsically linked to the higher PAH formation in the reactor section, resulting in increased deposits on the TLE inner wall [24-26]. The production of PAHs detected by GC×GC increased from 1.23 wt.% to 3.10 wt.% for the spiked single-ring aromatic and from 1.83 wt.% to 4.22 wt.% for the spiked naphthene-diaromatic when the temperature was raised from 950°C to 970°C.

A similar trend is consistently observed in the radiant section. Both the spiked single-ring aromatic (3 wt.%) and spiked naphthene-diaromatic (1.2 wt.%) samples exhibit a rise in coke formation when wall temperatures are increased. The increased coke formation must be attributed to the increased activity of coke precursors and the increased radical formation at elevated temperatures, thereby facilitating the coke formation.

Table 3. Comparison of coking rates at two different steam cracking operational temperature of 950°C (LT) and 970°C (HT).

	Radiant Coking Rate ($\times 10^3$ mg/s)	TLE Coking Rate ($\times 10^3$ mg/s)
Spiked single- ring aromatic (3 wt. %)- LT	14.71	6.02
Spiked single- ring aromatic (3 wt. %)-HT	18.28	10.27
Spiked naphthene- diaromatic (1.2 wt. %)-LT	21.28	6.92
Spiked naphthene- diaromatic (1.2 wt. %)-HT	25.98	13.59

CONCLUSION AND FUTURE PERSPECTIVE

The assessment of fouling in two sections of a steam cracker, namely the radiant and the TLE, is done using both online and offline methods in the Fouling Assessment SeTup (FAST). The study focuses on the impact on coke forming when adding small amounts of aromatics (single-ring aromatics, double-ring aromatics, and naphthene-diaromatics to the feedstock.

The results indicate that the introduction of single-ring aromatics has little to no significant effect on coke formation in both the TLE and radiant sections. However, as the number of aromatic rings in the hydrocarbon feedstock increase, fouling becomes more pronounced, especially in the TLE section. The increased fouling is primarily attributed to the condensation of polyaromatic hydrocarbons (PAHs) produced during the cracking of the spiked feedstocks. Furthermore, the study reveals that temperature influences the measured rate of coke formation. Even a modest temperature increase of 20°C, results in an increase of the coking rate by more than 70% in the TLE when spiked single-ring aromatics (3 wt.%) and naphthene-diaromatic (1.2 wt.%) samples are added to the naphtha feedstock.

The results of this study can assist steam cracking industries in gaining a deeper understanding of how the feedstocks they utilize affect coke formation in steam cracking reactors. However, this study specifically examined the impact of aromatics on coking in the radiant and TLE sections. It is recommended that future research explore the influence of other compound groups, such as naphthenes and olefins, and their interactions under steam cracking conditions, to further investigate their respective coking tendencies.

NOMENCLATURE

A, B, C, D	Parameters in coking curve fitting
BPR	Back Pressure Regulator
COP	Coil Outlet Pressure, bar
DFP	Dry Feed Preheater
DFPH	Dilute Feed PreHeater
FAST	Fouling Assessment SeTup
FID	Flame Ionization Detector
GC×GC	Comprehensive Two-Dimensional Gas Chromatography
HTTL	High Temperature Transfer Line
IR	Infra-Red gas analyzer
IS	Internal standard
m_c	Mass of deposited coke, kg
m_t	Mass of deposited coke at time t, kg
MM	Molecular Mass
MSB	Magnetic Suspension Balance
PAH	Polycyclic Aromatic Hydrocarbon
\dot{Q}_t	Volumetric combustion gases flow rate, m ³ /s
R	Gas constant, J/mol/K
r_f	Rate of coke mass deposition, Kg/s
R_f	Rate of coke mass deposition per unit surface area, kg.s ⁻¹ .m ⁻²
RGA	Refinery Gas Analyzer
SG	Steam Generator
T	Temperature, K
TCD	Thermal Conductivity Detector
TLE	Transfer Line Exchanger
$y_{x,i}$	Volumetric fraction of component x at time i

SUBSCRIPT

c	coke
i	time
x	component

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