

DETERMINING THE FOULING TENDENCY OF DIFFERENT FEEDSTOCKS IN THE FOULING ASSESSMENT SETUP (FAST)

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ABSTRACT

The use of heavier feedstocks has created new challenges for the steam cracking process, as severe fouling in the different sections of steam crackers is observed then. In order to obtain a more fundamental understanding about the fouling phenomenon and its relation to feedstock composition and process conditions the “Fouling Assessment SeTup (FAST)” was developed. This experimental unit was used to determine the fouling tendency of a heavy hydrocarbon mixture (HHM) in the different sections of a steam cracker, *i.e.* convection, radiant, and transfer line heat exchanger (TLE) sections via a post cracking decoking procedure and the continuous weighting of a suspended coupon in TLE with a Magnetic Suspension Balance (MSB). Additionally, a fouling mitigation concept of wetting fluid injection in TLE via an in-house apparatus was tested. The injection of a paraffinic fluid substantially reduced fouling in this section.

INTRODUCTION

Steam cracking is the dominant process for olefins production, which are key components of the chemical industry [1]. This technology is based on the thermal cracking of hydrocarbons inside tubular reactors suspended in a heated furnace [2]. Conventional feedstocks for steam crackers include ethane, propane and naphtha, however olefin producers have been encouraged to adopt heavier hydrocarbon sources that leads to severe fouling in different sections of steam crackers, especially on transfer line heat exchanger (TLE) [3].

The fouling phenomenon is not completely understood, although different mechanisms of coke formation and its relation to reactor material, process conditions and feedstock composition are described in literature. The different methods of fouling assessment are normally classified in four categories: weighing the equipment before and after the experiment [4], measuring of CO/CO₂ concentration during a decoking process in the fouled section [5-7], online measurement of heat transfer resistance during the experiment [8-10] and online measurement of mass deposited on a

suspended sample, *i.e.* thermo-gravimetric analysis [6, 11, 12]. The online fouling assessment methods, *i.e.* heat transfer resistance and thermos-gravimetric analysis have the advantage of continuous data acquisition. Further, it is possible to quickly detect experimental instabilities and to determine the effect of changes in experimental conditions in fouling rates. On the other hand, these methods are also more sensitive to fluctuations in experimental conditions, making the fine control of the experimental conditions and the use of data post-processing methods essential.

The Fouling Assessment SeTup (FAST) is an unit developed to assess the fouling tendencies independently in convection, radiant, and TLE sections during a single experimental run [13]. An apparatus for wetting fluid (WF) injection in TLE was developed in-house and installed in the FAST. The suppression of fouling in TLE by the injection of a wetting fluid is claimed by many patents [14-16]. The injection fluid would prevent the direct contact between the reactor effluent and the cold TLE wall avoiding the condensation of heavy hydrocarbons present in the reactor effluent, *e.g.* polyaromatics, which are the main precursors for fouling in TLE [12, 17]. Further, fouling mitigation would be achieved by decreasing the partial pressure and residence time of fouling precursors. From a process integration perspective, minimum amounts of wetting fluid should be used to avoid the excessive cooling of the effluent mixture which undermines the energy recovery in TLE [18].

In this work, the fouling tendency of a heavy hydrocarbon mixture (HHM) in the different sections of a steam cracker, *i.e.* convection, radiant and TLE sections was determined. Furthermore, the influence of the injection of a paraffinic wetting fluid (WF) in TLE fouling was studied. To the best of our knowledge, this is the first time that experiments applying the injection of a wetting fluid in TLE are reported in literature.

FOULING ASSESSMENT SETUP (FAST)

The Fouling Assessment Setup (FAST) is an experimental unit developed to assess the fouling tendency of a great variety of feedstocks in the convection and reaction sections of steam crackers.

The setup is divided in four sections, namely the feed, convection, reaction and analysis section. The reaction section corresponds to the radiant section and transfer line exchanger (TLE). Each section is denoted on the simplified schematic of the setup shown in Figure 1. The process conditions for each section of the setup are set and monitored using the Programmable Logical Controller (PLC).

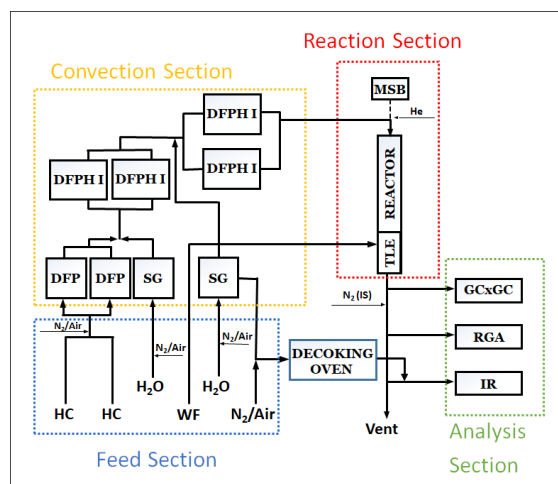


Fig. 1. Schematic representation of the FAST for studying coke formation in different sections of a steam cracking furnace.

Feeding section

Hydrocarbons (HC), water, nitrogen, air and a wetting fluid (WF) are fed to the unit. Mass flowrate is controlled via Coriolis mass flow controllers (Bronkhorst, the Netherlands) in combination with regulating valves for gasses and high precision rotary pumps for liquids (HNP, Germany). In order to avoid particle entrainment in the rotary pumps, sintered filters are placed upstream in two parallel cartridges, thus allowing switching between filters in case of blockages during the cracking run. Water and hydrocarbon vessels are pressurized with nitrogen gas to guarantee constant pump suction pressure. Hydrocarbon vessels are equipped with electrical impellers and electrical heat, assuring feedstock homogeneity. Lines upstream and downstream of the high precision pumps are electrically heated using tracing heaters, which decreases the density and viscosity of the feedstock. This feature is specially applied when using heavy hydrocarbon mixtures. Nitrogen is added using a separate line to the TLE outlet as the primary internal standard for the determination of product yields in the effluent [19, 20]. Similarly, helium is fed via a separate line through the Magnetic Suspension Balance (MSB) towards the inlet of the radiant section to protect the interior of the MSB from the convection section outlet stream [21].

Convection section

The convection section is composed by four different zones, namely steam generators (SG), Dry

Feed Preheater (DFP), Dilute Feed Preheater I (DFPH I), and Dilute Feed Preheater II (DFPH II). Hydrocarbons are fed without dilution to the DFP and water is fed to each SG. Downstream of the DFP, steam diluent is mixed with the hydrocarbons stream at two different locations, *i.e.* DFPH I and DFPH II. All heaters are vertically-positioned electrically-heated stainless steel 316L tubes with regulating K-type thermocouples placed on the outer wall. The DFP and SG are filled with quartz beads to enable smooth evaporation, while the DFPH I and DFPH II have inner stationary mixers that provide uniform mixing of feedstock and steam diluent. Each one of DFP, DFPH I and DFPH II zones consist of two evaporators in parallel, thus another evaporator can be used in case of blockages due to excessive fouling. In order to avoid cold spots in the lines of the convection section, all the elements of the convection section are located within four independently controlled electrically heated insulated boxes.

The amount of coke formed in the DFP, DFPH I and DFPH II zones during a cracking experiment are individually quantified by post-cracking decoking. More specifically, each heater is removed from its original position and mounted in the decoking oven to burn the accumulated coke deposits under air flow. The temperature of the decoking oven is set to 873 K with a nitrogen flow. Then the nitrogen flow stops and air is introduced enabling the combustion of coke deposits. The quantification of coke is performed according to the decoking procedure (see section Methods of fouling assessment)

Reaction section

The effluent of the convection section is transferred to the reaction section via a high temperature transferline (HTTL) that corresponds to the Crossover Temperature (XOT) of an industrial steam cracking.

Preserving the coke sample structure is critical for studying the morphology of deposits which can provide evidence of the dominant fouling mechanism [22]. The coupon can be removed without material loss using a balance lift. Helium is fed from the top side of the MSB to prevent the reacting gas entering the balance electromagnetic chamber.

The feed/diluent mixture enters from the top side of a vertically-positioned 0.6 m long, 10 mm internal diameter reactor tube, made of Incoloy 800HT (Ni, 30–35; Cr, 19–23; and Fe, >39.5 wt.%). The inner surface of the reactor is coated with hydrogenated amorphous silicon [23] in order to prevent extensive buildup of carbon deposits (SilcoTek®, Pennsylvania, USA). The coating can withstand 1373 K. Reaction section temperatures are set by radiation from four independently regulated electrically heated ovens (maximal temperature 1423 K). The outer wall temperature of the reactor

is measured at four positions and controlled, see Figure 2. Reaction temperature in the last zone can be reduced by injecting air through a spiral wrapped around the last 0.15 m of the reaction section. By combining heat input and cooling air flowrate, a temperature profile corresponding to both the steam cracking radiant and TLE conditions can be set.

Fouling in the reaction section is measured in two ways, *i.e.* fouling rate on a suspended coupon over time is measured via the MSB and the total fouling on the reactor wall during an experimental run is measured separately via decoking. The fouling rate changes during an experimental run are measured on a flat coupon (see Figure 2) connected with a Kanthal (diameter 0.5 mm) wire to a Magnetic Suspension Balance (MSB) from Linseis (Linseis Thermal Analysis, Germany), which records changes in mass of coupon with a frequency of 1 Hz. The resolution of the MSB is $\pm 5 \mu\text{g}$ and the maximum measurable mass 10 g. By changing the length of the Kanthal wire the preferred coupon position can be selected, *i.e.*, either in the radiant or TLE section. Process gas temperature is measured with a Movable Thermocouple (MT), positioned below the coupon in the corresponding section of the reactor. The position of the coupon and the movable thermocouple is set prior to an experimental run.

The total amount of fouling on the reactor wall can also be examined by post-cracking decoking. Initially the TLE is heated and air is introduced to facilitate the combustion of deposits. The total amount of deposits are calculated as described in the section Methods of Fouling Assessment. On sequence, the same procedure is repeated for the radiant section. Fouling on the suspended coupon is also burnt off during this procedure, but this amount is negligible compared to the total amount of carbon deposited on the reactor wall.

The pressure in the reaction section is controlled by a Back Pressure Regulator (BPR) positioned downstream of the reaction section. The pressure is monitored both at the reaction section inlet and outlet, thus increase of the pressure drop across the reaction section due to fouling can be monitored and logged.

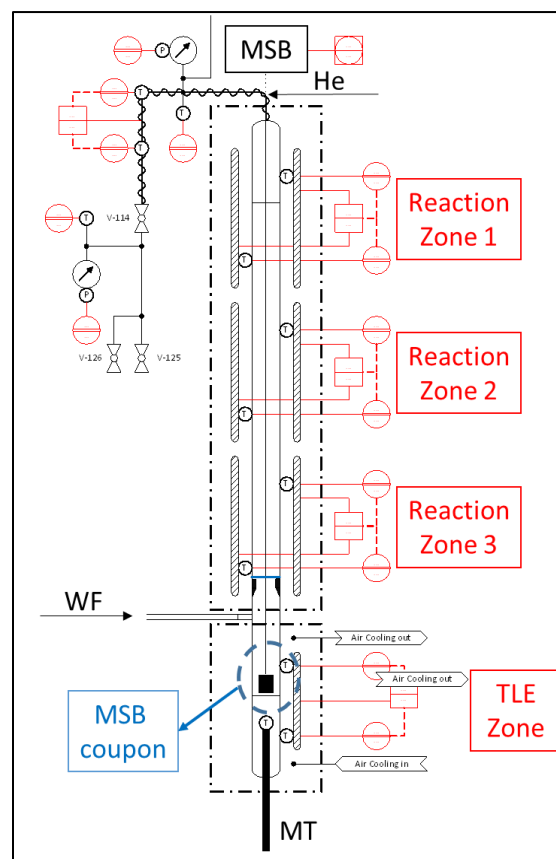


Fig. 2. Schematic of the radiant section of the Fouling Assessment Setup (FAST)

Wetting fluid injection apparatus in TLE

Based on the patent of Baumgartner, et al. [15], a wetting fluid injection apparatus was developed in-house and installed in the radiant section of the FAST. The paraffinic wetting fluid is fed in the TLE using a micro rotary pump controlled with a Coriolis mass flow controllers (Bronkhorst, the Netherlands). Upstream of the injection point, a one-way valve prevents the back flow of the wetting fluid. The line connected to TLE, the micro rotary pump and the mass flow controllers are kept at 323 K to reduce the viscosity of the wetting fluid and stabilize the flow rates of the wetting agent.

Four nozzles are used to inject the wetting fluid in TLE. Due to the ellipsoidal shape of the nozzles and the acute angle of the nozzles to TLE, the fluid agent swirls around the inner surface of the TLE tube avoiding interactions between the reactor effluent and the TLE walls. Elbow barriers located upstream of the wetting fluid injection point create a low pressure entry points for the wetting fluid. Moreover, the barriers prevent the back flow of the injected fluid to upstream sections.

Effluent composition analysis

The analysis section of the setup enables determination of a wide boiling point range reactor effluent composition, more specifically N_2 , H_2 , CO , CO_2 and hydrocarbons ranging from methane to

Polycyclic Aromatic Hydrocarbons (PAHs). Low boiling point hydrocarbon products (C₁ to C₄), N₂, H₂, CO, and CO₂ are chromatographically separated and detected using Refinery Gas Analyzer (RGA) coupled with Thermal Conductivity Detectors (TCD) and Flame Ionization Detector (FID). Further, all hydrocarbons ranging from methane to PAHs are analyzed on-line via comprehensive two-dimensional gas chromatography (GC×GC) before being detected with FID. Identification of major reaction products in the reactor effluent is based on their chromatographic retention times database established through injections of standard mixtures or using mass spectrometry identification. On the other hand, minor products are identified using Kovats retention indices and roof-tiles principle [19, 24]. The quantification procedure is based on the internal standard methodology [19, 20, 24].

Methods of fouling assessment

Coke deposits are quantified in two ways: The total amount of coke deposited in a specific section can be quantified via a post-cracking decoking procedure and the coke deposition on a coupon can be measured during the experiment via MSB measurements.

A dedicated carbon oxide infrared (IR) measurement is performed to determine the total amount of coke deposited in a certain section over the whole experimental run. The coke is burned off and the effluent analyzed during the decoking cycle.

The decoking effluent is cooled to 293 K and measured via a drum rotor volumetric gas meter (Ritter, Germany) under a controlled pressure of 120 kPa. The CO/CO₂ volumetric concentrations are measured with a frequency of 50 mHz using an infrared analyzer (Fuji Electric, Japan). Light intensity is measured and compared to a reference with inert nitrogen. Since carbon oxides absorb specific infra-red wavelengths, the calibration of the measuring cells with a calibration bottle enables the quantification of carbon oxides via the Lambert-Beer law. Finally, coke mass is calculated as a cumulative value over the complete decoking time with the following equation:

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

Where MM_c is the molecular mass of pure coke, \dot{Q}_t the volumetric flowrate, R the gas constant, y the volumetric concentration, p the pressure and T the temperature.

The amount of deposits during an experimental run is also measured by continuous weighing using the MSB with a coupon in the desired location. The raw balance signal contains high frequency noise that requires filtering using a MATLAB 8.6 2015b (The Mathworks, Inc., Natick, MA) low-pass filter. The filtered curve is further regressed by minimizing

the total sum of squares to equation 2 using parameters A , B , C and D .

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

Equation 2 is called the fitted mass curve, with m_t the mass of coke on the surface at time t . The corresponding time dependent mass increase can be obtained by differentiating equation 2:

$$r_{f,c} = \frac{dm_t}{dt} = A + \frac{B}{2} (Ce^{-Ct} + De^{-Dt}) \quad (3)$$

Finally, the fouling rate is determined by dividing equation 3 by the surface area of the coupon, S_c , which leads to the final coking rate form:

$$R_f = \frac{r_{f,c}}{S_c} \quad (4)$$

The fouling rate can also be calculated as a discrete derivative from the fitted mass curve as:

$$R_f = \frac{(m_{t_1} - m_{t_2})}{\Delta t \times S_{Coupon}} \quad (5)$$

where r_f is the fouling rate in $\text{kg} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$, m_{t_1} is the mass of deposits at time j , m_{t_2} is the mass of coke at time $j-1$ and Δt is the time increment. For details describing filtering, fitting and fouling rate calculation procedure the reader is referred to the work of Munoz et al. and Sarris et al. [21, 25, 26].

OPERATING PROCEDURES AND CONDITIONS

An overview of the applied operating conditions is presented in Table 1.

Table 1. Overview of the operating conditions, δ = dilution steam flowrate

Feed section			
HC [10 ⁻³ g·s ⁻¹]	δ_1 [10 ⁻³ g·s ⁻¹]	δ_2 [10 ⁻³ g·s ⁻¹]	
27.8	11.1	16.7	
N ₂ -IS [10 ⁻³ g·s ⁻¹]	He [10 ⁻³ g·s ⁻¹]	WF [10 ⁻³ g·s ⁻¹]	
2.8	1.2	27.8	
Convection section			
DFP [K]	DFPH-I [K]	DFPH-II [K]	
673	773	873	
SG-I [K]	SG-II [K]	XOT [K]	
673	673	873	
Radiant section			
Zone I [K]	Zone II [K]	Zone III [K]	TLE [K]
973	1043	1113	723
BPR [bar a]	RGA [bar a]	IR [bar a]	
1.8	1.5	1.2	

Dimethyl disulphide (DMS) is added to the heavy hydrocarbon mixture (HHM) in a 100 ppm concentration. The solution is fed to the convection section Dry Feed Preheater (DFP) kept at 673 K. Demineralized water is used as a diluent and fed to the Steam Generator (SGI), which is kept at 673 K. Steam and hydrocarbon streams are mixed in the Dilute Feed Preheater I (DFPH-I), where the temperature is kept at 773 K. Moreover, demineralized water is also fed to a second Steam Generator (SG II), that is kept at 673 K, and mixed with the diluted hydrocarbon stream in the Dilute Feed Preheater II (DFPH-II) kept at 873 K. The pressure in the convection section is set to 210 kPa with a manual needle valve positioned downstream of the DFPH II. The convection section effluent is transferred to the reaction section via a transfer line kept at a controlled crossover temperature of 873 K.

The reaction section temperature profile is controlled by setting temperature in the first three zones of the setup to 973 K, 1043 K and 1113 K, respectively. On the other hand, the temperature in the last zone corresponding to TLE is kept at 723 K. An Incoloy 800 HT coupon hanged on the MSB is positioned in the TLE mid-section. The process gas temperature is measured with a movable thermocouple positioned 10 mm below the hanged coupon. The magnetic coupling system of the MSB is protected from the reactor effluent by the injection of helium, thus further diluting the process stream. Nitrogen used as an internal standard for gas chromatography analyses is introduced downstream of the TLE section. The pressure in the reaction section is set to 180 kPa by means of a Back Pressure Regulator (BPR) positioned downstream. The reactor tube made of Incoloy 800HT (Ni, 30–35; Cr, 19–23; and Fe, >39.5 wt.%) is 0.6 m long with a 10 mm internal diameter. During the experiments with a paraffinic wetting fluid (HHM-WF) equivalent conditions were applied. The wetting fluid (WF) is injected with a micro rotary pump controlled via a cori-flow meter. A mass flow ratio of 1:1 between the hydrocarbon feed and the wetting fluid is applied.

FOULING ASSESSMENT IN THE CONVECTION SECTION

Fouling in the dry feed preheaters (DFP), dilute feed preheater I (DFPH-I) and dilute feed preheater II (DFPH-II) was measured via the post cracking decoking procedure (see section Methods of Fouling Assessment). Average coking rates were determined by dividing the total amount of coke by the duration of the experiment. In a second step, these values were divided by the coking rates of a wide range gas oil (WRGO). The relative coking rates of the HHM/WRGO and HHM-WF/WRGO for each element are shown in Figure 3. The error bars were estimated from relative standard deviations previously reported by Geerts et al. [13]. The

relative fouling rates of repeated experiments are included in the supplementary material (Table S1). This work also contains detailed information on the experimental conditions and the characteristics of the WRGO sample. The final boiling point (FBP) of the HHM is above 700 K, and for WRGO this is even above 800 K. Due to the blockage of downstream lines the experiment without the wetting fluid (HHM) lasted less than 3 hours, while the experiment with the wetting fluid (HHM-WF) lasted 50% longer.

Fouling in the convection section of steam crackers is initiated by the incomplete evaporation of heavy hydrocarbon compounds. High boiling point compounds form droplets that impinge in the hot tube walls of the convection section directly causing fouling on tubes, or rebound from the walls and form coke particles in the bulk of the reactor that also end up deposited on tube walls [27, 28]. In most of the cases, the fouling rates in HHM and HHM-WF experiments were one order of magnitude lower than the WRGO reference due to their lower final boiling point (FBP). The higher fouling rates obtained in the HHM-WF experiments could be related to experimental errors caused by the low amount of coke deposit detected and the different durations of the HHM and HHM-WF experiments. Furthermore, the use of the wetting fluid in TLE should not affect fouling in upstream sections, *e.g.* convection and radiant sections.

Despite the fact that the evaporation of HHM should be incomplete in DFP, the relative low temperatures applied should prevent fouling in this zone. In both DFPH-I and DFPH-II, the temperatures applied are above the final boiling point of the HHM sample. Therefore, fouling is suppressed in these zones by the complete evaporation of the sample.

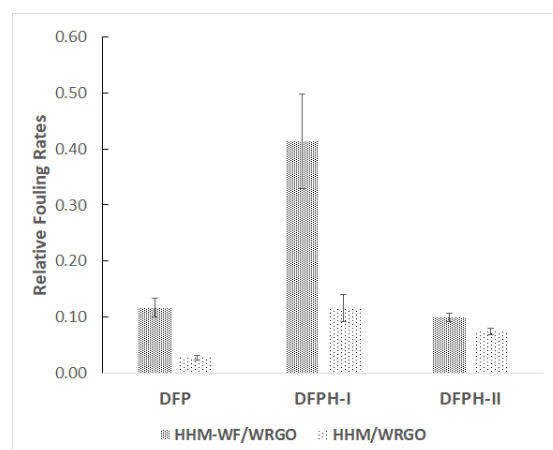


Fig. 3. Relative fouling rates in the convection section

FOULING ASSESSMENT IN THE REACTION SECTION

The post cracking decoking procedure was applied to determine the fouling rate in the radiant

and TLE sections (see section Methods of Fouling Assessment).

The online fouling assessment was performed in TLE by the continuous weighing a metal coupon positioned in TLE with the magnetic suspension balance (MSB). A comparison between the derived filtered coking curves and fitted coking curves of the HHM and HHM-WF experiments with dimensionless units is provided in Figure 4. The derived coking rates of the HHM and HHM-WF in dimensionless units is shown in Figure 5.

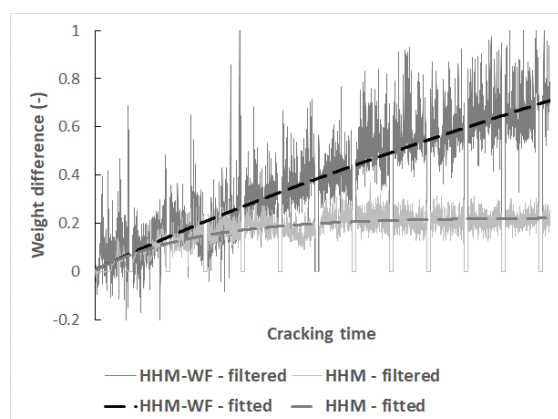


Fig. 4. Coking curve and fitted coking curve on the coupon in TLE

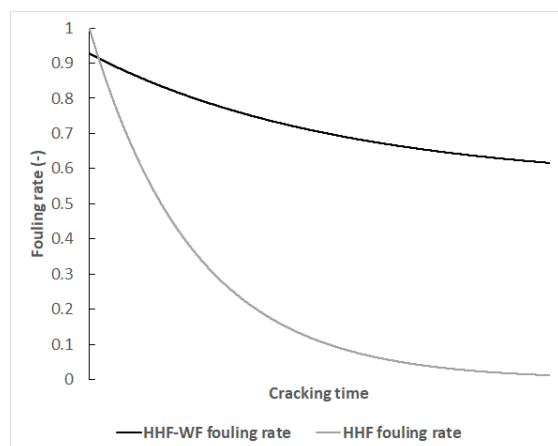


Fig. 5. Coking rate on the coupon in the TLE

Offline and Online fouling assessment

In radiant section, a small increase of 9.7% in the average coking rate was detected in the experiment with the wetting fluid injection. Because this value is very similar to the experimental deviations previously reported by Geerts, et al. [13], it can be concluded that the injection of the wetting fluid in the TLE did not affect fouling in upstream radiant sections. In the TLE the use of the wetting fluid suppressed fouling in 86% suggesting that the wetting agent can efficiently reduce the adhesion of heavy coke precursors in TLE inner tubes.

Despite the fact that much lower amounts of coke deposits were detected in the TLE via the decoking procedure during the experiment with the

wetting fluid, the MSB measurements reveals that fouling on the suspended coupon in the TLE was more than three times higher in the wetting fluid experiment. This apparent contradiction can be elucidated by the mechanisms of fouling suppression proposed below.

As described in the wetting fluid patent, fouling is mitigated by the wetting fluid action on the TLE tube walls [15]. It can be assumed that the wetting fluid removes the coke precursors from the TLE tube walls, but not from the bulk of the reactor. Because the suspended coupon is not wetted by the wetting agent, its surface is prone to fouling by coke precursors in the bulk. Due to the high sensitivity of the MSB measurements, the injection of the wetting fluid directly on the surface of the coupon is not possible. Moreover, higher fluctuations were already detected in the balance signals without the direct injection of wetting fluid on the coupon (see Figure 4).

In summary, the injection of a wetting fluid significantly reduced fouling in the TLE section, even though the presence of coke precursors in the bulk of the TLE was increased.

CONCLUSION

The fouling assessment of a heavy hydrocarbon mixture (HHM) in different sections of a steam cracker, *i.e.* convection, reactor and TLE sections was performed in the Fouling Assessment SeTup (FAST). Low fouling tendencies were determined for the HHM in the different zones of convection section, *i.e.* dry feed preheater (DFP), dilute feed preheater (DFPH-I) and dilute feed preheater II (DFPH-II). The concept of the injection of a wetting fluid for fouling suppression in TLE was investigated. The post cracking decoking of this section indicated that the injection of a paraffinic wetting fluid in a 1:1 wetting fluid to hydrocarbon feed mass ratio reduced fouling in TLE by 86%. Nevertheless, the higher fouling on the coupon in TLE detected by the MSB measurements, indicates that the injection of the wetting fluid increased the amount of coke precursors in the bulk of the TLE.

The injection of a wetting fluid in TLE is a promising fouling mitigation concept. Different aspects of this process, such as the composition of the wetting fluid, fluid flow patterns and wetting fluid to feed mass ratios, that has a great impact on the energy efficiency of the steam cracker deserves further investigation.

NOMENCLATURE

A, B, C, D	Parameters in coking curve fitting
BPR	Back Pressure Regulator
C_x	Carbon Number of Hydrocarbons
DFP	Dry Feed Preheater
DFPH	Dilute Feed PreHeater
DMDS	Dimethyl disulphide
FAST	Fouling Assessment SeTup

FID	Flame Ionization Detector
FBP	Final Boiling Point
GCxGC	Comprehensive Two-Dimensional Gas chromatography
HC	Hydrocarbons
HHM	Heavy hydrocarbon mixture
HTTL	High Temperature Transfer Line
IBP	Initial Boiling Point
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
MT	Moveable thermocouple
Nu	number, dimensionless
PAH	Polycyclic Aromatic Hydrocarbons
PLC	Programmable logical controller
\dot{Q}_t	Volumetric flow rate, m ³ /s
R	Gas constant, J/mol/K
r_f	Rate of mass deposition, Kg/s
R_f	Rate of mass deposition per surface area, Kg/s/m ²
RGA	Refinery Gas Analyzer
SG	Steam generator
S_c	Surface area of coupon, m ²
δ	Steam dilution mass flow rate, 10 ⁻³ g/s
T	Temperature, K
TCD	Thermal Conductivity Detector
TLE	Transfer Line Exchanger
WF	Wetting fluid
WRGO	Wide Range Gas Oil
$y_{x,i}$	Volumetric percentage concentration of component x at time i
XOT	Crossover Temperature

Subscript

c	coke
i	time
x	component

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