



Research article

Effect of composition of coke deposited in delayed coker furnace tubes on on-line spalling



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A B S T R A C T

Delayed coking is one of the most widely used residue upgradation process in crude oil refining where vacuum residue is thermally cracked and converted into distillates and petroleum coke. During heating of vacuum residue in coker furnace, coke is continuously deposited in furnace tubes which is removed at regular intervals by one of the three methods namely (i) pigging, (ii) steam air decoking or (iii) online spalling (OLS). OLS is one of the preferred methods of coke removal from coker furnace tubes. We have noticed very effective as well as “not so effective” OLS in a commercial delayed coker furnace. In present article, the changes in composition and properties of furnace coke during effective and ineffective OLS were systematically analyzed by various analytical tools such as Dilatometer, TGA, HRSEM, SEM-EDX and XRD. Based on these analyses, it was found that inorganic deposits such as iron sulphides and tube metal corrosion products play a major role in failure of OLS. Higher total acid number (TAN) of vacuum residue may be promoting the formation of iron sulfide deposits in furnace tube.

1. Introduction

Delayed coking is one of the most widely used residue upgradation process where vacuum residue (VR) is thermally cracked and converted into distillates and petroleum coke. Typically VR feed enters in a delayed coker furnace at 300–350 °C and comes out at 485–505 °C. On reaching cracking temperature of ~400 °C, thermal cracking of alkyl side chains of asphaltenes gets initiated, consequently the core of asphaltene molecules become less soluble in VR [1,2]. The cracked asphaltenes core agglomerate and start to precipitate out of solution phase. These agglomerates on further propagation in furnace tubes experience still higher temperature ~500 °C and start depositing on the furnace tubes as coke [3,4]. The thermal conductivity of deposited coke [5,6] is typically between 0.3–3 W/m·K and that of P9 metal used in furnace tube is ~30 W/m·K [7]. Thus coke being ~30 times less conductive than heater tubes reduces the heat transfer coefficient of furnace tubes [8,9]. In order to maintain the desired furnace outlet temperature of feed, tube metal temperature is continuously increased up to the maximum allowable working temperature (MAWT). P9 metal used in delayed coker furnace tubes contains ~89 wt% Fe, ~9 wt% Cr and ~1 wt% Mo along with small amount of C (~0.1 wt%), Si (~0.22 wt%), Mn (0.73 wt%) and Ni (0.27 wt%) [10].

Deposition rate of coke and other associated inorganic materials in delayed coker depends on several factors such as feed velocity inside furnace tubes, [11,12] suspended solids in coker feed, [13] roughness of tube surface [14] and temperature of tube metal surface [8,9,12]. Once MAWT is attained, furnace tubes are required to be cleaned by one of the following three methods viz. a) Pigging [15] b) Steam air decoking [16] c) On-line spalling (OLS) [17].

During pigging the entire furnace is shut down and cooled to ambient temperature. A plastic pig, embedded with metal studs, is inserted in the fouled furnace tubes and pushed with help of high pressure water. Size of plastic pig is sequentially increased to a diameter slightly less than the inner diameter of furnace tube to remove maximum amount of coke from furnace tubes. In steam air decoking the fouled furnace is heated in presence of steam-air mixture to slowly burn the deposited coke. This method is less effective when significant amount of inorganic material is deposited in furnace tubes.

OLS is one of the most economical methods of furnace decoking as it does not require complete furnace shutdown and external expert agencies to perform the spalling activities. OLS is done in one pass of furnace at a time whereas other passes of the same furnace are operated normally. Vacuum residue flow to the furnace pass where OLS is being carried out is reduced and steam flow is increased in tandem. Finally VR

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flow is completely stopped and steam flow is maximized to get steam velocity in the range of 90 to 100 m/s. After attaining the desired steam velocity, temperature of furnace tubes is gradually raised to MAWT, typically in the range of 650–700 °C and maintained for 1–2 h to dislodge any loosely bound coke. Then temperature of furnace tubes is quickly dropped to 450–500 °C by manipulating fuel supply to furnace to give a mild thermal shock. This mild shock is given to ensure heater tubes are not plugged due to excessive coke removal.

After mild thermal shock, temperature of furnace tubes is again increased to MAWT and hold for few hours. 2nd thermal shock is given by decreasing the tube temperature to 250–300 °C in < 1 h by manipulating fuel supply to furnace and introduction of boiler feed water in furnace tubes. 1 to 3 more shocks are given by repeating the sequence followed for 2nd deep shock to ensure maximum coke removal from tubes. After multiple thermal shocks, furnace tubes are heated again, vacuum residue is gradually introduced and steam flow is reduced to normal operation.

Success of OLS is measured by reduction in tube metal temperature when the spalled pass is taken back in line for regular operation to maintain desired feed outlet temperature. OLS efficiency depends upon difference in coefficient of thermal expansion (CTE) between deposited coke and tube metal as well as binding strength of coke with tube metal surface. The former is primarily dependent on crystallinity of coke such as graphite content, bonding characteristics of C in constituent molecules [18] whereas the latter is dependent on the elemental composition of coke layer and its inorganic contents [14]. Elemental analysis of the deposited coke in a lab scale foulant testing unit showed C, Fe and S as major constituents [19,20]. In literature source of Fe and S has been attributed to feed and it was suggested that iron naphthenates in feed decomposes and reacts with sulfur to form iron sulphide, predominantly as Pyrrhotite [15].

In this article, we have compared the composition and properties of furnace coke removed during pigging from a ~9 Million Metric Ton per Annum commercial delayed coker furnace situated in Jamnagar, India. These coke samples were collected during pigging operation when OLS was very effective and when OLS was not so effective. This study attempts to understand the root cause of good and bad spalling of coke in a commercial delayed coker furnace. It was found that significant amount of iron sulfide was present in the coke deposited in furnace tubes during bad spalling period which may be a result of higher corrosion of tube metals and upstream equipment due to increased total acid number (TAN) and reduced sulfur in VR feed. CTE of bad spalling coke was higher and closure to that of P9 metal making is more prone to sticking during thermal shock of OLS.

2. Material and methods

2.1. Vacuum residue (VR) feed

VR feed processed in delayed coker during good spalling and bad spalling period was produced from blends of 15–20 different crude oils. Although VR properties were maintained within specification window, there were some changes in feed properties during good spalling and bad spalling periods. Table 1 shows the average properties of VR feed processed during good spalling and bad spalling periods. Average TAN of VR was 0.47 mg KOH/g and 0.60 mg KOH/g during good spalling and bad spalling periods respectively. Average total sulfur in VR was 4.1 wt% during good spalling period whereas it has decreased to 3.9 wt% for bad spalling period. Other feed properties like CCR, metals, density were almost similar in both periods.

2.2. Furnace coke

Coke collected after pigging of delayed coker furnace when OLS was effective was named as “good spalling” and that collected when OLS was ineffective was named “bad spalling”. During pigging the scrapped

Table 1
Average VR properties during good and bad spalling periods.

Properties	Good spalling period	Bad spalling period
TAN, mg KOH/g	0.47	0.60
Sulfur, wt%	4.1	3.9
Density, g/cm ³	1.037	1.037
Asphaltene, wt%	14.1	15.1
CCR, wt%	25.5	25.2
Recovery at 565 °C, wt%	16	16
V, ppmw	410	439
Ni, ppmw	119	117
Fe, ppmw	11.1	13.3

coke and water mixture were collected from furnace tube outlet. This mixture was filtered through a mesh to collect coke flakes. The water along with finer coke powder was drained. The coke thus collected was kept in separate bags for each pass of the furnace. In this study, since the total thickness of coke layer was ~2 mm only, most of the coke flakes were intact having both tube side and feed side surfaces. In case, thickness of coke is higher there may be slicing of the coke layer into two or more layers hence care must be taken to identify the tube side and feed side surfaces. The screened coke samples were oven dried at 60 °C for 12 h to remove moisture. These coke samples have seen temperature of ~500 °C for more than 60 days in furnace tubes and were of different size and shape ranging from small granules to flakes of few centimeter sizes.

2.3. Hardgrove Grindability Index (HGI)

HGI of coke samples was measured in HGI apparatus from Chemicals and Instruments Corporation, Kolkata as per ASTM D409.

2.4. Real density

Real density of coke and ash samples was measured in Quantachrome Ultrapyc 1200e as per ASTM D2838. Coke samples were powdered to < 75 µm size before real density measurement.

2.5. X-ray diffraction

XRD analysis was carried out by using Rigaku Miniflex600 power diffraction instrument. X-ray was generated from Cu X-ray tube operated at 60 kV and 1 mA. Graphite monochromator was used to get monochromatic Cu K α radiation (1.54056 Å) which was used for XRD measurement. The samples were powdered and uniformly spread over XRD sample holder. Then sample holder was placed on an auto sampler of the X-ray system. XRD patterns of the samples were collected in 5–50° (2 θ) with scanning speed 1°/min and step size (0.01°). Phase identification in the sample was carried out using search match program of M/s Rigaku and using the JCPDS library.

2.6. Thermogravimetric analysis

TGA measurements were performed by using TA SDT-Q 600 instrument. Samples were placed in the analyzer and kept at 250 °C for 1 min. Subsequently, the temperature was increased from 250 °C to 900 °C at a heating rate of 100 °C/min. Decrease in weight of the sample w.r.t. the starting weight was recorded in percentage. Derivative of the curve was also determined in order to display peaks where the weight decrease was highest.

2.7. CHNS analysis

CHNS measurement was performed using Elementar Vario micro cube instrument, where combustion tube and reduction tube were set at

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