International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
SJIF (2024): 6.623

Root Cause Analysis and Engineering Measures for Furnace Tube Blockage in Ethylene Pyrolysis Furnaces

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Abstract: ***This study investigates the underlying causes of furnace tube blockage in pyrolysis furnaces within ethylene production facilities. Combining macroscopic and microscopic analyses, including SEM and EBSD techniques, the research identifies feedstock aromaticity, cracking temperature, and alloy composition as key contributors to coke formation. The presence of carbon-rich deposits and corrosion-related elements confirms the catalytic and structural vulnerabilities of furnace tubes. Mitigation strategies such as optimizing feedstock composition, introducing coking inhibitors like DMDS, and enhancing furnace design are proposed. These interventions aim to extend equipment lifespan and ensure consistent production efficiency.***

Keywords: pyrolysis furnace, coke formation, ethylene production, tube blockage, furnace optimization

1. Introduction

As a core component of ethylene plants, the blockage of pyrolysis furnace tubes is a complex issue. Pyrolysis furnace tubes are chronically exposed to extreme environments characterized by high temperatures and corrosive flue gas. Concurrently, throughout their service life, these tubes are exposed to multiple stressors such as process media corrosion, erosion from high-velocity fluid flow, and coking on the inner tube wall. The causes are multifaceted, involving coking, corrosion, material degradation, and improper operational conditions [1]-[3]. These persistent forms of damage lead to the gradual deterioration of the tube material, reducing its corrosion resistance and mechanical strength, and ultimately resulting in equipment failure [4],[5]. Such failures cause unplanned shutdowns, imposing significant economic losses and safety hazards on production facilities. A thorough analysis of these blockage mechanisms and their interactions is crucial for extending tube service life, enhancing production efficiency, and ensuring operational safety.

The cracking furnace is an indispensable piece of equipment in the petrochemical industry. Operating under extreme conditions, it is susceptible to various forms of degradation and operational challenges, among which coke deposition leading to furnace tube blockage is a significant issue [6]-[8]. Coke deposition not only exacerbates tube wall temperature irregularities but also progressively reduces the effective flow area inside the furnace tubes. This can ultimately lead to severe blockage, adversely affecting heat transfer efficiency and the service life of the furnace tubes. This blockage phenomenon can result in localized temperature increases, elevated pressure drops, and even deformation of the furnace tubes [9], posing operational safety hazards.

The study examines operational issues within an ethylene production unit of a petrochemical company. The cracking furnace at this facility has experienced multiple tube blockages during actual production, significantly impacting its operational cycle. This paper analyzes the aforementioned phenomena and proposes corresponding mitigation measures, aiming to achieve long-term stable operation of the cracking furnace. Understanding and addressing the root causes of tube blockage is crucial not only for minimizing unplanned shutdowns but also for improving operational safety and energy efficiency in ethylene production systems.

2. Coking Mechanism

During the pyrolysis reaction of hydrocarbon feedstocks inside the furnace tubes, coke fines are generated as a result of accompanying secondary reactions. The continuous deposition of these coke fines within the tubes ultimately leads to coking. This coking phenomenon increases the thermal resistance of the tube wall, alters the heat transfer coefficient, and causes localized overheating of the tube wall, thereby reducing the service life of the tubes and increasing energy consumption during the reaction process. The persistent deposition of the coke layer causes a continuous reduction in the inner diameter of the furnace tube. This leads to an increased pressure drop of the feedstock fluid flowing through the tube, a decrease in the amount of pyrolysis feedstock participating in the reaction, and a reduction in olefin yield. As the severity of coking progresses, it can eventually lead to furnace tube blockage.

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3. Analysis of Coking Causes in Cracking Furnace Tubes of Ethylene Plants

Coking and subsequent tube blockage are common issues during the operation of ethylene plants, primarily caused by coke formation during the cracking reactions. The gradual accumulation of coke directly impacts the operational stability and production efficiency of the plant. The coking substances mainly originate from aromatic hydrocarbons present in the feedstock and polycyclic aromatic hydrocarbons (PAHs) formed through reactions such as dehydrogenation and condensation of cracking products. Under high-temperature conditions, substances like aromatic hydrocarbons and PAHs undergo further polymerization. They gradually adhere to the inner wall of the furnace tubes and form a coke layer, ultimately leading to a progressive reduction in the effective flow area of the tubes and, in severe cases, complete blockage.

3.1 Macro Analysis

3.1.1 Feedstock Characteristics

The mass fraction of aromatics in the ethylene feedstock is a profound factor influencing the coking amount. The Bureau of Mines Correlation Index (BMCI) holds significant importance in the cracking unit of an ethylene plant, as it aids in predicting the cracking performance of feedstock oil fractions. It comprehensively considers factors such as the temperature, width, and density of the feedstock fraction, which are directly related to the feedstock's properties and cracking performance. The typical threshold value for BMCI is 20. When the feedstock's BMCI exceeds 20, it indicates a higher content of heavy components. These components are more prone to form coke during the cracking process, thereby increasing the risk of coking inside the pyrolysis furnace tubes, and concurrently resulting in lower ethylene yield. Conversely, when the feedstock's BMCI is below 20, the content of high-molecular-weight benzene and aromatics is lower, making it less susceptible to coking under high-temperature reactions. Therefore, in practical production, feedstock quality should be strictly controlled. Selecting feedstocks with a moderate BMCI, a reasonable distillation range, and appropriate density can effectively mitigate the risk of tube coking

3.1.2 Cracking Temperature

An increase in cracking temperature further promotes the enhancement of cracking severity. The primary reason for this is that high temperature provides sufficient energy to facilitate the cleavage of chemical bonds in hydrocarbon molecules, which is conducive to the generation of products such as ethylene and propylene. In practical production, an appropriate increase in temperature can effectively promote the occurrence of cracking reactions. However, excessively high temperatures can produce negative effects: on one hand, they promote secondary reactions, and on the other hand, they intensify side reactions such as coking and carbon deposition. Therefore, balancing cracking severity with coking inhibition is key to determining the optimal cracking temperature.

Table 1 shows the changes in effluent composition of a heavy oil furnace at different cracking temperatures. As can be seen from the data in the table, with increasing temperature, the ethylene volume fraction initially increases before declining, the volume fraction of propylene gradually decreases, while the volume fraction of acetylene continuously increases. This result further indicates that cracking temperature is directly related to cracking severity. A suitable temperature helps to improve the yield of target products, but excessively high temperatures may also affect ethylene selectivity.

In summary, to optimize the ethylene production process, precise control of the cracking temperature is essential. On the basis of ensuring the required cracking severity, the generation and adhesion of coke should be minimized as much as possible. Reasonable temperature regulation not only improves the quality and yield of ethylene products but also effectively prevents furnace tube blockages, thereby ensuring stable operation of the unit and increasing the economic benefits of the enterprise.

Table 1: Analysis of the components of the off-gas from the heavy oil furnace in the ethylene plant

Cracking Temperature/ °C	Propylene Volume Fraction/%	Ethylene Volume Fraction/%	Acetylene Volume Fraction/%
841	12.84	34.96	0.61
843	12.68	35.84	0.64
845	11.85	35.19	0.71

3.1.3 Furnace Tube Material and Structure

The cracking furnace tubes in ethylene plants are typically manufactured from iron-nickel-based superalloys. These materials exhibit excellent high-temperature resistance, corrosion resistance, and creep resistance. During the production process, iron elements within the alloy react with carbon free radicals generated from cracking, forming unstable carbides that are prone to decomposition under high-temperature conditions. Concurrently, chromium elements oxidize on the inner wall of the furnace tube to form an oxide film. This film effectively mitigates coke adhesion to the inner tube wall, inhibits further carbon penetration, and enhances the material's corrosion resistance at elevated temperatures. However, when the chromium content in the alloy exceeds a critical threshold, the oxide film may fail and spall under high temperatures, thereby diminishing its protective effect.

On the other hand, although the addition of nickel can reduce the solid solubility of carbon in the alloy, it also promotes coking reactions and exhibits a catalytic effect on coke formation. When process conditions such as cracking temperature and flow rate remain stable, the internal structure of the furnace tube directly influences the residence time of carbon-source gases within the tube. Additionally, the surface roughness of the inner wall significantly affects the initial deposition behavior of coke. Therefore, the coking phenomenon in ethylene cracking furnace tubes may be closely related to both the material composition and the physical structure of the tubes. In practical use or during tube replacement, strict control over the content of key elements such as nickel and chromium is required, while particular attention should be paid to the smoothness of the inner tube wall and the rationality of the structural design. This approach aims to delay coking and ensure sustained unit operation.

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3.2 Microscopic Analysis

Figure 1 shows the blockage material from the inner wall of a pyrolysis furnace pipeline in an ethylene plant of a petrochemical company in 2024, which was obtained by high-pressure water jet cleaning. The material primarily adhered to the internal fins of the pipeline and, after prolonged accumulation, severely obstructed the pipeline. To further investigate the composition of the blockage, this paper utilized the JSM-IT500 equipment from JEOL Company to conduct scanning electron microscopy and electronic sectioning analysis on the blockage.

Figure 1: Buildup on the inner wall of the cracking furnace tube

Figure 2 shows the electron microscope image of the clogging material in the cracking furnace pipeline, captured at a scanning voltage of 20 kV, a current of 60 nA, and with an amplification factor of 800. From the image, it can be seen that the surface of the clogging material consists of spherical black particles, which are randomly distributed, and there is a white crystalline substance adhering to the surface of the clogging material.

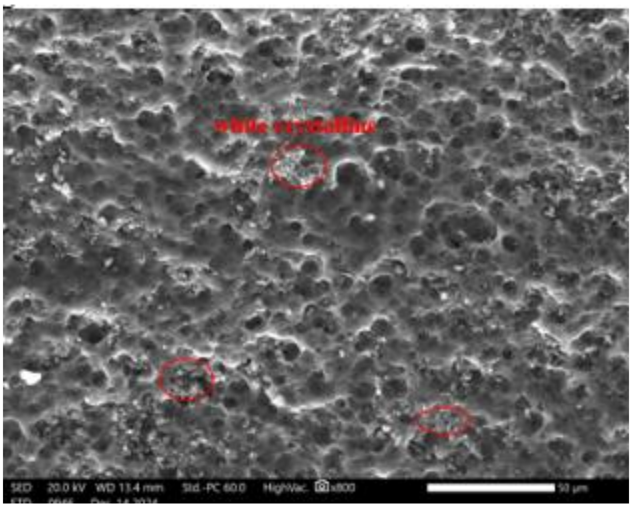

Figure 2: SEM Image of the Blockage

Figure 3 shows the layered SEM image of the deposit. It can be seen that the internal deposit within the tube is composed of numerous elements. From the composition analysis, it is evident that the black particles are primarily substances generated by coking. To determine the proportion and distribution of various elements, an area scan was performed on the deposit sample. The results are shown in Figures 3 and 4. It can be concluded that carbon has the highest content in the deposit, which is determined by the composition of the feedstock. However, the deposit also contains significant amounts of elements such as Si, Br, and Ni. The material of the pyrolysis furnace tube is composed of elements including Cr, Ni, Si, and B. Therefore, it can be inferred that the long-term adhesion of the deposit to the inner wall of the pyrolysis tube has a corrosive effect on the tube. This corrosion causes the degradation and detachment of alloy constituents, thereby reducing the service life of the tube. Furthermore, with prolonged operation, the corrosion becomes more severe, the roughness of the inner tube wall increases, and the pyrolysis furnace tube becomes more prone to blockage.

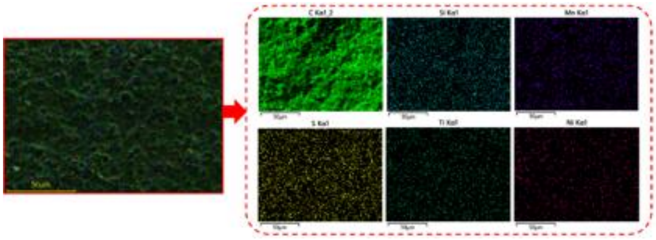

Figure 3: Electron Microscopy Layered Image of the Blockage

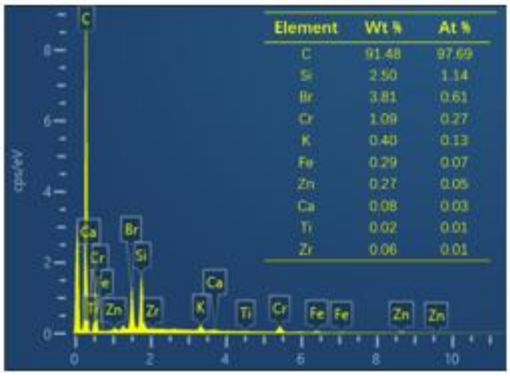

Figure 4: EDS Analysis of the Blockage

4. Measures to Mitigate Furnace Tube Blockage

4.1 Improvement of Cracking Feedstock

The coking tendency of cracking feedstock is closely related to its Bureau of Mines Correlation Index (BMCI) value. A higher BMCI value typically indicates more severe coking reactions during the thermal conversion process. Therefore, strict control over the aromatic hydrocarbon content of the feedstock must be implemented during the procurement stage to ensure feedstock quality from the source. This helps prevent a shortened operation cycle of the cracking furnace due to excessively high aromatic content.

4.2 Addition of Coking Inhibitors

Dimethyl disulfide (DMDS) is an effective coking inhibitor widely used in ethylene plants. Its composition primarily consists of sulfides, alkali metals, and phosphides. Under high-temperature conditions, the sulfides decompose to generate sulfhydryl groups, which can react with the iron on the inner wall of the furnace tube to form iron-sulfur compounds such as iron sulfide, thereby passivating the metal surface. The passivated inner wall of the furnace tube can delay the catalytic effect of metal elements such as iron and nickel on coking reactions, thus reducing the deposition of coke on the tube wall. Simultaneously, the alkali metals in DMDS can promote the reaction between steam and deposited carbon, converting the carbon into CO and CO_2,

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which are then discharged with the gas stream, thereby reducing coke adhesion on the furnace tube surface. The passivation by alkali metals also reduces the catalytic effect of active metal centers on coking. Furthermore, phosphides decompose under high temperatures, and their decomposition products can form a protective film on the metal surface. This film not only delays coking on the alloy material but also alters the physical structure of the coke, making it loose and brittle, and thus easier to be carried away by the gas flow.

4.3 Optimization of Furnace Tube Structure

To effectively prevent furnace tube blockage, it is necessary to optimize both material selection and structural design. In terms of material selection, the content of key elements such as nickel and chromium should be reasonably controlled to inhibit their catalytic coking effect while ensuring high-temperature resistance and corrosion resistance. The application of surface modification treatments or coating technologies is recommended to enhance the anti-coking performance of the furnace tube inner wall. Regarding structural design, the flow channel morphology of the furnace tube should be optimized to reduce flow dead zones, and the inner wall should maintain a high degree of smoothness to minimize coking. Furthermore, by improving process parameters—such as optimizing the pyrolysis temperature and feedstock residence time—and employing coking inhibitors, the generation and adhesion of coke can be further delayed, thereby ensuring the long-term stable operation of the unit.

5. Conclusions

Through analysis from both macroscopic and microscopic perspectives, the following conclusions are drawn:

Analysis of feedstock characteristics revealed that a higher Aromaticity Index (BMCI) in the feedstock is associated with an increased risk of coking within the pyrolysis furnace tubes. Conversely, a lower BMCI value indicates the feedstock is less prone to coking during high-temperature reactions. Therefore, in practical production, feedstock quality should be strictly controlled. Selecting feedstocks with a moderate BMCI, a reasonable distillation range, and appropriate density can effectively mitigate the risk of tube coking.

Appropriately increasing the pyrolysis temperature can effectively promote cracking reactions and achieve a higher degree of pyrolysis. However, excessively high temperatures can promote side reactions such as coking and carbon deposition. Further analysis on the relationship between pyrolysis severity and coking inhibition will be conducted in subsequent research.

The tubes of ethylene plant pyrolysis furnaces are typically fabricated from iron-nickel-based superalloys. Chromium (Cr) in the tube material oxidizes on the surface to form a dense oxide film. This film effectively retards coke deposition, inhibits further penetration of carbon, and enhances the material's corrosion resistance at high temperatures. However, when the chromium content in the alloy exceeds a certain critical value, the oxide film may become unstable and spall under high-temperature conditions, thereby diminishing its protective effect. Furthermore, the presence of nickel (Ni) can promote coking reactions and exhibits a catalytic effect on coke formation.

Analysis via electron microscopy images indicated that the tube blockages possess the highest carbon content, along with elements such as silicon (Si), bromine (Br), and nickel (Ni). This is attributed to the long-term adhesion of these deposits to the inner tube walls, which causes corrosion. This corrosion leads to the detachment of elements from the tube material, reducing the tube's service life. Furthermore, with prolonged operation, corrosion intensifies, increasing the inner wall roughness of the tubes. This increased roughness makes the pyrolysis furnace tubes more susceptible to blockage. These insights contribute to the ongoing development of predictive maintenance frameworks and inform the design of next-generation pyrolysis furnaces.

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ISSN (Online): 2347-3878
SJIF (2024): 6.623

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