Engineering Consulting & Training Services

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Petroleum Coke Formation

By Leo D. Brown

Unwanted coke formation in high temperature petroleum processing can result in significant effects on unit performance such as:

- Flow constriction in pipes and vessels
- Blockages on grids, sheds, and trays
- Increased back pressure on fixed catalyst beds
- Decrease in heat transfer efficiency (especially for fired heaters and heat exchangers)

These problems will not only reduce unit productivity but may also increase the frequency and duration of unit turnarounds.

All petroleum coke is not the same. In order to understand the cause of a specific coking problem, the type of coke must be determined. The vast majority of petroleum coke deposits are often referred to as "thermal coke" (the same class of coke as produced by the delayed coking process). The mechanism of formation involves heating a heavy hydrocarbon such as petroleum resid above 700°F during which a liquid crystal precursor called mesophase begins to form. Over time, the mesophase grows and coalesces in the liquid phase, which results in a degree of order in the final coke product. This order is observable under polarized light as distinct anisotropic regions in the coke called mosaics (ranging in size from 0.5 to 10 microns) and larger regions called flow domains (> 10 microns). The larger the mosaic or domain size, the greater the degree of order in the coke. Factors affecting mesophase growth include the properties of the heavy feed, the coking temperature and pressure, and the time spent at temperature (annealing time). Therefore, the observed anisotropic texture of a thermal coke can reveal qualitative information on the conditions in which the coke was formed. In addition, the H/C atomic ratio, thermal decomposition profile, and ash/metals content of the coke will provide further valuable characteristics related to the coking conditions and feed source.

Isotropic (unordered) coke can be formed by a polymerization mechanism or by thermal degradation of organics in the absence of a liquid phase. This type of coke occurs less often than the anisotropic thermal coke, but it has a distinct morphology that can readily reveal the mechanism of formation.

Work Highlights

Machinery Engineering

- *As part of consulting support being provided for a major refinery expansion project, machinery engineering design audits were made of the technical specifications prepared by others for long-lead time and critical rotating equipment items (e.g., centrifugal, reciprocating, and screw compressors). Recommendations were made to revise these specifications to improve the long-term reliability of the equipment.*

Process, Operations & Safety

- *Supporting a major refiner's proprietary upstream development program, process research, fouling, and technology assessments.*
- *Provided process and operations consultation during Fluid Coker upset and temporary shutdown in addition to mechanical specialist support.*
- *Providing analytical consultation on lubes feed characterizations, correlations, and process modeling research.*

A third type called “pyrolytic coke” is formed by vapor phase decomposition of organics at higher temperatures. The coke morphology shows a slow buildup of thin layers (*ca*. 1 micron). This unique structure reveals that the coke was formed in quiescent regions (cracks and interstices) where there is minimal turbulence over a long time period. Pyrolytic coke can act as a binder or cementing agent for catalyst particles or larger particles of coke material.

Whether or not the coke is anisotropic, isotropic, or pyrolytic, a fundamental understanding of the structure and mechanism of coke formation in refinery units will help to find the root cause of the coking problem. This will lead to solutions that can control or eliminate coke formation.

About the Author

Leo Brown was a technical researcher at ExxonMobil for over 30 years. He has in-depth expertise and insight for solving problems involving coking and inorganic chemistry both in commercial units and in R&D. Leo has a broad background in the structure and chemistry of a wide range of inorganic and heavy hydrocarbon materials with the ability to link observed properties to underlying causes and able to successfully apply a variety of analytical techniques to characterize materials, including optical microscopy, SEM, thermal analysis, surface science, etc. Leo has the ability to work effectively with operating facilities to find root causes of real world problems, rapidly put in place programs to address problems, and deliver answers the facility can use to improve operations.

Please contact Jerry Lacatena (jlacatena@carmagen.com) if you’d like more information on Carmagen’s expertise in this area.