Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *Curtailing Coke Formation in Ethylene Furnace Tubes (02/03S10)*.

In the production of ethylene via pyrolysis (thermal cracking), a major ongoing challenge to producers is to reduce coke deposition in the inside of the radiant section tubes and transfer line exchangers (i.e., coke formation is a side reaction from thermal cracking). The historical method for coke reduction and controlling carbon monoxide formation is the use of an inhibitor such as dimethylsulfide (DMS) and dimethyldisulfide (DMDS). Injection of DMDS results in the passivation of metal tubes in gas (e.g., ethane) and liquid (e.g., naphtha) steam crackers that produce ethylene, via adsorption of sulfur atoms produced by its pyrolysis. This passivation slows down the metal catalyzed formation of catalytic coke. The hydrogen sulfide (H₂S) formed from DMDS inhibits the formation of carbon monoxide (CO).

In addition, ethylene producers are faced with a demand that is growing faster than capacity and one method to boost output is to run plants hotter. The resulting higher temperatures mean that the inside of the tubes will build up coke faster, an undesirable side effect. Within the furnace tubes, the coke deposits on the wall of the tube and because the coke is a thermal insulator, it prevents efficient heat transfer from the furnace firebox to the reacting gas within the tubes. To compensate for this the furnace is fired harder being careful not to exceed the metallurgical limits set by the external tube skin temperature. Additionally, the effective coil diameter is reduced by increasing deposition of the coke on the tubes inside surface, thus raising the pressure drop across the coil. Consequently, the furnace inlet pressure must be raised. Both effects are detrimental when optimizing ethylene yield.

The transfer line exchanger (TLE) tube fouling raises the process gas outlet temperature since heat transfer is lowered. Consequently, as the TLE outlet temperature rises, less heat is recovered for steam generation. In addition the coke deposition increases the pressure drop through the exchanger. Depending on the coke deposition rate, the cracking operations must be periodically terminated or shut down for cleaning (i.e., decoking). Cleaning operations are carried out either mechanically or by passing steam and/or air through the coils and TLEs to burn off the coke buildup.

The run length for a pyrolysis furnace is usually controlled by coke build-up. (Run length is the operating time between cleanings). The limiting parameters can be either an increase in pressure drop (usually limiting for small diameter coils) or an increase in the tube wall metal temperature (usually limiting for large diameter coils). Pressure drop increase is the limiting parameter because any increase in hydrocarbon partial pressure will decrease selectivity and as a result degrade desirable products to fuels – methane and fuel oil. Tube metal temperature (TMT) affects mechanical strength and tube life. Since the run length for small diameter coils is often quite low
(10 to 15 days versus 30 to 60 days for split coils with large outlet tubes), it is necessary to frequently decoke small diameter tubes, on-line, in order to remove coke and tars from the inside of the radiant tubes and the TLE tubes, in order to achieve acceptable on-stream efficiencies.

Since TLE tube fouling (or inlet-tube sheet coking for cracking of natural gas liquids, NGLs) controls coil run length for high severity cracking of naphtha and heavier feeds in split coil designs, use of the techniques described herein can extend heater run lengths, reduce cycling, reduce tube replacement, and increase heater on-stream efficiency as well.

The removal of the coke requires frequent decokes of the furnace tubes and each decoke operation is a non-productive downtime for the furnace. The figure below shows the consequence that the loss of productive time (shown by operating rate) has on the cost of production of an ethylene plant. The difference between operating between 85 and 100 percent of the time is 1.7 cents per pound ($37 per metric ton).

This shows that there is an obvious economic incentive to reduce the downtime needed to decoke the furnaces. The type of furnace has an influence on the coking rate - short residence time furnaces require more frequent decokes, but provide higher ethylene yields.

There are two proven methods for suppressing coke deposition in pyrolysis furnaces. Anti-coking coatings, which are applied to the inside of the tubes (usually before installation) and antifoulant
additives added to the process upstream of the furnaces. The former solution requires additional capital investment, while the latter is maintenance intensive (i.e., may require additional operating costs).

This new report from Nexant/ChemSystems compares the features of several competing approaches for curtailing coke formation. These include Alon’s Alcroplex®, Nova’s ANK400, SK Corp’s PY-COAT™, SEP’s CoatAlloy™, Atofina’s CLX, CPChem’s CCA500, and Ondeo Nalco’s COKE-LESS®.