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IMPROVING DELAYED COKER HEATER RUN LENGTH

BY

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- Thermal Cracking Process converting residual oils to liquid products
- Byproducts Offgas and Petroleum Coke
- Feedstocks characteristics vary widely
- Some feedstocks pose challenges which affect heater and therefore unit run length
- It is important to maintain the Delayed Coker on line for as long as possible and at maximum throughput.
- If the refinery did not have the Delayed Coker in operation it would have to cut back on the Crude Unit and shut down or cut back various other units that rely on the products for feed stock.

- The Fired Heater run length is the key component affecting the Delayed Coking Unit Onstream Factor.
- All the heat for the Process is supplied by the Fired Heater
- Heater Run Length has a direct role in the profitability of the unit and ultimately the entire refinery
- Even considering the ability to spall and decoke online, there is still loss of production and maintenance costs associated with short run lengths.

Feed Stocks

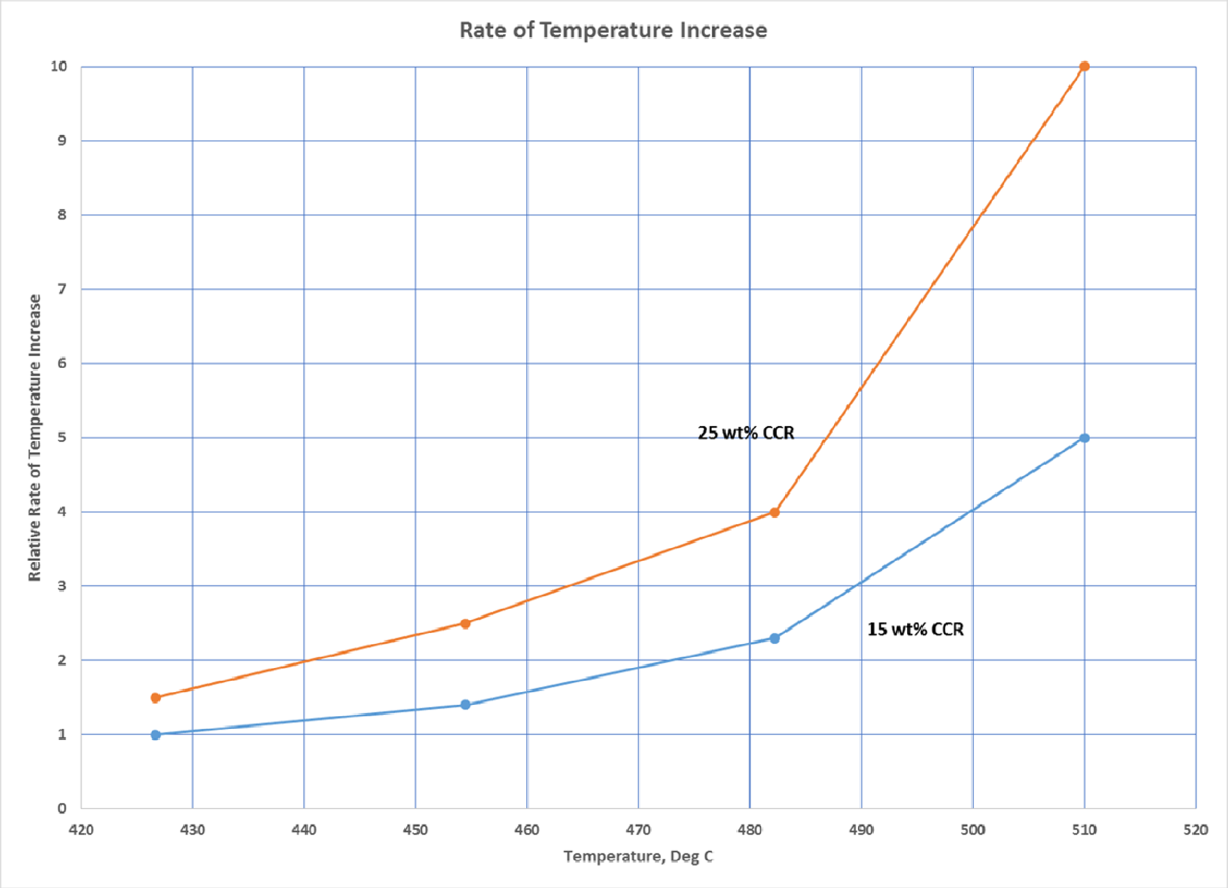
- Shift to lower quality heavier Crudes
- Higher levels of asphaltenes, metals, sulfur and naphthenic acids
- No longer operating on fixed feed slate. A variety of available crudes are selected from the market
- Some feeds are not compatible
- Refinery expansion requiring higher severity operation
- All have contributed to shorter run lengths

Heater Run Length

- Limited by fouling inside the tubes that increase:
  - pressure drop limiting throughput, or
  - Tube Wall Temperature to design level beyond which operation is unsafe
- Causes and Mechanisms need to be identified
- Predicting fouling rates is difficult due to number of variables
- In most cases it is function of time, temperature, and asphaltene content

Heater Run Length

- Good indicator of expected run length is CCR and asphaltene content of feed
- Higher CCR and asphaltene content = shorter run length



- Heater Duty – The total heat duty for the unit is provided by the coking heater. It includes the total heat of reaction for conversion of feed to products. It also includes the sensible heat and heat of vaporization including the recycle plus the heat loss for the coke drums and transfer lines.
- Recycle Rate – Depending on the configuration of the unit, a recycle stream is specified to meet the desired heavy coker gas oil product specifications.
- Coil Outlet Temperature – The Coil Outlet Temperature required to meet the required conversion and product specifications as well as the Volatile Combustible Matter (VCM) of the coke is specified.

Maximum Heat Flux Rate

- Objective - heat as quickly as possible with as little coking in the heater as possible.
- Requires a balance between the residence time and the heat rate.
- Too high a heat rate will cause excessive coke laydown on the tube wall.
- For a given mass velocity, too low a heat rate will require a longer coil length which will result in a longer residence time.

Mass Velocity and Tube Size

- Generally speaking, a higher mass velocity results in a longer run length.
- However, if the mass velocity is too high the pressure drop will be high and the run terminated by high pressure drop rather than high tube metal temperature.
- Number of coils required has to consider the number of coke drum pairs
- Has to be an even number of coils per heater and per pair of coke drums.
- Cold oil velocity should be in the range of 1.83 meters per second (6 feet per second).
- Tube size should be in the range of 4 - 4.5 inch OD. Smaller tubes will experience high pressure drop. Larger tubes will have higher tube wall temperatures even at the same mass velocity and heat rates.

Steam Injection

- Steam injection is used to increase the linear velocity to decrease the residence time in the coil.
- Quantity calculated to increase the Cold Oil Velocity to 3.05 meters per second (10 feet per second) at the point where reaction begins.
- Amount of steam required is calculated by the heater designer and provided in a graphic form or table as a function of the process flow
- At turndown the quantity required is higher to maintain the desired cold oil velocity.

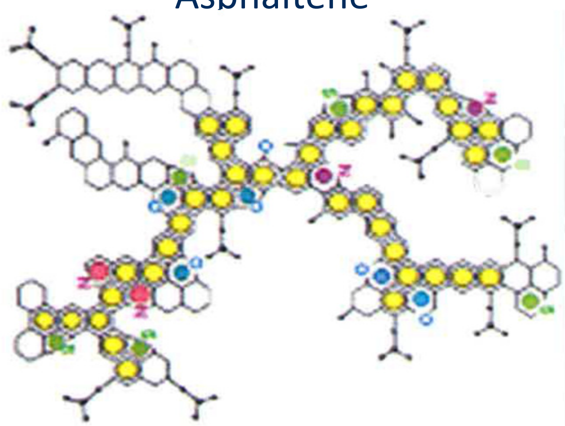
Other Factors

- Burner Arrangement - Number and arrangement is determined to provide uniform heating and remove the possibility of hot spots. Normal practice is to use a large number of small liberation burners.
- Crossover Temperature – low enough that there will not be any coke laydown in the convection section. Convection section coke can not be removed by on-line spalling or steam air decoking.
- Metallurgy and End of Run Temperature – Tube metallurgy has to consider the characteristics of the feed and level of contaminants. In most cases the material used is 9% Chrome - 1% Moly tubes with thickness required to meet the maximum End of Run temperature and design pressure. In some case special alloys may be required such as TP317L due to high Total Acid Number (TAN) in the feed.

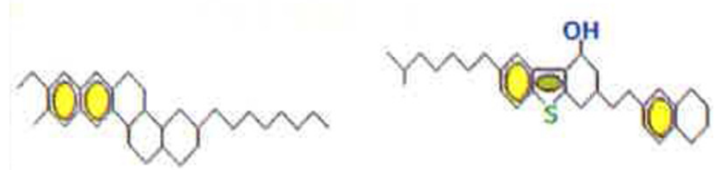
Crude is a complex mixture of hydrocarbons that for simplicity are classified into four categories

- Saturates – can be either Paraffinic or Naphthenic with long alkyl chains
- Aromatics – made up of many unsaturated rings with short alkyl chains
- Resins -40-53% aromatic with intermediate paraffin chain length on naphthenic structure. Also contain aromatic rings.
- Asphaltenes – Normally stabilized, highly condensed naphthenic and aromatic molecules with small side chains
- Almost all crude oils are comprised of different quantities of each of these classes

Asphaltene

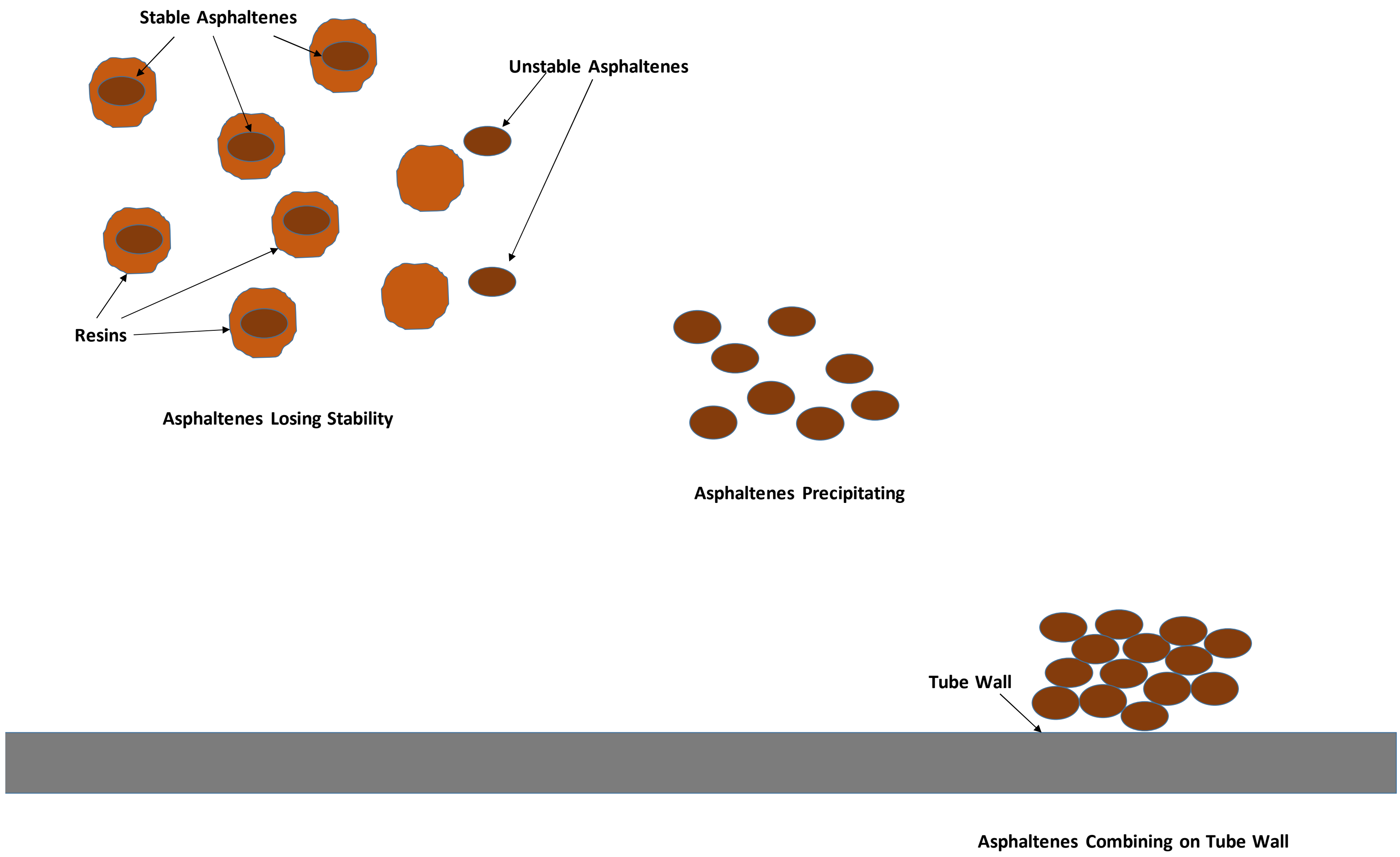


Resins



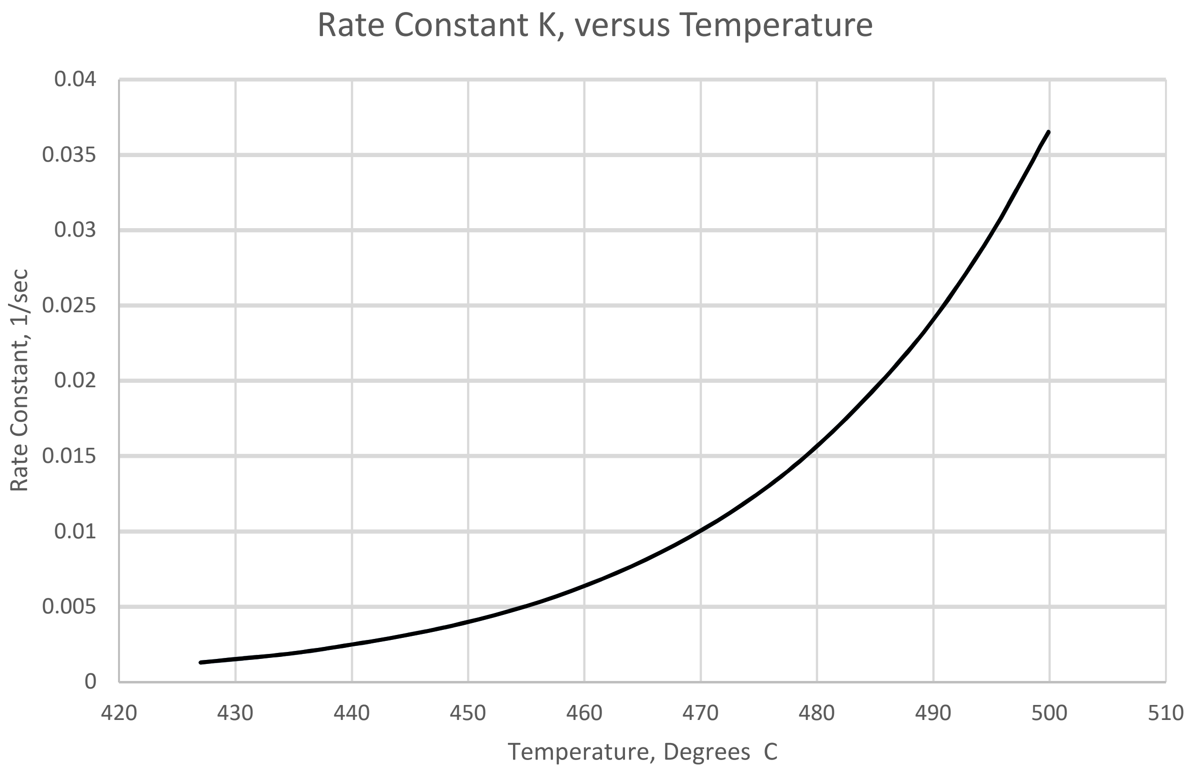
- Soluble in aromatics
- Insoluble in paraffins
- Exist as a highly dispersed colloid in the oil held in solution by resins.
- There is a saturation concentration beyond which they precipitate
- The balance can be disturbed by heating, change in quantity of saturates or both
- Heating above the reaction temperature can cause some asphaltenes to become unstable and affect their solubility in the oil.
- Eventually some will begin to precipitate

Asphaltene Precipitation



Coking Reactions

- Generally Reactions start at 425°C
- Extent of reaction is a function of the residence time above this temperature
- The rate of reaction increases with temperature



Coking Reactions

- Many reactions are taking place
- In addition to thermal reactions there is also asphaltene precipitation
- First reactions are breaking of alkyl bonds
- Long chain molecules are cracked into shorter molecules
- Alkyl chains are broken off aromatic and naphthenic molecules, resins, and asphaltenes creating free radicals

- Next are dehydrogenation of naphthene rings to form aromatics which creates more free radicals
- Combination of free radicals leads to condensation of heavier polynuclear aromatics and formation of surface coke at the tube wall.
- Long residence time favors the combination reactions.
- As aromatics and resins are combined the concentration of asphaltenes increases, the concentration of resins to hold them in solution decreases.
- The cracking of the alkyl chains results in an increase in alkanes further reducing solubility.
- The result is that asphaltenes precipitate from solution

Coke Build Up on the Tube Wall

Initial Temperature Rise

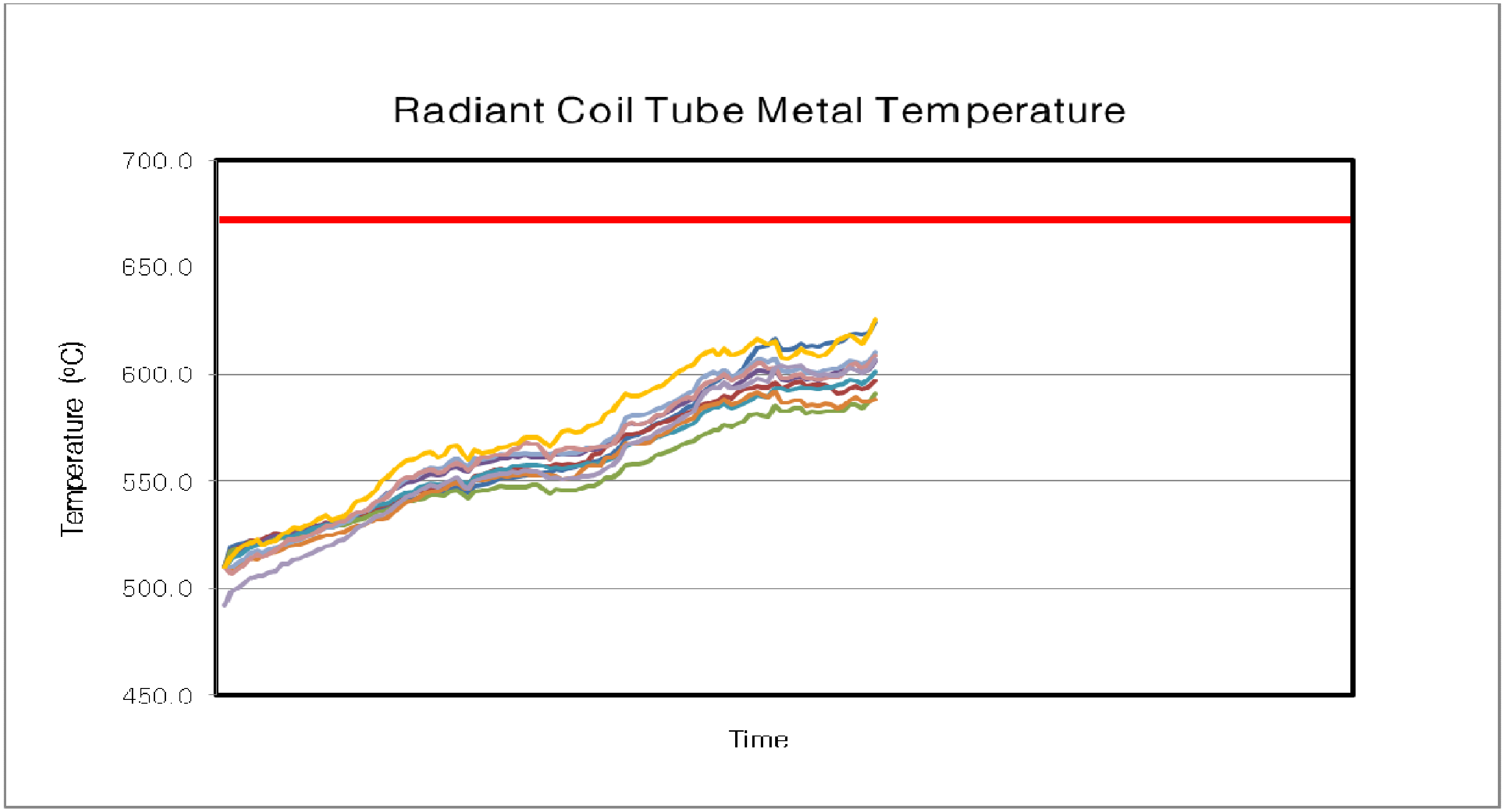
- Catalytic reaction
- Factors that can act as catalyst:
- Metals such as iron, nickel, and their oxides, chromium and titanium catalyze the coking reaction
- In other words – the tube itself acts as catalyst
- Initiated at 355°C
- Quick increase in temperature until the metal surface is covered with a thin layer of coke.

Coke Build Up on the Tube Wall

Additional Coke Buildup

- Primarily caused by radical condensation and precipitation of asphaltenes
- A well designed heater with proper mass velocity and steam injection will have turbulent flow but the area at the tube wall will be slow moving and possibly stagnant
- Temperature at the tube wall (film) is higher and residence time is longer.
- Material at the tube wall will undergo the cracking reactions but because the velocities are low there is more time for the condensation reactions to occur.
- The heavy molecules formed together with the precipitated asphaltenes form a porous layer of coke on the tube wall.
- The oil trapped in the pores continues to react and condense, filling the pores with more coke which eventually makes a solid layer.
- Additional porous coke is formed on top of this layer which will also go through the same process

- Assuming stable heater operation with uniform heating and steady state operation, after the initial temperature rise the tube metal temperature can be expected to rise at a steady rate until it reaches End of Run



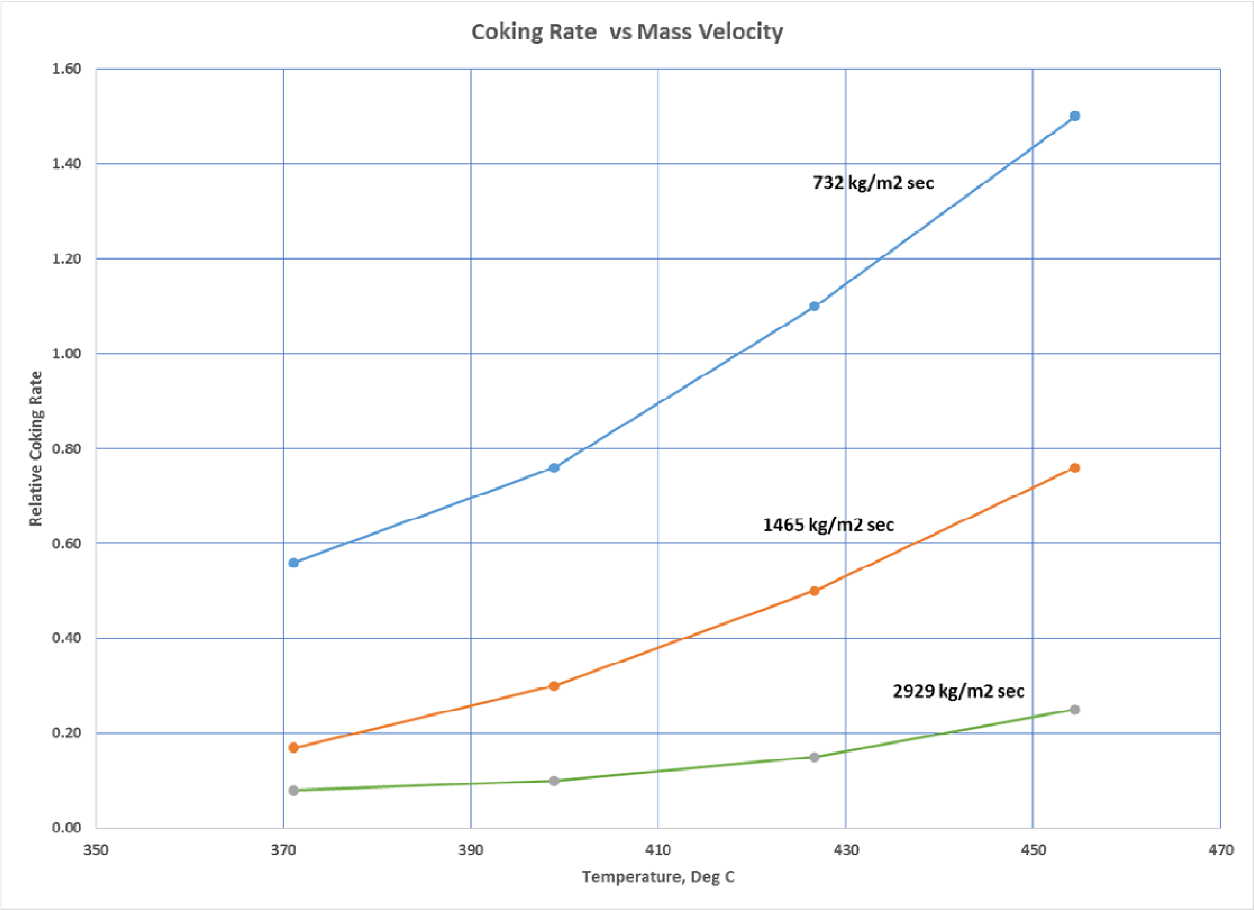
Other Forms of Fouling

- Precipitation of suspended material such as clay from surface mined Tar Sands Bitumen
- Alumino Silicate clay particles dispersed in a colloidal system
- Lose solubility and deposit on heating
- Deposits are silicates which have low thermal conductivities
- Usually occur in the convection section or the top of the radiant section
- Deposits can not be removed by spalling or steam air decoking only by pigging.

Causes of Rapid Fouling

- Sodium Chloride in Crude
- Usually removed in the desalter. Can be carried over due to poor desalter operation
- Sodium and Calcium act as catalyst in formation and laydown of coke on the heater tubes.
- Sodium should be limited to 20 ppmw and preferably 15 ppmw.
- A spike in the sodium level will lead to rapid increase in tube metal temperature.
- Sodium Hydroxide is used in some refineries to control chlorides.
- Excess caustic will also accelerate fouling

- Low Mass Velocity – Depending on the mass velocity some of the precipitated asphaltenes and other deposits can be sheared and pushed downstream. If the mass velocity is low more will collect on the tube wall.



Factors Contributing to Coking

- Long Residence Time – The coking reactions are a function of temperature and time. Longer residence time favors the condensation reactions. The longer the material is in the tube the more likely that coke is to form on the tube wall.
- High Coil Outlet Temperature – Requires higher heat rates which increases the local tube metal temperature. It pushes the initiating temperature further back in the coil. This will result in a higher tube metal profile and longer residence time above 425°C
- Feed Interruptions – This is one of the most common causes of shortened run lengths. Unplanned trips result in high tube metal temperatures due to loss of flow which results in coke formation.

Factors Contributing to Coking

- Improper Burner Operation – Operation with insufficient air or combustion air improperly distributed can result in afterburning if the fuel rich gas comes in contact with excess oxygen. This can result in hot spots in the area where the afterburning occurs
- Maldistribution of fuel to the burners can result in hot spots due to higher amounts of heat released by some burners in relation to the others. This can be due to plugging of fuel tips due to operation with dirty fuels or due to attempts to bias heating by pinching the manual fuel valves to the burners
- Operation with dirty fuels can also result in misdirected flames which can cause flame impingement on the tubes.
- Tips removed for cleaning should always be put back in the same position as they were originally. The tips have the drilling with angles to create the flame shape desired. If the tips are reinstalled in the wrong position the resulting flames may be misdirected. Some burner manufacturer’s designs prevent putting tips back in the wrong position.

Factors Contributing to Coking

- Change in Burner Type – Changing the burner type can change the flame pattern and change the heat input from uniform to non-uniform. Changing from conventional to low NOx or low NOx to Ultra Low NOx will result in longer flames and a change in the heat distribution. In older furnaces with tubes on the roof, change to burners with longer flames may result in flame impingement.
- Increased Throughput – Increasing the throughput above the design level will increase the heater duty and the heat rate. The higher heat rate will increase the temperature at the tube wall and increase the coking rate.
- Changing Feedstocks – Changing to heavier feedstocks with higher CCR and/or asphaltenes will laydown coke faster. Blending of crudes from different sources without considering compatibility can result in asphaltene precipitation and rapid fouling. For example, blending a paraffinic crude with a crude high in asphaltenes. A compatability matrix can be used to predict the impact on the heater performance.

Avoid Interruptions in Feed

- Heater walls, floor and roof have a certain degree of heat storage.
- If feed is lost, even if the fuel valves close and the firing is stopped the coils will remain hot.
- Any material remaining in the coil will continue to be heated and coke will laydown in the tubes
- Upon loss of flow the coil should be immediately purged with a sufficient quantity of steam to force the oil out of the coil.
- Availability of a sufficient quantity of emergency steam at all times is of paramount importance.

Means to Maximize Run Length

Monitor Burner Operation

- All burners should have the same fuel pressure at the burner and the same air amount.
- If burners are forced draft all should have the same damper or register opening
- If burners are natural draft all registers or dampers should have the same setting.
- Do not attempt to operate at excess air levels too low. Especially in forced draft systems with multiple burners, operating at excess air levels too low will almost guarantee that some burners will have insufficient air.
- Heater firebox should be monitored daily to insure all burners are firing properly and all flames look uniform.
- Any burner whose flame looks suspect should be taken off line and the tips cleaned.
- Heater should also be checked for the appearance of haze which is an indication of secondary combustion.

Monitor Tube Skin Temperatures

- Heaters typically equipped with Tube Skin Thermocouples
- These give an indication of the tube wall temperature at fixed locations in the coil
- They may miss hot spots
- They may read the wrong temperature if they go bad which they frequently do
- A scan of the coil should be made periodically using a digital pyrometer to look for hot spots and to verify the readings from the Tube Skin Thermocouples

Monitor the Feed for Sodium and Calcium

- Sodium and Calcium can cause rapid tube metal temperature increase due to catalytic effect on the coking reactions.
- Feedstock should be sampled at regular intervals and analyzed for contaminants that accelerate coking in the heater tubes.
- Levels should preferably be less than 15 ppmw and no more than 20 ppmw.

Means to Maximize Run Length

Blend Feedstocks with Caution

- Highly paraffinic feedstocks when blended with feedstocks containing high asphaltenes can lead to premature precipitation of asphaltenes and fouling of the heater tubes.
- Asphaltenes are suspended in solution and the solution can become unstabilized when the concentration of paraffinic constituents increases forcing the asphaltenes to precipitate
- Blending of high TAN crudes must consider in addition to corrosion issues, calcium naphthenate present in certain crudes such as Doba, Kuito, etc. These can cause the sodium and calcium content of the feed to spike.

Means to Maximize Run Length

Maintain Design Feed Rate

- The heater is designed to have a high mass velocity at the design feed rate.
- The high velocity will clean some of the deposited coke and precipitating asphaltenes from the coil and keep them from accumulating on the tube walls.
- At lower feed rates, even using the velocity steam to maintain the cold oil velocity, the feed will not have the same shear force to clean the tubes as well.
- At higher feed rates although the mass velocity will be improved, the heat rate will be higher leading to a shortened run length.

Maintain Specified Recycle

- Reducing the recycle rate will make less coke and more distillate
- Throughput limited units can substitute additional fresh feed for recycle
- However it could have negative affects on the quality of the heavy coker gas oil and the heater run length
- Recycle stream contains aromatics that improve the solubility of the asphaltenes
- Most of the recycle material will vaporize in the coil increasing the velocity in the heater tube thus reducing the residence time.

Maintain Steam Injection Rate

- Steam injection is important to limit residence time in the coil.
- If the unit has to be turned down the injection rate should be increased to maintain cold oil velocity
- Operation at turndown is possible within limits.
- Below a certain level the mass velocity will be too low to clean the tubes of precipitated asphaltenes and additional steam will not compensate.
- Adding additional steam may have downstream consequences such as increasing risk of coke drum foamover and flooding the overhead in the fractionator.

Operate with the Optimum Coil Outlet Temperature

- The Coil Outlet Temperature (COT) shown on the heater data sheet is a maximum for which the heater is designed. The most optimum in most cases is lower than the design COT.
- The design COT provides the unit with flexibility for adjustment when feedstock characteristics change.
- Variation in the COT is possible within a narrow range. Operation outside the range can result in production of tar or rapid coking of the heater tubes.
- Changes within the acceptable range also need to consider the net benefit of making such an adjustment.
- Operation at higher COT than required will result in additional cracking of the feed which improves liquid yield. However, it requires higher duty and increased heat rate and increases the coke formation in the tubes.
- Additionally it can lead to harder coke inside the coke drum requiring longer time for cutting.
- The economic advantage of incremental liquid yield has to be weighed against the impact on unit throughput as a result of more frequent online decoking and longer cutting time.

Add Decant Oil to the Feed

- Decant oil (FCC Slurry Oil) is highly aromatic and will improve the solubility of asphaltenes.
- Adding at a rate of 3-5% will increase the heater duty and heat rate slightly but it will have a net effect of increasing the run length.

Means to Maximize Run Length - Revamp Opportunity

Replace the Coil

- Replace the existing coil with a new coil having thicker tube wall.
- This will allow higher End of Run Temperatures but will also increase the pressure drop which could result in an overhaul of the heater charge circuit.
- 9 Chrome – 1 Moly has a limiting design temperature according to API 530 of 704°C (1300°F) but is subject to oxidation above 650°C (1200°F). This means the tubes will scale at the higher temperatures which will reduce tube life.
- If pressure drop is a limitation TP347H can be used to replace the coil material. Due to the higher strength at elevated temperatures the thickness required will be less and the end of run temperature will be higher.
- TP347H is a stabilized alloy but is susceptible to stress corrosion cracking. During down times it will need to be alkaline washed to get rid of polythionic acid.

- Replace the Coil (Continued)
- If the TP347H coils are cleaned by pigging., an alkaline solution instead of water can be used for the pigging.
- Chloride content should be limited to no more than 25 ppm with any austenitic stainless steel to prevent stress corrosion cracking.

- Heater Run Length impacts unit and ultimately refinery profitability.
- Impact of on-line spalling and pigging features
  - Increase unit on line time between off-line decoke, but
  - Decreases maximum unit throughput utilization
  - Increases operating costs
- Understanding cause(s) of coke formation specific to each unit helps to:
  - Slow it's rate of deposition by
    - Identifying key performance indicators on the process and combustion side to monitor
    - Identifying operating changes to the heater and process affecting run length
- Changes must be evaluated considering the affect on the unit operating costs and throughput to maximize the unit profitability.

Thank You!!