

COKING

INTRODUCTION

❖ Coking process is the process by which coal is converted in to coke.

There are two type of coal :

1. Coking coal,
2. Non coking coal,

❖ Coking process accurse in presence of air.

❖ Coking process are the more severe form of thermal cracking.

TYPES OF COKING

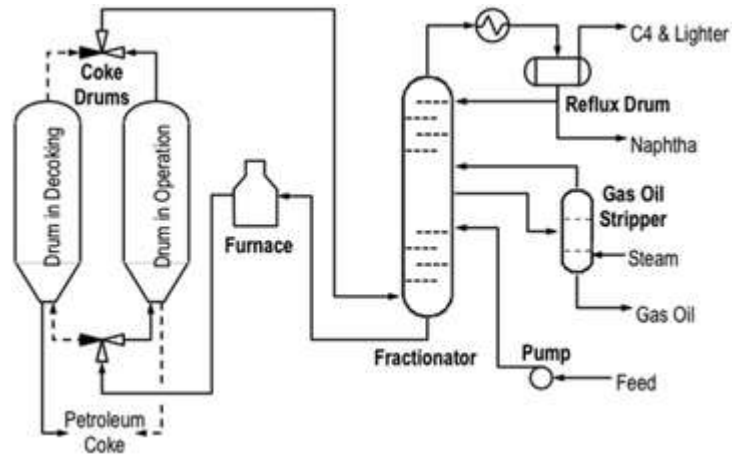
There are three main type of coking

- ❖ Delayed coking
- ❖ Fluid coking
- ❖ Flexi coking

DELAYED COKING

- ❖ Delayed coking is a thermal cracking process used in petroleum refineries to upgrade and convert petroleum residuum into liquid and gas product streams leaving behind a solid concentrated carbon material, petroleum coke.
- ❖ Three physical structures of petroleum coke: shot, sponge, or needle coke can be produced by delayed coking.
- ❖ Delayed coking is a key technology for residue upgrading or zero fuel oil production.

FLOW DIAGRAM OF DELAYED COKING



DELAYED COKING CHEMICAL REACTION

- ❖ Carbonization is the thermal conversion of organic materials to carbon/ coke.
- ❖ Carbonization involves a complex series of chemical reactions and diffusion processes in both liquid and solid state.
- ❖ The reaction sequence consists of the elimination of substituent atoms and groups from the organic molecule and atoms subsequent polymerization to a large aromatic carbon frame work.

CHEMICAL REACTION OF CARBONIZATION

Dehydrogenation -The initial reaction in carbonization involves the loss of hydrogen atom from an aromatic hydrocarbon and formation of aromatic free radical intermediate.

Rearrangement Reactions-Thermal rearrangement usually leads to formation of more stabilised aromatic ring system which forms building aromatic block of graphite growth.

Polymerisation of aromatic -Aromatic free radicals get polymerised in the process of coking reaction. This process is initiated in the liquid phase and continued in different steps.

DELAYED COKING PROCESS

Delayed Coking is a batch cum continuous process :

- ❖ Flow through the furnace coil is continuous.
- ❖ Feed is switched between two or more drums in batch wise fashion.
- Delayed Coker drum cycle length varies from unit to unit. However, drum typically it is kept within 16 to 24 hours.
- Adequate time should be given for coke drum cooling/heating to avoid any thermal shock/ degradation of coke drum metallurgy

PRODUCT OF DELAYED COKING

- ❖ Delayed Coker produces desirable liquid products (naphtha and gas produces oil) and byproducts Coker gas and solid coke.
- ❖ Coker off gas goes to the gas plant where C3 and C4 is recovered as LPG and the lighter end can be used as fuel gas in the refinery LPG refinery.
- ❖ Naphtha ex coker unit contains high olefin content and this stream is unit usually sent to hydrotreater for for stabilisation.
- ❖ Light Coker Gas Oil (LCGO) is sent to diesel hydrotreater for for production of diesel.

DELAYED COKING PROCESS VARIABLES

- ❖ Three operating parameters govern the yield pattern and product quality of Delayed Coker :
 - Temperature
 - Pressure
 - Recycle Ratio (RR)

DELAYED COKING PROCESS VARIABLES

Temperature: Increasing coking temperature decreases coke and increases liquid yield and gas oil endpoint. However, temperature can be adjusted only a narrow range to control volatilities left in coke.

Pressure: Increasing pressure and/or Recycle Ratio (RR) increases gas and coke make and decreases liquid yield and gas oil endpoint. RR can be varied from 0% to d 120%.

Recycle Ratio:

$$\frac{\text{(Composite feed to Coker Heater)}}{\text{(Primary feed to Fractionators bottom)}}$$

FEEDSTOCK CHARACTERISTICS

- ❖ Feedstock can have considerable amount of metal, Sulphur , Resins and Asphaltenes.
- ❖ Contaminants present in feedstock mostly gets eliminated with Contaminants coke.
- ❖ Most typical feedstock is Vacuum Residue (530°C). It can also process refinery slop oil/ sludge.
- ❖ Atmospheric residue is also occasionally processed

NEEDLE COKE PROCESSING

- ❖ Needle Coke is a premium grade, high value petroleum coke used in the manufacturing of graphite electrodes of very low Coefficient of Thermal Expansion (CTE) for the electric arc furnaces in the steel industry.
- ❖ Production of Needle Coke requires specific feed stocks, coking conditions and calcinations conditions. The hardware employed is similar to that of conventional Delayed Coker

ADVANTAGES OF NEEDLE COKE PROCESSING

- ❖ Significant improvement in refinery margin owing to very high price of Needle Coke
- ❖ Does not require special design of Delayed Coker unit and can produce Needle Coke in existing unit without major modification
- ❖ Produces Needle Coke using heavier petroleum streams of refinery without major pre-treatment .

Petroleum Assignment

- Other coking process
- **CALCINATION OF GREEN COKE**

OTHER COKING PROCESSES

Other coking processes which are in commercial operation include;

It have three types of process.

- I. Eureka steam cracking,
- II. ART process,
- III. Dynacracking,


Eureka steam cracking

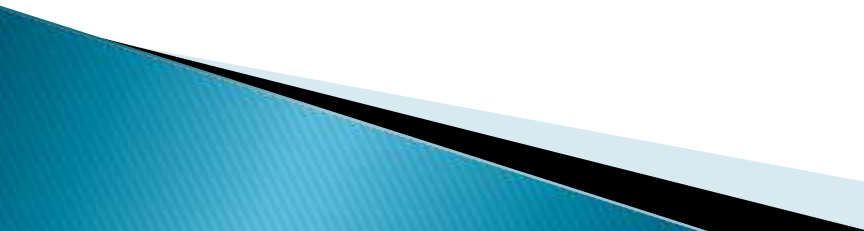
It is similar to delayed coking process but is operated at a lower temperature. Hot liquid residue is solidified separately . Net distillate recovery is higher compared to delayed coking.

ART process

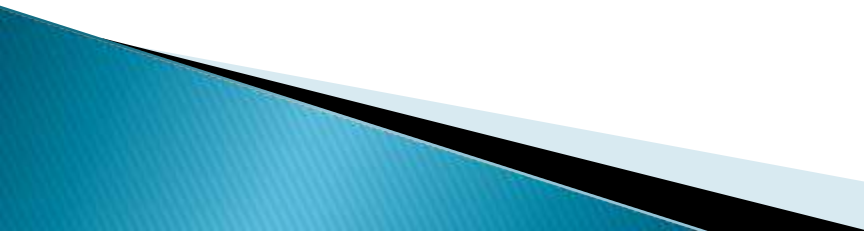
The process configuration is similar to a fluid catalytic cracking unit. Coke is burnt off in the regenerator. Most of the metals and some sulphur and nitrogen are removed with the coke. The distillate product is a better feedstock for downstream residue conversion processes.

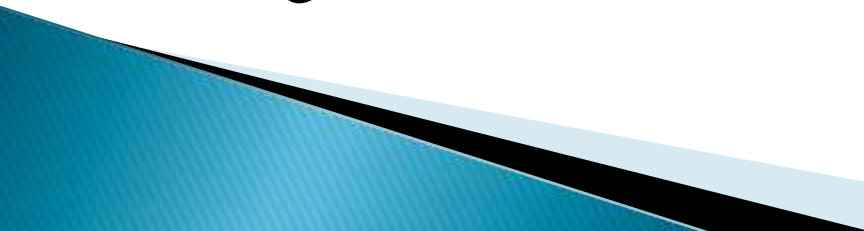
Dynacracking process

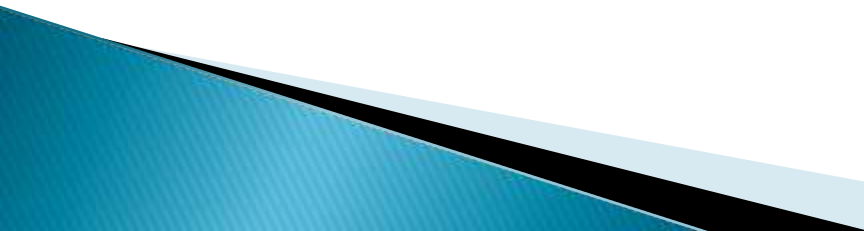
- Dynacracking process, developed by hydrocarbon Research , uses an unique reactor design.
 - Heated feedstock is cracked at a temperature of 538 degree C and a pressure of 28 atm in the presence of an inert carrier and in a hydrogen medium in the upper bed of reactor.
 - Coke is deposited in the carrier along with the metals in the feedstock.
 - The inert carrier flows downward in to the lower section of the reactor, where it is stripped with steam.
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- Deposited coke is gasified at a temperature of 932 degree C with steam and oxygen to produce hydrogen rich gas.
 - The hydrogen rich gas supplies the hydrogen medium in the upper reaction zone.
 - The decoked carrier is lifted to the upper section through a riser using steam or product gas .
 - Hydrocarbon products leave the reactor from the upper section. part of the liquid product is recycled.
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CALCINATION OF GREEN COKE

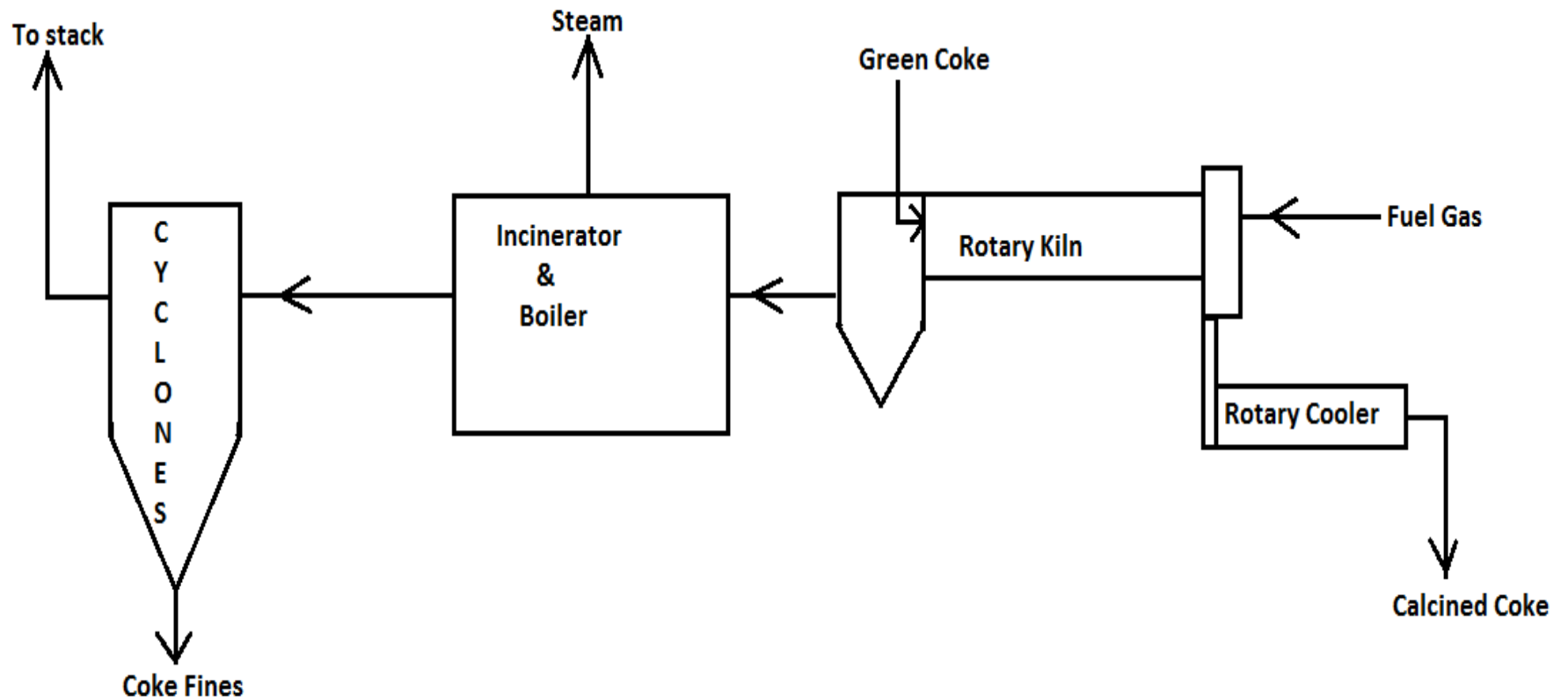
- Petroleum coke is produced as delayed sponge coke, delayed needle coke, fluid coke and flexicoke.
 - Calcined coke is mostly used by aluminium industry in the manufacture of anodes for alumina reduction.
 - Calcination of green coke is essential a high temp treatment.
 - It may be carried out in a rotary kiln or rotary hearth.
 - Calcination of green coke can take place in either an inert atmosphere or an active atmosphere of flue gas.
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- If the volatile matter and moisture content of green coke are high, sudden variation in coke volume can occur to cause cracks and produce fines.
 - Coke calcined in the presence of active flue gases can burn and reduced coke yields.
 - The calcination process is considered to be terminated around 1300degree C. At higher temp, a crystallization called graphitization starts.
 - The loss of water during calcination occurs at coke temperature from ambient to 150degree C, which are developed over the first 10 to 15 percent of kiln length.
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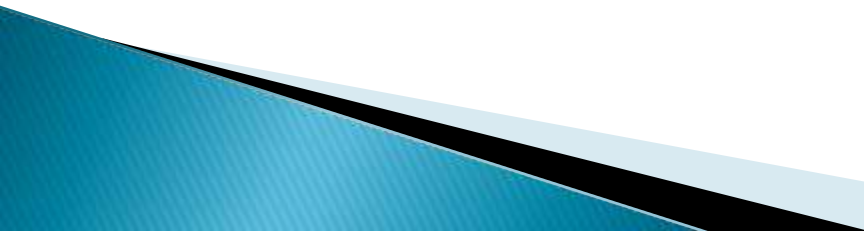
- The release of volatile matters starts in the coke temp range of 150-200degree C and may overlap moisture removal.
 - As calcination temp increases, hydrogen formation is enhanced.
 - In range of 480-700degree C, the volatile matter of coke is reduced to 3-4 percent of the initial value. Above 760degree C hydrogen continuous to be evolved.
 - Carbon dioxide and moisture have secondary endothermic reaction with coke at 900-1000degree C which can lower temp in the calcination zone.
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- Several factor such as heat-up rate, duration of calcination and green coke properties affect the properties of calcined coke.
 - Therefore, optimum calcination condition are specified for each coke.
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Process Description

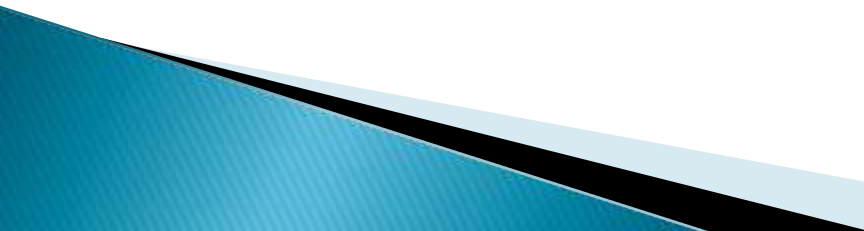


COKE CALCINATION PROCESS

- Green coke is fed continuously into the rotary kiln through either a feed pipe or a feed scope assembly.
 - The feed rate of green coke is controlled by a continuous weigh feeder equipped with a variable-speed drive.
 - Rotary kiln is completely equipped with all component like refractory, tires, carrying stations, seals and a drive train, which includes girth gear, pinion, speed reducer, variable-speed unit and motor.
 - The moisture content of green coke is kept at 8 to 10 percent to minimize loss of coke fines inside the kiln during calcination.
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- The temp of rotary kiln at the feed zone varies from 700 to 800degree C.
- The coke travel inside the kiln from the feed end to the discharge end due to its inclination and rotation with a gradual rise in temp.
- The moisture present in the coke evaporates at the feed end of the kiln.
- By the time coke passes through the calcining zone, the release of volatile matters from coke is completed.
- Calcining zone is maintained at a temp of about 1300degreeC.
- Calcined coke at a temp of about 1300degree C is discharged from the discharge end of the kiln into a rotary cooler where coke temp is gradually reduced to 90-120degree C.

- Several type of coolers are used. The most commonly used rotary cooler cools the hot calcined coke by a direct water quench as well as by a cocurrent flow of ambient air.
- After discharge from the cooler and before going to storage, coke is very often sprayed with an oil to reduce dusting in handling
- After discharge from the cooler and before going to storage, coke is very often sprayed with an oil to reduce dusting in handling.
- Evolved volatile matter not burned in the kiln together with combustion products and particulates are carried into the incinerator at a temp of about 680degree C where combustion is generally completed.

- The two main sections in the incinerator are:
 - 1) A modest size chamber equipped with auxiliary burners, where bulk of residual volatile matter is burned,
 - 2) A box type chamber in which combustion of volatile matter is completed and particulate matter is burned.
 - These days waste heat boiler are also used to recover a large percentage of the heat released in the incinerator in order to conserve energy. Steam generated may be used directly or in cogeneration.
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Thanks

