Republic of Iraq

Ministry of Higher Education

and Scientific Research

Al-Mustaqbal University College

Chemical Engineering and Petroleum Industries Department

Subject: Properties of Petroleum Fuels

3nd Class

Lecture two

PETROLEUM COKE

• Petroleum coke is a black carbonaceous solid material produced as a by-product of delayed coking or fluid coking units in refineries.
• There is a large world market for petroleum coke as fuel because of its – high calorific value,
– low ash.
– and discount pricing relative to coal.

• The largest single nonfuel use of petroleum coke is in the manufacture of – carbon anodes for the aluminum smelling industry which accounts for almost 80 percent of all petroleum coke produced.
– Other important uses of petroleum coke are in the manufacture of graphite anodes for electric arc furnaces (used in steel plants, phosphoric acid, and calcium carbide manufacture) and in titanium dioxide (TiO,) manufacture. Each end use requires a different quality of petroleum coke.
– Both physical and chemical characteristics of petroleum coke determine its suitability for a specific use.

Coking is a thermal cracking process used in refineries to maximize residuum conversion to distillates and thus minimize low-value fuel oil production.
– Petroleum coke is a by-product of coker units. • If the coke produced has high sulfur and metals, it is sold as fuel for power generation or cement plants.
• If the by-product coke is of a low sulfur and low metal content, it can be further upgraded in value by the coke calcining process.

Manufacturing processes

• Raw petroleum coke is a by-product of coking units of refineries.
• There are two coking processes: – the fluid coking process and
– the delayed coking process.

Due to their lower capital cost, most of the coker units built in refineries use the delayed coking process.
Also the properties of the coke produced in the fluid coker units are much inferior to that produced in delayed coker units
• For these reasons, most of the petroleum coke produced in the refineries is from delayed coker units.
• Coking is a noncatalylic thermal cracking process based on the concept of carbon rejection.
• The heaviest hydrogen-deficient portion of feed (asphaltenes, resins, etc.) are rejected as coke, which contain essentially all the feed metals and ash and a substantial portion of feed sulfur and nitrogen.

PETROLEUM COKE TYPES

Different physical forms of coke are produced in the delayed coker:

- Sponge coke
- Needle coke
- Shot cokeSponge Coke
- Sponge coke is dull black with an amorphous appearance.
- It is produced from vacuum resids of low to moderate asphaltene concentration.
- Straight run vacuum residues tends to produce a large percentage of isotropic or amorphous cokes.
- These are visibly very porous and are called “sponge coke.”
- Petroleum coke with a high sulfur and high metal content that is not suitable for anode making is used as a fuel in various applications and known as “fuel grade.”
- Its use is frequently limited by its high sulfur content, which restricts its use in power generation.

Properties of calcined coke

Density

- The real density (RD) of raw green coke, 1.3 to 1.4 g/cc, is measured on -200 mesh particles using a helium pyknometer.
- After calcinations, anode grade coke density increased from 2.05 to 2.08 g/cm3.
- Calcined needle coke for graphite electrodes can reach an RD of 2.13 g/cm3.

Electrical Resistivity

- The electrical resistivity of calcined coke decreases with increasing calcination temperatures.
- Petroleum coke actually changes from an insulating material to an electrical conductor upon calcination.

Mercury Apparent Density

- The Hg (mercury) apparent density (AD) is a measure of the porosity and density of calcined coke.
- Anisotropic needle-type coke produces a higher AD upon calcining than isotropic sponge coke or shot coke.
- Calcination above 2280°F decreases AD for all coke types with the exception of low-sulfur cokes.
- Low-sulfur coke decreases in AD only beyond 2460°F.
- AD decreases very rapidly in high- sulfur cokes with the onset of desulfurization.

Vibrated Bulk Density

- Vibrated bulk density (VBD) of calcined petroleum coke is of great importance for the aluminum industry.
- VBD is measured on screened particle fraction.

HardgroveGrindability Index

- The HGI (HardgroveGrindability Index) is a measure of the hardness of coke and can be measured on both raw/green coke and calcined coke.
- The property is most useful for green coke and is important for fuel-grade cokes that need to be crushed before burning in a power plant.

Air and Carbon Dioxide Reactivity

- Reactivities of calcined coke in air at two different heat-up rates and in carbon dioxide (C02) are determined to provide information as to how an anode will behave in a smelting pot.

Shot Coke Content

- Shot coke cannot be used for making anodes in the aluminum smelting industry.
- Shot coke balls are made of two layers of materials with different CTE values. These small balls (2 to 4 mm in diameter) fracture at the interface of the layers when calcined, due to the difference in their CTEs.

Screen Sizing

- Aluminum smelters require strict specifications on the amount of different size fractions of the calcined coke.
- To make carbon anodes, calcined coke is first screened in the calciner plant to separate out different size fractions.

Chemical Properties

• Volatile Matter. – Volatile matter (VM) is a weight loss on heating of coke. The test is done on a 60-mesh sample.

– The coke is placed in a covered platinum crucible and heated to 1740°F at a controlled rate in a furnace.

– The weight loss of the sample as the percentage of feed is the volatile matter of the coke.

– Typically the VM of green coke is between 8.5 and 12.5 percent by weight.

– This is reduced to approximately 0.4 percent after calcining at 1650 to 1830°F.

– The VM of the raw coke is correlated with the VBD.

– Some VM is burned during calcinations, which accounts for some of the calcining yield loss.

• Hydrogen Content. – Hydrogen content is determined by combustion in oxygen.

– This property provides a measure of the calcination of the product.

– During calcination, most of the hydrogen is evolved before a temperature of 1800°F is reached.

• Moisture and Ash. – Moisture is determined by oven drying.

– Ash is determined by muffle furnace ashing of the coke sample.

– Calcined coke must be dry to avoid problems with screening and the fabrication of carbon anodes.
– The ash content of the calcined coke is in the range of 0.1 to 0.3 percent by weight.

Sulfur and Metals (V, Si, Fe, Ca. Na).

- In aluminum smelting, any excess metal in the coke migrates to the aluminum metal because coke is consumed during the process.
- Some grades of aluminum metal require very low values of certain metals depending on the end use of aluminum.
- Sulfur and some metals also affect the air and CO, reactivity of calcined coke.
- The concentration of metal in coke increases upon calcining due to the loss of volatile matter, sulfur, hydrogen, nitrogen, and moisture.

USES OF PETROLEUM COKE

Carbon Anodes

- Aluminum reduction cell in modem smelters use two types of carbon anodes.
- Carbon anodes must be dense, strong, electrically conductive, and of high carbon purity.
- Anode properties depend on the quality of the calcined petroleum coke and the pitch used for binding anodes.
- The uniformity of the coke is important to permit suitable anode fabrication.