Calcinations of Petroleum coke

Aliasghar Rohani, Khashayar Sharifi, and Rahmatollah Golpasha

Abstract—Petroleum coke is a process that involves steps such as thermal decomposition, polymerization and condensation. The Petroleum Coke category consists of two substances; green coke and calcined coke. These two substances are grouped together in a category based on their similarity of manufacturing processes which results in similar physical chemical characteristics and chemical composition. The principal difference is the amount of residual hydrocarbon (also termed volatile matter) in the two products. Petroleum coke (both green and calcined) is a black-colored solid produced by the high pressure thermal decomposition of heavy (high boiling) petroleum process streams and residues. Green coke is the initial product from the cracking and carbonization of the feedstock's to produce a substance with a high carbon-to-hydrogen ratio. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in a lower potential for toxicity for calcined coke.

Calcinations of coke are usually done in a rotary kiln at about 1300°C to 1500°C. During the process the coke is further decomposed, increasing in the carbon to hydrogen ratio from 20 of green coke to 100 for calcined coke. Along with increasing in the fixed carbon of the coke to over 95%, electrical conductivity improved and real density increase when coke is calcined. Sulfur content of the calcined coke is dependent on the sulfur in the green coke as feed of process. Typically, since low sulfur content is usually required for calcined product, only low sulfur green cookes are calcined.

Keywords—Calcination, green coke, petroleum coke, rotary kiln

I. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons, sometimes characterized as "a useless mixture of useful products." Petroleum coke is, essentially, the "bottom of the crude barrel" - the carbon in the crude charge that cannot be recovered in normal refining processes - comprising about 5-7 wt% of each barrel of crude. A refiner must carefully balance crude characteristics against refining unit capacities and product slates. If the facility produces anode-grade carbon, other impacts must be considered. Consistent quality coke begins with consistent quality crudes; "trim" crudes introduced at the "front end" of the refining process to control eventual

Carbon quality results in much more consistent finished carbon product to the end user/smelter as opposed to trying to blend solids (green and/or calcined) to spec. "after the fact". World calcinations coke demand in 2016 is shown in figure 1.

Proper distillation in the Vacuum Unit is critical to reside (Coker feed) quality control. Specifically, the amount of vacuum gas oil sent to the Coker with the vacuum residuum (determined by the efficiency of the fractionation in the Vacuum tower itself) must be carefully monitored and controlled to insure adequate hardness of the green coke produced by the Coker. An "optimal" reside yield for a refiner more concerned about downstream catalytic units may not necessarily be optimal for eventual calcined coke properties [1]. Petroleum cokes are produced at refineries using three different types of coking processes: delayed, hid, and flexi coking. The delayed coker is mostly used at forty-nine U.S. refineries processing [2]. The other fluid coker and flexicoker are less utilized at a relatively smaller capacity. Coke products from a delayed coker are classified as shot, sponge, (sometimes honeycomb), or needle coke depending on their chemical and physical characteristics. Shot coke (almost always sold as fuel) is hard, having spherical form, and physically produced through precipitating asphaltenes; sponge coke (mostly used for anode-grade) is dull and black, having porous, amorphous structure, and is considered as a mixture of shot and needle cokes; and needle coke (not used in anode production) is silver-gray, having crystalline broken needle structure, and chemically produced through cross linking of
condensed aromatic hydrocarbons during coking reactions [3,4]. Most of fluid coke does not enter the anode pool and flexi coke has never been used in aluminum smelting.[5] Crude oil contains of various compound of hydrocarbons but low concentrations of inorganic compounds or metals found in crude oil. Vanadium and Nickel are the most common metals in crude oil. These metals usually exist in solution in the oil and residual fuel oil in the refining process is condensed. Delerious effects of metals in petroleum have been known for some time. These metals not only contaminate the product but also cause intoxication and loss of catalyst and corrosion to equipment. In this study removal heavy metals and petroleum residues were investigated. These methods include physical and chemical and biological treatment processes. For example, Processes such as solvent extraction and hydro-catalytic and catalytic methods are effective and practical methods, but typically often have high costs and environmental pollution. Furthermore, biological methods have been discussed in recent years and don't have environmental pollution. But these methods have not yet been industrialized [6-9].

II. PETROLEUM COKE

A. Desulphurization of pet coke

Petroleum coke is no longer a left-over by-product of “bottom-of-the-barrel” refinery operations whose chief aims are the production of other materials. Pet coke has become a valuable product in its own right, and the demand for high-quality low-sulphur coke is increasing. However, more coke with high sulphur content is being produced, and means whereby such sulphur content is reduced to an acceptable level or eliminated altogether are called for, in particular with the ever-tightening restrictions on sulphur oxides emissions for environmental considerations. The desulphurization of pet coke involves in general desorption of the inorganic sulphur present in the coke pores or on the coke surface, and the partition and removal of the organic sulphur attached to the aromatic carbon skeleton. The desulphurization techniques proposed fall generally under these headings

- Solvent extraction.
- Chemical treatment.
- Thermal desulphurization.
- Desulphurization in an oxidizing atmosphere.
- Desulphurization in an atmosphere of sulphur-bearing gas.
- Desulphurization in an atmosphere of hydrocarbon gases.
- Hydrodesulphurization.

B. Calcined petroleum coke

Calcined petroleum coke (CPC) is the product from calcining petroleum coke. This coke is the product of the Coker unit in a crude oil refinery. The calcined petroleum coke is used to make anodes for the aluminum, steel and titanium smelting industry. Calcined petroleum coke is shown in figure 2.

---

III. ELECTRODE PRODUCTION

Depending on its physical form, coke may also be classified as shot, sponge or needle coke. Shot coke occurs as hard spheres and is produced from high asphaltene precursors. Needle coke appears as silver-gray crystalline needles and is derived from feedstocks with high aromatic hydrocarbon content. Sponge coke is dull black with a macroscopically amorphous appearance but is a mixture of shot and needle coke structures.
In the calcining process, the green coke feed is heated to a sufficiently high temperature to drive off any residual moisture, and to drive off and combust any residual hydrocarbons (the combustion of the evolved volatile materials provides the necessary heat for the calcination process) in the green coke feed.

The production of electrodes is closely controlled process. Flow scheme of general electrode production shown in figure 3.

Fig. 3 diagram for manufacturing of graphite electrodes

IV. CONCLUSION

Petroleum coke calcining is taking green coke or anode grade green coke from the refining process and convert this coke to different structures of carbon. The calcined coke is used to produce carbon anodes for the aluminum industry. To obtain the calcined coke properties required by the carbon and graphite industries, the temperature of coke must be reached to 1200-1450°C or higher to refine its crystalline structure. Calcined coke is a very dusty material, and without adequate provision for containing the dust a calcining plant can be a very dirty operation, with excessive atmospheric discharge. Calcination processes is a process whereby green or raw petroleum coke is upgraded with high temperature to remove associated moisture and volatile combustion matter and to otherwise improve in critical physical properties, electrical conductivity, real density and oxidation characteristics. It is known that at the temperature of calcining some sulfur oxidation also take place. the average rate of desulfurization of delayed coke is 2 to 3 times higher than that of coke from fluid or contact cokers. The calcining process is essentially a time-temperature function with the most important control variables being heating rate, VCM/air ratio and final calcinations temperature. The final quality of the calcined coke is directly related to the specific characteristics and quality of the green coke fed to the calciner. The demand for low sulfur coke for electrode manufacture is hardly satisfied from feedstock.

REFERENCES