

CARBONIZATION OF COAL

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Summary

For hundreds of years, coke from coal has been used for the production of iron. With the increasing use of coke in iron smelting, more and more investigations were carried out to establish the types of coal best suitable for coke-making. Different coals have different coking properties.

The coking characteristics of coking coals during high-temperature carbonizing processes are described by a plastic caking mechanism and mesophase caking mechanism. The methods of widening coking coal sources are by blending and pretreatment technology of coals, for example, stamping, preheating, and so on.

Coke-making equipment from coals has developed from the beehive oven to the jumbo coking reactor. Modern coke ovens are mainly composed of carbonization chambers, combustion chambers, regenerators, and coke-oven machinery.

The prepared coal is charged into carbonization chambers by a larry car. The coals in the carbonization chamber are carbonized by heat transferred from the combustion chamber.

When the coking process is completed, the oven doors are opened, the pusher is spotted opposite the pusher-side door, and the hot coke is forced out of the oven by means of the ram, through the coke guide into the quenching car or tank placed in position at the coke-side door. The quenching car travels from the coke oven to the quenching station, and the hot coke is quickly doused with water or cooled with inert gas.

The raw gas leaving from the coke oven contains various compounds. It is cooled to recover tar and to remove water. Crude benzol is recovered from the gas by absorption, and gas is purified by absorption to remove ammonia, hydrogen sulfide, hydrogen cyanide, and so on.

The development of the modern iron and steel industry requires cokes with high specification and high quality. Some of the processes under developing coke-making technologies from coals are the increasing capacity of the carbonization chamber, the developing non-recovery coking process, and the formed coke process.

1. Introduction

Carbonization of coal, thermal decomposition of coals in the absence of air, represents one of the largest utilizations of coal, and is an essential process for production of a carbonaceous residue (coke), gas, and tar. The first attempts to coke bituminous coal date back to Duke Julius of Braunschweig. It was reported that coke was used in large-scale experiments for the reduction of ores in the year 1585, especially for copper schist. The results did not lead to any commercial application. The commercial importance of coke as an affective reducing agent in iron-making began with the year 1708, when A. Darby the Elder (1676–1717) succeeded in extracting coke from bituminous coal to produce suitable hot metal from iron ores.

Around 1850 the so-called Schaumburg kilns were used, which are half-open brick kilns with circular mounds emitting odoriferous tar-containing distillation gases directly into the atmosphere. The next development was the closed “beehive” oven, which in its original form discharged the distillation and flue gases through a chimney at a greater height. The heat required for coke-making in the pile, in the Schaumburg and the beehive oven, was produced by partial combustion of the coal. This practice resulted in a substantial loss of material by combustion; therefore the coke yield in these ovens was at most 55 percent of the coal.

The further development of the pile led to the so-called flame oven, in which the coal was carbonized in chambers heated from the outside. Gas of high calorific value leaving the oven chamber was immediately burned in flues built into the oven wall. The coke yield was about 75 percent resulting in a throughput of 7 tons per oven within 48 hr coking time, which was a remarkable result at that time. The first coke ovens producing sufficient blast furnace or foundry coke as the main product, tar, ammonia, and later also benzene as byproducts, were built around 1856.

The first regenerative heat recovery oven was built in Germany in 1884. These ovens were heated by burning parts of the gas produced, the other gas, the byproducts, however, were recovered. Since 1830, fire clay brick has been used as a raw material for the oven. Silica brick was introduced for building coke ovens around 1900 and is a common material since 1914. The further developing technologies of the current coke making include increasing capacity of the oven chamber, thinning the chamber walls, and raising the flue temperature. In 1992 Kaizerstuhl coke-making plant with perfect environmental protection measures had been built. The new Kaizerstuhl plant represents the latest state of the art concerning the “multi-chamber system”, with 610mm-chamber width, 7.63 m height, 18 m length, 78.84 cubic meters in volume and a 95 mm thickness of the chamber wall.

This article focuses on production of high quality metallurgical coke from coals, and includes the following contents:

1. Caking mechanism and blending of coals.
2. Properties of the high-temperature coke.
3. Structure and operation of the coke-oven.
4. Purification and recovery of the byproducts of the coke-oven gas.

2. Coal Preparation for Coke-oven Use

Since the reserves of good coking coals are being depleted, coal preparation is necessary for a modern coke-oven plant. In addition, with the development of large capacity units in coke-making and blast furnace technology, the better quality and uniformity of feed coals has been required.

2.1 The Coking Process of Coal in the Oven Chamber

When coal is charged into a hot coke oven, that portion of the coal directly in contact with the walls is heated very rapidly. When its fusing is reached, the thin layer of heated coal softens and fuses. Destructive-distillation reactions proceed rapidly in the plastic layer, with copious evolution of volatile products. The gas and condensable vapors are entrapped in the plastic mass and, as they expand, tend to distend it. As the reactions proceed and as the temperature of the fused zone increases, the plasticity of the charge begins to decrease. With continued heating and evolution of gas the fused layer gradually resolidifies to the typical, cellular, coke structure. The coke left after solidification of the plastic zone still contains considerable volatile matter, as its temperature is raised still higher, the destructive-distillation reactions continue with evolution of gas and a little tar. The final reactions that take place in the coke appear to be largely splitting off hydrogen from the extremely complex, high-molecular-weight hydrocarbons of which it is composed. With increasing temperature the coke tends to pull away from the oven walls, and shrinkage cracks develop, which run from the oven walls inward toward the center of the coke mass. The two plastic zones move slowly from the opposite walls of the oven toward each other and finally meet at the center of the oven. The junction of the zones appears as a vertical crack running lengthwise through the oven at the center of the charge. When an oven is pushed, the coke divides vertically at this crack.

As the plastic zones move inward, their rate of travel tends to decrease because of the increasing distances through which the heat must be conducted. Increasing in the sensible heat carried off by the gas passing upward through the coke, and any heat absorbed in the cracking reactions that occur in the gaseous, these also tend to slow down the rate of travel of the zones. The temperature and behavior of the charges that are in the different zones of oven are different at different coking times.

2.2 The Caking Mechanism of Coals

The caking characteristics of coking coals have been investigated during high-temperature carbonizing processes by many researchers in the world, and some hypotheses of coal caking mechanism have been given. Two of them are plastic caking mechanism and mesophase caking mechanism.

2.2.1 Plastic Caking Mechanism of Coal

D. W. Van Krevelen has given three continuous reactions of conversion from coals into cokes through the plastic phase. When coking coals are heated up above 620 K in the absence of air, the organic matter of the coal begins thermal decomposition. The

mixtures of the gas, liquid and softened coal, that are the thermally decomposed from coal, are called a plastic mass. The coking coals soften, melt, fuse, swell, and cohere within a plastic stage. When the temperature is raised to 720 K to 820 K, a part of the plastic mass is evolved in gas and condensable vapor; the others resolidify to the semicoke. With further increasing in temperature above 820 K, the organic matter of the semicoke decomposes and condenses further, the methane and hydrogen are evolved, the carbon lamellae of the semicoke increase continuously, the coke is then finally formed. The two main stages that are converted from coals into coke are the caking phase of producing a plastic mass and the shrinking phase of the semicoke.

2.2.2 The Caking Mechanism by Mesophase

The formation of anisotropic carbon from the isotropic melt of coal, pitch or selected model organic compounds were first attributed to the development of a distinctive phase of liquid crystals by Brooks and Taylor. When the coking coal is carbonizing, the plastic mass of optical isotropic is first formed, and then forms lamellar nematic liquid crystals gradually. This polymeric phase is termed mesophase. That is the intermediate phase between the isotropic fluid coal and the solid anisotropic semicoke ultimately formed from the mesophase, and has properties of intermediate between solids and liquids. If the fluidity of the intermediate phase is sufficiently high, mesophase coalesce immediately into a single larger unit. Over a range of increasing temperature mesophase is formed continuously, grows in size and ultimately touches each other. Thus the mesophase can solidify and convert from coking coal into optical anisotropic textures of cokes.

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Biographical Sketch

Dexiang ZHANG is a professor of chemical engineering for energy sources at East China University of Science and Technology. He was a visiting scholar at Department of Chemistry in Western Kentucky University where he studied the instrument analytical methods of coals in a laboratory, and the cleaning utilization of high sulfur coals. He has been a teacher in Huainan Mining Institute where he had made preparations for the setting up of the Coal Chemical Processing Laboratory; given lectures on Chemical Engineering at the Technology of Coal Chemical Processing, Fuel Combustion and so on. He has received support for coal research from the PR China Department of Coal Industry and other agencies. He has published numerous papers in technical publications for co-pyrolysis of coal and heavy oils, and analysis and utilization of coal minerals. He received his Master in Organic Chemical Technology from East China University of Chemical Technology in 1985.