

How is Crude Coal Tar Derived?

INTRODUCTION

Crude Coal Tar is a by product of the Coking process. Coking is the process of heating coal in coke ovens to drive volatile matter from it. Metallurgical Coke is used as a fuel and reducing agent in the production of iron, steel, ferro-alloys, elemental phosphorus, calcium carbide and numerous other processes. It is also used to produce carbon electrodes and to agglomerate sinter and iron ore pellets.

COKE PRODUCTION

The coke making process involves carbonization of coal to high temperatures (1100°C) in an oxygen deficient atmosphere in order to concentrate the carbon. The commercial coke making process can be broken down into two categories: a) By-product Coke making and b) Non-Recovery/Heat Recovery Coke making. A brief description of each coking process is presented here.

a) By-product Coke Production:

The majority of coke produced in the United States comes from wet-charge, by-product coke oven batteries (Figure 1). The entire coke making operation is comprised of the following steps: Before carbonization, the selected coals from specific mines are blended, pulverized, and oiled for proper bulk density control. The blended coal is charged into a number of slot type ovens wherein each oven shares a common heating flue with the adjacent oven. Coal is carbonized in a reducing atmosphere and the off-gas is collected and sent to the by-product plant where various by-products are recovered. Hence, this process is called by-product coke making.



Figure 1: "Coke Side" of a By-Product Coke Oven Battery. The oven has just been "pushed" and railroad car is full of incandescent coke that will now be taken to the "quench station".

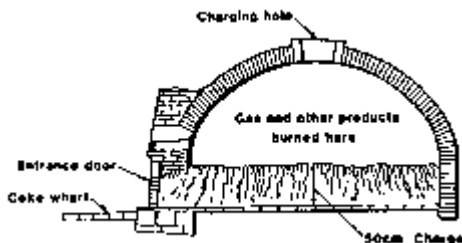


The coal-to-coke transformation takes place as follows: The heat is transferred from the heated brick walls into the coal charge. From about 375°C to 475°C, the coal decomposes to form plastic layers near each wall. At about 475°C to 600°C, there is a marked evolution of tar, and aromatic hydrocarbon compounds, followed by re-solidification of the plastic mass into semi-coke. At 600°C to 1100°C, the coke stabilization phase begins. This is characterized by contraction of coke mass, structural development of coke and final hydrogen evolution. During the plastic stage, the plastic layers move from each wall towards the center of the oven trapping the liberated gas and creating in gas pressure build up which is transferred to the heating wall. Once, the plastic layers have met at the center of the oven, the entire mass has been carbonized (Figure 2). The incandescent coke mass is pushed from the oven and is wet or dry quenched prior to its shipment to the blast furnace.

Figure 2: Incandescent coke in the oven waiting to be "pushed".

b) Non-Recovery/Heat Recovery Coke Production:

In Non-Recovery coke plants (originally referred to as beehive ovens) the coal is carbonized in large oven chambers (Figure 3). The carbonization process takes place from the top by radiant heat transfer and from the bottom by conduction of heat through the sole floor. Primary air for combustion is introduced into the oven chamber through several ports located above the charge level in both pusher and coke side doors of the oven. Partially combusted gases exit the top chamber through "down comer" passages in the oven wall and enter the sole flue, thereby heating the sole of the oven. Combusted gases collect in a common tunnel and exit via a stack which creates a natural draft in the oven. Since the by-products are not recovered, the process is called Non-Recovery coke making. In one case, the waste gas exits into a waste heat recovery boiler (Figure 3) which converts the excess heat into steam for power generation; hence, the process is called Heat Recovery coke making.



Generalised cross-section of a beehive coke oven with a charge of coal (Roger 1998)

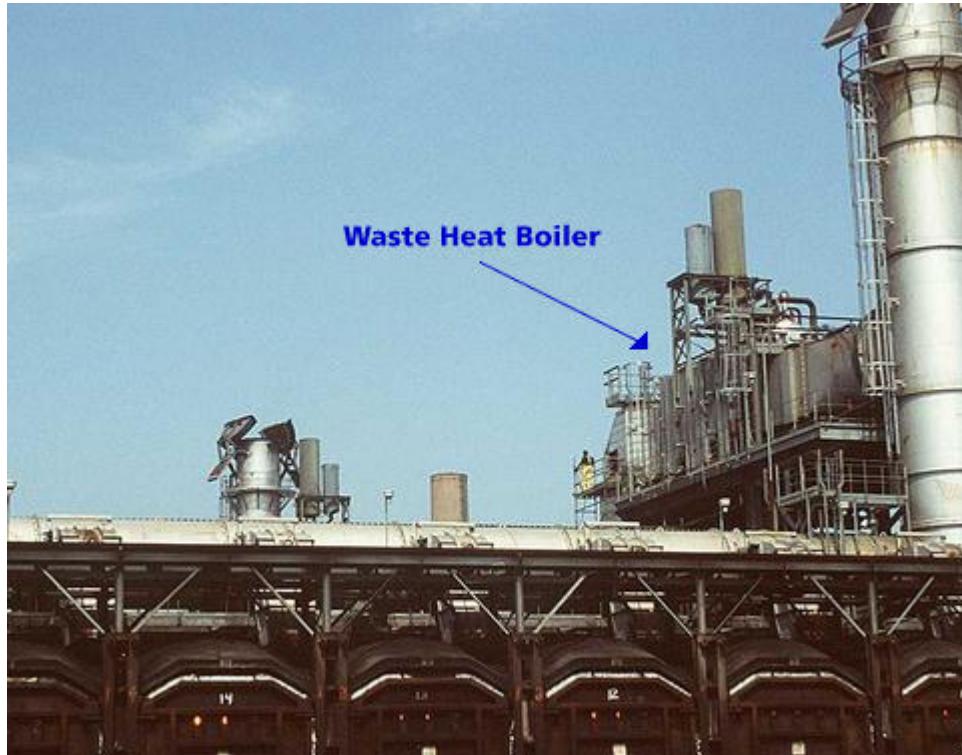


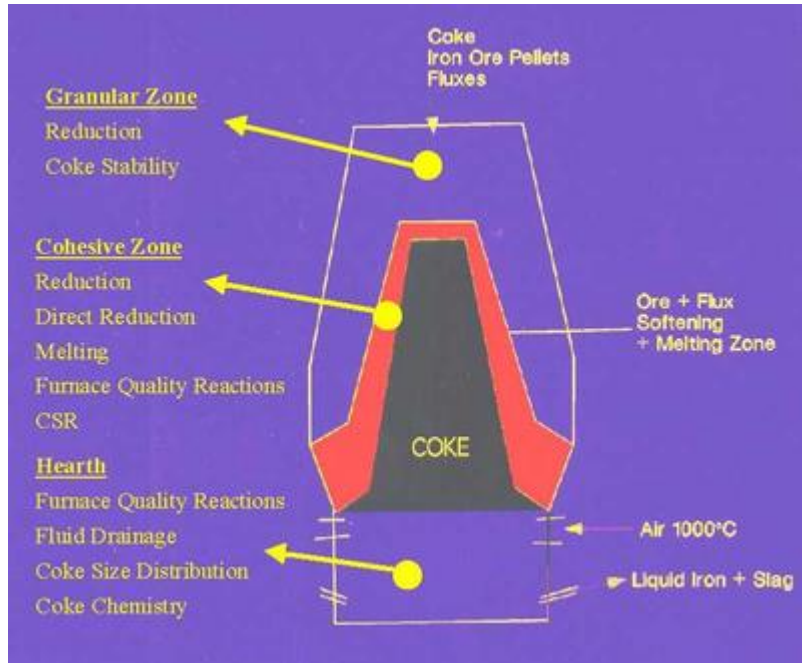
Figure 3: Heat Recovery Coke Plant.

COKE PROPERTIES

High quality coke is characterized by a definite set of physical and chemical properties that can vary within narrow limits. The coke properties can be grouped into following two groups: a) Physical properties and b) Chemical properties.

a) Physical Properties:

Measurement of physical properties aid in determining coke behavior both inside and outside the blast furnace (Figure 4). In terms of coke strength, the coke stability and Coke Strength After Reaction with CO_2 (CSR) are the most important parameters. The stability measures the ability of coke to withstand breakage at room temperature and reflects coke behavior outside the blast furnace and in the upper part of the blast furnace. CSR measures the potential of the coke to break into smaller size under a high temperature CO/CO_2 environment that exists throughout the lower two-thirds of the blast furnace. A large mean size with narrow size variations helps maintain a stable void fraction in the blast furnace permitting the upward flow of gases and downward of molten iron and slag thus improving blast furnace productivity.



Blast Furnace Operating Zones and Coke Behavior.

b) Chemical Properties:

The most important chemical properties are moisture, fixed carbon, ash, sulfur, phosphorus, and alkalis. Fixed carbon is the fuel portion of the coke; the higher the fixed carbon, the higher the thermal value of coke. The other components such as moisture, ash, sulfur, phosphorus, and alkalis are undesirable as they have adverse effects on energy requirements, blast furnace operation, hot metal quality, and/or refractory lining. Coke quality specifications for one large blast furnace in North America are shown in Table I.

Table I. Coke Quality Specifications:

Physical: (measured at the blast furnace)	Mean	Range
Average Coke Size (mm)	52	45-60
Plus 4" (% by weight)	1	4 max
Minus 1"(% by weight)	8	11 max
Stability	60	58 min
CSR	65	61 min
Physical: (% by weight)		
Ash	8.0	9.0 max
Moisture	2.5	5.0 max
Sulfur	0.65	0.82 max
Volatile Matter	0.5	1.5 max
Alkali (K ₂ O+Na ₂ O)	0.25	0.40 max
Phosphorus	0.02	0.33 max

FACTORS AFFECTING COKE QUALITY

A good quality coke is generally made from carbonization of good quality coking coals. Coking coals are defined as those coals that on carbonization pass through softening, swelling, and resolidification to coke. One important consideration in selecting a coal blend is that it should not exert a high coke oven wall pressure and should contract sufficiently to allow the coke to be pushed from the oven. The properties of coke and coke oven pushing performance are influenced by following coal quality and battery operating variables: rank of coal, petrographic, chemical and rheologic characteristics of coal, particle size, moisture content, bulk density, weathering of coal, coking temperature and coking rate, soaking time, quenching practice, and coke handling. Coke quality variability is low if all these factors are controlled. Coke producers use widely differing coals and employ many procedures to enhance the quality of the coke and to enhance the coke oven productivity and battery life.

Typical Coke Oven Yield

Yield from Coke Oven	
Yield from One Ton of Coke	
1200-1400 lb.	Coke
100-200 lb.	Coke Breeze
8-12 gal.	Tar
20-28 lb.	Ammonium Sulfate
15-35 gal.	Ammonia Liquor
2.5-4 gal.	Light Oil
9,500-11,500 scf	Coke Oven Gas
	▪ 574 Btu/scf HHV
	▪ 514 Btu/scf LHV

Ferrous and non-ferrous foundries specialize in melting and casting metal into desired shapes. Foundry products are most often used in automobiles, plumbing fixtures, train locomotives, airplanes and as metal pieces in other kinds of equipment.

In 1990, iron and steel accounted for 84% of metals cast (McKinley, 1994). The remaining 15% of foundry operations come from aluminum, copper, zinc and lead production. The foundry industry currently produces 11 million tons of metal product per year, with a shipment value of \$19 billion.

Foundry Processes

Cast Making

The first step in metal casting (Figure 3) involves the creation of a mold into which the molten metal will be poured and cooled. The materials used to make the molds depend on the type of metal being cast and the desired shape of the final product. Sand is the most common molding material; however, metals, investment materials, and other compounds may also be used.

Figure 3. Metal Casting Process (USEPA, 1981)

Green sand mold are used in 85% of foundries. Green sand is a mixture of sand, clay, carbonaceous material and water (Figure 4). The sand provides the structure for the mold, the clay binds the sand together and the carbonaceous materials prevent rust. Water is used to activate the clay. The green sand mixture is packed around a pattern of the metal piece and allowed to harden. The mold is carefully removed from the pattern and prepared for the molten metal.

Figure 4. Green Sand Composition

Sand molds are used only once. Molten metal is poured into the mold and allowed to cool. After cooling, the mold is broken away from the metal piece in a process called shakeout. Most of the sand from green sand molds is reused to make future molds.

Sand mixtures are also often used to create cores. Cores are pieces that fit into the mold to create detailed internal passages in the metal piece. Cores must be strong and hard to withstand the molten metal, and collapsible so they can be removed from the metal piece after it has cooled. To obtain these properties, resins or chemical binders are usually added to sand mixtures. Depending on the binder used, molds may be either air or thermally set.

Other molding materials include chemically bonded sand, metal or refractories. These materials are used in the remaining 15% of foundry applications. Shell molds use chemically bonded sand to make the molds. Permanent metal molds may be used in foundries that produce large quantities of the same piece. Investment molds are made from ceramic substances called refractories. They are used in high precision metal castings.

Metal Melting

Foundries melt metals in one of several types of furnaces depending on the type of metal being used (Table 1). Furnaces types include cupolas, electric arc, induction, hearth or reverberatory and crucible. Because of the different nature of metals, different inputs are required and different pollution is released from each type.

Table 1. Common Types of Metal Melting Furnaces

Furnace Type	Raw Materials	Outputs	Process
Cupola Furnace	Iron ore, scrap iron, lime, coke	Molten iron	Alternative layers of metal and coke are fed into the top of the furnace. The metal is melted by the hot gasses from the coke combustion. Impurities react with the lime and are separated.
Electric Arc Furnace	Scrap iron, flux	Molten iron and steel	Electric arcs from carbon electrodes melt the scrap metal. The flux reacts with impurities.
Induction Furnace	Scrap iron or non-ferrous metals	Molten iron or non-ferrous metals	Induction furnaces are the most common type used by both ferrous and non-ferrous foundries. Copper coils heat the metal using alternating currents. The flux reacts with impurities.
Reverberatory, Hearth, or Crucible Furnace	Non-ferrous metals, flux	Molten non-ferrous metals	Reverberatory furnaces melt metals in batches using a pot-shaped crucible that holds the metal over an electric heater or fuel-free burner. The flux

			reacts with impurities.
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Cupola Furnaces

Cupola furnaces are the oldest type of furnaces used in foundries. They are tall and roughly cylindrical and are most often used for melting iron and ferro alloys. . Alternating layers of metal and ferro alloys, coke, and limestone are fed into the furnace from the top. Coke makes up 8 - 16% of the total charge to provide the heat that melts the metal (USEPA, 1992). Limestone is added to react with impurities in the metal and floats to the top of the metal as it melts. As in steel melting, this limestone/impurities combination is called slag. By floating on top of the metal while it melts, the slag protects the metal from oxidation.

Cupola furnaces are lined with refractories, or hard, heat resistant substances such as fire clay, bricks or blocks. The refractory protects the furnace shell from abrasion, heat and oxidation. Over time the refractory breaks down and eventually becomes part of the slag.

Cupola furnaces are usually attached to emissions control systems to capture air emissions. Usually, the air emission systems use either high energy wet scrubbers that use water to remove air pollution from the gas stream or dry baghouse systems that use fabric filters to capture the emissions.

A world class blast furnace operation demands the highest quality of raw materials, operation, and operators. Coke is the most important raw material fed into the blast furnace in terms of its effect on blast furnace operation and hot metal quality. A high quality coke should be able to support a smooth descent of the blast furnace burden with as little degradation as possible while providing the lowest amount of impurities, highest thermal energy, highest metal reduction, and optimum permeability for the flow of gaseous and molten products. Introduction of high quality coke to a blast furnace will result in lower coke rate, higher productivity and lower hot metal cost.

Reference

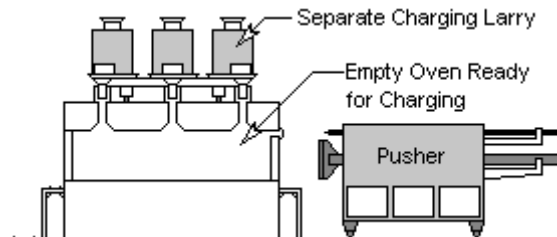
Website

By Hardarshan S. Valia, Scientist, <http://www.steel.org> :
Ispat Inland Inc

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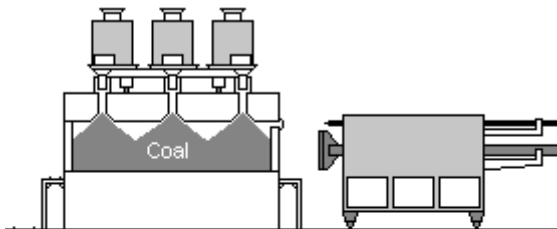
Coal is converted to coke in large coke oven batteries like the one pictured. The coking process consists of heating coal in the absence of air to drive off the volatile compounds; the resulting coke is a hard, but porous carbon material that is used for reducing the iron in the blast furnace. The modern by-product coke oven recovers volatile chemicals in the form of coke oven gas, tars, and oils.

Coke Oven Operation



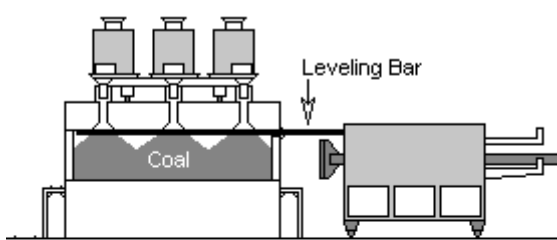
The charging larry, with hoppers containing measured amounts of coal is in position over charging holes from which covers have been removed. The pusher has been moved into position.

First Step



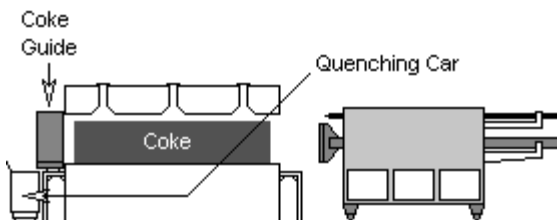
The coal from the larry hoppers has dropped into the oven chamber, forming peaked piles.

Second Step



The leveling door at the top of the oven door on the pusher side has been opened, and the leveling bar on the pusher side has been moved back and forth across the peaked coal piles to level them. The bar next is withdrawn from the oven, the leveling door and charging holes are closed, and the coking operation begins.

Third Step



Coking of the coal originally charged into the oven has been completed (in about 18 hours) and the oven is ready to be "pushed". The oven doors are removed from each end, and the pusher, coke guide and quenching car are moved into position.

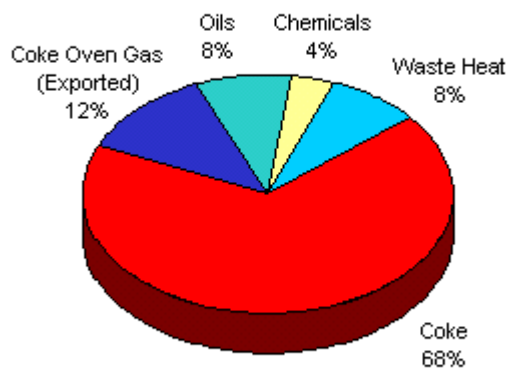
Fourth Step

A coke oven battery consists of 10-100 individual coke ovens with batteries of 45 or more being preferred in the U.S. The long thin coking chambers (Height 6-22 ft., Length: 3-52 ft, Width: 1-2 ft) alternate with the heating chambers so that there are heating chambers on both sides of each coking chamber to provide even heating. This alternating row of heating and coking chambers sits atop regenerative chambers that recover the flue gas heat for preheating the combustion air. The burners/regenerators are alternated on a 15-30 minute cycle determined by the need to maintain temperature control within the coking chambers. On top of the coke oven battery are coal charging cars. On the pusher side of the battery is the large pusher/leveler that levels the input charge and then pushes the hot coke out of the oven. On the coke side of the oven, quench cars take the incandescent coke to the quenching system.

Coke production has been declining due to the associated environmental clean-up issues. Over 25 million tons of metallurgical coal are used to produce 18 million tons of coke. Each ton of coke produced requires 1.37 tons of coal. In the wet quench process most common in the U.S., 0.6 million Btu of steam is required per ton of coke for chemical recovery. In the dry quench process, enough heat is recovered in quenching to provide all of the steam requirements of the process and provide some steam for export as well. The energy required for the coking process, virtually all of which comes from the recovered coke oven gas itself or blast furnace gas which ultimately derives from the coke, equals 3.2 million Btu per ton of coke produced. Approximately 40% of the coke oven gas produced is returned to the coke ovens to supply this energy.

About 68% of the input coal energy goes into the coke itself. Coke oven gas (exported, i.e. the 60% not needed by the coking process itself) equals 12% of the input coal energy. Recovered tars, oils, and other chemicals contain about 12% of the input energy, and about 8% is consumed as fuel for the process.

Energy Breakdown of Coke Production (% Share of Coal Energy Input)



The iron and steel industry would need to invest \$4-6 billion in their coke oven batteries to replace or repair current capacity to bring them into compliance with environmental regulations. Of the 79 batteries operating, about half are more than 30 years old. Work is underway to minimize leakage from doors and to improve the process of chemicals recovery and air and process water cleanup. Systems to utilize lower quality coals for coking are also of interest, such as the continuous form-coking process. However, the focus of R&D in the industry is more toward reducing or eliminating the coke requirements in iron-making through pulverized or granular coal injection in blast furnaces (PCI/GCI) or completely new direct iron/steel making technologies that could utilize coal or some other fuel directly.