

The Coke Oven By-Product Plant

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WHAT IS IT AND WHAT DOES IT DO?

The coke oven by-product plant is an integral part of the by-product cokemaking process. In the process of converting coal into coke using the by-product coke oven, the volatile matter in the coal is vaporized and driven off. This volatile matter leaves the coke oven chambers as hot, raw coke oven gas. After leaving the coke oven chambers, the raw coke oven gas is cooled which results in a liquid condensate stream and a gas stream. The functions of the by-product plant are to take these two streams from the coke ovens, to process them to recover by-product coal chemicals and to condition the gas so that it can be used as a fuel gas. Historically, the by-product chemicals were of high value in agriculture and in the chemical industry, and the profits made from their sale were



often of greater importance than the coke produced. Nowadays however most of these same products can be more economically manufactured using other technologies such as those of the oil industry. Therefore, with some exceptions depending on local economics, the main emphasis of a modern coke by-product plant is to treat the coke oven gas sufficiently so that it can be used as a clean, environmentally friendly fuel.

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Coke oven / by-product plant interface

In a by-product coke oven the evolved coke oven gas leaves the coke oven chambers at high temperatures approaching 2000(°)F. This hot gas is immediately quenched by direct contact with a spray of aqueous liquor (flushing liquor). The resulting cooled gas is water saturated and has a temperature of 176(°)F. This gas is collected in the coke oven battery gas collecting main. From the gas collecting main the raw coke oven gas flows into the suction main. The amount of flushing liquor sprayed into the hot gas leaving the oven chambers is far more than is required for cooling, and the remaining unevaporated flushing liquor provides a liquid stream in the gas collecting main that serves to flush away condensed tar and other compounds. This stream of flushing liquor flows under gravity into the suction main along with the raw coke oven gas. The raw coke oven gas and the flushing liquor are separated using a drain pot (the downcomer) in the suction main. The flushing liquor and the raw coke oven gas then flow separately to the by-product plant for treatment.

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Composition of coke oven gas

Raw coke oven gas coming from the coke oven battery has the following typical composition:

	Dry basis	Actual composition (water saturated at 176°F)
Water vapor	-	47%
Hydrogen	55%	29%
Methane	25%	13%
Nitrogen	10%	5%
Carbon Monoxide	6%	3%
Carbon Dioxide	3%	2%

Hydrocarbons (ethane, propane etc.)	2%	1%
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Raw coke oven gas also contains various contaminants, which give coke oven gas its unique characteristics. These consist of:

- Tar vapors
- Light oil vapors (aromatics), consisting mainly of benzene, toluene and xylene (BTX)
- Naphthalene vapor
- Ammonia gas
- Hydrogen sulfide gas
- Hydrogen cyanide gas

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Duties of the by-product plant

In order to make raw coke oven gas suitable for use as a fuel gas at the coke oven battery and elsewhere in the steelmaking facility the by-product plant must:

- Cool the coke oven gas to condense out water vapor and contaminants
 - Remove tar aerosols to prevent gas line/equipment fouling
 - Remove ammonia to prevent gas line corrosion
 - Remove naphthalene to prevent gas line fouling by condensation
- Other duties may include:
- Remove light oil for recovery and sale of benzene, toluene and xylene
 - Remove hydrogen sulfide to meet local emissions regulations governing the combustion of coke oven gas.

In addition to treating the coke oven gas, the by-product plant must also condition the flushing liquor that is returned to the coke oven battery, and treat the waste water that is generated by the coke making process.

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The by-product plant gas train

The gas treatment processes in the by-product plant typically consist of the following plant items, arranged in the order in which they are described.

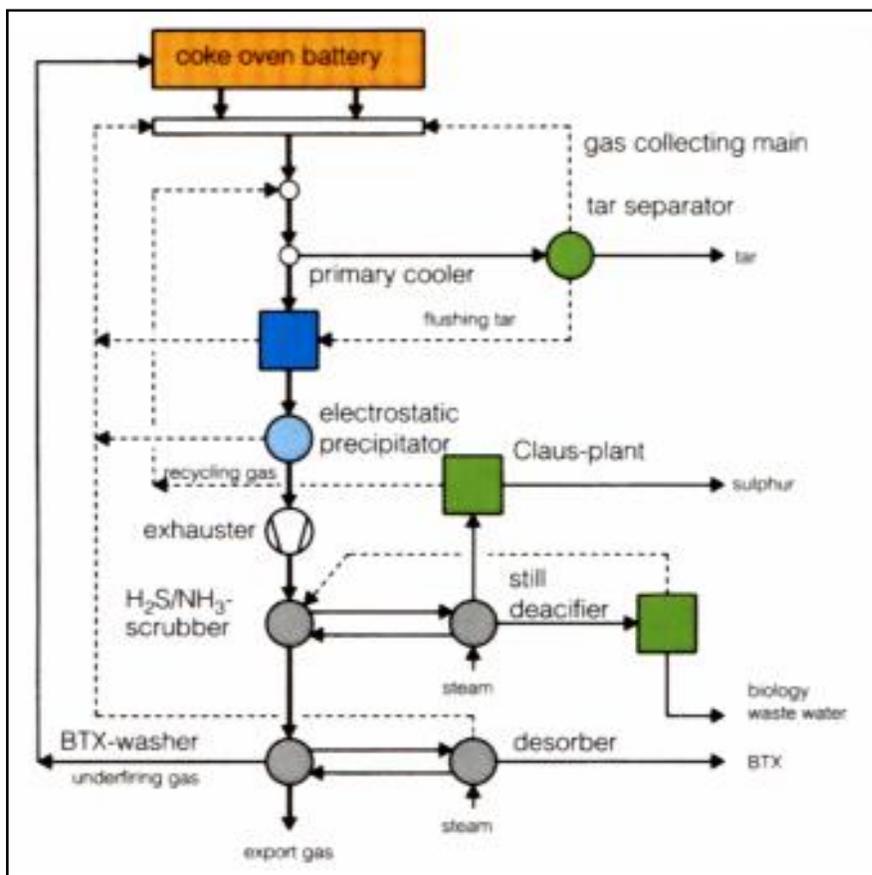
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Primary cooler

The first step in the treatment of raw coke oven gas is to cool it to remove water vapor and so greatly reduce its volume. This is done in the Primary Cooler. There are two basic types, the spray type cooler and the horizontal tube type. In a spray type cooler the coke oven gas is cooled by direct contact with a recirculated water spray, with the contact cooling water being itself cooled externally in heat exchangers. In the tubular type, the coke oven gas is cooled indirectly by flowing across horizontally mounted tubes through which cooling water is pumped. In this

case, the cooling water does not come into contact with the coke oven gas and so it can be cooled in a cooling tower for example.

As the coke oven gas is cooled, water, tar and naphthalene condense out. The condensate collects in the primary cooler system and is discharged to the tar & liquor plant.



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Tar precipitators

As the raw coke oven gas is cooled, tar vapor condenses and forms aerosols which are carried along with the gas flow. These tar particles would contaminate and foul downstream processes and would foul gas lines and burner nozzles if allowed to continue in the gas stream. The tar precipitators typically use high voltage electrodes to charge the tar particles and then collect them from the gas by means of electrostatic attraction. The tar precipitators can be installed before, or after the exhauster. The usual practice in North America is to place them immediately after the exhauster.

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Exhauster

The exhauster is a large blower that provides the motive force to induce the coke oven gas to flow from the coke oven battery and through the by-product plant.

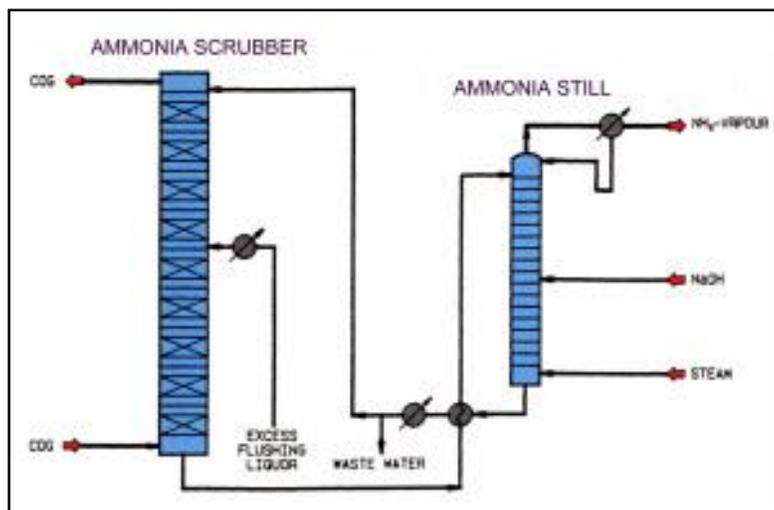
The exhauster is of prime importance to the operation of the coke oven battery. It allows the close control of the gas pressure in the collecting main, which in turn affects the degree of emissions, for example door emissions, from the battery. A failure of the exhauster will immediately result in venting to atmosphere, through the battery flares, of all of the raw coke oven gas produced.

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Ammonia removal

Because of the corrosive nature of ammonia, its removal is a priority in coke oven by-product plants. Historically the removal of ammonia from coke oven gas has yielded one of the more profitable by-products, that of ammonium sulfate. The ammonium sulfate process can take various forms but all basically involve contacting the coke oven gas with a solution of sulfuric acid. Variations include the use of an absorber, in which the sulfuric acid solution is sprayed into the gas, or the use of a saturator in which the gas is bubbled through a bath of sulfuric acid solution. The sulfuric acid reacts readily with the ammonia in the coke oven gas to form ammonium sulfate. This is then crystallized out, removed from the solution and dried for sale typically as a fertilizer. Nowadays the cost to produce ammonium sulfate often outweighs the revenue from the product, however there are still very many coke plants around the world producing ammonium sulfate.

More modern processes for ammonia removal include the water wash process in which the coke oven gas is scrubbed by water, which dissolves the ammonia, along with some hydrogen sulfide and hydrogen cyanide. The resulting scrubbing solution is pumped to an ammonia still where steam is used to strip out the ammonia. The ammonia vapors from the still can be processed to form ammonium sulfate similar to the processes



described above, condensed to form a strong ammonia solution, incinerated or catalytically converted to nitrogen and hydrogen which are then recycled back into the coke oven gas. The incineration of the ammonia vapors is usually not an option in areas where environmental laws restrict the emission of NO_x and sulfur dioxide.

Another process for ammonia removal from coke oven gas is the PHOSAM process developed by US Steel. This process absorbs the ammonia from the coke oven gas using a solution of monoammonium phosphate. The process produces saleable anhydrous ammonia.

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Final cooler

The duty of the final cooler is to remove the heat of compression from the coke oven gas that it gained on flowing through the exhauster. This is necessary because the efficiency of many of the by-product plant processes, including the water wash ammonia removal process, is greatly improved at lower temperature. The final cooler is therefore placed upstream of water wash ammonia scrubbers if these are installed. Final coolers typically cool the coke oven gas by direct contact with a cooling medium, either water or wash oil. An important aspect of final cooler operation is that when the coke oven gas is cooled below the outlet temperature of the primary cooler, naphthalene will condense from the gas. This naphthalene readily crystallizes out from the cooling medium and will foul equipment if not disposed of. In wash oil final coolers the naphthalene dissolves in the wash oil and a side stream of oil is steam stripped to remove the naphthalene. If water is used to cool the coke oven gas, the condensed naphthalene must be absorbed using tar. The tar is either entrained in the cooling water, with a portion of the flow being continuously blown down for treatment, or it takes the form of a tar layer through which the cooling water flows. The tar is continuously exchanged with fresh tar from the tar and liquor plant to dispose of the absorbed naphthalene.

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Naphthalene removal

Naphthalene is removed from coke oven gas using wash oil in a gas scrubbing vessel. The vessel may be packed or it may be the "void" type in which the wash oil is sprayed into the gas in several stages. The wash oil is regenerated by stripping out the naphthalene from the wash oil using steam in a still. In many plants, naphthalene removal is integrated with the similar process of light oil removal. The naphthalene is typically recovered as a heavier oil stream that is then often mixed with the tar that is produced in the by-product plant.

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Light oil removal

Light oil is a general term for a mixture of similar chemicals consisting mainly of benzene, toluene and xylene. The removal of light oil from coke oven gas uses wash oil in a similar process to that described for naphthalene removal. The light oil is stripped from the wash oil in a still and is then condensed to form crude light oil. This can be sold for further refining offsite or it can be refined in the by-product plant using several distillation steps in the light oil plant. The light oil can actually be left in the coke oven gas, where it increases the calorific value. Its removal has historically been extremely cost effective, as benzene toluene and xylene from coke oven gas were once vital raw materials for the developing chemical industry. However these materials can nowadays be obtained at lower cost and in greater quantities from other sources

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Coke oven gas desulfurization

There are several different processes for removal of hydrogen sulfide from coke oven gas. The specific process determines where in the gas train it is installed. The main desulfurization processes in use are

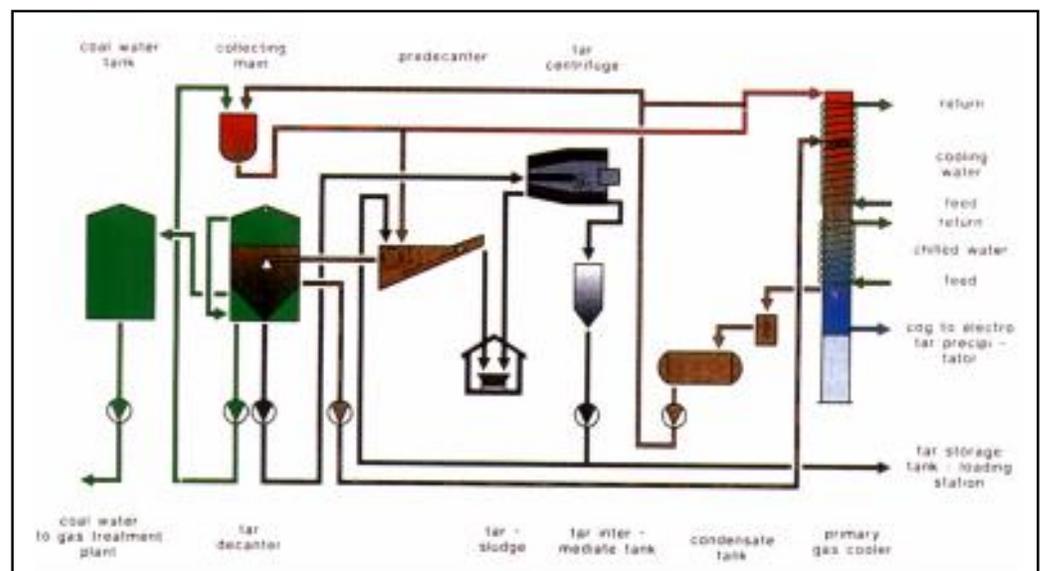
Vacuum Carbonate Process	Hydrogen Sulfide is absorbed from the coke oven gas using a solution of Potassium Carbonate, then stripped out in a still
Ammonia Wash Process	Hydrogen sulfide is absorbed from the coke oven gas using a solution of ammonia, then stripped out in a still - this process is often combined with the ammonia removal system
Sulfiban Process	Hydrogen sulfide is absorbed from the coke oven gas using a solution of Monoethanolamine (MEA) then stripped out in a still

The hydrogen sulfide is converted into elemental sulfur, using the Claus process, or it can be used for the production of sulfuric acid.

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Tar and Liquor Plant

The tar and liquor plant handles the flushing liquor that circulates between the by-product plant and the coke oven battery. It also processes the waste water that is generated by the cokemaking process and which results from coal moisture and chemically bound water in the coal. The flushing liquor flows into tar decanters where the tar separates out from



the water and is pumped to storage for later sale. Heavier solid particles separate out from the tar layer and these are removed as tar decanter sludge (TDS). The aqueous liquor is then pumped back to the battery, with a portion bled off from the circuit which is the coke plant "excess liquor" or waste water. This contains ammonia and, after the further removal of tar particles, it is steam stripped in a still. An alkali such as sodium hydroxide is added in the still to decompose ammonia compounds dissolved in the liquor. The ammonia vapor from the still is then either fed into the coke oven gas upstream of the ammonia removal system, or the still itself is often integrated into the ammonia removal system. Either way, the ultimate fate of the ammonia removed from both the coke oven gas and the waste water is the same. The stripped still effluent is either discharged to a municipal sewer or it can be treated in an on-site biological effluent treatment plant to remove residual ammonia, phenol and cyanides.

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Conclusion

The above describes the main features of the majority of coke oven byproducts plants around the world. The resultant main output streams are shown in the table below. The quantities shown are intended to be indicative only and relate to a typical facility producing 1 million tons per year of blast furnace coke. Coal properties and plant design and operation influence the actual quantities.

Stream	Destination	Typical quantities, based on 1 million tons per year coke
Coke Oven Gas	Used as fuel gas at the coke oven battery and steel works	50 million std.cu. ft./day
Flushing Liquor	Recirculated back to the coke oven battery	Varies with plant design
Waste Water	Discharged to treatment plant	Varies with plant design
Tar	Sold as product	29,000 gallons/day
Ammonia/ Ammonium Sulfate	Sold as product	12 tons/day (as ammonia)
Light Oil (if recovered)	Sold as product	12,500 gallons/day

Sulfur/Sulfuric Acid (if gas is desulfurized)	Sold as product	Varies with coal properties and local requirements
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