

6.1 Carbon Black

6.1.1 Process Description

Carbon black is produced by the reaction of a hydrocarbon fuel such as oil or gas with a limited supply of combustion air at temperatures of 1320 to 1540°C (2400 to 2800°F). The unburned carbon is collected as an extremely fine black fluffy particle, 10 to 500 nanometers (nm) in diameter. The principal uses of carbon black are as a reinforcing agent in rubber compounds (especially tires) and as a black pigment in printing inks, surface coatings, paper, and plastics. Two major processes are presently used in the United States to manufacture carbon black, the oil furnace process and the thermal process. The oil furnace process accounts for about 90 percent of production, and the thermal, about 10 percent. Two others, the lamp process for production of lamp black and the cracking of acetylene to produce acetylene black, are each used at 1 plant in the U. S. However, these are small-volume specialty black operations that constitute less than 1 percent of total production in this country. The gas furnace process is being phased out, and the last channel black plant in the U. S. was closed in 1976.

6.1.1.1 Oil Furnace Process -

In the oil furnace process (Figure 6.1-1 and Table 6.1-1), an aromatic liquid hydrocarbon feedstock is heated and injected continuously into the combustion zone of a natural gas-fired furnace, where it is decomposed to form carbon black. Primary quench water cools the gases to 500°C (1000°F) to stop the cracking. The exhaust gases entraining the carbon particles are further cooled to about 230°C (450°F) by passage through heat exchangers and direct water sprays. The black is then separated from the gas stream, usually by a fabric filter. A cyclone for primary collection and particle agglomeration may precede the filter. A single collection system often serves several manifolded furnaces.

The recovered carbon black is finished to a marketable product by pulverizing and wet pelletizing to increase bulk density. Water from the wet pelletizer is driven off in a gas-fired rotary dryer. Oil or process gas can be used. From 35 to 70 percent of the dryer combustion gas is charged directly to the interior of the dryer, and the remainder acts as an indirect heat source for the dryer. The dried pellets are then conveyed to bulk storage. Process yields range from 35 to 65 percent, depending on the feed composition and the grade of black produced. Furnace designs and operating conditions determine the particle size and the other physical and chemical properties of the black. Generally, yields are highest for large particle blacks and lowest for small particle blacks.

6.1.1.2 Thermal Process -

The thermal process is a cyclic operation in which natural gas is thermally decomposed (cracked) into carbon particles, hydrogen, and a mixture of other organics. Two furnaces are used in normal operation. The first cracks natural gas and makes carbon black and hydrogen. The effluent gas from the first reactor is cooled by water sprays to about 125°C (250°F), and the black is collected in a fabric filter. The filtered gas (90 percent hydrogen, 6 percent methane, and 4 percent higher hydrocarbons) is used as a fuel to heat a second reactor. When the first reactor becomes too cool to crack the natural gas feed, the positions of the reactors are reversed, and the second reactor is used to crack the gas while the first is heated. Normally, more than enough hydrogen is produced to make the thermal black process self-sustaining, and the surplus hydrogen is used to fire boilers that supply process steam and electric power.

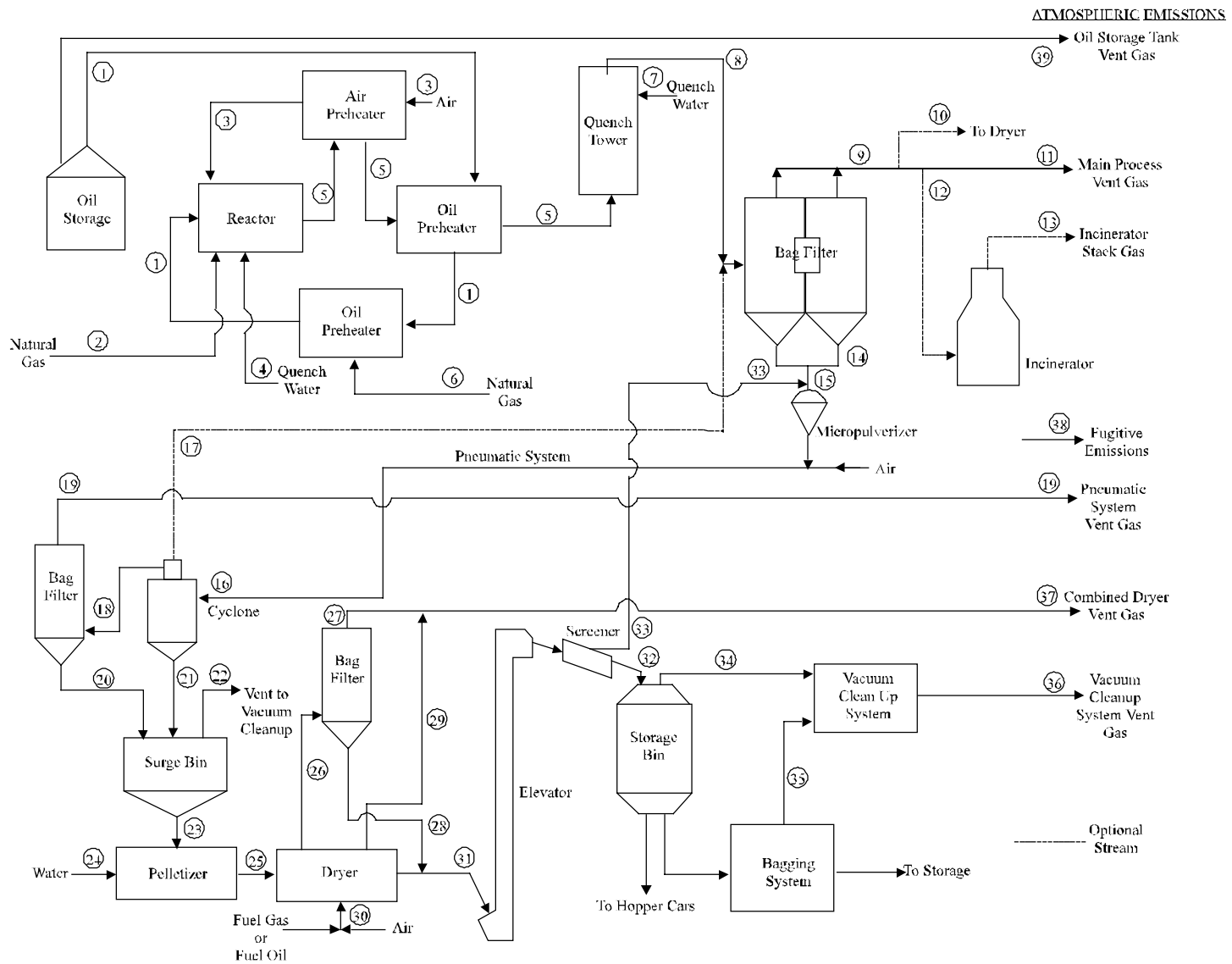


Figure 6.1-1. Flow diagram for the oil furnace carbon black process.

Table 6.1-1. STREAM IDENTIFICATION FOR THE OIL FURNACE PROCESS (FIGURE 6.1-1)

Stream	Identification
1	Oil feed
2	Natural gas feed
3	Air to reactor
4	Quench water
5	Reactor effluent
6	Gas to oil preheater
7	Water to quench tower
8	Quench tower effluent
9	Bag filter effluent
10	Vent gas purge for dryer fuel
11	Main process vent gas
12	Vent gas to incinerator
13	Incinerator stack gas
14	Recovered carbon black
15	Carbon black to micropulverizer
16	Pneumatic conveyor system
17	Cyclone vent gas recycle
18	Cyclone vent gas
19	Pneumatic system vent gas
20	Carbon black from bag filter
21	Carbon black from cyclone
22	Surge bin vent
23	Carbon black to pelletizer
24	Water to pelletizer
25	Pelletizer effluent
26	Dryer direct heat source vent
27	Dryer heat exhaust after bag filter
28	Carbon black from dryer bag filter
29	Dryer indirect heat source vent
30	Hot gases to dryer

Table 6.1-1 (cont.).

Stream	Identification
31	Dried carbon black
32	Screened carbon black
33	Carbon black recycle
34	Storage bin vent gas
35	Bagging system vent gas
36	Vacuum cleanup system vent gas
37	Combined dryer vent gas
38	Fugitive emissions
39	Oil storage tank vent gas

The collected thermal black is pulverized and pelletized to a final product in much the same manner as is furnace black. Thermal process yields are generally high (35 to 60 percent), but the relatively coarse particles produced, 180 to 470 nm, do not have the strong reinforcing properties required for rubber products.

6.1.2 Emissions And Controls

6.1.2.1 Oil Furnace Process -

Emissions from carbon black manufacture include particulate matter, carbon monoxide (CO), organics, nitrogen oxides, sulfur compounds, polycyclic organic matter (POM), and trace elements.

The principal source of emissions in the oil furnace process is the main process vent. The vent stream consists of the reactor effluent and the quench water vapor vented from the carbon black recovery system. Gaseous emissions may vary considerably according to the grade of carbon black being produced. Organic and CO emissions tend to be higher for small particle production, corresponding with the lower yields obtained. Sulfur compound emissions are a function of the feed sulfur content. Tables 6.1-2, 6.1-3, and 6.1-4 show the normal emission ranges to be expected, with typical average values.

The combined dryer vent (stream 37 in Figure 6.1-1) emits carbon black from the dryer bag filter and contaminants from the use of the main process vent gas if the gas is used as a supplementary fuel for the dryer. It also emits contaminants from the combustion of impurities in the natural gas fuel for the dryer. These contaminants include sulfur oxides, nitrogen oxides, and the unburned portion of each of the species present in the main process vent gas (see Table 6.1-2). The oil feedstock storage tanks are a source of organic emissions. Carbon black emissions also occur from the pneumatic transport system vent, the plantwide vacuum cleanup system vent, and from cleaning, spills, and leaks (fugitive emissions).

Gaseous emissions from the main process vent may be controlled with CO boilers, incinerators, or flares. The pellet dryer combustion furnace, which is, in essence, a thermal incinerator, may also be employed in a control system. CO boilers, thermal incinerators, or combinations of these devices can achieve essentially complete oxidation of organics and can oxidize

Table 6.1-2 (Metric And English Units). EMISSION FACTORS FOR CHEMICAL SUBSTANCES FROM OIL FURNACE CARBON BLACK MANUFACTURE^a

Chemical Substance	Main Process Vent Gas ^b	
	kg/Mg	lb/ton
Carbon disulfide	30	60
Carbonyl sulfide	10	20
Methane	25	50
	(10 - 60)	(20 - 120)
Nonmethane VOC		
Acetylene	45	90
	(5 - 130)	(10 - 260)
Ethane	0 ^c	0 ^c
Ethylene	1.6	3.2
Propylene	0 ^c	0 ^c
Propane	0.23	0.46
Isobutane	0.10	0.20
n-Butane	0.27	0.54
n-Pentane	0 ^c	0 ^c
POM	0.002	0.004
Trace elements ^d	<0.25	<0.50

^a Expressed in terms of weight of emissions per unit weight of carbon black produced. VOC = volatile organic compounds.

^b These chemical substances are emitted only from the main process vent. Average values are based on 6 sampling runs made at a representative plant (Reference 1). Ranges given in parentheses are based on results of a survey of operating plants (Reference 4).

^c Below detection limit of 1 ppm.

^d Beryllium, lead, and mercury, among several others.

sulfur compounds in the process flue gas. Combustion efficiencies of 99.6 percent for hydrogen sulfide and 99.8 percent for CO have been measured for a flare on a carbon black plant. Particulate emissions may also be reduced by combustion of some of the carbon black particles, but emissions of sulfur dioxide and nitrogen oxides are thereby increased.

6.1.2.2 Thermal Process -

Emissions from the furnaces in this process are very low because the offgas is recycled and burned in the next furnace to provide heat for cracking, or sent to a boiler as fuel. The carbon black is recovered in a bag filter between the 2 furnaces. The rest is recycled in the offgas. Some adheres to the surface of the checkerbrick where it is burned off in each firing cycle.

Table 6.1-3 (Metric Units). EMISSION FACTORS FOR CARBON BLACK MANUFACTURE^a

EMISSION FACTOR RATING: C

Process	Particulate ^b	Carbon Monoxide	Nitrogen Oxides	Sulfur Oxides	Methane	Nonmethane VOC ^c	Hydrogen Sulfide
Oil furnace process							
Main process vent	3.27 ^d (0.1 - 5)	1,400 ^e (700 - 2,200)	0.28 ^e (1 - 2.8)	0 ^{e,f} (0 - 12)	25 ^e (10 - 60)	50 ^e (10 - 159)	30 ^e (5S - 13S) ^g
Flare	1.35 (1.2 - 1.5)	122 (108 - 137)	ND	25 (21.9 - 28)		1.85 (1.7 - 2)	1
CO boiler and incinerator	1.04	0.88	4.65	17.5		0.99	0.11
Combined dryer vent ^h							
Bag filter	0.12 (0.01 - 0.40)		0.36 (0.12 - 0.61)	0.26 (0.03 - 0.54)			
Scrubber	0.36 (0.01 - 0.70)		1.10	0.20			
Pneumatic system vent ^h							
Bag filter	0.29 (0.06 - 0.70)						
Oil storage tank vent ⁱ							
Uncontrolled						0.72	
Vacuum cleanup system vent ^h							
Bag filter	0.03 (0.01 - 0.05)						
Fugitive emissions ^h	0.10						
Solid waste incinerator ^j	0.12	0.01	0.04	0.01		0.01	
Thermal process ^k	Neg	Neg	ND	Neg		Neg	Neg

Table 6.1-3 (cont.).

- ^a Expressed in terms of weight of emissions per unit weight of carbon black produced. Blanks indicate no emissions. Most plants use bag filters on all process trains for product recovery except solid waste incineration. Some plants may use scrubbers on at least one process train. ND = no data.
- ^b The particulate matter is carbon black.
- ^c Emission factors do not include organic sulfur compounds that are reported separately in Table 6.1-2. Individual organic species comprising the nonmethane VOC emissions are included in Table 6.1-2.
- ^d Average values based on surveys of plants (References 4-5).
- ^e Average values based on results of 6 sampling runs conducted at a representative plant with a mean production rate of 5.1×10 Mg/yr (5.6×10 ton/yr). Ranges of values are based on a survey of 15 plants (Reference 4). Controlled by bag filter.
- ^f Not detected at detection limit of 1 ppm.
- ^g S is the weight % sulfur in the feed.
- ^h Average values and corresponding ranges of values are based on a survey of plants (Reference 4) and on the public files of Louisiana Air Control Commission.
- ⁱ Emission factor calculated using empirical correlations for petrochemical losses from storage tanks (vapor pressure = 0.7 kPa). Emissions are mostly aromatic oils.
- ^j Based on emission rates obtained from the National Emissions Data System. All plants do not use solid waste incineration. See Section 2.1.
- ^k Emissions from the furnaces are negligible. Emissions from the dryer vent, pneumatic system vent, vacuum cleanup system, and fugitive sources are similar to those for the oil furnace process.

Table 6.1-4 (English Units). EMISSION FACTORS FOR CARBON BLACK MANUFACTURE^a

EMISSION FACTOR RATING: C

Process	Particulate ^b	Carbon Monoxide	Nitrogen Oxides	Sulfur Oxides	Methane	Nonmethane VOC ^c	Hydrogen Sulfide
Oil furnace process							
Main process vent	6.53 ^d (0.2 - 10)	2,800 ^e (1,400 - 4,400)	0.56 ^e (2 - 5.6)	0 ^{e,f} (0 - 24)	50 ^e (20 - 120)	100 ^e (20 - 300)	60 ^e (10S - 26S) ^g
Flare	2.70 (2.4 - 3)	245 (216 - 274)	ND	50 (44 - 56)		3.7 (3.4 - 4)	2
CO boiler and incinerator	2.07	1.75	9.3	35.2		1.98	0.22
Combined dryer vent ^h							
Bag filter	0.24 (0.02 - 0.80)		0.73 (0.24 - 1.22)	0.52 (0.06 - 1.08)			
Scrubber	0.71		2.20	0.40			
Pneumatic system vent ^h	(0.02 - 1.40)						
Bag filter	0.58 (0.12 - 1.40)						
Oil storage tank vent ⁱ							
Uncontrolled							
Vacuum cleanup system vent ^h						1.44	
Bag filter	0.06 (0.02 - 0.10)						
Fugitive emissions ^h	0.20						
Solid waste incinerator ^j	0.24	0.02	0.08	0.02		0.02	
Thermal process ^k	Neg	Neg	ND	Neg		Neg	Neg

Table 6.1-4 (cont.).

- ^a Expressed in terms of weight of emissions per unit weight of carbon black produced. Blanks indicate no emissions. Most plants use bag filters on all process trains for product recovery except solid waste incineration. Some plants may use scrubbers on at least one process train. ND = no data.
- ^b The particulate matter is carbon black.
- ^c Emission factors do not include organic sulfur compounds that are reported separately in Table 6.1-2. Individual organic species comprising the nonmethane VOC emissions are included in Table 6.1-2.
- ^d Average values based on surveys of plants (References 4-5).
- ^e Average values based on results of 6 sampling runs conducted at a representative plant with a mean production rate of 5.1×10 Mg/yr (5.6×10 tons/yr). Ranges of values are based on a survey of 15 plants (Reference 4). Controlled by bag filter.
- ^f Not detected at detection limit of 1 ppm.
- ^g S is the weight % sulfur in the feed.
- ^h Average values and corresponding ranges of values are based on a survey of plants (Reference 4) and on the public files of Louisiana Air Control Commission.
- ⁱ Emission factor calculated using empirical correlations for petrochemical losses from storage tanks (vapor pressure = 0.7 kPa). Emissions are mostly aromatic oils.
- ^j Based on emission rates obtained from the National Emissions Data System. All plants do not use solid waste incineration. See Section 2.1.
- ^k Emissions from the furnaces are negligible. Emissions from the dryer vent, pneumatic system vent, vacuum cleanup system, and fugitive sources are similar to those for the oil furnace process.

Emissions from the dryer vent, the pneumatic transport system vent, the vacuum cleanup system vent, and fugitive sources are similar to those for the oil furnace process, since the operations that give rise to these emissions in the 2 processes are similar. There is no emission point in the thermal process that corresponds to the oil storage tank vents in the oil furnace process. Also in the thermal process, sulfur compounds, POM, trace elements, and organic compound emissions are negligible, because low-sulfur natural gas is used, and the process offgas is burned as fuel.

References For Section 6.1

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