from: Air Pollutant Emission Factors
April 1970
Contract No. CPA-22-69-119

4.3 CARBON BLACK

Process Description

Carbon black is produced by reacting a hydrocarbon fuel such as oil and/or gas with a limited supply of air at temperatures of 2500°F - 3000°F. Part of the fuel is burned to CO_2, CO, and water thus generating heat for the combustion of fresh feed. The unburnt carbon is collected as a black fluffy particle. Three basic processes currently exist in the United States for producing this compound. They are: The furnace process accounting for about 83% of production; the older channel process which accounts for about 6% of production; and the thermal process. Atmospheric pollutants from the thermal process are negligible since the exit gases which are rich in hydrogen are used as fuel in the process. In contrast, the pollutants emitted from the channel process are excessive and characterized by copious amounts of highly visible black smoke. Emissions from the furnace process consist of carbon dioxide, nitrogen, carbon monoxide, hydrogen, hydrocarbons, some particulate matter, and some sulfur compounds.

In the channel black process, natural gas is burned with a limited air supply in long low buildings containing 3000 to 4000 small burners. The flame impinges on long steel channel sections that swing continuously over the flame. Carbon black, deposited on the channels, is scraped off and falls into collecting hoppers. The combustion gases containing solid carbon not collected on the channels, in addition to carbon monoxide and other combustion products, are then vented directly from the building. Approximately 1 to 1.5 pounds of carbon black are produced from the 32 pounds of carbon available in 1000 ft^3 of natural gas.[1,2,3] The balance of the carbon is lost as CO, CO_2, hydrocarbons, and particulate.

The furnace process is sub-divided into either the gas or oil process depending on the primary fuel used to produce the carbon black. In either case, gas (gas process) or gas and oil (oil process) are injected into a reactor with a limited supply of combustion air. Common practice currently consists of also feeding some oil to the reactor in the gas process. This enrichment is on the order of 5.65 gallons of oil per 1000 ft^3 gas.[1] Part of the feed is burned with the combustion air to provide heat for decomposing the balance of the feed at a temperature of about 2600 - 2900°F. The combustion gases containing the hot carbon are then rapidly cooled to a temperature of about 500°F by water sprays and by radiant cooling. Yields of 10 to 30% are obtained in the gas process (i.e., 10 to 30% of the carbon in the feed is recovered as carbon black). Approximately 55% of the oil feed is recovered as carbon in the oil process.

The largest and most important portion of the furnace process consists of the particulate or carbon black removal equipment. While many combinations of control equipment exist, common practice as shown in Figure 4.3-1 is to provide an electrostatic precipitator, a cyclone, and a fabric filter system in series to collect the carbon black. In newer plants, the electrostatic precipitator may be omitted. In some older plants the final fabric filter system is not used, or a scrubber may be used in its place. Control of gaseous emissions of carbon monoxide and hydrocarbons is not practiced in the United States. Incineration of these gases is feasible, however, and is practiced in Great Britain.

In thermal black plants, natural gas is decomposed by heat in the absence of air or flame. In this cyclic operation, methane is pyrolyzed or decomposed by passing it over a heated brick checkerwork at a temperature of about 3000°F. ($CH_4 \rightarrow C + 2H_2$).

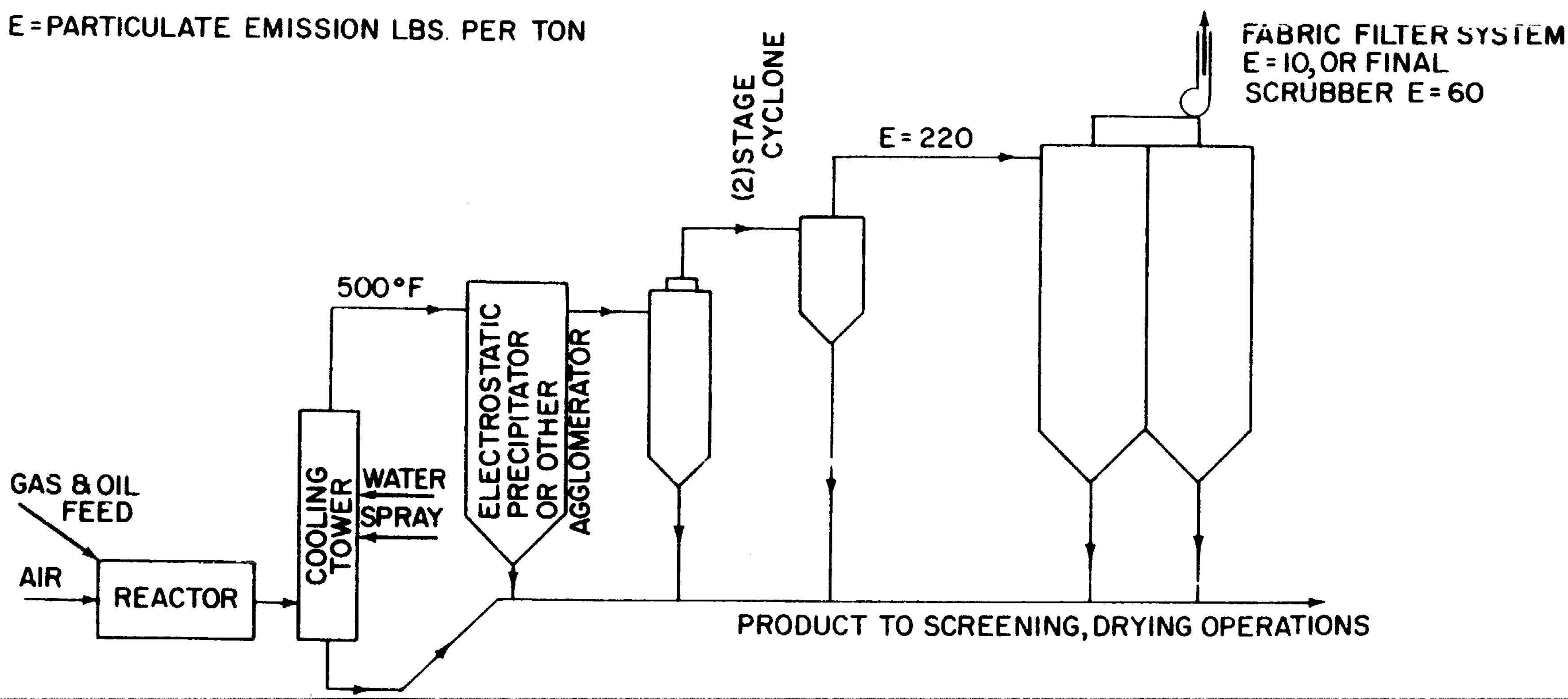

Figure 4.3-1. General process flow of furnace process carbon black manufacturing 1, 3.

This checkerwork is first heated by burning hydrogen generated in the decomposition reaction and/or by additional gas fuel. While one set of checkerwork is decomposing gas to produce carbon black, the other set is being heated. The gas flows are then switched and the heating/decomposition cycle is repeated. The decomposed gas is then cooled and the carbon black removed by a series of cyclones and fabric filters. The exit gas consisting largely of hydrogen (85%), methane (5%), and nitrogen is then recycled to the process burners or used to generate steam in a boiler. Due to the recycling of the effluent gases, there are essentially no atmospheric emissions from this process. Particulate emissions can, of course, occur from product handling.

Factors Affecting Emissions

The most important factor affecting emissions is the basic manufacturing process and its inherent efficiency. Thus, emissions from the channel black process are excessive, while those from the thermal process are negligible. Particulate emissions from the furnace process are affected by the type of control equipment used. Gaseous emissions are largely determined by the overall yield, type of fuel (that is, liquid or gas), the reaction time and temperature, the ratio of gas to oil in the feed, and the amount of combustion air.

Emissions

Table 4.3-1 presents the calculated emissions from the various carbon black processes. Nitrogen oxide emissions are not included since data are not available and they are believed to be low due to the lack of available oxygen in the reaction.

Table 4.3-1. Emissions From Carbon Black Manufacturing Processes, lbs/ton of product

Process	Particulate	CO	H_2S	HC[a]
Channel[f]	2300(2000 to 5000)	33,500 (26,000 to 44,000)	-	11,500(5000 to 15,[illegible]
Thermal	neg.	neg.	neg.	neg.
Furnace				
Gas	220[b] 60[c] 10[d]	5,300(4200 to 6400)	neg.	1,800
Oil		4,500(3600 to 5400)	38S[e]	400

a) As methane.

b) 90% overall collection efficiency, that is, no collection after cyclone.

c) 97% overall collection efficiency, that is, cyclones followed by scrubber.

d) 99.5% overall collection efficiency, that is, fabric filter system.

e) S = weight % sulfur in feed.

f) Based on yield of 1.5 pounds of carbon black per 1000 $ft.^3$ of gas feed.

Note: Emission ranges are due to variations in operating conditions and not any specific factors.

Trace quantities of carbonyl sulfide, thiophene and carbon disulfide have also been reported when oil is used in the feed. Most of the gas used in the carbon black industry is scrubbed to remove sulfur compounds. Oil feeds may, however, contain more than 1% of sulfur. When sulfur contents increase beyond about 1.2% by weight, additional H_2S is not produced and free sulfur is formed.

Additional emissions may occur from the grinding, screening, and drying operations at a carbon black plant. These emissions are usually controlled by a pneumatic system which exhausts into a bag filter system. However, poorly designed or maintained equipment can result in spills and leaks. Due to the variability of these emissions, no emission estimate is possible.

Reliability of Emission Factors

Factors for the channel black process are questionable due to a complete absence of emission data. Factors for furnace black plants are considered good since exit gas concentrations and considerable process throughput data were available. Table 4.3-2 presents the factor ranking.

Table 4.3-2. Carbon Black Emission Factor Ranking

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Channel Process	0	5	5	10
Furnace Process	7	8	8	23

No major assumptions were made in determining the emissions from the furnace process. For the channel black process, gaseous emissions were assumed to be similar in composition to those from the gas furnace process. Product yield was based on reported data, and the balance of the feed was lost to the atmosphere. Variations in emissions due to these assumptions are shown in Table 4.3-1.

APPENDIX 4.3

A. CARBON BALANCE TO ESTIMATE EXIT GAS VOLUMES - FURNACE PROCESS

1. Oil Furnace Process Input[1] (Intermediate super abrasion gra

220 gal oil/hr
12,200 ft^3 gas/hr
190,000 ft^3 air/hr

220 gal oil/hr x 7.1 lb/gal x .90 C = 1408 lbC/hr entering reactor in oil

12,200 ft^3 gas/hr x $\frac{12}{380}$ x .97 C = 374 lbC/hr entering reactor in gas

55% of oil feed is converted to carbon black.[1]

0.55 x 1408 = 774 lb carbon black produced

0.45 x 1408 = 634 lb carbon not converted to carbon black

634 lbs C from oil + 374 lbs C from gas = 1008 lbs C in ex

Exit gas carbon composition is:[1,4,5]

4.9% CO_2
11.4% CO
0.8% CH_4
0.5% C_2H_2

Exit gas rate may be calculated from carbon mass balance, namely:

$$(\%\ \text{Carbon})(\text{exit gas rate}) \times \frac{12\ \text{lbs/lb mol}}{380\ \text{ft}^3\text{/lb mol}} = \text{lbs carbon in exit gas}$$

Let Q = exit gas rate

$$\left[(0.049\,Q_{CO_2} + 0.114\,Q_{CO} + 0.008\,Q_{CH_4})\frac{12}{380}\right] + \left[0.005\,Q\frac{(24 \text{ lbs C/lb mol } C_2H_2)}{380 \text{ ft}^3\text{/lb mol}}\right]$$

= 1008 lbs carbon/hr

0.00534 Q + 0.00032 Q = 1008

Q = 180,000 ft^3/hr (dry basis rounded off)

= 3000 SCFM @ 60°F, dry basis

or 3000 SCFM per 774 lbs carbon black produced/hr

$\frac{3000}{0.774}$ = 3900 SCFM per 1000 lbs carbon black/hr dry basis (calculated).

Calculations based on data in article by Reinke and Ruble[4] gives 25,700 SCFM (wet) per 3000 lbs of product/hr, or

$\frac{25,700 \times .60\ H_2O \times 10^{-3}}{3000}$ = 5140 SCFM/1000 lb C/hr (dry)

Therefore use an average value of 4500 SCFM (dry basis) per 1000 lbs of carbon black produced or 9000 SCFM per ton of carbon black.

2. Gas Furnace Process[1]

560 ft^3/min of gas[a]

2520 ft^3/min of air

560 ft^3/min x $\frac{12}{380}$ x .97 x 60 min/hr = 1030 lb C/hr entering

a) Oil is sometimes added at the rate of 5.5 gallons per 1000 ft^3 of gas. This has very little effect on the overall emission rate per ton of product.

25% conversion to carbon black = 258 lb carbon black/hr pr

Lbs gaseous carbon in exit gas = (1030 - 258) = 772 lb/hr.

Exit gas carbon composition is (dry basis):

CO_2	5%
CO	5%
CH_4	1%
C_2H_2	1%

Let Q = ft^3/hr of exit gas flow

$$[(.05 + .05 + .01) \times \frac{12}{380}] Q + [.01 \times \frac{24}{380}] Q = 772 \text{ lbs carbon in exit gas}$$

$$.00348\ Q + .00063\ Q = 772$$

$$.00411\ Q = 772$$

$$Q = 187{,}000\ ft^3/hr \text{ (dry basis)}$$

$$= 3130 \text{ SCFM dry basis for 258 lb/hr of product}$$

For 1000 lbs of product, $\frac{3130}{.258}$ = 12,100 SCFM dry basis at 60

Use 24,000 SCFM/ton of carbon black.

B. GASEOUS EMISSIONS - FURNACE PROCESSES

Average Exit Gas Composition, percent by volume, dry basis.

	Oil Process[1,4,5]	Gas Process[1]
CO_2	4.9	5 ± 20%
CO	11.4	5 ± 20% (The range was estimated.)
CH_4	0.8	1
C_2H_2	0.5	1
H_2	13.5	17 - 18
H_2S	0.035	-
N_2	Balance	Balance

1. <u>Oil Process</u> - per ton of product

CO: $9000 \frac{ft^3}{min}$ (dry basis) x 60 min/hr x .114 x $\frac{28 \text{ lb/mol}}{380 \text{ ft}^3\text{/mol}}$

= 4550 lbs/ton

CH_4: 540,000 ft^3/hr x .008 x $\frac{16}{380}$ = 181 lbs/ton

C_2H_2: (expressed as CH_4): 540,000 ft^3/hr x .005 x $\frac{32}{380}$

= 228 lbs/ton

H_2S: 540,000 ft^3/hr x 0.00035 x $\frac{34}{380}$ = 16.9 lbs/ton

(See later calculation for H_2S emissions).

2. <u>Gas Process</u> - per ton of product

CO: 24,000 ft^3/min x 60 min/hr x .05 x $\frac{28}{380}$ = 5300 lbs/ton[a] ± 20%

CH_4: 1,440,000 ft^3/hr x .01 x $\frac{16}{380}$ = 606 lbs/ton[b]

C_2H_2: (as CH_4): 1,440,000 ft^3/hr x .01 x $\frac{32}{380}$ = 1212 lbs/ton[c]

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a) Represents 2280 lbs of carbon (5300 x 12/28), CO_2 also represents 2280 lbs of carbon

b) Represents 460 lbs of carbon

c) Represents 910 lbs of carbon

Nitrogen Oxide Emissions

Due to lack of oxygen in the high temperature zones, very little nitric oxide will form. No emission data are available.

Sulfur Emissions

Drogin reports 90% of S goes to effluent gas.[1] For low sulfur feeds this sulfur appears largely as H_2S, not SO_2. Free sulfur could also be formed but this would be collected as a particulate.

Based on 90% S emitted as H_2S, emission factor for oil process is:

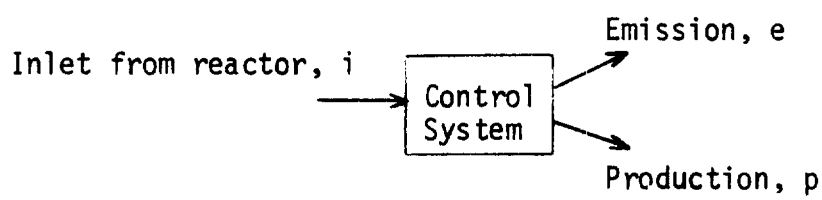
$$\frac{34\ H_2S}{32\ S} \times .90 \times \frac{S}{100} \times \frac{570 \text{ gal oil}}{\text{ton prod}} \times \frac{7.1 \text{ lb}}{\text{gal}} = 38.6S$$

Where S is weight % in feed

$$\frac{570 \text{ gal of oil}}{\text{ton}} = 220 \times \frac{2000 \text{ lbs/ton}}{774 \text{ lbs/220 gal}}$$

C. PARTICULATE EMISSIONS - FURNACE PROCESS - (either gas or oil)

Since production is the amount collected in the particulate control system, the efficiency of the control system can be mathematically related to the production:



$$i = e + p$$

$$E = \text{Collector Efficiency} = \frac{i - e}{i} = \frac{p}{i}$$

$$iE = i - e$$

$$i\,(1-E) = e$$

$$\text{and } i = \frac{p}{E}$$

$$\text{Therefore } e = \frac{p}{E}\,(1-E)$$

Particulate Emissions per ton of production are therefore:

@ 90% collection efficiency, that is, no collection after cyclone[1,4,5]

$$e = \frac{2000}{.90}\,(1 - .90) = 220 \text{ lbs/ton}$$

@ 97% collection efficiency, that is, with a scrubber following cyclone

$$e = \frac{2000}{.97}\,(1 - .97) = 61.9 \text{ lbs/ton}$$

@ 99.5% (good fabric filter system)

$$e = \frac{2000}{.995}\,(1 - .995) = 10.05 \text{ lbs/ton}$$

D. CHANNEL PROCESS

Yield is 1 to 1.5 lb per 1000 ft^3 of gas.[1,2]

1000 ft^3 gas contains about 32 lb of available carbon $(1000 \times \frac{12}{380} = 32 \text{ lb})$

Therefore 30.5 lbs of carbon are lost as particulate, CO_2, CO and hydrocarbons for each 1.5 lb of product (32-1.5 = 30.5).

Due to the higher excess air (open flame) less particulate is initially formed as compared to the furnace process, and more CO and CO_2 are formed.

In the gas furnace process about 25% of the feed (by weight) is converted to solid carbon. Assume in channel black process that about 10% of feed is converted to solid carbon and balance is split between CO, CO_2, and HC. For 1000 ft^3 of gas entering (32 lb carbon), 1.5 lb is product, and 1.7 lb is lost in smoke (3.2-1.5). This could vary up to 3-4 lbs, depending on amount of feed converted to solid carbon. Remaining 28.2 lb carbon (32-3.2) appears as a gas with the following assumed composition, based on gas furnace process:

38.4% of carbon appeared as CO_2 in the exit gas (probably varies from 30 to 50%)

38.4% of carbon appeared as CO in the exit gas (probably varies from 30 to 50%)

23.2% of carbon appeared as HC in the exit gas (probably varies from 10 to 30%)

on a lbs per ton basis:

$$1.7 \text{ lb part} \times \frac{2000 \text{ lb/ton}}{1.5 \text{ lb/product}} = 2{,}260 \text{ lb part/ton of product}$$ (200 to 5000)

$$28.2 \times \frac{2000}{1.5} \times 0.384 \times \frac{28}{12} = 33{,}600 \text{ lb CO/ton}$$ (Varies from 26,000 to 44,000)

$$28.2 \times \frac{2000}{1.5} \times 0.232 \times \frac{16}{12} = 11{,}500 \text{ lb } CH_4\text{/ton}$$ (Varies from 5,000 to 15,000)

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