

Note: This is an early version of the AP 42, *Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources*. EPA has made this available for historical reference purposes. The latest emission factors are available on the AP42 webpage.

The most recent updates to AP42 are located on the EPA web site at [www.epa.gov/ttn/chief/ap42/](http://www.epa.gov/ttn/chief/ap42/)

# **SUPPLEMENT NO. 7**

## **FOR**

# **COMPILATION OF AIR POLLUTANT EMISSION FACTORS**

## **SECOND EDITION**

**U.S. ENVIRONMENTAL PROTECTION AGENCY**

**Office of Air and Waste Management  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711**

**April 1977**

**INSTRUCTIONS  
FOR INSERTING SUPPLEMENT NO. 7  
INTO  
COMPILATION OF AIR POLLUTANT EMISSION FACTORS**

- Replace pages ii through xxi with new pages ii through xxiii.
- Replace pages 1.2-1 through 1.2-3 dated 4/73 with new pages 1.2-1 through 1.2-4 dated 4/77.
- Replace pages 1.3-1 through 1.3-2 dated 4/76 with new pages 1.3-1 through 1.3-2 dated 4/77.
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- Replace pages 8.15-1 through 8.15-2 dated 2/72 with new pages 8.15-1 through 8.15-5 dated 4/77.
- Replace pages 10.1-3 through 10.1-7 dated 5/74 with new pages 10.1-3 through 10.1-10 dated 4/77.
- Replace pages B-1 through B-4 dated 1/75 with new pages B-1 through B-5 dated 4/77.

## PREFACE

This document reports data available on those atmospheric emissions for which sufficient information exists to establish realistic emission factors. The information contained herein is based on Public Health Service Publication 999-AP-42, *Compilation of Air Pollutant Emission Factors*, by R.L. Duprey, and on three revised and expanded editions of *Compilation of Air Pollutant Emission Factors* that were published by the Environmental Protection Agency in February 1972, April 1973, and February 1976. This document is a reprint of the second edition and includes the supplements issued in July 1973, September 1973, July 1974, January 1975, December 1975, April 1976, and April 1977 (see page iv). It contains no new information not already presented in the previous issuances.

Chapters and sections of this document have been arranged in a format that permits easy and convenient replacement of material as information reflecting more accurate and refined emission factors is published and distributed. To speed dissemination of emission information, chapters or sections that contain new data will be issued—separate from the parent report—whenever they are revised.

To facilitate the addition of future materials, the punched, loose-leaf format was selected. This approach permits the document to be placed in a three-ring binder or to be secured by rings, rivets, or other fasteners; future supplements or revisions can then be easily inserted. The lower left- or right-hand corner of each page of the document bears a notation that indicates the date the information was issued.

Information on the availability of future supplements to *Compilation of Air Pollutant Emission Factors* can be obtained from the Environmental Protection Agency, Library Services, MD-35, Research Triangle Park, N.C. 27711 (Telephone: 919-549-8411 ext. 2777).

Comments and suggestions regarding this document should be directed to the attention of Director, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, Environmental Protection Agency, Research Triangle Park, N.C. 27711.

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Issuance	Release Date
Compilation of Air Pollutant Emission Factors (second edition)	4/73
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Section 4.3 Storage of Petroleum Products	
Section 4.4 Marketing and Transportation of Petroleum Products	
Supplement No. 2	9/73
Introduction	
Section 3.1.1 Average Emission Factors for Highway Vehicles	
Section 3.1.2 Light-Duty, Gasoline-Powered Vehicles	
Supplement No. 3	7/74
Introduction	
Section 1.4 Natural Gas Combustion	
Section 1.5 Liquefied Petroleum Gas Combustion	
Section 1.6 Wood/Bark Waste Combustion in Boilers	
Section 2.5 Sewage Sludge Incineration	
Section 7.6 Lead Smelting	
Section 7.11 Secondary Lead Smelting	
Section 10.1 Chemical Wood Pulping	
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- Section 2.4 Open Burning
- Section 3.3-2 Heavy-Duty, Natural-Gas-Fired Pipeline Compressor Engines
- Section 6.1 Alfalfa Dehydrating
- Section 6.12 Sugar Cane Processing
- Section 9.2 Natural Gas Processing
- Section 10.4 Woodworking Operations

**Supplement to No. 7**

4/77

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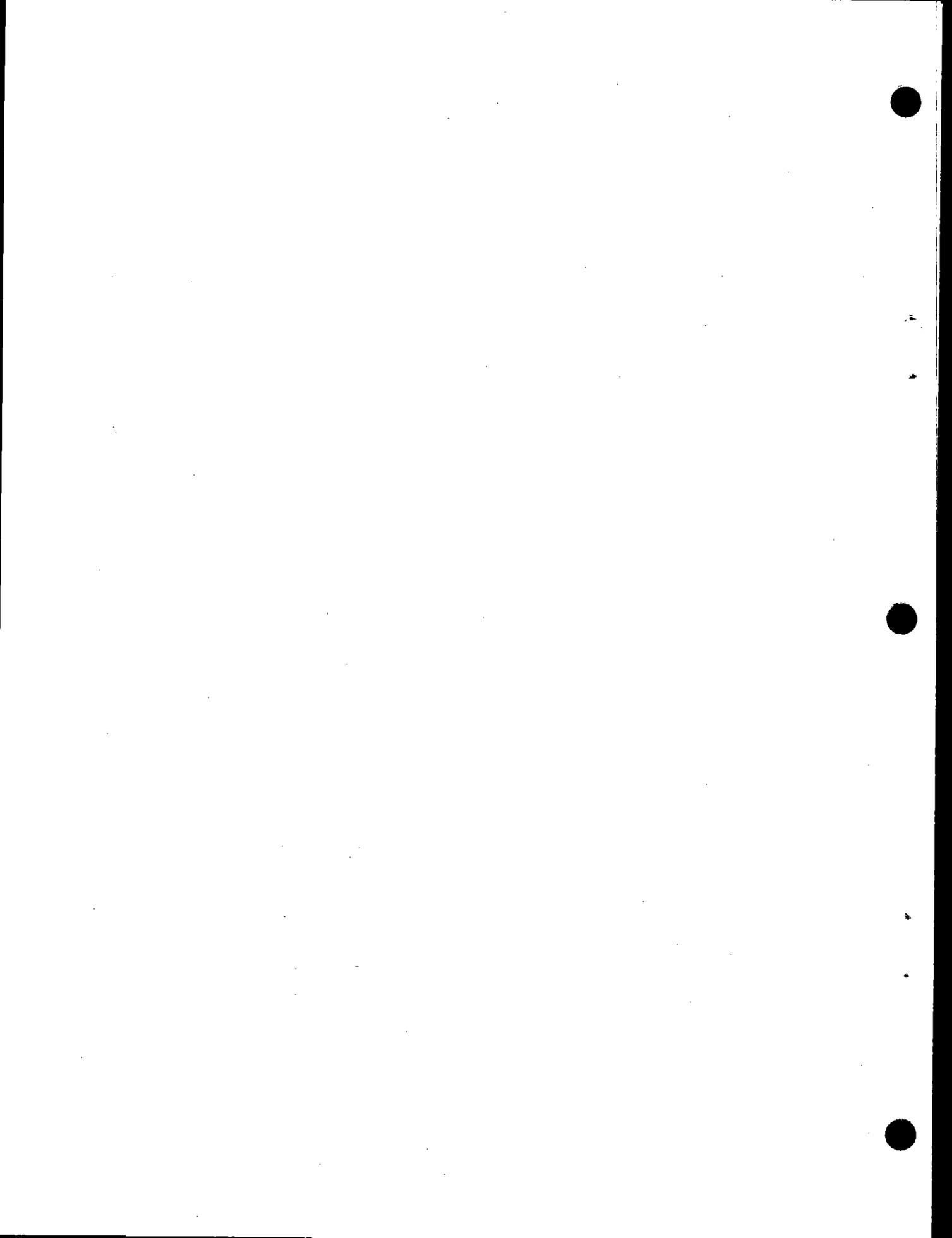
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## ABSTRACT

Emission data obtained from source tests, material balance studies, engineering estimates, etc., have been compiled for use by individuals and groups responsible for conducting air pollution emission inventories. Emission factors given in this document, the result of the expansion and continuation of earlier work, cover most of the common emission categories: fuel combustion by stationary and mobile sources; combustion of solid wastes; evaporation of fuels, solvents, and other volatile substances; various industrial processes; and miscellaneous sources. When no source-test data are available, these factors can be used to estimate the quantities of primary pollutants (particulates, CO, SO<sub>2</sub>, NO<sub>x</sub>, and hydrocarbons) being released from a source or source group.

**Key words:** fuel combustion, stationary sources, mobile sources, industrial processes, evaporative losses, emissions, emission data, emission inventories, primary pollutants, emission factors.



## 1.2 ANTHRACITE COAL COMBUSTION

*revised by Tom Lahre*

### 1.2.1 General<sup>1,2</sup>

Anthracite is a high-rank coal having a high fixed-carbon content and low volatile-matter content relative to bituminous coal and lignite. It is also characterized by higher ignition and ash fusion temperatures. Because of its low volatile-matter content and non-clinkering characteristics, anthracite is most commonly fired in medium-sized traveling-grate stokers and small hand-fired units. Some anthracite (occasionally along with petroleum coke) is fired in pulverized-coal-fired boilers. None is fired in spreader stokers. Because of its low sulfur content (typically less than 0.8 percent, by weight) and minimal smoking tendencies, anthracite is considered a desirable fuel where readily available.

In the United States, all anthracite is mined in Northeastern Pennsylvania and consumed primarily in Pennsylvania and several surrounding states. The largest use of anthracite is for space heating; lesser amounts are employed for steam-electric production, coke manufacturing, sintering and pelletizing, and other industrial uses. Anthracite combustion currently represents only a small fraction of the total quantity of coal combusted in the United States.

### 1.2.2 Emissions and Controls<sup>2-9</sup>

Particulate emissions from anthracite combustion are a function of furnace-firing configuration, firing practices (boiler load, quantity and location of underfire air, sootblowing, flyash reinjection, etc.), as well as of the ash content of the coal. Pulverized-coal-fired boilers emit the highest quantity of particulate per unit of fuel because they fire the anthracite in suspension, which results in a high percentage of ash carryover into the exhaust gases. Traveling-grate stokers and hand-fired units, on the other hand, produce much less particulate per unit of fuel fired. This is because combustion takes place in a quiescent fuel bed and does not result in significant ash carryover into the exhaust gases. In general, particulate emissions from traveling-grate stokers will increase during sootblowing, flyash reinjection, and with higher underfeed air rates through the fuel bed. Higher underfeed air rates, in turn, result from higher grate loadings and the use of forced-draft fans rather than natural draft to supply combustion air. Smoking is rarely a problem because of anthracite's low volatile-matter content.

Limited data are available on the emission of gaseous pollutants from anthracite combustion. It is assumed, based on data derived from bituminous coal combustion, that a large fraction of the fuel sulfur is emitted as sulfur oxides. Moreover, because combustion equipment, excess air rates, combustion temperatures, etc., are similar between anthracite and bituminous coal combustion, nitrogen oxide and carbon monoxide emissions are assumed to be similar, as well. On the other hand, hydrocarbon emissions are expected to be considerably lower because the volatile-matter content of anthracite is significantly less than that of bituminous coal.

Air pollution control of emissions from anthracite combustion has mainly been limited to particulate matter. The most efficient particulate controls--fabric filters, scrubbers, and electrostatic precipitators--have been installed on large pulverized-anthracite-fired boilers. Fabric filters and venturi scrubbers can effect collection efficiencies exceeding 99 percent. Electrostatic precipitators, on the other hand, are typically only 90 to 97 percent efficient due to the characteristic high resistivity of the low-sulfur anthracite flyash. Higher efficiencies can reportedly be achieved using larger precipitators and flue gas conditioning. Mechanical collectors are frequently employed upstream from these devices for large-particle removal.

Traveling-grate stokers are often uncontrolled. Indeed, particulate control has often been considered unnecessary because of anthracite's low smoking tendencies and due to the fact that a significant fraction of the large-sized flyash from stokers is readily collected in flyash hoppers as well as in the breeching and base of the stack. Cyclone collectors have been employed on traveling-grate stokers;

limited information suggests these devices may be up to 75 percent efficient on particulate. Flyash reinjection, frequently employed in traveling-grate stokers to enhance fuel-use efficiency, tends to increase particulate emissions per unit of fuel combusted.

Emission factors for anthracite combustion are presented in Table 1.2-1.

Table 1.2-1. EMISSION FACTORS FOR ANTHRACITE COMBUSTION, BEFORE CONTROLS  
EMISSION FACTOR RATING: B

Type of furnace	Emissions <sup>a</sup>									
	Particulate		Sulfur oxides <sup>b</sup>		Hydrocarbons <sup>c</sup>		Carbon monoxide <sup>d</sup>		Nitrogen oxides <sup>e</sup>	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Pulverized coal	17A <sup>f</sup>	8.5A <sup>f</sup>	38S	19S	Neg	Neg	1	0.5	18	9
Traveling grate	1A <sup>g</sup>	0.5A <sup>g</sup>	38S	19S	Neg	Neg	1	0.5	10	5
Hand-fired	10 <sup>h</sup>	5 <sup>h</sup>	38S	19S	2.5	1.25	90	45	3	1.5

<sup>a</sup>All emission factors are per unit of anthracite fired.

<sup>b</sup>These factors are based on the assumption that, as with bituminous coal combustion, most of the fuel sulfur is emitted as sulfur oxides. Limited data in Reference 5 verify this assumption for pulverized-anthracite-fired boilers. Generally most of these emissions are sulfur dioxide; however, approximately 1 to 3 percent are sulfur trioxide.

<sup>c</sup>Hydrocarbon emissions from anthracite combustion are assumed to be lower than from bituminous coal combustion because of anthracite's much lower volatile-matter content. No emissions data are available to verify this assumption.

<sup>d</sup>The carbon monoxide factors for pulverized-anthracite-fired boilers and hand-fired units are from Table 1.1-2 and are based on the similarity between anthracite and bituminous coal combustion. The pulverized-coal-fired boilers factor is substantiated by additional data in Reference 10. The factor for traveling-grate stokers is based on limited information in Reference 8. Carbon monoxide emissions may increase by several orders of magnitude if a boiler is not properly operated or well maintained.

<sup>e</sup>The nitrogen oxide factors for pulverized-anthracite-fired boilers and hand-fired units are assumed to be similar to those for bituminous coal combustion given in Table 1.1-2. The factors for traveling-grate stokers are based on Reference 8.

<sup>f</sup>These factors are based on the similarity between anthracite and bituminous coal combustion and on limited data in Reference 5. Note that all pulverized-anthracite-fired boilers operate in the dry tap or dry bottom mode due to anthracite's characteristically high ash-fusion temperature. The letter A on units other than hand-fired equipment indicates that the weight percentage of ash in the coal should be multiplied by the value given.

<sup>g</sup>Based on information in References 2,4,8, and 9. These factors account for limited fallout that may occur in fallout chambers and stack breeching. Emission factors for individual boilers may vary from 0.5A lb/ton (0.25A kg/MT) to 3A lb/ton (1.5A kg/MT), and as high as 5A lb/ton (2.5A kg/MT) during soot blowing.

<sup>h</sup>Based on limited information in Reference 2.

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1.3.1 General<sup>1,2</sup>

Fuel oils are broadly classified into two major types: distillate and residual. Distillate oils (fuel oil grades 1 and 2) are used mainly in domestic and small commercial applications in which easy fuel burning is required. Distillates are more volatile and less viscous than residual oils as well as cleaner, having negligible ash and nitrogen contents and usually containing less than 0.3 percent sulfur (by weight). Residual oils (fuel oil grades 4, 5, and 6), on the other hand, are used mainly in utility, industrial, and large commercial applications in which sophisticated combustion equipment can be utilized. (Grade 4 oil is sometimes classified as a distillate; grade 6 is sometimes referred to as Bunker C.) Being more viscous and less volatile than distillate oils, the heavier residual oils (grades 5 and 6) must be heated for ease of handling and to facilitate proper atomization. Because residual oils are produced from the residue left over after the lighter fractions (gasoline, kerosene, and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur. Properties of typical fuel oils are given in Appendix A.

## 1.3.2 Emissions

Emissions from fuel oil combustion are dependent on the grade and composition of the fuel, the type and size of the boiler, the firing and loading practices used, and the level of equipment maintenance. Table 1.3-1 presents emission factors for fuel oil combustion in units without control equipment. Note that the emission factors for industrial and commercial boilers are divided into distillate and residual oil categories because the combustion of each produces significantly different emissions of particulates,  $SO_x$ , and  $NO_x$ . The reader is urged to consult the references cited for a detailed discussion of all of the parameters that affect emissions from oil combustion.

1.3.2.1 Particulates<sup>3-6, 12, 13</sup> – Particulate emissions are most dependent on the grade of fuel fired. The lighter distillate oils result in significantly lower particulate formation than do the heavier residual oils. Among residual oils, grades 4 and 5 usually result in less particulate than does the heavier grade 6.

In boilers firing grade 6, particulate emissions can be described, on the average, as a function of the sulfur content of the oil. As shown in Table 1.3-1 (footnote c), particulate emissions can be reduced considerably when low-sulfur grade 6 oil is fired. This is because low-sulfur grade 6, whether refined from naturally occurring low-sulfur crude oil or desulfurized by one of several processes currently in practice, exhibits substantially lower viscosity and reduced asphaltene, ash, and sulfur content – all of which result in better atomization and cleaner combustion.

Boiler load can also affect particulate emissions in units firing grade 6 oil. At low load conditions, particulate emissions may be lowered by 30 to 40 percent from utility boilers and by as much as 60 percent from small industrial and commercial units. No significant particulate reductions have been noted at low loads from boilers firing any of the lighter grades, however. At too low a load condition, proper combustion conditions cannot be maintained and particulate emissions may increase drastically. It should be noted, in this regard, that any condition that prevents proper boiler operation can result in excessive particulate formation.

1.3.2.2 Sulfur Oxides ( $SO_x$ )<sup>1-5</sup> – Total sulfur oxide emissions are almost entirely dependent on the sulfur content of the fuel and are not affected by boiler size, burner design, or grade of fuel being fired. On the average, more than 95 percent of the fuel sulfur is converted to  $SO_2$ , with about 1 to 3 percent further oxidized to  $SO_3$ . Sulfur trioxide readily reacts with water vapor (both in the air and in the flue gases) to form a sulfuric acid mist.

Table 1.3-1. EMISSION FACTORS FOR FUEL OIL COMBUSTION  
EMISSION FACTOR RATING: A

Pollutant	Type of boiler <sup>a</sup>							
	Power plant		Industrial and commercial				Domestic	
	Residual oil		Residual oil		Distillate oil		Distillate oil	
	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liter	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liter	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liter	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liter
Particulate <sup>b</sup>	c	c	c	c	2	0.25	2.5	0.31
Sulfur dioxide <sup>d</sup>	157S	19S	157S	19S	142S	17S	142S	17S
Sulfur trioxide <sup>d</sup>	2S	0.25S	2S	0.25S	2S	0.25S	2S	0.25S
Carbon monoxide <sup>e</sup>	5	0.63	5	0.63	5	0.63	5	0.63
Hydrocarbons (total, as CH <sub>4</sub> ) <sup>f</sup>	1	0.12	1	0.12	1	0.12	1	0.12
Nitrogen oxides (total, as NO <sub>2</sub> ) <sup>g</sup>	105(50) <sup>h,i</sup>	12.6(6.25) <sup>h,i</sup>	60 <sup>j</sup>	7.5 <sup>j</sup>	22	2.8	18	2.3

<sup>a</sup>Boilers can be classified, roughly, according to their gross (higher) heat input rate, as shown below.

Power plant (utility) boilers:  $>250 \times 10^6$  Btu/hr  
( $>63 \times 10^6$  kg-cal/hr)

Industrial boilers:  $>15 \times 10^6$ , but  $<250 \times 10^6$  Btu/hr  
( $>3.7 \times 10^6$ , but  $<63 \times 10^6$  kg-cal/hr)

Commercial boilers:  $>0.5 \times 10^6$ , but  $<15 \times 10^6$  Btu/hr  
( $>0.13 \times 10^6$ , but  $<3.7 \times 10^6$  kg-cal/hr)

Domestic (residential) boilers:  $<0.5 \times 10^6$  Btu/hr  
( $<0.13 \times 10^6$  kg-cal/hr)

<sup>b</sup>Based on References 3 through 6. Particulate is defined in this section as that material collected by EPA Method 5 (front half catch)<sup>7</sup>.

<sup>c</sup>Particulate emission factors for residual oil combustion are best described, on the average, as a function of fuel oil grade and sulfur content, as shown below.

Grade 6 oil: lb/10<sup>3</sup> gal = 10 (S) + 3  
(kg/10<sup>3</sup> liter = 1.25 (S) + 0.38)

Where: S is the percentage, by weight, of sulfur in the oil

Grade 5 oil: 10 lb/10<sup>3</sup> gal (1.25 kg/10<sup>3</sup> liter)

Grade 4 oil: 7 lb/10<sup>3</sup> gal (0.88 kg/10<sup>3</sup> liter)

<sup>d</sup>Based on References 1 through 5. S is the percentage, by weight, of sulfur in the oil.

<sup>e</sup>Based on References 3 through 5 and 8 through 10. Carbon monoxide emissions may increase by a factor of 10 to 100 if a unit is improperly operated or not well maintained.

<sup>f</sup>Based on References 1, 3 through 5, and 10. Hydrocarbon emissions are generally negligible unless unit is improperly operated or not well maintained, in which case emissions may increase by several orders of magnitude.

<sup>g</sup>Based on References 1 through 5 and 8 through 11.

<sup>h</sup>Use 50 lb/10<sup>3</sup> gal (6.25 kg/10<sup>3</sup> liter) for tangentially fired boilers and 105 lb/10<sup>3</sup> gal (12.6 kg/10<sup>3</sup> liter) for all others, at full load, and normal (>15 percent) excess air. At reduced loads, NO<sub>x</sub> emissions are reduced by 0.5 to 1 percent, on the average, for every percentage reduction in boiler load.

<sup>i</sup>Several combustion modifications can be employed for NO<sub>x</sub> reduction: (1) limited excess air firing can reduce NO<sub>x</sub> emissions by 5 to 30 percent, (2) staged combustion can reduce NO<sub>x</sub> emissions by 20 to 45 percent, and (3) flue gas recirculation can reduce NO<sub>x</sub> emissions by 10 to 45 percent. Combinations of the modifications have been employed to reduce NO<sub>x</sub> emissions by as much as 60 percent in certain boilers. See section 1.4 for a discussion of these NO<sub>x</sub>-reducing techniques.

<sup>j</sup>Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are strongly dependent on the fuel nitrogen content and can be estimated more accurately by the following empirical relationship:

lb NO<sub>2</sub>/10<sup>3</sup> gal = 22 + 400 (N)<sup>2</sup>  
(kg NO<sub>2</sub>/10<sup>3</sup> liters = 2.75 + 50 (N)<sup>2</sup>)

Where: N is the percentage, by weight, of nitrogen in the oil. Note: For residual oils having high (>0.5%, by weight) nitrogen contents, one should use 120 lb NO<sub>2</sub>/10<sup>3</sup> gal (15 kg NO<sub>2</sub>/10<sup>3</sup> liter) as an emission factor.

## 1.5 LIQUEFIED PETROLEUM GAS COMBUSTION

*Revised by Thomas Lahre*

### 1.5.1 General<sup>1</sup>

Liquefied petroleum gas, commonly referred to as LPG, consists mainly of butane, propane, or a mixture of the two, and of trace amounts of propylene and butylene. This gas, obtained from oil or gas wells as a by-product of gasoline refining, is sold as a liquid in metal cylinders under pressure and, therefore, is often called bottled gas. LPG is graded according to maximum vapor pressure with Grade A being predominantly butane, Grade F being predominantly propane, and Grades B through E consisting of varying mixtures of butane and propane. The heating value of LPG ranges from 97,400 Btu/gallon (6,480 kcal/liter) for Grade A to 90,500 Btu/gallon (6,030 kcal/liter) for Grade F. The largest market for LPG is the domestic-commercial market, followed by the chemical industry and the internal combustion engine.

### 1.5.2 Emissions<sup>1</sup>

LPG is considered a "clean" fuel because it does not produce visible emissions. Gaseous pollutants such as carbon monoxide, hydrocarbons, and nitrogen oxides do occur, however. The most significant factors affecting these emissions are the burner design, adjustment, and venting.<sup>2</sup> Improper design, blocking and clogging of the flue vent, and lack of combustion air result in improper combustion that causes the emission of aldehydes, carbon monoxide, hydrocarbons, and other organics. Nitrogen oxide emissions are a function of a number of variables including temperature, excess air, and residence time in the combustion zone. The amount of sulfur dioxide emitted is directly proportional to the amount of sulfur in the fuel. Emission factors for LPG combustion are presented in Table 1.5-1.

### References for Section 1.5

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.
2. Clifford, E.A. A Practical Guide to Liquefied Petroleum Gas Utilization. New York, Moore Publishing Co. 1962.

Table 1.5-1. EMISSION FACTORS FOR LPG COMBUSTION<sup>a</sup>  
EMISSION FACTOR RATING: C

Pollutant	Industrial process furnaces				Domestic and commercial furnaces			
	Butane		Propane		Butane		Propane	
	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liters	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liters	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liters	lb/10 <sup>3</sup> gal	kg/10 <sup>3</sup> liters
Particulates	1.8	0.22	1.7	0.20	1.9	0.23	1.8	0.22
Sulfur oxides <sup>b</sup>	0.09S	0.01S	0.09S	0.01S	0.09S	0.01S	0.09S	0.01S
Carbon monoxide	1.6	0.19	1.5	0.18	2.0	0.24	1.9	0.23
Hydrocarbons	0.3	0.036	0.3	0.036	0.8	0.096	0.7	0.084
Nitrogen oxides <sup>c</sup>	12.1	1.45	11.2	1.35	(8 to 12) <sup>d</sup>	(1.0 to 1.5) <sup>d</sup>	(7 to 11) <sup>d</sup>	(0.8 to 1.3) <sup>d</sup>

<sup>a</sup>LPG emission factors calculated assuming emissions (excluding sulfur oxides) are the same, on a heat input basis, as for natural gas combustion.

<sup>b</sup>S equals sulfur content expressed in grains per 100 ft<sup>3</sup> gas vapor; e.g., if the sulfur content is 0.16 grain per 100 ft<sup>3</sup> (0.366 g/100 m<sup>3</sup>) vapor, the SO<sub>2</sub> emission factor would be 0.09 x 0.16 or 0.014 lb SO<sub>2</sub> per 1000 gallons (0.01 x 0.366 or 0.0018 kg SO<sub>2</sub>/10<sup>3</sup> liters) butane burned.

<sup>c</sup>Expressed as NO<sub>2</sub>.

<sup>d</sup>Use lower value for domestic units and higher value for commercial units.

## 1.8 BAGASSE COMBUSTION IN SUGAR MILLS

by Tom Lahre

### 1.8.1 General<sup>1</sup>

Bagasse is the fibrous residue from sugar cane that has been processed in a sugar mill. (See Section 6.12 for a brief general description of sugar cane processing.) It is fired in boilers to eliminate a large solid waste disposal problem and to produce steam and electricity to meet the mill's power requirements. Bagasse represents about 30 percent of the weight of the raw sugar cane. Because of the high moisture content (usually at least 50 percent, by weight) a typical heating value of wet bagasse will range from 3000 to 4000 Btu/lb (1660 to 2220 kcal/kg). Fuel oil may be fired with bagasse when the mill's power requirements cannot be met by burning only bagasse or when bagasse is too wet to support combustion.

The United States sugar industry is located in Florida, Louisiana, Hawaii, Texas, and Puerto Rico. Except in Hawaii, where raw sugar production takes place year round, sugar mills operate seasonally, from 2 to 5 months per year.

Bagasse is commonly fired in boilers employing either a solid hearth or traveling grate. In the former, bagasse is gravity fed through chutes and forms a pile of burning fibers. The burning occurs on the surface of the pile with combustion air supplied through primary and secondary ports located in the furnace walls. This kind of boiler is common in older mills in the sugar cane industry. Newer boilers, on the other hand, may employ traveling-grate stokers. Underfire air is used to suspend the bagasse, and overfired air is supplied to complete combustion. This kind of boiler requires bagasse with a higher percentage of fines, a moisture content not over 50 percent, and more experienced operating personnel.

### 1.8.2 Emissions and Controls<sup>1</sup>

Particulate is the major pollutant of concern from bagasse boilers. Unless an auxiliary fuel is fired, few sulfur oxides will be emitted because of the low sulfur content (<0.1 percent, by weight) of bagasse. Some nitrogen oxides are emitted, although the quantities appear to be somewhat lower (on an equivalent heat input basis) than are emitted from conventional fossil fuel boilers.

Particulate emissions are reduced by the use of multi-cyclones and wet scrubbers. Multi-cyclones are reportedly 20 to 60 percent efficient on particulate from bagasse boilers, whereas scrubbers (either venturi or the spray impingement type) are usually 90 percent or more efficient. Other types of control equipment have been investigated but have not been found to be practical.

Emission factors for bagasse fired boilers are shown in Table 1.8-1.

**Table 1.8-1. EMISSION FACTORS FOR UNCONTROLLED BAGASSE BOILERS  
EMISSION FACTOR RATING: C**

	Emission factors			
	lb/10 <sup>3</sup> lb steam <sup>a</sup>	g/kg steam <sup>a</sup>	lb/ton bagasse <sup>b</sup>	kg/MT bagasse <sup>b</sup>
Particulate <sup>c</sup>	4	4	16	8
Sulfur oxides	d	d	d	d
Nitrogen oxides <sup>e</sup>	0.3	0.3	1.2	0.6

<sup>a</sup> Emission factors are expressed in terms of the amount of steam produced, as most mills do not monitor the amount of bagasse fired. These factors should be applied only to that fraction of steam resulting from bagasse combustion. If a significant amount (>25% of total Btu input) of fuel oil is fired with the bagasse, the appropriate emission factors from Table 1.3-1 should be used to estimate the emission contributions from the fuel oil.

<sup>b</sup> Emissions are expressed in terms of wet bagasse, containing approximately 50 percent moisture, by weight. As a rule of thumb, about 2 pounds (2 kg) of steam are produced from 1 pound (1 kg) of wet bagasse.

<sup>c</sup> Multi-cyclones are reportedly 20 to 60 percent efficient on particulate from bagasse boilers. Wet scrubbers are capable of effecting 90 or more percent particulate control. Based on Reference 1.

<sup>d</sup> Sulfur oxide emissions from the firing of bagasse alone would be expected to be negligible as bagasse typically contains less than 0.1 percent sulfur, by weight. If fuel oil is fired with bagasse, the appropriate factors from Table 1.3-1 should be used to estimate sulfur oxide emissions.

<sup>e</sup> Based on Reference 1.

### Reference for Section 1.8

1. **Background Document: Bagasse Combustion in Sugar Mills.** Prepared by Environmental Science and Engineering, Inc., Gainesville, Fla., for Environmental Protection Agency under Contract No. 68-02-1402, Task Order No. 13. Document No. EPA-450/3-77-007. Research Triangle Park, N.C. October 1976.

### 1.9.1 General<sup>1,2</sup>

Fireplaces are utilized mainly in homes, lodges, etc., for supplemental heating and for their aesthetic effect. Wood is most commonly burned in fireplaces; however, coal, compacted wood waste "logs," paper, and rubbish may all be burned at times. Fuel is generally added to the fire by hand on an intermittent basis.

Combustion generally takes place on a raised grate or on the floor of the fireplace. Combustion air is supplied by natural draft, and may be controlled, to some extent, by a damper located in the chimney directly above the firebox. It is common practice for dampers to be left completely open during the fire, affording little control of the amount of air drawn up the chimney.

Most fireplaces heat a room by radiation, with a significant fraction of the heat released during combustion (estimated at greater than 70 percent) lost in the exhaust gases or through the fireplace walls. In addition, as with any fuel-burning, space-heating device, some of the resulting heat energy must go toward warming the air that infiltrates into the residence to make up for the air drawn up the chimney. The net effect is that fireplaces are extremely inefficient heating devices. Indeed, in cases where combustion is poor, where the outside air is cold, or where the fire is allowed to smolder (thus drawing air into a residence without producing appreciable radiant heat energy) a net heat loss may occur in a residence due to the use of a fireplace. Fireplace efficiency may be improved by a number of devices that either reduce the excess air rate or transfer some of the heat back into the residence that is normally lost in the exhaust gases or through the fireplace walls.

### 1.9.2 Emissions<sup>1,2</sup>

The major pollutants of concern from fireplaces are unburnt combustibles—carbon monoxide and smoke. Significant quantities of these pollutants are produced because fireplaces are grossly inefficient combustion devices due to high, uncontrolled excess air rates, low combustion temperatures, and the absence of any sort of secondary combustion. The last of these is especially important when burning wood because of its typically high (80 percent, on a dry weight basis)<sup>3</sup> volatile matter content.

Because most wood contains negligible sulfur, very few sulfur oxides are emitted. Sulfur oxides will be produced, of course, when coal or other sulfur-bearing fuels are burned. Nitrogen oxide emissions from fireplaces are expected to be negligible because of the low combustion temperatures involved.

Emission factors for wood and coal combustion in residential fireplaces are given in Table 1.9-1.

**Table 1.9-1. EMISSION FACTORS FOR RESIDENTIAL FIREPLACES  
EMISSION FACTOR RATING: C**

Pollutant	Wood		Coal <sup>a</sup>	
	lb/ton	kg/MT	lb/ton	kg/MT
Particulate	20 <sup>b</sup>	10 <sup>b</sup>	30 <sup>c</sup>	15 <sup>c</sup>
Sulfur oxides	0 <sup>d</sup>	0 <sup>d</sup>	36S <sup>e</sup>	36S <sup>e</sup>
Nitrogen oxides	1 <sup>f</sup>	0.5 <sup>f</sup>	3	1.5
Hydrocarbons	5 <sup>g</sup>	2.5 <sup>g</sup>	20	10
Carbon monoxide	120 <sup>h</sup>	60 <sup>h</sup>	90	45

<sup>a</sup>All coal emission factors, except particulate, are based on data in Table 1.1-2 of Section 1.1 for hand-fired units.

<sup>b</sup>This includes condensable particulate. Only about 30 percent of this is filterable particulate as determined by EPA Method 5 (front-half catch).<sup>4</sup> Based on limited data from Reference 1.

<sup>c</sup>This includes condensable particulate. About 50 percent of this is filterable particulate as determined by EPA Method 5 (front-half catch).<sup>4</sup> Based on limited data from Reference 1.

<sup>d</sup>Based on negligible sulfur content in most wood.<sup>3</sup>

<sup>e</sup>S is the sulfur content, on a weight percent basis, of the coal.

<sup>f</sup>Based on data in Table 2.3-1 in Section 2.3 for wood waste combustion in conical burners.

<sup>g</sup>Nonmethane volatile hydrocarbons. Based on limited data from Reference 1.

<sup>h</sup>Based on limited data from Reference 1.

## References for Section 1.9

1. Snowden, W.D., et al. Source Sampling Residential Fireplaces for Emission Factor Development. Valentine, Fisher and Tomlinson. Seattle, Washington. Prepared for Environmental Protection Agency, Research Triangle Park, N.C., under Contract 68-02-1992. Publication No. EPA-450/3-76-010. November 1975.
2. Snowden, W.D., and I.J. Primplani. Atmospheric Emissions From Residential Space Heating. Presented at the Pacific Northwest International Section of the Air Pollution Control Association Annual Meeting. Boise, Idaho. November 1974.
3. Kreisinger, Henry. Combustion of Wood-Waste Fuels. Mechanical Engineering. 61:115, February 1939.
4. Title 40 - Protection of Environment. Part 60: Standards of Performance for New Stationary Sources. Method 5 - Determination of Emission from Stationary Sources. Federal Register. 36 (247): 24888-24890, December 23, 1971.

## 2.4 OPEN BURNING

revised by Tom Lahre  
and Pam Canova

### 2.4.1 General<sup>1</sup>

Open burning can be done in open drums or baskets, in fields and yards, and in large open dumps or pits. Materials commonly disposed of in this manner are municipal waste, auto body components, landscape refuse, agricultural field refuse, wood refuse, bulky industrial refuse, and leaves.

### 2.4.2 Emissions<sup>1-19</sup>

Ground-level open burning is affected by many variables including wind, ambient temperature, composition and moisture content of the debris burned, and compactness of the pile. In general, the relatively low temperatures associated with open burning increase the emission of particulates, carbon monoxide, and hydrocarbons and suppress the emission of nitrogen oxides. Sulfur oxide emissions are a direct function of the sulfur content of the refuse. Emission factors are presented in Table 2.4-1 for the open burning of municipal refuse and automobile components.

Table 2.4-1. EMISSION FACTORS FOR OPEN BURNING OF NONAGRICULTURAL MATERIAL  
EMISSION FACTOR RATING: B

	Particulates	Sulfur oxides	Carbon monoxide	Hydrocarbons (CH <sub>4</sub> )	Nitrogen oxides
Municipal refuse <sup>a</sup>					
lb/ton	16	1	85	30	6
kg/MT	8	0.5	42	15	3
Automobile components <sup>b,c</sup>					
lb/ton	100	Neg.	125	30	4
kg/MT	50	Neg.	62	15	2

<sup>a</sup>References 2 through 6.

<sup>b</sup>Upholstery, belts, hoses, and tires burned in common.

<sup>c</sup>Reference 2.

Emissions from agricultural refuse burning are dependent mainly on the moisture content of the refuse and, in the case of the field crops, on whether the refuse is burned in a headfire or a backfire. (Headfires are started at the upwind side of a field and allowed to progress in the direction of the wind, whereas backfires are started at the downwind edge and forced to progress in a direction opposing the wind.) Other variables such as fuel loading (how much refuse material is burned per unit of land area) and how the refuse is arranged (that is, in piles, rows, or spread out) are also important in certain instances. Emission factors for open agricultural burning are presented in Table 2.4-2 as a function of refuse type and also, in certain instances, as a function of burning techniques and/or moisture content when these variables are known to significantly affect emissions. Table 2.4-2 also presents typical fuel loading values associated with each type of refuse. These values can be used, along with the corresponding emission factors, to estimate emissions from certain categories of agricultural burning when the specific fuel loadings for a given area are not known.

Emissions from leaf burning are dependent upon the moisture content, density, and ignition location of the leaf piles. Increasing the moisture content of the leaves generally increases the amount of carbon monoxide, hydrocarbon, and particulate emissions. Increasing the density of the piles increases the amount of hydrocarbon and particulate emissions, but has a variable effect on carbon

**Table 2.4-2. EMISSION FACTORS AND FUEL LOADING FACTORS FOR OPEN BURNING  
OF AGRICULTURAL MATERIALS<sup>a</sup>  
EMISSION FACTOR RATING: B**

Refuse category	Emission factors						Fuel loading factors (waste production)	
	Particulate <sup>b</sup>		Carbon monoxide		Hydrocarbons (as C <sub>6</sub> H <sub>14</sub> )			
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	ton/acre	MT/hectare
Field crops <sup>c</sup>								
Unspecified Burning technique not significant <sup>d</sup>	21	11	117	58	23	12	2.0	4.5
Asparagus <sup>e</sup>	40	20	150	75	85	42	1.5	3.4
Barley	22	11	157	78	19	10	1.7	3.8
Corn	14	7	108	54	16	8	4.2	9.4
Cotton	8	4	176	88	6	3	1.7	3.8
Grasses	16	8	101	50	19	10		
Pineapple <sup>f</sup>	8	4	112	56	8	4		
Rice <sup>g</sup>	9	4	83	41	10	5	3.0	6.7
Safflower	18	9	144	72	26	13	1.3	2.9
Sorghum	18	9	77	38	9	4	2.9	6.5
Sugar cane <sup>h</sup>	7	4	71	35	10	5	11.0	24.0
Headfire burning <sup>i</sup>								
Alfalfa	45	23	106	53	36	18	0.8	1.8
Bean (red)	43	22	186	93	46	23	2.5	5.6
Hay (wild)	32	16	139	70	22	11	1.0	2.2
Oats	44	22	137	68	33	16	1.6	3.6
Pea	31	16	147	74	38	19	2.5	5.6
Wheat	22	11	128	64	17	9	1.9	4.3
Backfire burning <sup>j</sup>								
Alfalfa	29	14	119	60	37	18	0.8	1.8
Bean (red), pea	14	7	148	72	25	12	2.5	5.6
Hay (wild)	17	8	150	75	17	8	1.0	2.2
Oats	21	11	136	68	18	9	1.6	3.6
Wheat	13	6	108	54	11	6	1.9	4.3
Vine crops	5	3	51	26	7	4	2.5	5.6
Weeds								
Unspecified	15	8	85	42	12	6	3.2	7.2
Russian thistle (tumbleweed)	22	11	309	154	2	1	0.1	0.2
Tules (wild reeds)	5	3	34	17	27	14		
Orchard crops <sup>c,k,l</sup>								
Unspecified	6	3	52	26	10	5	1.6	3.6
Almond	6	3	46	23	8	4	1.6	3.6
Apple	4	2	42	21	4	2	2.3	5.2
Apricot	6	3	49	24	8	4	1.8	4.0
Avocado	21	10	116	58	32	16	1.5	3.4
Cherry	8	4	44	22	10	5	1.0	2.2
Citrus (orange, lemon)	6	3	81	40	12	6	1.0	2.2
Date palm	10	5	56	28	7	4	1.0	2.2
Fig	7	4	57	28	10	5	2.2	4.9

Table 2.4-2 (continued). EMISSION FACTORS AND FUEL LOADING FACTORS FOR OPEN BURNING OF AGRICULTURAL MATERIALS<sup>a</sup>  
EMISSION FACTOR RATING: B

Refuse category	Emission factors						Fuel loading factors (waste production)	
	Particulate <sup>b</sup>		Carbon monoxide		Hydrocarbons (as C <sub>6</sub> H <sub>14</sub> )			
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	ton/acre	MT/hectare
Orchard crops <sup>c,k,l</sup> (continued)								
Nectarine	4	2	33	16	4	2	2.0	4.5
Olive	12	6	114	57	18	9	1.2	2.7
Peach	6	3	42	21	5	2	2.5	5.6
Pear	9	4	57	28	9	4	2.6	5.8
Prune	3	2	42	21	3	2	1.2	2.7
Walnut	6	3	47	24	8	4	1.2	2.7
Forest residues								
Unspecified <sup>m</sup>	17	8	140	70	24	12	70	157
Hemlock, Douglas fir, cedar <sup>n</sup>	4	2	90	45	5	2		
Ponderosa pine <sup>o</sup>	12	6	195	98	14	7		

<sup>a</sup>Factors expressed as weight of pollutant emitted per weight of refuse material burned.

<sup>b</sup>Particulate matter from most agricultural refuse burning has been found to be in the submicrometer size range.<sup>12</sup>

<sup>c</sup>References 12 and 13 for emission factors; Reference 14 for fuel loading factors.

<sup>d</sup>For these refuse materials, no significant difference exists between emissions resulting from headfiring or backfiring.

<sup>e</sup>These factors represent emissions under typical high moisture conditions. If ferns are dried to less than 15 percent moisture, particulate emissions will be reduced by 30 percent, CO emission by 23 percent, and HC by 74 percent.

<sup>f</sup>When pineapple is allowed to dry to less than 20 percent moisture, as it usually is, the firing technique is not important. When headfired above 20 percent moisture, particulate emission will increase to 23 lb/ton (11.5 kg/MT) and HC will increase to 12 lb/ton (6 kg/MT). See Reference 11.

<sup>g</sup>This factor is for dry (<15 percent moisture) rice straw. If rice straw is burned at higher moisture levels, particulate emission will increase to 29 lb/ton (14.5 kg/MT), CO emission to 161 lb/ton (80.5 kg/MT), and HC emission to 21 lb/ton (10.5 kg/MT).

<sup>h</sup>See Section 6.12 for discussion of sugar cane burning.

<sup>i</sup>See accompanying text for definition of headfiring.

<sup>j</sup>See accompanying text for definition of backfiring. This category, for emission estimation purposes, includes another technique used occasionally for limiting emissions, called into-the-wind striplighting, which involves lighting fields in strips into the wind at 100-200 m (300-600 ft) intervals.

<sup>k</sup>Orchard prunings are usually burned in piles. No significant difference in emission results from burning a "cold pile" as opposed to using a roll-on technique, where prunings are bulldozed onto a bed of embers from a preceding fire.

<sup>l</sup>If orchard removal is the purpose of a burn, 30 ton/acre (66 MT/hectare) of waste will be produced.

<sup>m</sup>Reference 10. Nitrogen oxide emissions estimated at 4 lb/ton (2 kg/MT).

<sup>n</sup>Reference 15.

<sup>o</sup>Reference 16.

monoxide emissions. Arranging the leaves in conical piles and igniting around the periphery of the bottom proves to be the least desirable method of burning. Igniting a single spot on the top of the pile decreases the hydrocarbon and particulate emissions. Carbon monoxide emissions with top ignition decrease if moisture content is high but increase if moisture content is low. Particulate, hydrocarbon, and carbon monoxide emissions from windrow ignition (piling the leaves into a long row and igniting one end, allowing it to burn toward the other end) are intermediate between top and bottom ignition. Emission factors for leaf burning are presented in Table 2.4-3.

For more detailed information on this subject, the reader should consult the references cited at the end of this section.

**Table 2.4-3. EMISSION FACTORS FOR LEAF BURNING<sup>18,19</sup>**  
**EMISSION FACTOR RATING: B**

Leaf species	Particulate <sup>a,b</sup>		Carbon monoxide <sup>a</sup>		Hydrocarbons <sup>a,c</sup>	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Black Ash	36	18	127	63.5	41	20.5
Modesto Ash	32	16	163	81.5	25	12.5
White Ash	43	21.5	113	57	21	10.5
Catalpa	17	8.5	89	44.5	15	7.5
Horse Chestnut	54	27	147	73.5	39	19.5
Cottonwood	38	19	90	45	32	16
American Elm	26	13	119	59.5	29	14.5
Eucalyptus	36	18	90	45	26	13
Sweet Gum	33	16.5	140	70	27	13.5
Black Locust	70	35	130	65	62	31
Magnolia	13	6.5	55	27.5	10	5
Silver Maple	66	33	102	51	25	12.5
American Sycamore	15	7.5	115	57.5	8	4
California Sycamore	10	5	104	52	5	2.5
Tulip	20	10	77	38.5	16	8
Red Oak	92	46	137	68.5	34	17
Sugar Maple	53	26.5	108	54	27	13.5
Unspecified	38	19	112	56	26	13

<sup>a</sup>These factors are an arithmetic average of the results obtained by burning high- and low-moisture content conical piles ignited either at the top or around the periphery of the bottom. The windrow arrangement was only tested on Modesto Ash, Catalpa, American Elm, Sweet Gum, Silver Maple, and Tulip, and the results are included in the averages for these species.

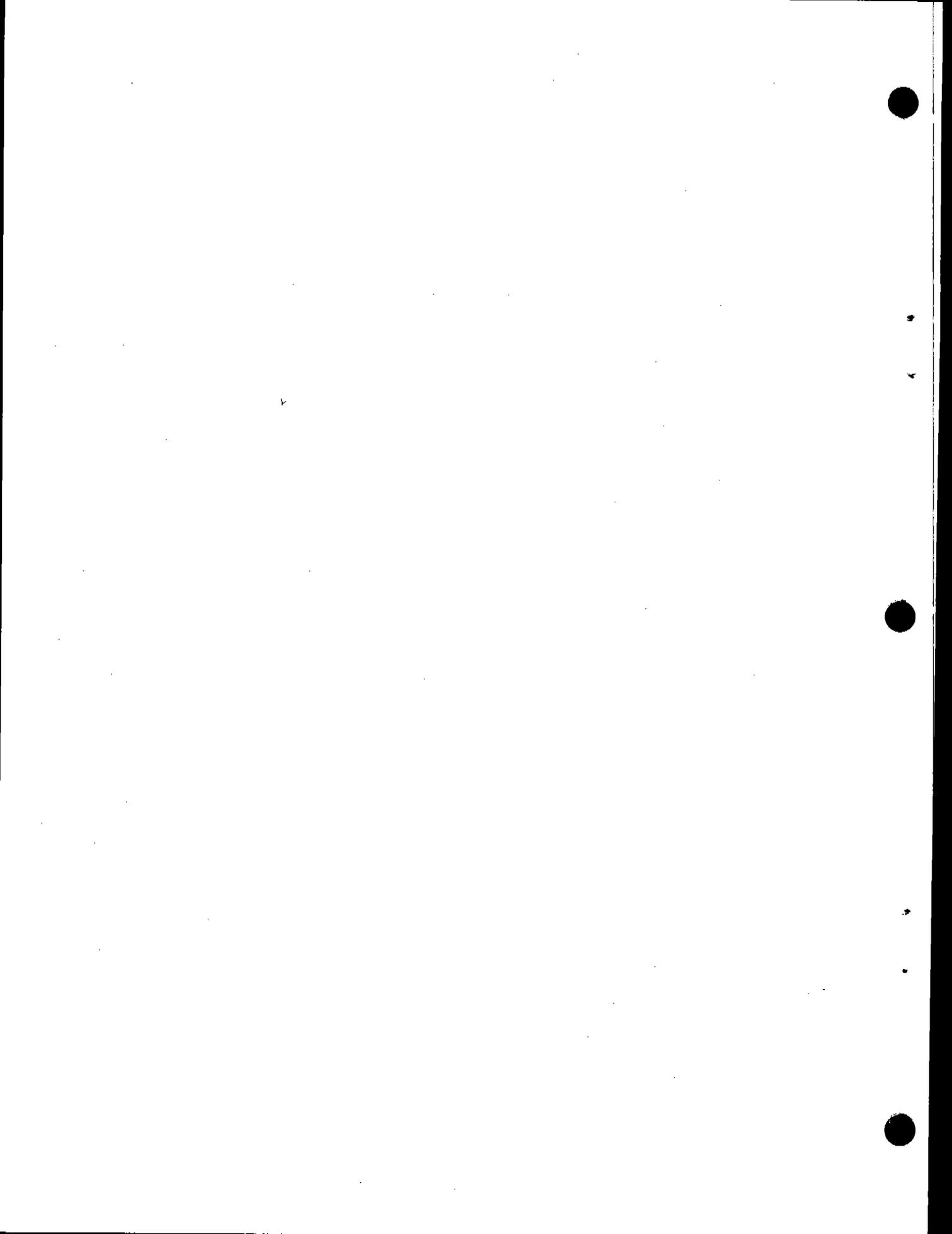
<sup>b</sup>The majority of particulates are submicron in size.

<sup>c</sup>Tests indicate hydrocarbons consist, on the average, of 42% olefins, 32% methane, 8% acetylene, and 13% other saturates.

#### References for Section 2.4

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## 4. EVAPORATION LOSS SOURCES

Evaporation losses include the organic solvents emitted from dry-cleaning plants and surface-coating operations as well as the volatile matter in petroleum products. This chapter presents the hydrocarbon emissions from these sources, including liquid petroleum storage and marketing. Where possible, the effect of controls to reduce the emissions of organic compounds has been shown.

### 4.1 DRY CLEANING

*by Susan Sercer*

#### 4.1.1 General<sup>1,2</sup>

Dry cleaning involves the cleaning of fabrics with non-aqueous organic solvents. The dry cleaning process requires three steps: (1) washing the fabric in solvent, (2) spinning to extract excess solvent, and (3) drying by tumbling in a hot airstream.

Two general types of cleaning fluids are used in the industry: petroleum solvents and synthetic solvents. Petroleum solvents, such as Stoddard or 140-F, are inexpensive, combustible hydrocarbon mixtures similar to kerosene. Operations using petroleum solvents are known as petroleum plants. Synthetic solvents are nonflammable but more expensive halogenated hydrocarbons. Perchloroethylene and trichlorotrifluoroethane are the two synthetic dry cleaning solvents presently in use. Operations using these synthetic solvents are called "perc" plants and fluorocarbon plants, respectively.

There are two basic types of dry cleaning machines: transfer and dry-to-dry. Transfer machines accomplish washing and drying in separate machines. Usually the washer extracts excess solvent from the clothes before they are transferred to the dryer, however, some older petroleum plants have separate extractors for this purpose. Dry-to-dry machines are single units that perform all of the washing, extraction, and drying operations. All petroleum solvent machines are the transfer type, but synthetic solvent plants can be either type.

The dry cleaning industry can be divided into three sectors: coin-operated facilities, commercial operations, and industrial cleaners. Coin-operated facilities are usually part of a laundry and supply "self-service" type dry cleaning for consumers. Only synthetic solvents are used in coin-operated dry cleaning machines. Such machines are small, with a capacity of 8 to 25 lb (3.6 to 11.5 kg) of clothing.

Commercial operations, such as small neighborhood or franchise dry cleaning shops, clean soiled apparel for the consumer. Generally, perchloroethylene and petroleum solvents are used in commercial operations. A typical "perc" plant operates a 30 to 60 lb (14 to 27 kg) capacity washer/extractor and an equivalent size reclaiming dryer.

Industrial cleaners are larger dry cleaning plants which supply rental service of uniforms, mats, mops, etc., to businesses or industries. Although petroleum solvents are used extensively, perchloroethylene is used by approximately 50% of the industrial dry cleaning establishments. A typical large industrial cleaner has a 500 lb (230 kg) capacity washer/extractor and three to six 100 lb (38 kg) capacity dryers.

A typical perc plant is shown in Figure 4.1-1. Although one solvent tank may be used, the typical perc plant uses two tanks for washing. One tank contains pure solvent; the other tank contains "charged" solvent—used solvent to which small amounts of detergent have been added to aid in cleaning. Generally, clothes are cleaned in charged solvent and rinsed in pure solvent. A water bath may also be used.



After the clothes have been washed, the used solvent is filtered, and part of the filtered solvent is returned to the charged solvent tank for washing the next load. The remaining solvent is then distilled to remove oils, fats, greases, etc., and returned to the pure solvent tank. The resulting distillation bottoms are typically stored on the premises until disposed of. The filter cake and collected solids (muck) are usually removed from the filter once a day. Before disposal, the muck may be "cooked" to recover additional solvent. Still and muck cooker vapors are vented to a condenser and separator where more solvent is reclaimed. In many perc plants, the condenser off-gases are vented to a carbon adsorption unit for additional solvent recovery.

After washing, the clothes are transferred to the dryer where they are tumbled in a heated airstream. Exhaust gases from the dryer, along with a small amount of exhaust gases from the washer/extractor, are vented to a water-cooled condenser and water separator. Recovered solvent is returned to the pure solvent storage tank. In 30-50 percent of the perc plants, the condenser off-gases are vented to a carbon adsorption unit for additional solvent recovery. To reclaim this solvent, the unit must be periodically desorbed with steam—typically at the end of each day. Desorbed solvent and water are condensed and separated; recovered solvent is returned to the pure solvent tank.

A petroleum plant would differ from Figure 4.1-1 chiefly in that there would be no recovery of solvent from the washer and dryer and no muck cooker. A fluorocarbon plant would differ in that a non-vented refrigeration system would be used in place of a carbon adsorption unit. Another difference would be that a typical fluorocarbon plant would use a cartridge filter which is drained and disposed of after several hundred cycles.

### Emissions and Controls<sup>1,2,3</sup>

The solvent material itself is the primary emission of concern from dry cleaning operations. Solvent is given off by the washer, dryer, solvent still, muck cooker, still residue and filter muck storage areas, as well as leaky pipes, flanges, and pumps.

Petroleum plants have generally not employed solvent recovery because of the low cost of petroleum solvents and the fire hazards associated with collecting vapors. Some emission control, however, can be obtained by maintaining all equipment in good condition (e.g., preventing lint accumulation, preventing solvent leakage, etc.) and by using good operating practices (e.g., not overloading machinery). Both carbon adsorption and incineration appear to be technically feasible controls for petroleum plants, but costs are high.

Solvent recovery is necessary in perc plants due to the higher cost of perchloroethylene. As shown in Figure 4.1-1, recovery is effected on the washer, dryer, still, and muck cooker through the use of condensers, water/solvent separators, and carbon adsorption units. Periodically (typically once a day), solvent collected in the carbon adsorption unit is desorbed with steam, condensed, separated from the condensed water, and returned to the pure solvent storage tank. Residual solvent emitted from treated distillation bottoms and muck is not recovered. As in petroleum plants, good emission control can be obtained by good housekeeping practices (maintaining all equipment in good condition and using good operating practices).

All fluorocarbon machines are of the dry-to-dry variety to conserve solvent vapor, and all are closed systems with built-in solvent recovery. High emissions can occur, however, as a result of poor maintenance and operation of equipment. Refrigeration systems are installed on newer machines to recover solvent from the washer/dryer exhaust gases.

Emission factors for dry cleaning operations are presented in Table 4.1-1.

**Table 4.1-1. SOLVENT LOSS EMISSION FACTORS FOR DRY CLEANING OPERATIONS  
EMISSION FACTOR RATING: B**

Solvent type (Process used)	Source	Emission rate <sup>a</sup>	
		Typical systems	Well-controlled system
		lb/100 lb (kg/100 kg)	lb/100 lb (kg/100 kg)
Petroleum (transfer process)	washer/dryer <sup>f</sup>	18	2 <sup>b</sup>
	filter disposal		
	uncooked (drained)	5	
	centrifuged		0.5 - 1
	still residue disposal	2	0.5 - 1
	miscellaneous <sup>c</sup>	3	1
Perchloroethylene (transfer process)	washer/dryer/still/muck cooker	8 <sup>d</sup>	0.3 <sup>b</sup>
	filter disposal		
	uncooked muck	14	
	cooked muck	1.3	0.5 - 1.3
	cartridge filter	1.1	0.5 - 1.1
	still residue disposal	1.6	0.5 - 1.6
	miscellaneous <sup>c</sup>	1.5	1
Trichlorotrifluoroethane (dry-to-dry process)	washer/dryer/still <sup>e</sup>	0	0
	cartridge filter disposal	1	1
	still residue disposal	0.5	0.5
	miscellaneous <sup>c</sup>	1 - 3	1 - 3

<sup>a</sup>Units are in terms of weight of solvent per weight of clothes cleaned (capacity x loads). Emissions may be estimated on an alternative basis by determining the amount of solvent consumed. Assuming that all solvent input to dry cleaning operations is eventually evaporated to the atmosphere, an emission factor of 2000 lb/ton of solvent consumed can be applied. All emission factors are based on References 1, 2 and 3.

<sup>b</sup>Emissions from the washer, dryer, still, and muck cooker are collectively passed through a carbon adsorber.

<sup>c</sup>Miscellaneous sources include fugitive emissions from flanges, pumps, pipes, storage tanks, fixed losses (for example, opening and closing the dryer), etc.

<sup>d</sup>Uncontrolled emissions from the washer, dryer, still, and muck cooker average about 8 lb/100 lb (8 kg/100 kg). Roughly 15% of the solvent emitted comes from the washer, 75% from the dryer, and 5% from both the still and the muck cooker.

<sup>e</sup>Emission factors are based on the typical refrigeration system installed in fluorocarbon plants.

<sup>f</sup>Different materials in the wash retain varying amounts of solvent (synthetic: 10 kg/100 kg, cotton: 20 kg/100 kg, leather: 40 kg/100 kg).

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Fundamentally, the petroleum industry consists of three operations: (1) petroleum production and transportation, (2) petroleum refining, and (3) transportation and marketing of finished petroleum products. All three operations require some type of storage for petroleum liquids. Storage tanks for both crude and finished products can be sources of evaporative emissions. Figure 4.3-1 presents a schematic of the petroleum industry and its points of emissions from storage operations.

#### 4.3.1 Process Description

Four basic tank designs are used for petroleum storage vessels: fixed roof, floating roof (open type and covered type), variable vapor space, and pressure (low and high).

**4.3.1.1 Fixed Roof Tanks<sup>2</sup>** - The minimum accepted standard for storage of volatile liquids is the fixed roof tank (Figure 4.3-2). It is usually the least expensive tank design to construct. Fixed roof tanks basically consist of a cylindrical steel shell topped by a coned roof having a minimum slope of 3/4 inch in 12 inches. Fixed roof tanks are generally equipped with a pressure/vacuum vent designed to contain minor vapor volume changes. For large fixed roof tanks, the recommended maximum operating pressure/vacuum is +0.03 psig/-0.03 psig (+2.1 g/cm<sup>2</sup>/-2.1 g/cm<sup>2</sup>).

**4.3.1.2 Floating Roof Tanks<sup>3</sup>** - Floating roof tanks reduce evaporative storage losses by minimizing vapor spaces. The tank consists of a welded or riveted cylindrical steel wall, equipped with a deck or roof which is free to float on the surface of the stored liquid. The roof then rises and falls according to the depth of stored liquid. To ensure that the liquid surface is completely covered, the roof is equipped with a sliding seal which fits against the tank wall. Sliding seals are also provided at support columns and at all other points where tank appurtenances pass through the floating roof.

Until recent years, the most commonly used floating roof tank was the conventional open-type tank. The open-type floating roof tank exposes the roof deck to the weather; provisions must be made for rain water drainage, snow removal, and sliding seal dirt protection. Floating roof decks are of three general types: pan, pontoon, and double deck. The pan-type roof consists of a flat metal plate with a vertical rim and sufficient stiffening braces to maintain rigidity (Figure 4.3-3). The single metal plate roof in contact with the liquid readily conducts solar heat, resulting in higher vaporization losses than other floating roof decks. The roof is equipped with automatic vents for pressure and vacuum release. The pontoon roof is a pan-type floating roof with pontoon sections added to the top of the deck around the rim. The pontoons are arranged to provide floating stability under heavy loads of water and snow. Evaporation losses due to solar heating are about the same as for pan-type roofs. Pressure/vacuum vents are required on pontoon roof tanks. The double deck roof is similar to a pan-type floating roof, but consists of a hollow double deck covering the entire surface of the roof (Figure 4.3-4). The double deck adds rigidity, and the dead air space between the upper and lower deck provides significant insulation from solar heating. Pressure/vacuum vents are also required.

The covered-type floating roof tank is essentially a fixed-roof tank with a floating roof deck inside the tank (Figure 4.3-5). The American Petroleum Institute has designated the term "covered floating" roof to describe a fixed roof tank with an internal steel pan-type floating roof. The term "internal floating cover" has been chosen by the API to describe internal covers constructed of materials other than steel. Floating roofs and covers can be installed inside existing fixed roof tanks. The fixed roof protects the floating roof from the weather, and no provision is necessary for rain or snow removal, or for seal

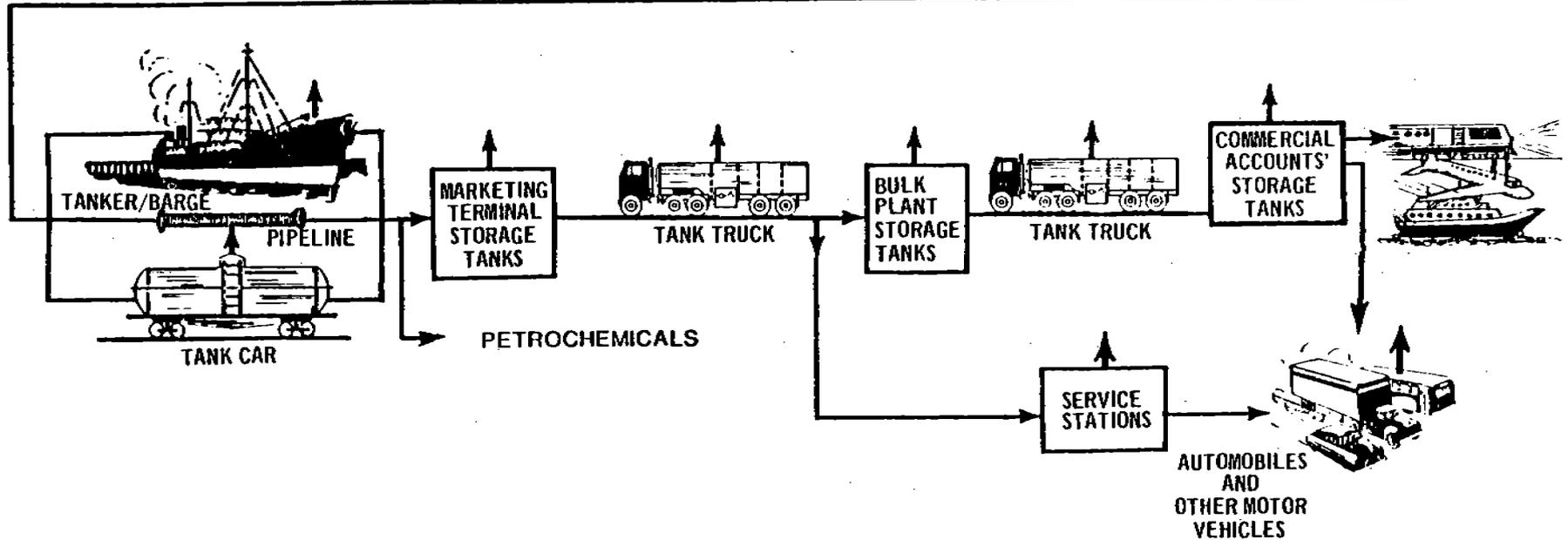
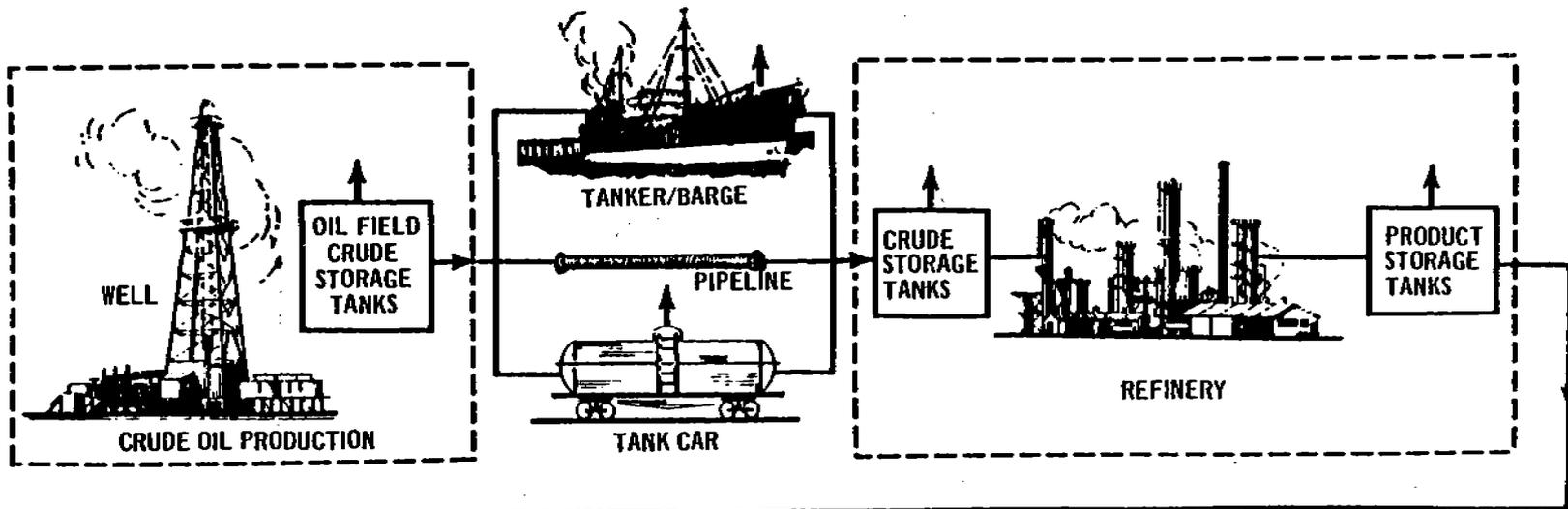


Figure 4.3-1. Flowsheet of petroleum production, refining, and distribution systems. (Sources of organic evaporative emissions are indicated by vertical arrows.)

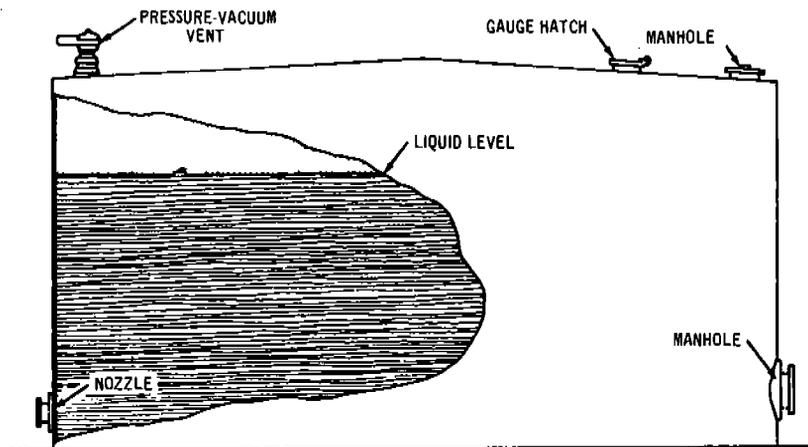


Figure 4.3-2. Fixed roof storage tank.

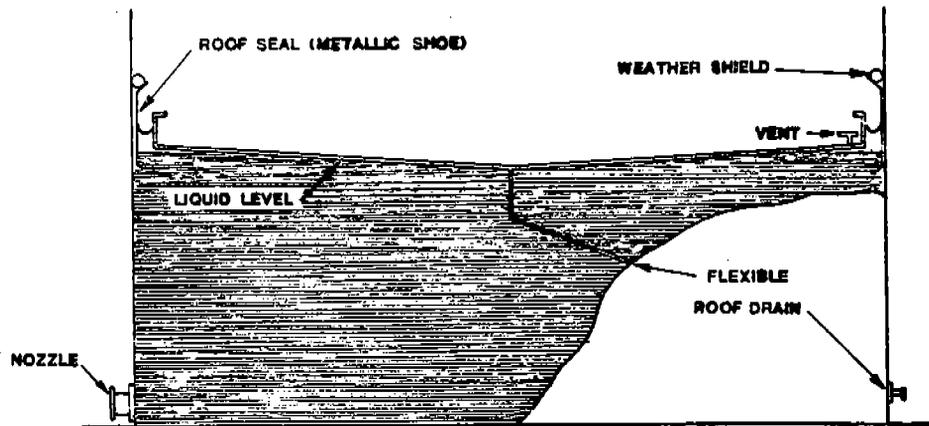


Figure 4.3-3. Pan-type floating roof storage tank (metallic seals).

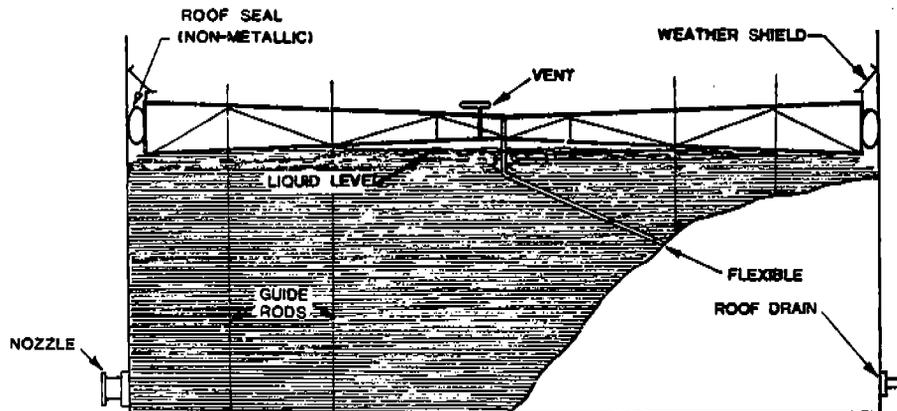


Figure 4.3-4. Double deck floating roof storage tank (non-metallic seals).

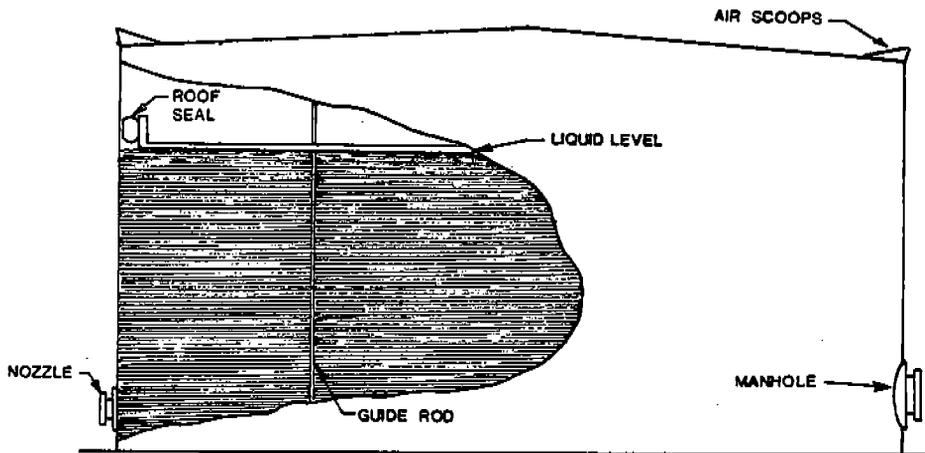


Figure 4.3-5. Covered floating roof storage tank.

protection. Antirotational guides must be provided to maintain roof alignment, and the space between the fixed and floating roofs must be vented to prevent the possible formation of a flammable mixture.

**4.3.1.3 Variable Vapor Space Tanks<sup>4</sup>** - Variable vapor space tanks are equipped with expandable vapor reservoirs to accommodate vapor volume fluctuations attributable to temperature and barometric pressure changes. Although variable vapor space tanks are sometimes used independently, they are normally connected to the vapor spaces of one or more fixed roof tanks. The two most common types of variable vapor space tanks are lifter roof tanks and flexible diaphragm tanks.

Lifter roof tanks have a telescoping roof that fits loosely around the outside of the main tank wall. The space between the roof and the wall is closed by either a wet seal, which consists of a trough filled with liquid, or a dry seal, which employs a flexible coated fabric in place of the trough (Figure 4.3-6).

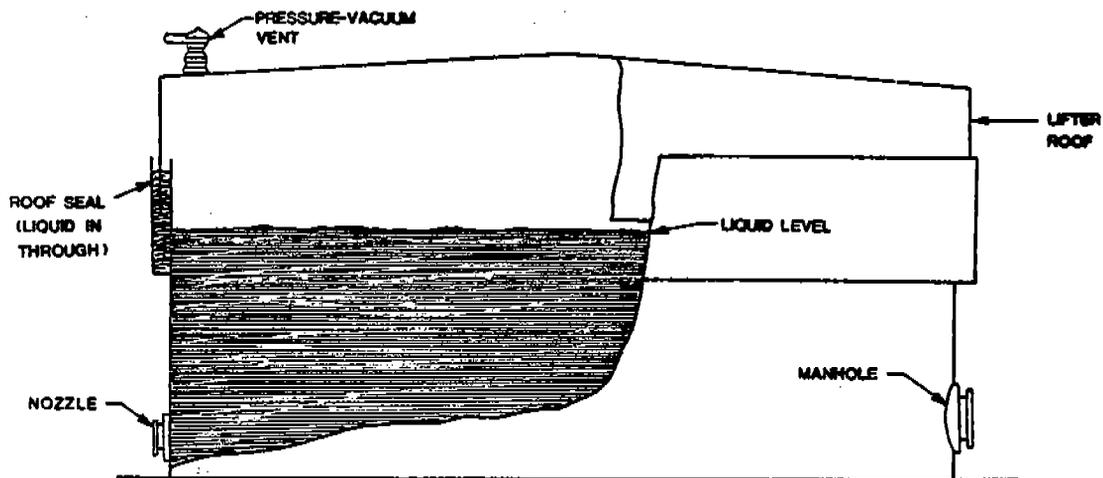


Figure 4.3-6. Lifter roof storage tank (wet seal).

Flexible diaphragm tanks utilize flexible membranes to provide the expandable volume. They may be separate gasholder type units, or integral units mounted atop fixed roof tanks (Figure 4.3-7).

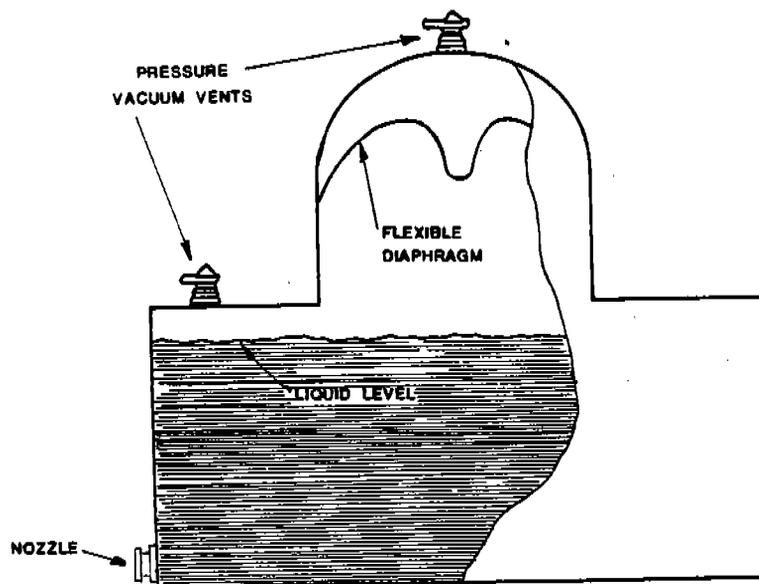


Figure 4.3-7. Flexible diaphragm tank (integral unit).

4.3.1.4 Pressure Tanks<sup>5</sup> - Pressure tanks are designed to withstand relatively large pressure variations without incurring a loss. They are generally used for storage of high volatility stocks, and they are constructed in many sizes and shapes, depending on the operating range. The noded spheroid and noded hemispheroid shapes are generally used as low-pressure tanks (17 to 30 psia or 12 to 21 mg/m<sup>2</sup>), while the horizontal cylinder and spheroid shapes are generally used as high-pressure tanks (up to 265 psia or 186 mg/m<sup>2</sup>).

#### 4.3.2 Emissions and Controls

There are six sources of emissions from petroleum liquids in storage: fixed roof breathing losses, fixed roof working losses, floating roof standing storage losses, floating roof withdrawal losses, variable vapor space filling losses, and pressure tank losses.<sup>6</sup>

Fixed roof breathing losses consist of vapor expelled from a tank because of the thermal expansion of existing vapors, vapor expansion caused by barometric pressure changes, and/or an increase in the amount of vapor due to added vaporization in the absence of a liquid-level change.

Fixed roof working losses consist of vapor expelled from a tank as a result of filling and emptying operations. Filling loss is the result of vapor displacement by the input of liquid. Emptying loss is the expulsion of vapors subsequent to product withdrawal, and is attributable to vapor growth as the newly inhaled air is saturated with hydrocarbons.

Floating roof standing storage losses result from causes other than breathing or changes in liquid level. The largest potential source of this loss is attributable to an improper fit of the seal and shoe to the shell, which exposes some liquid surface to the atmosphere. A small amount of vapor may escape between the flexible membrane seal and the roof.

Floating roof withdrawal losses result from evaporation of stock which wets the tank wall as the roof descends during emptying operations. This loss is small in comparison to other types of losses.

Variable vapor space filling losses result when vapor is displaced by the liquid input during filling operations. Since the variable vapor space tank has an expandable vapor storage capacity, this loss is not as large as the filling loss associated with fixed roof tanks. Loss of vapor occurs only when the vapor storage capacity of the tank is exceeded.

Pressure tank losses occur when the pressure inside the tank exceeds the design pressure of the tank, which results in relief vent opening. This happens only when the tank is filled improperly, or when abnormal vapor expansion occurs. These are not regularly occurring events, and pressure tanks are not a significant source of loss under normal operating conditions.

The total amount of evaporation loss from storage tanks depends upon the rate of loss and the period of time involved. Factors affecting the rate of loss include:

1. True vapor pressure of the liquid stored.
2. Temperature changes in the tank.
3. Height of the vapor space (tank outage).
4. Tank diameter.
5. Schedule of tank filling and emptying.
6. Mechanical condition of tank and seals.
7. Type of tank and type of paint applied to outer surface.

The American Petroleum Institute has developed empirical formulae, based on field testing, that correlate evaporative losses with the above factors and other specific storage factors.

4.3.2.1 Fixed Roof Tanks<sup>2,7</sup> - Fixed roof breathing losses can be estimated from:

$$L_B = 2.21 \times 10^{-4} M \left[ \frac{P}{14.7 - P} \right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_p C K_c \quad (1)$$

where:  $L_B$  = Fixed roof breathing loss (lb/day).

$M$  = Molecular weight of vapor in storage tank (lb/lb mole). (see Table 4.3-1).

$P$  = True vapor pressure at bulk liquid conditions (psia); see Figures 4.3-8, 4.3-9, or Table 4.3-1.

$D$  = Tank diameter (ft).

$H$  = Average vapor space height, including roof volume correction (ft); see note (1).

$\Delta T$  = Average ambient temperature change from day to night ( $^{\circ}F$ ).

$F_p$  = Paint factor (dimensionless); see Table 4.3-2.

$C$  = Adjustment factor for small diameter tanks (dimensionless); see Figure 4.3-10.

$K_c$  = Crude oil factor (dimensionless); see note (2).

Note: (1) The vapor space in a cone roof is equivalent in volume to a cylinder which has the same base diameter as the cone and is one-third the height of the cone.

(2)  $K_c = (0.65)$  for crude oil,  $K_c = (1.0)$  for gasoline and all other liquids.

API reports that calculated breathing loss from Equation (1) may deviate in the order of  $\pm 10$  percent from actual breathing loss.

Table 4.3-1. PHYSICAL PROPERTIES OF HYDROCARBONS 7,9

Hydrocarbon	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	Vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
<b>Fuels</b>										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel No. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil No. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
<b>Petrochemicals</b>										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1, 2 - Dichlorethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.5	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methyl-ethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methyl-methacrylate	100	7.9	7.9	0.1	0.2	0.3	0.5	0.8	1.1	1.4
1, 1, 1 - Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.6
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

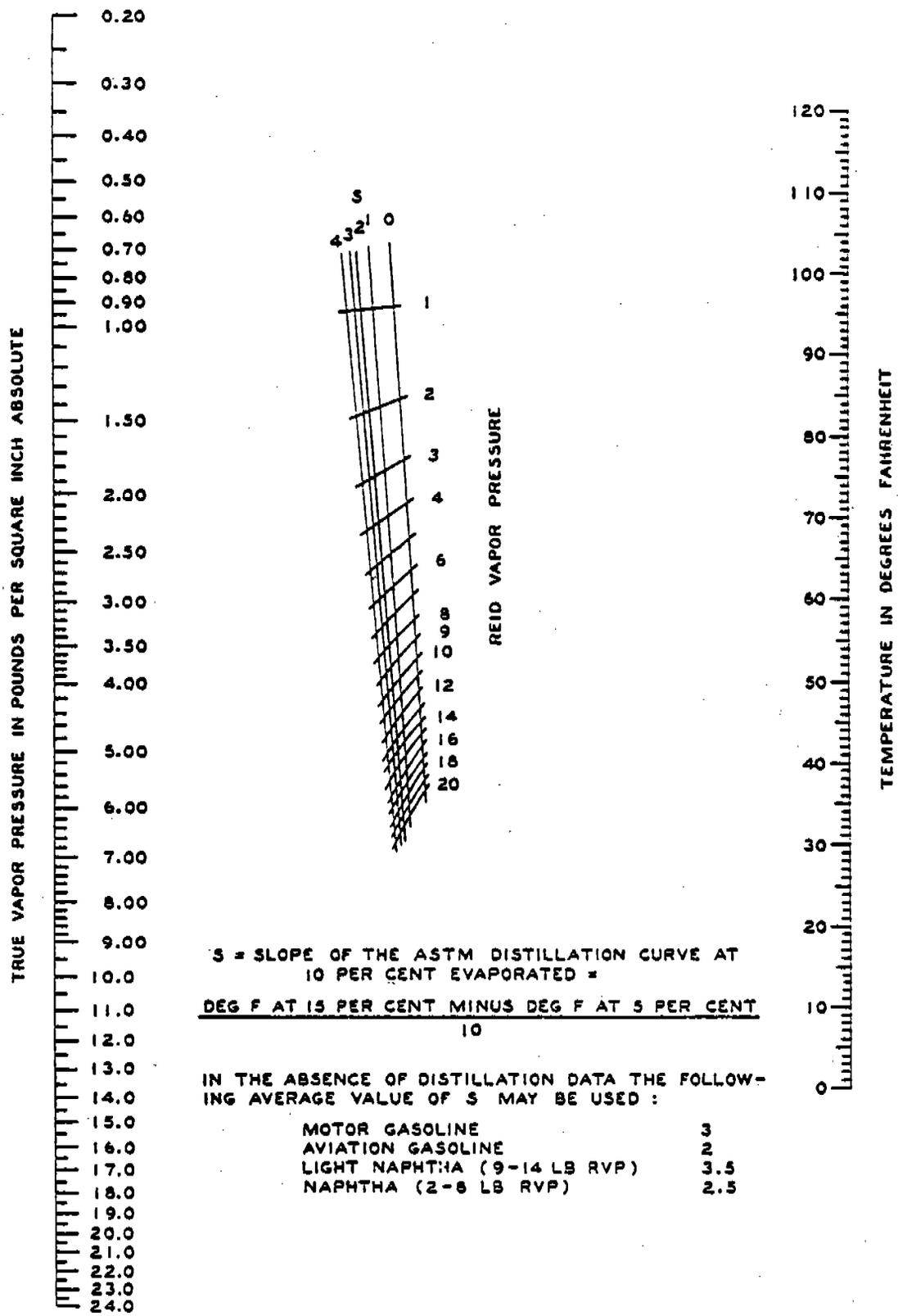


Figure 4.3-8. Vapor pressures of gasolines and finished petroleum products.

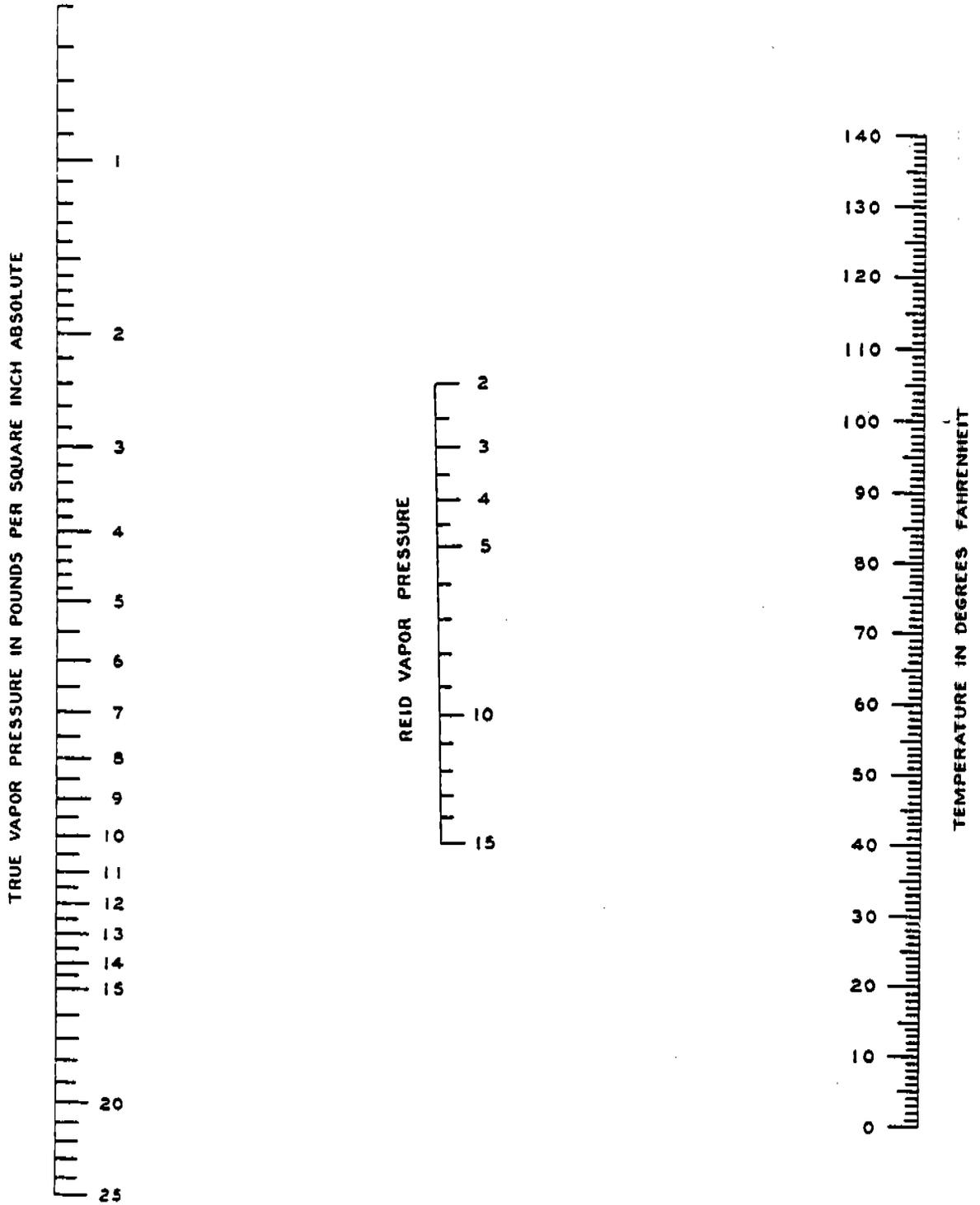


Figure 4.3-9. Vapor pressures of crude oil.

Table 4.3-2. PAINT FACTORS FOR FIXED ROOF TANKS<sup>2</sup>

Tank color		Paint factors (F <sub>p</sub> )	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44 <sup>a</sup>
Medium gray	Medium gray	1.40	1.58 <sup>a</sup>

<sup>a</sup>Estimated from the ratios of the seven preceding paint factors.

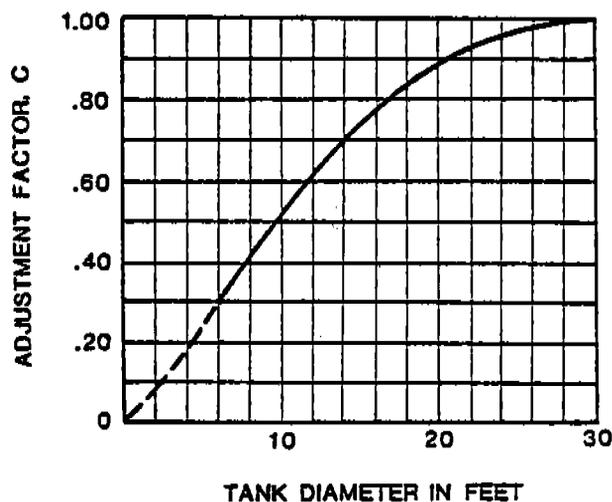


Figure 4.3-10. Adjustment factor (C) for small diameter tanks.

Fixed roof working losses can be estimated from:

$$L_W = 2.40 \times 10^{-2} M P K_N K_C \quad (2)$$

where:  $L_W$  = Fixed roof working loss (lb/10<sup>3</sup> gal throughput).

$M$  = Molecular weight of vapor in storage tank (lb/lb mole). see Table 4.3-1.

$P$  = True vapor pressure at bulk liquid conditions (psia); see Figures 4.3-8, 4.3-9, or Table 4.3-1.

$K_N$  = Turnover factor (dimensionless); see Figure 4.3-11.

$K_c$  = Crude oil factor (dimensionless); see note.

Note:  $K_c = (0.84)$  for crude oil,  $K_c = (1.0)$  for gasoline and all other liquids.

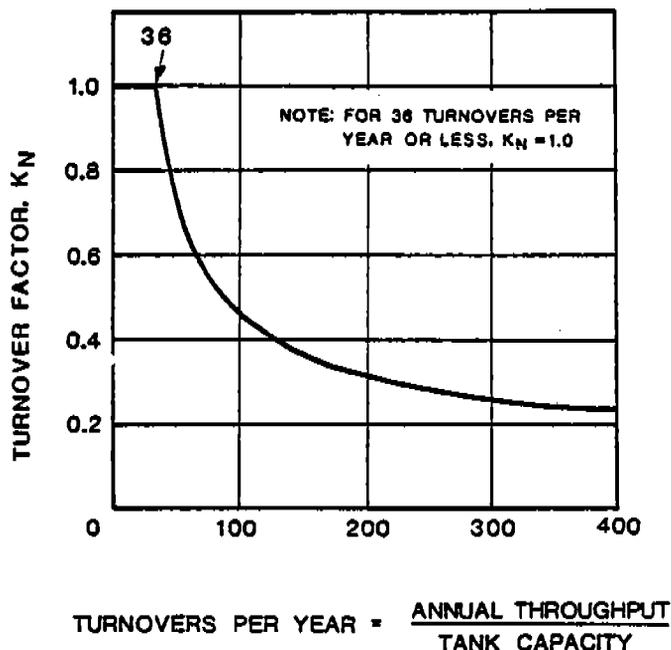


Figure 4.3-11. Turnover factor ( $K_N$ ) for fixed roof tanks.

The fixed roof working loss ( $L_W$ ) is the sum of the loading and unloading loss. API reports that special tank operating conditions may result in actual losses which are significantly greater or lower than the estimates provided by Equation (2).

The API recommends the use of these storage loss equations only for cases in which the stored petroleum liquids exhibit vapor pressures in the same range as gasolines. However, in the absence of any correlation developed specifically for naphthas, kerosenes, and fuel oils, it is recommended that these storage loss equations also be used for the storage of these heavier fuels.

The method most commonly used to control emissions from fixed roof tanks is a vapor recovery system that collects emissions from the storage vessels and converts them to liquid product. To recover vapor, one or a combination of four methods may be used: vapor/liquid absorption, vapor compression, vapor cooling, and vapor/solid adsorption. Overall control efficiencies of vapor recovery systems vary

from 90 to 95 percent, depending on the method used, the design of the unit, the composition of vapors recovered, and the mechanical condition of the system.

Emissions from fixed roof tanks can also be controlled by the addition of an internal floating cover or covered floating roof to the existing fixed roof tank. API reports that this can result in an average loss reduction of 90 percent of the total evaporation loss sustained from a fixed roof tank.<sup>8</sup>

Evaporative emissions can be minimized by reducing tank heat input with water sprays, mechanical cooling, underground storage, tank insulation, and optimum scheduling of tank turnovers.

4.3.2.2 Floating Roof Tanks<sup>3,7</sup> - Floating roof standing storage losses can be estimated from:

$$L_S = 9.21 \times 10^{-3} M \left[ \frac{P}{14.7-P} \right]^{0.7} D^{1.5} V_w^{0.7} K_t K_s K_p K_c \quad (3)$$

where:  $L_S$  = Floating roof standing storage loss (lb/day).

$M$  = Molecular weight of vapor in storage tank (lb/lb mole); see Table 4.3-1.

$P$  = True vapor pressure at bulk liquid conditions (psia); see Figures 4.3-8, 4.3-9, or Table 4.3-1.

$D$  = Tank diameter (ft); see note (1).

$V_w$  = Average wind velocity (mi/hr); see note (2).

$K_t$  = Tank type factor (dimensionless); see Table 4.3-3.

$K_s$  = Seal factor (dimensionless); see Table 4.3-3.

$K_p$  = Paint factor (dimensionless); see Table 4.3-3.

$K_c$  = Crude oil factor (dimensionless); see note (3).

Note: (1) For  $D \geq 150$ , use  $D\sqrt{150}$  instead of  $D$ .<sup>1,5</sup>

(2) API correlation was derived for minimum wind velocity of 4 mph. If  $V_w \leq 4$  mph, use  $V_w = 4$  mph.

(3)  $K_c = (0.84)$  for crude oil,  $K_c = (1.0)$  for all other liquids.

API reports that standing storage losses from gasoline and crude oil storage calculated from Equation (3) will not deviate from the actual losses by more than  $\pm 25$  percent for tanks in good condition under normal operation. However, losses may exceed the calculated amount if the seals are in poor condition. Although the API recommends the use of these correlations only for petroleum liquids exhibiting vapor pressures in the range of gasoline and crude oils, in the absence of better correlations, these correlations are also recommended with caution for use with heavier naphthas, kerosenes, and fuel oils.

Table 4.3-3. TANK, TYPE, SEAL, AND PAINT FACTORS FOR FLOATING ROOF TANKS<sup>2</sup>

Tank type	$K_t$	Seal type	$K_s$
Welded tank with pan or pontoon roof, single or double seal	0.045	Tight fitting (typical of modern metallic and non-metallic seals)	1.00
Riveted tank with pontoon roof, double seal	0.11	Loose fitting (typical of seals built prior to 1942)	1.33
Riveted tank with pontoon roof, single seal	0.13	Paint color of shell and roof	$K_p$
Riveted tank with pan roof, double seal	0.13	Light gray or aluminum	1.0
		White	0.9
Riveted tank with pan roof, single seal	0.14		

API has developed a correlation based on laboratory data for calculating floating roof withdrawal loss for gasoline storage.<sup>5</sup> Floating roof withdrawal loss for gasoline can be estimated from:

$$L_{WD} = \frac{22.4 d C_F}{D} \quad (4)$$

where:  $L_{WD}$  = Floating roof gasoline withdrawal loss (lb/10<sup>3</sup> gal throughput).

$d$  = Density of stored liquid at bulk liquid conditions (lb/gal); see Table 4.3-1.

$C_F$  = Tank construction factor (dimensionless); see note.

$D$  = Tank diameter (ft).

Note:  $C_F$  = (0.02) for steel tanks,  $C_F$  = (1.0) for gunite-lined tanks.

Because Equation (4) was derived from gasoline data, its applicability to other stored liquids is uncertain. No estimate of accuracy of Equation (4) has been given.

API has not presented any correlations that specifically pertain to internal floating covers or covered floating roofs. Currently, API recommends the use of Equations (3) and (4) with a wind speed of 4 mph for calculating the losses from internal floating covers and covered floating roofs.

Evaporative emissions from floating roof tanks can be minimized by reducing tank heat input.

4.3.2.3 Variable Vapor Space Systems<sup>4,7</sup>- Variable vapor space system filling losses can be estimated from:

$$L_V = (2.40 \times 10^{-2}) \frac{MP}{V_1} [(V_1) - (0.25 V_2 N)] \quad (5)$$

where:  $L_V$  = Variable vapor space filling loss (lb/10<sup>3</sup> gal throughput).

$M$  = Molecular weight of vapor in storage tank (lb/lb mole); see Table 4.3-1.

$P$  = True vapor pressure at bulk liquid conditions (psia); see Figures 4.3-8, 4.3-9, or Table 4.3-1.

$V_1$  = Volume of liquid pumped into system: throughput (bb1).

$V_2$  = Volume expansion capacity of system (bb1); see note (1).

$N$  = Number of transfers into system (dimensionless); see note (2).

Note: (1)  $V$  is the volume expansion capacity of the variable vapor space achieved by roof-lifting or diaphragm-flexing.

(2)  $N$  is the number of transfers into the system during the time period that corresponds to a throughput of  $V_1$ .

The accuracy of Equation (5) is not documented; however, API reports that special tank operating conditions may result in actual losses which are significantly different from the estimates provided by Equation (5). It should also be noted that, although not developed for use with heavier petroleum liquids such as kerosenes and fuel oils, Equation (5) is recommended for use with heavier petroleum liquids in the absence of better data.

Evaporative emissions from variable vapor space tanks are negligible and can be minimized by optimum scheduling of tank turnovers and by reducing tank heat input. Vapor recovery systems can be used with variable vapor space systems to collect and recover filling losses.

Vapor recovery systems capture hydrocarbon vapors displaced during filling operations and recover the hydrocarbon vapors by the use of refrigeration, absorption, adsorption, and/or compression. Control efficiencies range from 90 to 98 percent, depending on the nature of the vapors and the recovery equipment used.

**4.3.2.4 Pressure Tanks** - Pressure tanks incur vapor losses when excessive internal pressures result in relief valve venting. In some pressure tanks vapor venting is a design characteristic, and the vented vapors must be routed to a vapor recovery system. However, for most pressure tanks vapor venting is not a normal occurrence, and the tanks can be considered closed systems. Fugitive losses are also associated with pressure tanks and their equipment, but with proper system maintenance they are insignificant. Correlations do not exist for estimating vapor losses from pressure tanks.

### 4.3.3 Emission Factors

Equations (1) through (5) can be used to estimate evaporative losses, provided the respective parameters are known. For those cases where such parameters are unknown, Table 4.3-4 provides emission factors for the typical systems and conditions. It should be emphasized that these emission factors are rough estimates at best for storage of liquids other than gasoline and crude oil, and for storage conditions other than the ones they are based upon. In areas where storage sources contribute a substantial portion of the total evaporative emissions or where they are major factors affecting the air quality, it is advisable to obtain the necessary parameters and to calculate emission estimates using Equations (1) through (5).

Table 4.3-4. EVAPORATIVE EMISSION FACTORS FOR STORAGE TANKS WITHOUT CONTROLS<sup>2-4,6,7</sup>

Product Stored	Fixed roof tanks						Floating roof tanks						Variable vapor space tanks	
	Breathing loss				Working loss		Standing storage loss				Withdrawal loss		10,500 bbl	
	"New tank" conditions		"Old tank" conditions				"New tank" conditions		"Old tank" conditions				Filling loss	
	lb/day-10 <sup>3</sup> gal	kg/day-10 <sup>3</sup> liters	lb/day-10 <sup>3</sup> gal	kg/day-10 <sup>3</sup> liters	lb/10 <sup>3</sup> gal throughput	kg/10 <sup>3</sup> liters throughput	lb/day-10 <sup>3</sup> gal	kg/day-10 <sup>3</sup> liters	lb/day-10 <sup>3</sup> gal	kg/day-10 <sup>3</sup> liters	lb/10 <sup>3</sup> gal throughput	kg/10 <sup>3</sup> liters throughput	lb/10 <sup>3</sup> gal throughput	kg/10 <sup>3</sup> liters throughput
<b>Fuels - 67,000 bbl tanks</b>														
1. Gasoline RVP 13	0.30	0.036	0.34	0.041	10.0	1.2	0.044	0.0052	0.10	0.012	0.023	0.0028	9.6	1.2
2. Gasoline RVP 10	0.23	0.028	0.26	0.031	8.2	0.99	0.033	0.0040	0.078	0.0094	0.023	0.0028	7.7	0.93
3. Gasoline RVP 7	0.16	0.019	0.18	0.022	5.7	0.68	0.023	0.0028	0.055	0.0066	0.023	0.0028	5.4	0.65
4. Crude oil RVP 5	0.064	0.0077	0.073	0.0088	2.8	0.34	0.012	0.0014	0.028	0.0034			Not used	Not used
5. Jet naphtha (JP-4)	0.086	0.010	0.098	0.011	2.5	0.30	0.012	0.0014	0.028	0.0034			Not used	Not used
6. Jet kerosene	0.0043	0.00052	0.0049	0.00059	0.027	0.0032	0.00054	0.000065	0.0013	0.00016			0.025	0.0030
7. Distillate fuel no. 2	0.0039	0.00047	0.0044	0.00053	0.023	0.0028	0.00049	0.000058	0.0011	0.00014			0.022	0.0026
8. Residual oil no. 6	0.00016	0.000019	0.00018	0.000022	0.00018	0.000022	0.000018	0.0000022	0.000043	0.0000052			0.00017	0.000020
<b>Fuels - 250,000 bbl tanks</b>														
9. Gasoline RVP 13	0.22	0.026	0.25	0.030	10.0	1.2	0.025	0.0030	0.057	0.0068	0.013	0.0015	Not used	Not used
10. Gasoline RVP 10	0.17	0.020	0.19	0.023	8.2	0.99	0.019	0.0023	0.044	0.0053	0.013	0.0015	Not used	Not used
11. Gasoline RVP 7	0.12	0.014	0.13	0.016	5.7	0.68	0.013	0.0016	0.031	0.0037	0.013	0.0015	Not used	Not used
12. Crude oil RVP 5	0.046	0.0055	0.052	0.0062	2.8	0.34	0.0077	0.0092	0.018	0.0022			Not used	Not used
13. Jet naphtha (JP-4)	0.062	0.0074	0.071	0.0085	2.5	0.30	0.0068	0.00082	0.016	0.0019			Not used	Not used
14. Jet kerosene	0.0031	0.00037	0.0035	0.00042	0.027	0.0032	0.00031	0.000037	0.00074	0.000089			Not used	Not used
15. Distillate fuel no. 2	0.0028	0.00034	0.0032	0.00038	0.023	0.0028	0.00028	0.000034	0.00068	0.000082			Not used	Not used
16. Residual fuel no. 6	0.00012	0.000014	0.00014	0.000017	0.00018	0.000022	0.000010	0.0000012	0.000024	0.0000029			Not used	Not used
<b>Petrochemicals* - 67,000 bbl tanks</b>														
17. Acetone	0.12	0.014	0.14	0.016	4.0	0.48	0.017	0.0020	0.039	0.0047			3.8	0.45
18. Acrylonitrile	0.060	0.0072	0.068	0.0082	1.8	0.21	0.0084	0.0010	0.020	0.0024			1.7	0.20
19. Benzene	0.079	0.0094	0.090	0.011	2.2	0.27	0.011	0.0013	0.026	0.0031			2.1	0.25
20. Carbon disulfide	0.24	0.029	0.28	0.033	8.8	1.1	0.035	0.0042	0.083	0.0099			6.2	0.98
21. Carbon tetrachloride	0.17	0.021	0.20	0.024	5.2	0.62	0.024	0.0029	0.056	0.0069			4.8	0.58
22. Chloroform	0.21	0.025	0.24	0.029	7.1	0.86	0.030	0.0036	0.071	0.0085			6.7	0.80
23. Cyclohexane	0.085	0.010	0.096	0.012	2.4	0.29	0.012	0.0014	0.028	0.0034			2.3	0.27
24. 1,2-Dichloroethane	0.087	0.010	0.10	0.012	2.4	0.28	0.012	0.0014	0.029	0.0034			2.2	0.27
25. Ethyl acetate	0.083	0.010	0.095	0.011	2.3	0.28	0.012	0.0014	0.027	0.0033			2.2	0.26
26. Ethyl alcohol	0.028	0.0034	0.032	0.0038	0.66	0.079	0.0039	0.00046	0.0091	0.0011			0.62	0.074
27. Isopropyl alcohol	0.031	0.0038	0.036	0.0043	0.72	0.086	0.0043	0.00052	0.010	0.0012			0.68	0.082
28. Methyl alcohol	0.036	0.0044	0.042	0.0050	1.1	0.13	0.0051	0.00061	0.012	0.0014			1.0	0.12
29. Methylene chloride	0.31	0.037	0.35	0.042	11.0	1.3	0.044	0.0053	0.10	0.012			10.0	1.2
30. Methyl-ethyl-ketone	0.073	0.0087	0.083	0.0099	2.1	0.25	0.010	0.0012	0.024	0.0029			1.9	0.23
31. Methyl methacrylate	0.038	0.0046	0.043	0.0052	0.72	0.086	0.0051	0.00061	0.012	0.0015			0.68	0.082
32. 1,1,1-Trichloroethane	0.17	0.020	0.19	0.023	5.1	0.61	0.023	0.0028	0.055	0.0066			4.8	0.58
33. Trichloroethylene	0.11	0.013	0.12	0.014	2.8	0.34	0.015	0.0018	0.035	0.0042			2.6	0.31
34. Toluene	0.035	0.0042	0.040	0.0048	0.66	0.079	0.0048	0.00058	0.011	0.0014			0.62	0.074
35. Vinyl acetate	0.092	0.011	0.10	0.013	2.7	0.32	0.013	0.0016	0.030	0.0037			2.5	0.30

\*Due to safety and health regulations, toxicity, and value of these petrochemicals, they are normally stored in tanks with vapor recovery controls which are 90 to 98 percent efficient.

Emission factors based on the following parameters:

Ambient conditions:

Storage temperature: 60°F (15.6°C).  
Daily ambient temperature change: 15°F (8.3°C).  
Wind velocity: 10 mi/hr (4.5 m/sec).

Typical fixed roof tanks:

Outage: 50 percent of tank height.  
Turnovers per year (N): 30 for crude; 13 for all other liquids.  
Paint factor (F<sub>p</sub>): New tank-white paint-1.00;  
Old tank-white/aluminum paint-1.14.

For 67,000 bbl tankage (10.7 x 10<sup>6</sup> liters)  
Height: 48 ft. (14.6m)  
Diameter: 110 ft. (33.5m)

For 250,000 bbl tankage (39.7 x 10<sup>6</sup> liters)  
Height: 44 ft. (11.4m)  
Diameter: 200 ft. (60.8m)

Emission factors based on the following parameters:

Typical floating roof tanks:

Paint factor (K<sub>p</sub>): New tank-white paint-0.090;  
Old tank-white/aluminum paint-0.95.  
Seal factor (K<sub>s</sub>): New tank-modern seals-1.00;  
Old tank-50 percent old seals-1.14.  
Tank type factor (K<sub>t</sub>): New tank-welded-0.045;  
Old tank-50 percent riveted-0.088.

Typical variable space tank:

Diameter: 50 ft. (15.2m)  
Height: 30 ft. (9.1m)  
Capacity: 10,500 bbl (1.67 x 10<sup>6</sup> liters)  
Turnovers per year (N): 6  
Volume expansion capacity: one fourth of liquid capacity - 2625 bbl (0.42 x 10<sup>6</sup> liters).

4.3.3.1 Sample Calculation - Breathing losses from a fixed roof storage tank would be calculated as follows, using Equation (1).

Design basis:

Tank capacity - 100,000 bbl.  
 Tank diameter - 125 ft.  
 Tank height - 46 ft.  
 Average diurnal temperature change - 15°F.  
 Gasoline RVP - 9 psia.  
 Gasoline temperature - 70°F.  
 Specular aluminum painted tank.  
 Roof slope is 0.1 ft/ft.

Fixed roof tank breathing loss equation:

$$L_B = 2.21 \times 10^{-4} M \left[ \frac{P}{14.7 - P} \right]^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_p C K_c$$

where: M = Molecular weight of gasoline vapors (see Table 4.3-1) = 66.

P = True vapor of gasoline (see Figure 4.3-8) = 5.6 psia.

D = Tank diameter = 125 ft.

$\Delta T$  = average diurnal temperature change = 15°F.

$F_p$  = paint factor (see Table 4.3-2) = 1.20.

C = tank diameter adjustment factor (see Figure 4.3-10) = 1.0.

$K_c$  = crude oil factor (see note for equation (1)) = 1.0.

H = average vapor space height. For a tank which is filled completely and emptied, the average liquid level is 1/2 the tank rim height, or 23 ft. The effective cone height is 1/3 of the cone height. The roof slope is 0.1 ft/ft and the tank radius is 62.5 ft. Effective cone height = (62.5 ft) (0.1 ft/ft) (1/3) = 2.08 ft.

H = average vapor space height = 23 ft + 2 ft = 25 ft.

Therefore:

$$L_B = 2.21 \times 10^{-4} (66) \left[ \frac{5.6}{14.7 - 5.6} \right]^{0.68} (125)^{1.73} (25)^{0.51} (15)^{0.50} (1.2) (1.0) (1.0)$$

$$L_B = 1068 \text{ lb/day}$$

### References for Section 4.3

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## 4.4 TRANSPORTATION AND MARKETING OF PETROLEUM LIQUIDS<sup>1</sup>

by Charles C. Masser

### 4.4.1 Process Description

As Figure 4.4-1 indicates, the transportation and marketing of petroleum liquids involves many distinct operations, each of which represents a potential source of hydrocarbon evaporation loss. Crude oil is transported from production operations to the refinery via tankers, barges, tank cars, tank trucks, and pipelines. In the same manner, refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries by tankers, barges, tank cars, tank trucks, and pipelines. From the fuel marketing terminals, the fuels are delivered via tank trucks to service stations, commercial accounts, and local bulk storage plants. The final destination for gasoline is usually a motor vehicle gasoline tank. A similar distribution path may also be developed for fuel oils and other petroleum products.

### 4.4.2 Emissions and Controls

Evaporative hydrocarbon emissions from the transportation and marketing of petroleum liquids may be separated into four categories, depending on the storage equipment and mode of transportation used:

1. Large storage tanks: Breathing, working, and standing storage losses.
2. Marine vessels, tank cars, and tank trucks: Loading, transit, and ballasting losses.
3. Service stations: Bulk fuel drop losses and underground tank breathing losses.
4. Motor vehicle tanks: Refueling losses.

(In addition, evaporative and exhaust emissions are also associated with motor vehicle operation. These topics are discussed in Chapter 3.)

4.4.2.1 Large Storage Tanks - Losses from storage tanks are thoroughly discussed in Section 4.3.

4.4.2.2 Marine Vessels, Tank Cars, and Tank Trucks - Losses from marine vessels, tank cars, and tank trucks can be categorized into loading losses, transit losses, and ballasting losses.

Loading losses are the primary source of evaporative hydrocarbon emissions from marine vessel, tank car, and tank truck operations. Loading losses occur as hydrocarbon vapors residing in empty cargo tanks are displaced to the atmosphere by the liquid being loaded into the cargo tanks. The hydrocarbon vapors displaced from the cargo tanks are a composite of (1) hydrocarbon vapors formed in the empty tank by evaporation of residual product from previous hauls and (2) hydrocarbon vapors generated in the tank as the new product is being loaded. The quantity of hydrocarbon losses from loading operations is, therefore, a function of the following parameters:

- Physical and chemical characteristics of the previous cargo.
- Method of unloading the previous cargo.

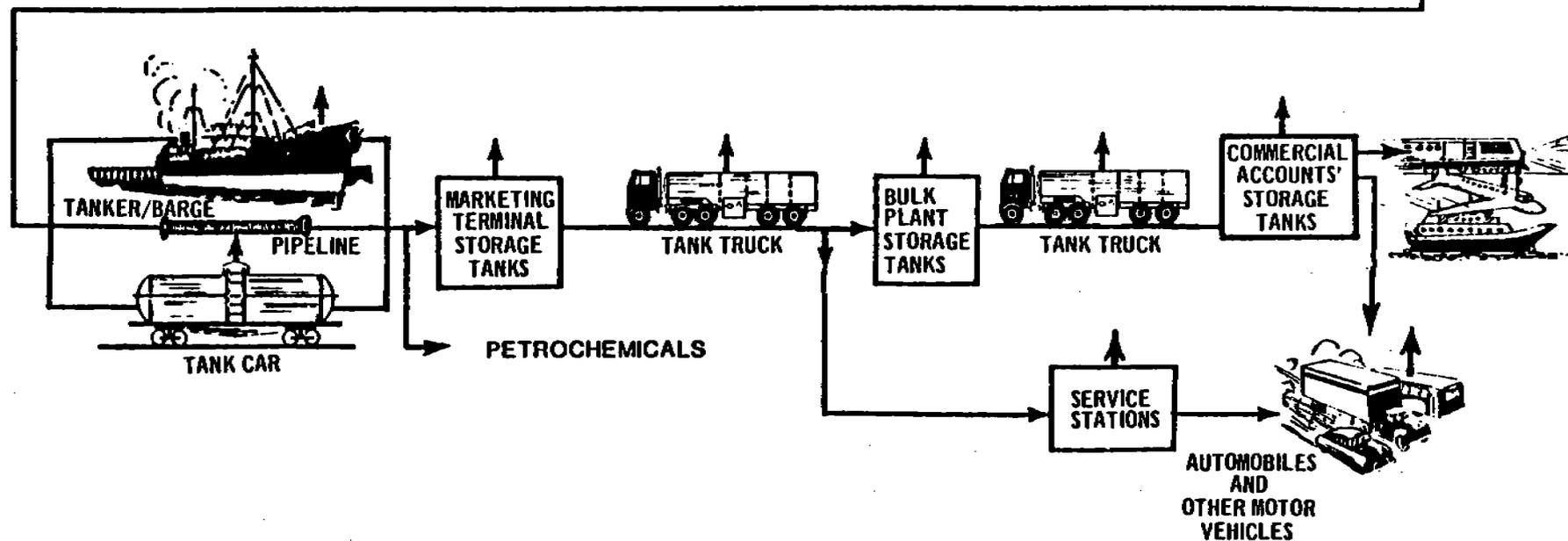
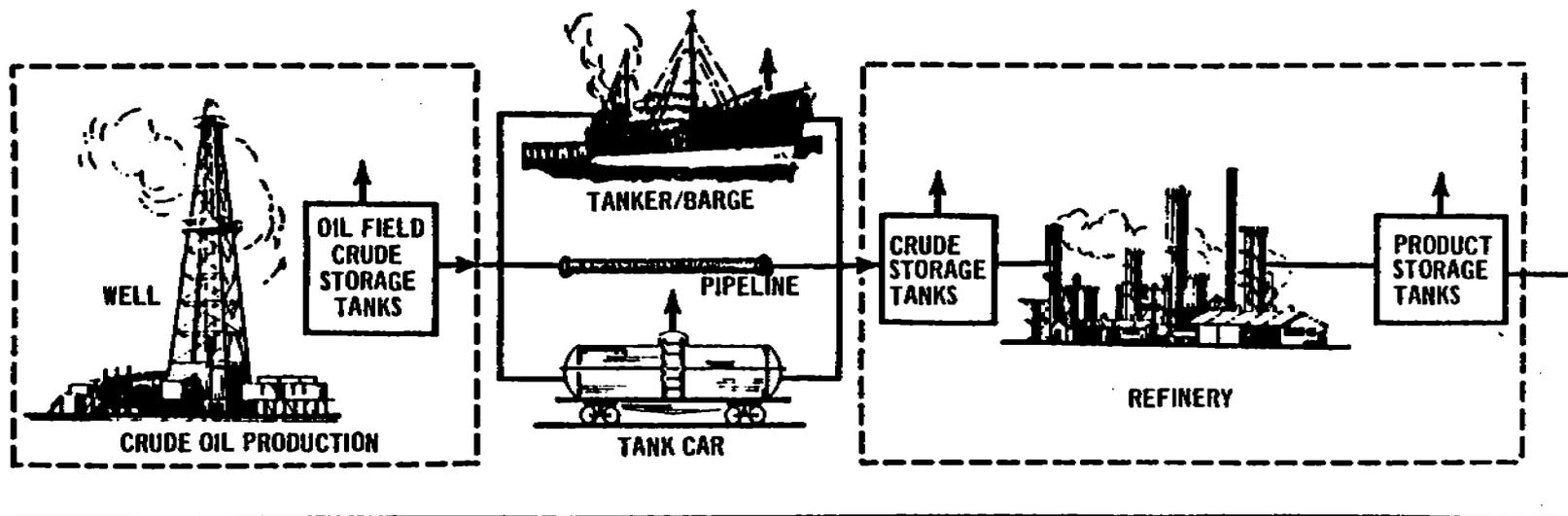


Figure 4.4-1. Flowsheet of petroleum production, refining, and distribution systems. (Sources of organic evaporative emissions are indicated by vertical arrows.)

- Operations during the transport of the empty carrier to the loading terminal.
- Method of loading the new cargo.
- Physical and chemical characteristics of the new cargo.

The principal methods of loading cargo carriers are presented in Figures 4.4-2, 4.4-3, and 4.4-4. In the splash loading method, the fill pipe dispensing the cargo is only partially lowered into the cargo tank. Significant turbulence and vapor-liquid contacting occurs during the splash loading operation, resulting in high levels of vapor generation and loss. If the turbulence is high enough, liquid droplets will be entrained in the vented vapors.

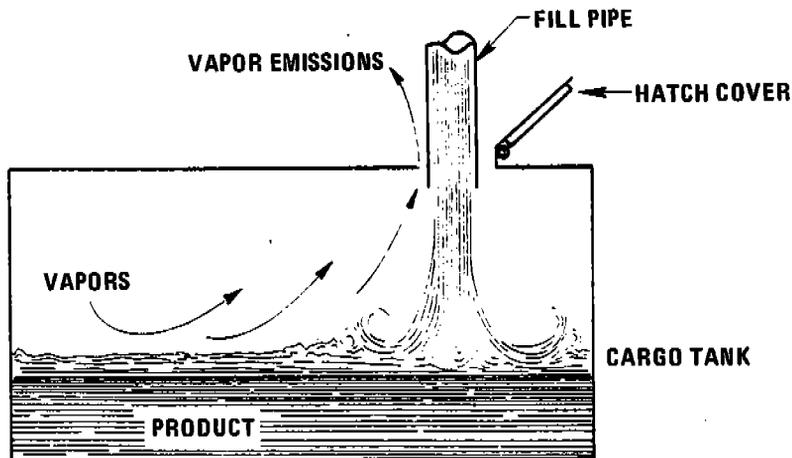


Figure 4.4-2. Splash loading method.

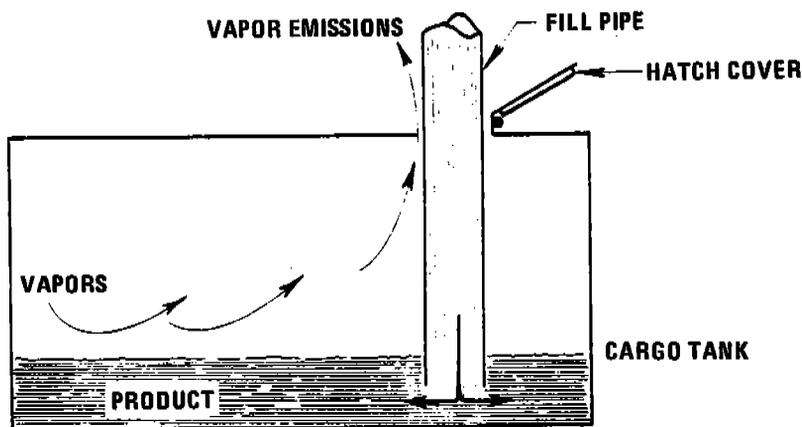


Figure 4.4-3. Submerged fill pipe.

A second method of loading is submerged loading. The two types of submerged loading are the submerged fill pipe method and the bottom loading method. In the submerged fill pipe method, the fill pipe descends almost to the bottom of the cargo tank. In the bottom loading method, the fill pipe enters the cargo tank from the bottom. During the major portion of both forms of submerged loading

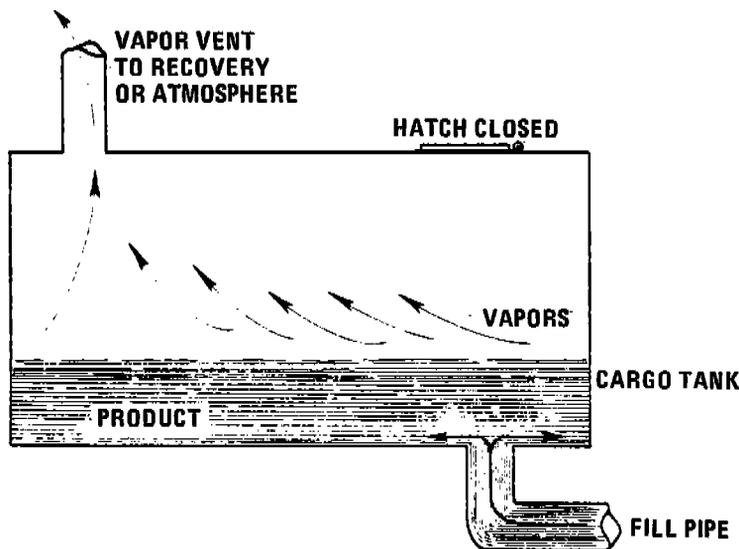


Figure 4.4-4. Bottom loading.

methods, the fill pipe opening is positioned below the liquid level. The submerged loading method significantly reduces liquid turbulence and vapor-liquid contacting, thereby resulting in much lower hydrocarbon losses than encountered during splash loading methods.

The history of a cargo carrier is just as important a factor in loading losses as the method of loading. Hydrocarbon emissions are generally lowest from a clean cargo carrier whose cargo tanks are free from vapors prior to loading. Clean cargo tanks normally result from either carrying a non-volatile liquid such as heavy fuel oils in the previous haul, or from cleaning or venting the empty cargo tank prior to loading operations. An additional practice, specific to marine vessels, that has significant impact on loading losses is ballasting. After unloading a cargo, empty tankers normally fill several cargo tanks with water to improve the tanker's stability on the return voyage. Upon arrival in port, this ballast water is pumped from the cargo tanks before loading the new cargo. The ballasting of cargo tanks reduces the quantity of vapor returning in the empty tanker, thereby reducing the quantity of vapors emitted during subsequent tanker loading operations.

In normal dedicated service, a cargo carrier is dedicated to the transport of only one product and does not clean or vent its tank between trips. An empty cargo tank in normal dedicated service will retain a low but significant concentration of vapors which were generated by evaporation of residual product on the tank surfaces. These residual vapors are expelled along with newly generated vapors during the subsequent loading operation.

Another type of cargo carrier is one in "dedicated balance service." Cargo carriers in dedicated balance service pick up vapors displaced during unloading operations and transport these vapors in the empty cargo tanks back to the loading terminal. Figure 4.4-5 shows a tank truck in dedicated vapor balance service unloading gasoline to an underground service station tank and filling up with displaced gasoline vapors to be returned to the truck loading terminal. The vapors in an empty cargo carrier in dedicated balance service are normally saturated with hydrocarbons.

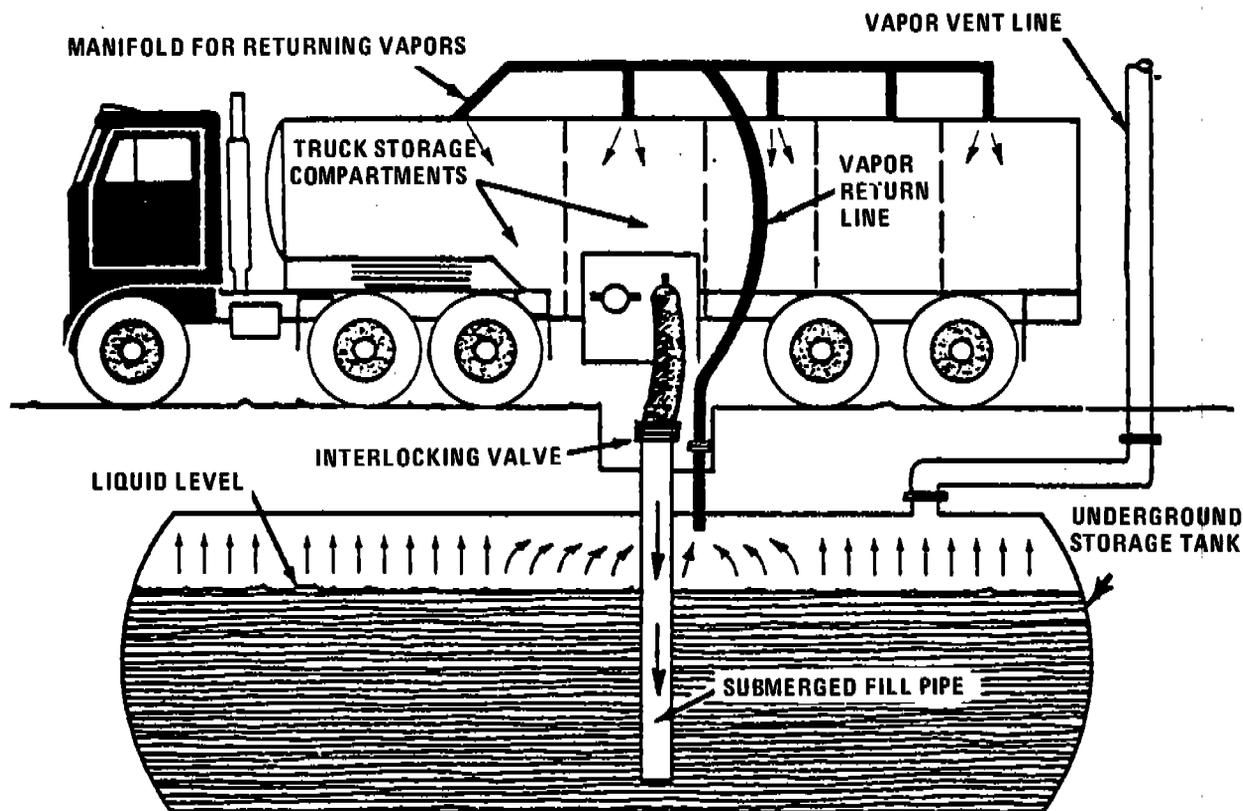


Figure 4.4-5. Tanktruck unloading into an underground service station storage tank. Tanktruck is practicing "vapor balance" form of vapor control.

Emissions from loading hydrocarbon liquid can be estimated (within 30 percent) using the following expression:

$$L_L = 12.46 \frac{SPM}{T} \quad (1)$$

where:  $L_L$  = Loading loss, lb/10<sup>3</sup> gal of liquid loaded.

$M$  = Molecular weight of vapors, lb/lb-mole (see Table 4.3-1).

$P$  = True vapor pressure of liquid loading, psia (see Figures 4.3-8 and 4.3-9, and Table 4.3-1).

$T$  = Bulk temperature of liquid loaded, °R.

$S$  = A saturation factor (see Table 4.4-1).

The saturation factor (S) represents the expelled vapor's fractional approach to saturation and accounts for the variations observed in emission rates from the different unloading and loading methods. Table 4.4-1 lists suggested saturation factors (S).

**Table 4.4-1. S FACTORS FOR CALCULATING PETROLEUM LOADING LOSSES**

Cargo carrier	Mode of operation	S factor
Tank trucks and tank cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedicated service	1.45
	Submerged loading: dedicated, vapor balance service	1.00
	Splash loading: dedicated, vapor balance service	1.00
Marine vessels <sup>a</sup>	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

<sup>a</sup>To be used for products other than gasoline; use factors from Table 4.4-2 for marine loading of gasoline.

Recent studies on gasoline loading losses from ships and barges have led to the development of more accurate emission factors for these specific loading operations. These factors are presented in Table 4.4-2 and should be used instead of Equation (1) for gasoline loading operations at marine terminals.<sup>2</sup>

Ballasting operations are a major source of hydrocarbon emissions associated with unloading petroleum liquids at marine terminals. It is common practice for large tankers to fill several cargo tanks with water after unloading their cargo. This water, termed ballast, improves the stability of the empty tanker on rough seas during the subsequent return voyage. Ballasting emissions occur as hydrocarbon-laden air in the empty cargo tank is displaced to the atmosphere by ballast water being pumped into the empty cargo tank. Although ballasting practices vary quite a bit, individual cargo tanks are ballasted about 80 percent, and the total vessel is ballasted approximately 40 percent of capacity. Ballasting emissions from gasoline and crude oil tankers are approximately 0.8 and 0.6 lb/10<sup>3</sup> gal, respectively, based on total tanker capacity. These estimates are for motor gasolines and medium volatility crudes (RVP ≈ 5 psia).<sup>2</sup>

An additional emission source associated with marine vessel, tank car, and tank truck operations is transit losses. During the transportation of petroleum liquids, small quantities of hydrocarbon vapors are expelled from cargo tanks due to temperature and barometric pressure changes. The most significant transit loss is from tanker and barge operations and can be calculated using Equation (2).<sup>3</sup>

**Table 4.4-2. HYDROCARBON EMISSION FACTORS FOR GASOLINE LOADING OPERATIONS**

Vessel tank condition	Hydrocarbon emission factors					
	Ships		Ocean barges		Barges	
	Range	Average	Range	Average	Range	Average
Cleaned and vapor free						
lb/10 <sup>3</sup> gal transferred	0 to 2.3	1.0	0 to 3	1.3	a	1.2
kg/10 <sup>3</sup> liter transferred	0 to 0.28	0.12	0 to 0.36	0.16		0.14
Ballasted						
lb/10 <sup>3</sup> gal transferred	0.4 to 3	1.6	0.5 to 3	2.1	b	b
kg/10 <sup>3</sup> liter transferred	0.05 to 0.36	0.19	0.06 to 0.36	0.25		
Uncleaned - dedicated service						
lb/10 <sup>3</sup> gal transferred	0.4 to 4	2.4	0.5 to 5	3.3	1.4 to 9	4.0
kg/10 <sup>3</sup> liter transferred	0.05 to 0.48	0.29	0.06 to 0.60	0.40	0.17 to 1.08	0.48
Average cargo tank condition						
lb/10 <sup>3</sup> gal transferred	a	1.4	a	a	a	4.0
kg/10 <sup>3</sup> liter transferred		0.17				0.48

<sup>a</sup>These values are not available.

<sup>b</sup>Barges are not normally ballasted.

$$L_T = 0.1 PW \quad (2)$$

where:  $L_T$  = Transit loss, lb/week-10<sup>3</sup> gal transported.

$P$  = True vapor pressure of the transported liquid, psia  
(see Figures 4.3-8 and 4.3-9, and Table 4.3-1).

$W$  = Density of the condensed vapors, lb/gal (see Table 4.3-1).

In the absence of specific inputs for Equations (1) and (2), typical evaporative hydrocarbon emissions from loading operations are presented in Table 4.4-3. It should be noted that, although the crude oil used to calculate the emission values presented in Table 4.4-3 has an RVP of 5, the RVP of crude oils can range over two orders of magnitude. In areas where loading and transportation sources are major factors affecting the air quality it is advisable to obtain the necessary parameters and to calculate emission estimates from Equations (1) and (2).

Control measures for reducing loading emissions include the application of alternate loading methods producing lower emissions and the application of vapor recovery equipment. Vapor recovery equipment captures hydrocarbon vapors displaced during loading and ballasting operations and recovers the hydrocarbon vapors by the use of refrigeration, absorption, adsorption, and/or compression. Figure 4.4-6 demonstrates the recovery of gasoline vapors from tank trucks during loading operation at bulk terminals. Control efficiencies range from 90 to 98 percent depending on the nature of the vapors and the type of recovery equipment employed.<sup>4</sup>

**Table 4.4-3. HYDROCARBON EMISSION FACTORS FOR PETROLEUM LIQUID TRANSPORTATION AND MARKETING SOURCES**

Emission source	Product emission factors					
	Gasoline	Crude oil	Jet naphtha (JP-4)	Jet kerosene	Distillate oil No. 2	Residual oil No. 6
<b>Tank cars/trucks</b>						
Submerged loading-normal service						
lb/10 <sup>3</sup> gal transferred	5	3	1.5	0.02	0.01	0.0001
kg/10 <sup>3</sup> liters transferred	0.6	0.4	0.18	0.002	0.001	0.00001
Splash loading-normal service						
lb/10 <sup>3</sup> gal transferred	12	7	4	0.04	0.03	0.0003
kg/10 <sup>3</sup> liters transferred	1.4	0.8	0.5	0.005	0.004	0.00004
Submerged loading-balance service						
lb/10 <sup>3</sup> gal transferred	8	5	2.5	a	a	a
kg/10 <sup>3</sup> liters transferred	1.0	0.6	0.3			
Splash loading-balance service						
lb/10 <sup>3</sup> gal transferred	8	5	2.5	a	a	a
kg/10 <sup>3</sup> liters transferred	1.0	0.6	0.3			
<b>Marine vessels</b>						
Loading tankers						
lb/10 <sup>3</sup> gal transferred	b	0.7	0.5	0.005	0.005	0.00004
kg/10 <sup>3</sup> liters transferred		0.08	0.06	0.0006	0.0006	5x10 <sup>-6</sup>
Loading barges						
lb/10 <sup>3</sup> gal transferred	b	1.7	1.2	0.013	0.012	0.00009
kg/10 <sup>3</sup> liters transferred		0.20	0.14	0.0016	0.0014	1.1x10 <sup>-5</sup>
Tanker ballasting						
lb/10 <sup>3</sup> gal cargo capacity	0.8	0.6	c	c	c	c
kg/10 <sup>3</sup> liters cargo capacity	0.10	0.07				
Transit						
lb/week-10 <sup>3</sup> gal transported	3	1	0.7	0.02	0.005	3x10 <sup>-5</sup>
kg/week-10 <sup>3</sup> liters transported	0.4	0.1	0.08	0.002	0.0006	4x10 <sup>-6</sup>

1. Emission factors are calculated for dispensed fuel temperature of 60°F.
  2. The example gasoline has an RVP of 10 psia.
  3. The example crude oil has an RVP of 5 psia.
- a. Not normally used.  
b. See Table 4.4-2 for these emission factors.  
c. Not Available.

Emissions from controlled loading operations can be calculated by multiplying the uncontrolled emission rate calculated in Equations (1) and (2) by the control efficiency term:

$$\left[ 1 - \frac{\text{efficiency}}{100} \right]$$

**4.4.2.3 Sample Calculation - Loading losses from a gasoline tank truck in dedicated balance service and practicing vapor recovery would be calculated as follows using Equation (1).**

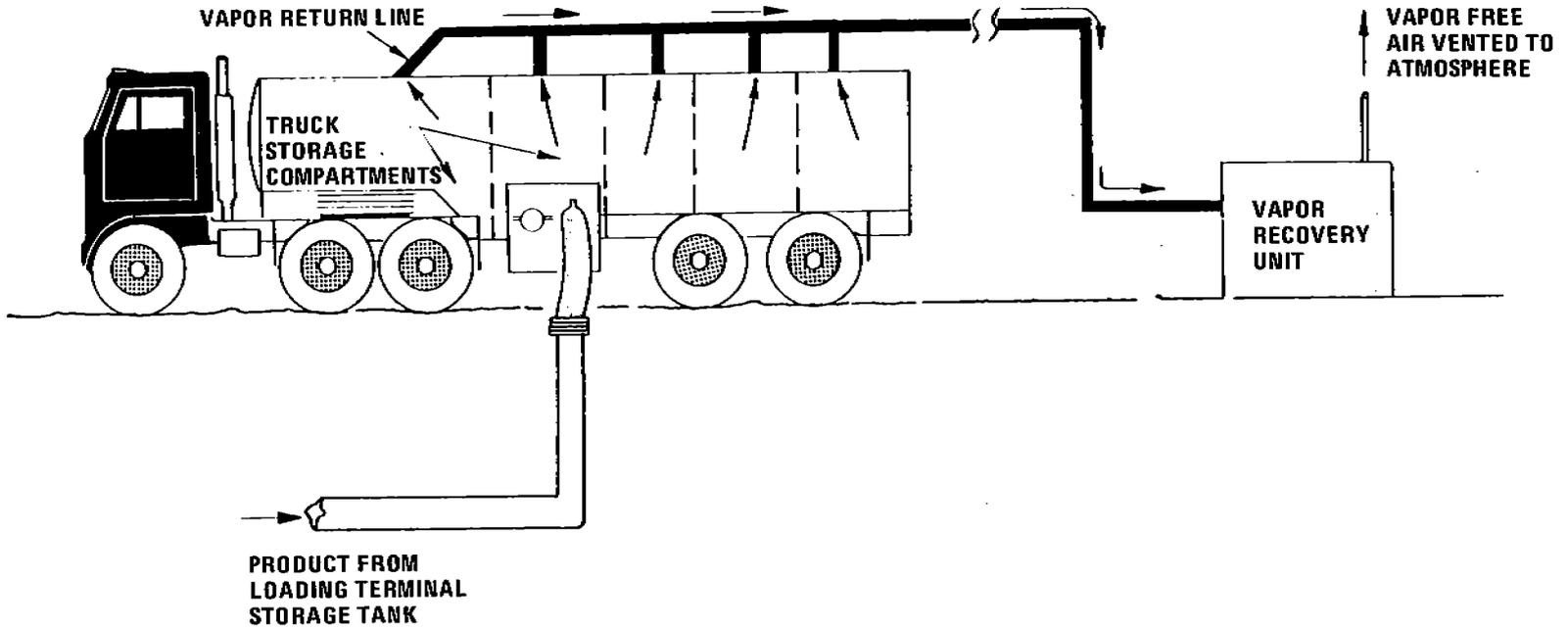


Figure 4.4-6. Tanktruck loading with vapor recovery.

Design basis:

Tank truck volume is 8000 gallons

Gasoline RVP is 9 psia

Dispensing temperature is 80° F

Vapor recovery efficiency is 95%

Loading loss equation:

$$L_L = 12.46 \frac{SPM}{T} \left(1 - \frac{eff}{100}\right)$$

- where: S = Saturation factor (see Table 4.4-1) = 1.0  
P = True vapor pressure of gasoline (see Figure 4.3-8) = 6.6 psia  
M = Molecular weight of gasoline vapors (see Table 4.3-1) ≈ 66  
T = Temperature of gasoline = 540° R  
eff = The control efficiency = 95%

$$L_L = 12.46 \frac{(1.0)(6.6)(66)}{540} \left(1 - \frac{95}{100}\right)$$
$$= 0.50 \text{ lb}/10^3 \text{ gal}$$

Total loading losses are

$$(0.50 \text{ lb}/10^3 \text{ gal}) (8.0 \times 10^3 \text{ gal}) = 4.0 \text{ lb of hydrocarbon}$$

4.4.2.4 Service Stations - Another major source of evaporative hydrocarbon emissions is the filling of underground gasoline storage tanks at service stations. Normally, gasoline is delivered to service stations in large (8000 gallon) tank trucks. Emissions are generated when hydrocarbon vapors in the underground storage tank are displaced to the atmosphere by the gasoline being loaded into the tank. As with other loading losses, the quantity of the service station tank loading loss depends on several variables including the size and length of the fill pipe, the method of filling, the tank configuration, and the gasoline temperature, vapor pressure, and composition. An average hydrocarbon emission rate for submerged filling is 7.3 lb/10<sup>3</sup> gallons of transferred gasoline, and the rate for splash filling is 11.5 lb/10<sup>3</sup> gallons of transferred gasoline (Table 4.4-4).<sup>4</sup>

Emissions from underground tank filling operations at service stations can be reduced by the use of the vapor balance system (Figure 4.4-5). The vapor balance system employs a vapor return hose which returns gasoline vapors displaced from the underground tank to the tank truck storage compartments being emptied. The control efficiency of the balance system ranges from 93 to 100 percent. Hydrocarbon emissions from underground tank filling operations at a service station employing the vapor balance system and submerged filling are not expected to exceed 0.3 lb/10<sup>3</sup> gallons of transferred gasoline.

**Table 4.4-4. HYDROCARBON EMISSIONS FROM GASOLINE SERVICE STATION OPERATIONS**

Emission source	Emission rate	
	lb/10 <sup>3</sup> gal throughput	kg/10 <sup>3</sup> liters throughput
Filling underground tank		
Submerged filling	7.3	0.88
Splash filling	11.5	1.38
Balanced submerged filling	0.3	0.04
Underground tank breathing	1	0.12
Vehicle refueling operations		
Displacement losses (uncontrolled)	9	1.08
Displacement losses (controlled)	0.9	0.11
Spillage	0.7	0.084

A second source of hydrocarbon emissions from service stations is underground tank breathing. Breathing losses occur daily and are attributed to temperature changes, barometric pressure changes, and gasoline evaporation. The type of service station operation also has a large impact on breathing losses. An average breathing emission rate is 1 lb/10<sup>3</sup> gallons throughput.<sup>5</sup>

**4.4.2.5 Motor Vehicle Refueling** - An additional source of evaporative hydrocarbon emissions at service stations is vehicle refueling operations. Vehicle refueling emissions are attributable to vapors displaced from the automobile tank by dispensed gasoline and to spillage. The quantity of displaced vapors is dependent on gasoline temperature, auto tank temperature, gasoline RVP, and dispensing rates. Although several correlations have been developed to estimate losses due to displaced vapors, significant controversy exists concerning these correlations. It is estimated that the hydrocarbon emissions due to vapors displaced during vehicle refueling average 9 lb/10<sup>3</sup> gallons of dispensed gasoline.<sup>4,5</sup>

The quantity of spillage loss is a function of the type of service station, vehicle tank configuration, operator technique, and operation discomfort indices. An overall average spillage loss is 0.7 lb/10<sup>3</sup> gallons of dispensed gasoline.<sup>6</sup>

Control methods for vehicle refueling emissions are based on conveying the vapors displaced from the vehicle fuel tank to the underground storage tank vapor space through the use of a special hose and nozzle (Figure 4.4-7). In the "balance" vapor control system, the vapors are conveyed by natural pressure differentials established during refueling. In "vacuum assist" vapor control systems, the conveyance of vapors from the auto fuel tank to the underground fuel tank is assisted by a vacuum pump. The overall control efficiency of vapor control systems for vehicle refueling emissions is estimated to be 88 to 92 percent.<sup>4</sup>

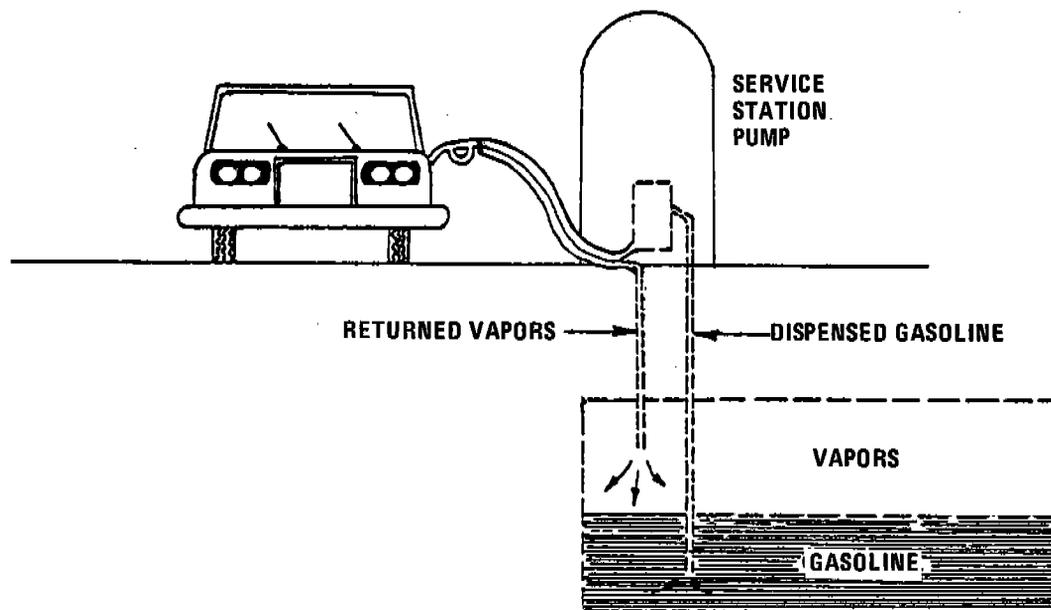


Figure 4.4-7. Automobile refueling vapor-recovery system.

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## 5. CHEMICAL PROCESS INDUSTRY

This section deals with emissions from the manufacture and use of chemicals or chemical products. Potential emissions from many of these processes are high, but because of the nature of the compounds they are usually recovered as an economic necessity. In other cases, the manufacturing operation is run as a closed system allowing little or no escape to the atmosphere.

In general, the emissions that reach the atmosphere from chemical processes are primarily gaseous and are controlled by incineration, adsorption, or absorption. In some cases, particulate emissions may also be a problem. The particulates emitted are generally extremely small and require very efficient treatment for removal. Emission data from chemical processes are sparse. It was therefore frequently necessary to make estimates of emission factors on the basis of material balances, yields, or similar processes.

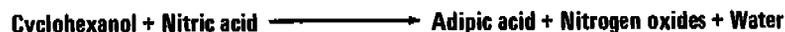
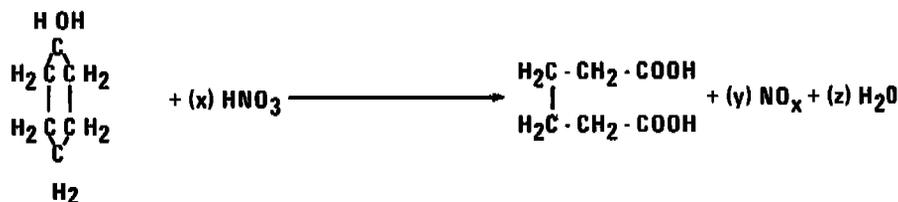
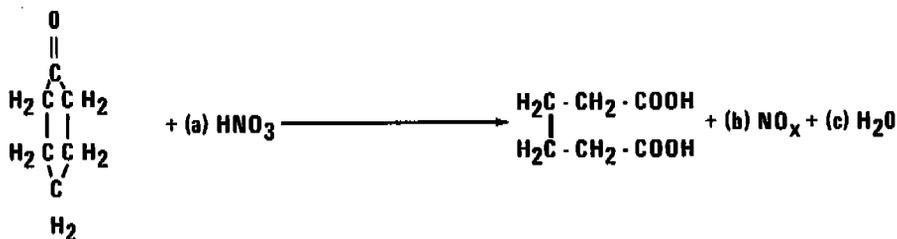
### 5.1 ADIPIC ACID

by Pam Canova

#### 5.1.1 General<sup>1,2</sup>

Adipic acid,  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ , is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Ninety percent of all adipic acid produced in the United States is used in manufacturing Nylon 6,6. Cyclohexane is generally the basic raw material used to produce adipic acid; however, one plant uses cyclohexanone, which is a by-product of another process. Phenol has also been utilized, but has proved to be more expensive and less readily available than cyclohexane.

During adipic acid production, the raw material, cyclohexane or cyclohexanone, is transferred to a reactor, where it is oxidized at 260 to 330°F (130 to 170°C) to form a cyclohexanol/cyclohexanone mixture. The mixture is then transferred to a second reactor and oxidized with nitric acid and a catalyst (usually a mixture of cupric nitrate and ammonium vanadate) at 160 to 220°F (70 to 100°C) to form adipic acid. The chemistry of these reactions is shown below.



Dissolved  $\text{NO}_x$  gas plus any light hydrocarbon by-products are stripped from the adipic acid/nitric acid solution with air and steam. Various organic acid by-products, namely acetic acid, glutaric acid, and succinic acid, are also formed and may be recovered and sold by some plants.

The adipic acid/nitric acid solution is then chilled, and sent to a crystallizer where adipic acid crystals are formed. The solution is centrifuged to separate the crystals. The remaining solution is sent to another crystallizer, where any residual adipic acid is crystallized and centrifugally separated. The crystals from the two centrifuges are combined, dried, and stored. The remaining solution is distilled to recover nitric acid, which is routed back to the second reactor for re-use. Figure 5.1-1 presents a general schematic of the adipic acid manufacturing process.

### 5.1.2 Emissions and Controls

Nitrogen oxides, hydrocarbons, and carbon monoxide are the major pollutants produced in adipic acid production. The cyclohexane reactor is the largest source of CO and HC, and the nitric acid reactor is the predominant source of  $\text{NO}_x$ . Particulate emissions are low because baghouses are generally employed for maximum product recovery and air pollution control. Figure 5.1-1 shows the points of emission of these pollutants.

The most significant emissions of HC and CO come from the cyclohexane oxidation unit, which is equipped with high- and low-pressure scrubbers. Scrubbers have a 90 percent collection efficiency of HC and are used for economic reasons to recover expensive hydrocarbons as well as for pollution control. Thermal incinerators, flaring, and carbon absorbers can all be used to limit HC emissions from the cyclohexane oxidation unit with greater than 90 percent efficiency. CO boilers control CO emissions with 99.99 percent efficiency and HC emissions with practically 100 percent efficiency. The combined use of a CO boiler and a pressure scrubber results in essentially complete HC and CO control.

Three methods are presently used to control emissions from the  $\text{NO}_x$  absorber: water scrubbing, thermal reduction, and flaring or combustion in a powerhouse boiler. Water scrubbers have a low collection efficiency of approximately 70 percent because of the extended length of time needed to remove insoluble NO in the absorber offgas stream. Thermal reduction, in which offgases containing  $\text{NO}_x$  are heated to high temperatures and reacted with excess fuel in a reducing atmosphere, operates at up to 97.5 percent efficiency and is believed to be the most effective system of control. Burning off-gas in a powerhouse or flaring has an estimated efficiency of 70 percent.

Emission factors for adipic acid manufacture are listed in Table 5.1-1.

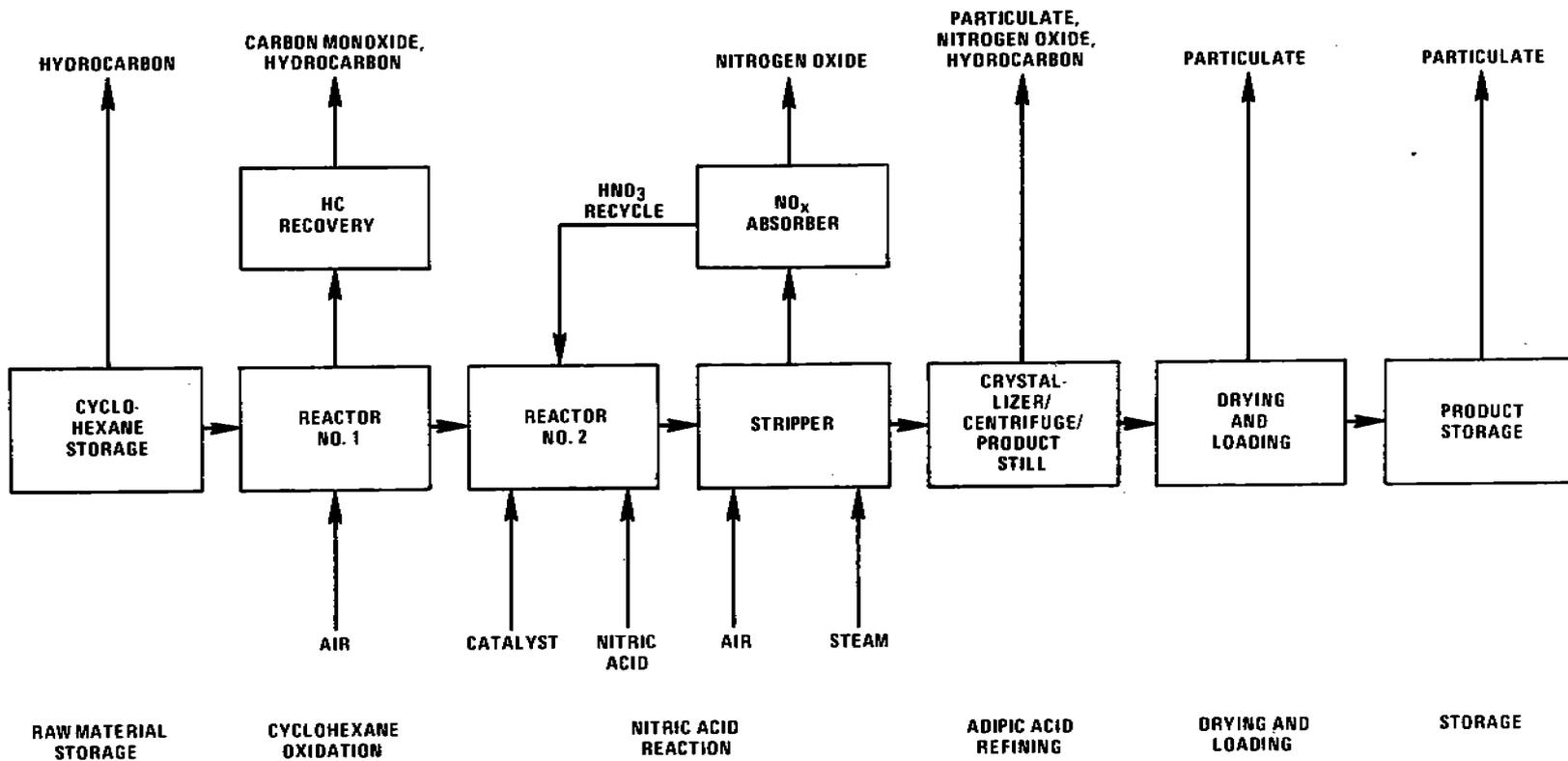


Figure 5.1-1. General flow diagram of adipic acid manufacturing process.

**Table 5.1-1. EMISSION FACTORS FOR ADIPIC ACID MANUFACTURE<sup>1,a</sup>**  
**EMISSION FACTOR RATING: B**

Process	Particulate		Nitrogen oxides <sup>b</sup>		Hydrocarbon		Carbon monoxide	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Raw material storage Uncontrolled	0	0	0	0	2.2	1.1	0	0
Cyclohexane oxidation Uncontrolled <sup>c</sup>	0	0	0	0	40	20	115	58
W/boiler	0	0	0	0	Neg <sup>l</sup>	Neg	1	0.5
W/thermal incinerator <sup>d</sup>	0	0	0	0	Neg	Neg	Neg	Neg
W/flaring <sup>e</sup>	0	0	0	0	4	2	12	6
W/carbon absorber <sup>f</sup>	0	0	0	0	2	1	115	58
W/scrubber plus boiler	0	0	0	0	Neg	Neg	Neg	Neg
Nitric acid reaction Uncontrolled <sup>g</sup>	0	0	53	27	0	0	0	0
W/water scrubber <sup>h</sup>	0	0	16	8	0	0	0	0
W/thermal reduction <sup>i</sup>	0	0	1	0.5	0	0	0	0
W/flaring or combustion <sup>h</sup>	0	0	16	8	0	0	0	0
Adipic acid refining <sup>j</sup> Uncontrolled <sup>k</sup>	<0.1	<0.1	0.6	0.3	0.5	0.3	0	0
Adipic acid drying, loading, and storage Uncontrolled <sup>k</sup>	0.8	0.4	0	0	0	0	0	0

<sup>a</sup>Emission factors are in units of pounds of pollutant per ton and kilograms of pollutant per metric ton of adipic acid produced.

<sup>b</sup>NO<sub>x</sub> is in the form of NO and NO<sub>2</sub>. Although large quantities of N<sub>2</sub>O are also produced, N<sub>2</sub>O is not considered a criteria pollutant and is not, therefore, included in these factors.

<sup>c</sup>Uncontrolled emission factors are after scrubber processing since hydrocarbon recovery using scrubbers is an integral part of adipic acid manufacturing.

<sup>d</sup>A thermal incinerator is assumed to reduce HC and CO emissions by approximately 99.99%.

<sup>e</sup>A flaring system is assumed to reduce HC and CO emissions by 90%.

<sup>f</sup>A carbon absorber is assumed to reduce HC emissions by 94% and to be ineffective in reducing CO emissions.

<sup>g</sup>Uncontrolled emission factors are after NO<sub>x</sub> absorber since nitric acid recovery is an integral part of adipic acid manufacturing.

<sup>h</sup>Based on estimated 70% control.

<sup>i</sup>Based on estimated 97.5% control.

<sup>j</sup>Refining includes chilling, crystallization, centrifuging, and purification.

<sup>k</sup>Particulate emission factors are after baghouse control device.

<sup>l</sup>Negligible.

## References for Section 5.1

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### 5.3.1 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 2500 to 3000°F (1370 to 1650°C). The unburned carbon is collected as an extremely fine (10- to 400-nm diameter), black, fluffy particle. The three processes for producing carbon black are the furnace process, thermal process, and channel process. In 1973 the furnace process accounted for over 90 percent of production; the thermal process, 9 percent; and the channel process, less than 1 percent. The primary use for carbon black is for strengthening rubber products (mainly rubber tires); it is also used in printing inks, surface coatings, and plastics.

**5.3.1.1 Furnace Process** - Furnace black is produced by combustion of hydrocarbon feed in a refractory-lined furnace. Oil-fired furnaces now predominate. In this process (Figure 5.3-1) a heavy, aromatic oil feed is preheated and fed into the furnace with about half of the air required for complete combustion and a controlled amount of natural gas. The flue gases, which contain entrained carbon particles, are cooled to about 450°F (235°C) by passage through heat exchangers and water sprays. The carbon 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 a number of furnaces that are manifolded together.

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 an indirect-fired rotary dryer. The dried pellets are then conveyed to bulk storage. Process yields range from 35 to 65 percent, depending on the particle size of the carbon black produced and the efficiency of the process. Furnace designs and operating characteristics influence the particle size of the oil black. Generally, yields are highest for large particle blacks and lowest for small particle sizes.

The older gas-furnace process is basically the same as the oil-furnace process except that a light hydrocarbon gas is the primary feedstock and furnace designs are different. Some oil may also be added to enrich the gas feed. Yields range from 10 to 30 percent, which is much less than in the oil process, and comparatively coarser particles (40- to 80-nm diameter compared to 20- to 50-nm diameter for oil-furnace blacks) are produced. Because of the scarcity of natural gas and the comparatively low efficiency of the gas process, carbon black production by this method has been declining.

**5.3.1.2 Thermal Process** - The thermal process is a cyclic operation in which natural gas is thermally decomposed to carbon particles, hydrogen, methane, and a mixture of other hydrocarbons. To start the cycle, natural gas is burned to heat a brick checkerwork in the process furnace to about 3000°F (1650°C). After this temperature is reached, the air supply is cut off, the furnace stack is closed, and natural gas is introduced into the furnace. The natural gas is decomposed by the heat from the hot bricks. When the bricks become cool, the natural gas flow is shut off. The effluent gases, containing the thermal black particles, are flushed out of the furnace and cooled by water sprays to about 250°F (125°C) before passing through cyclonic collectors and fabric filters, which recover the thermal black.

The effluent gases, consisting of about 90 percent hydrogen, 6 percent methane, and a mixture of other hydrocarbons, are cooled, compressed, and used as a fuel to reheat the furnaces. 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.

The collected thermal black is pulverized and pelletized to a final product in much the same manner as furnace black. Thermal-process yields are generally high (35 to 60 percent), but the relatively

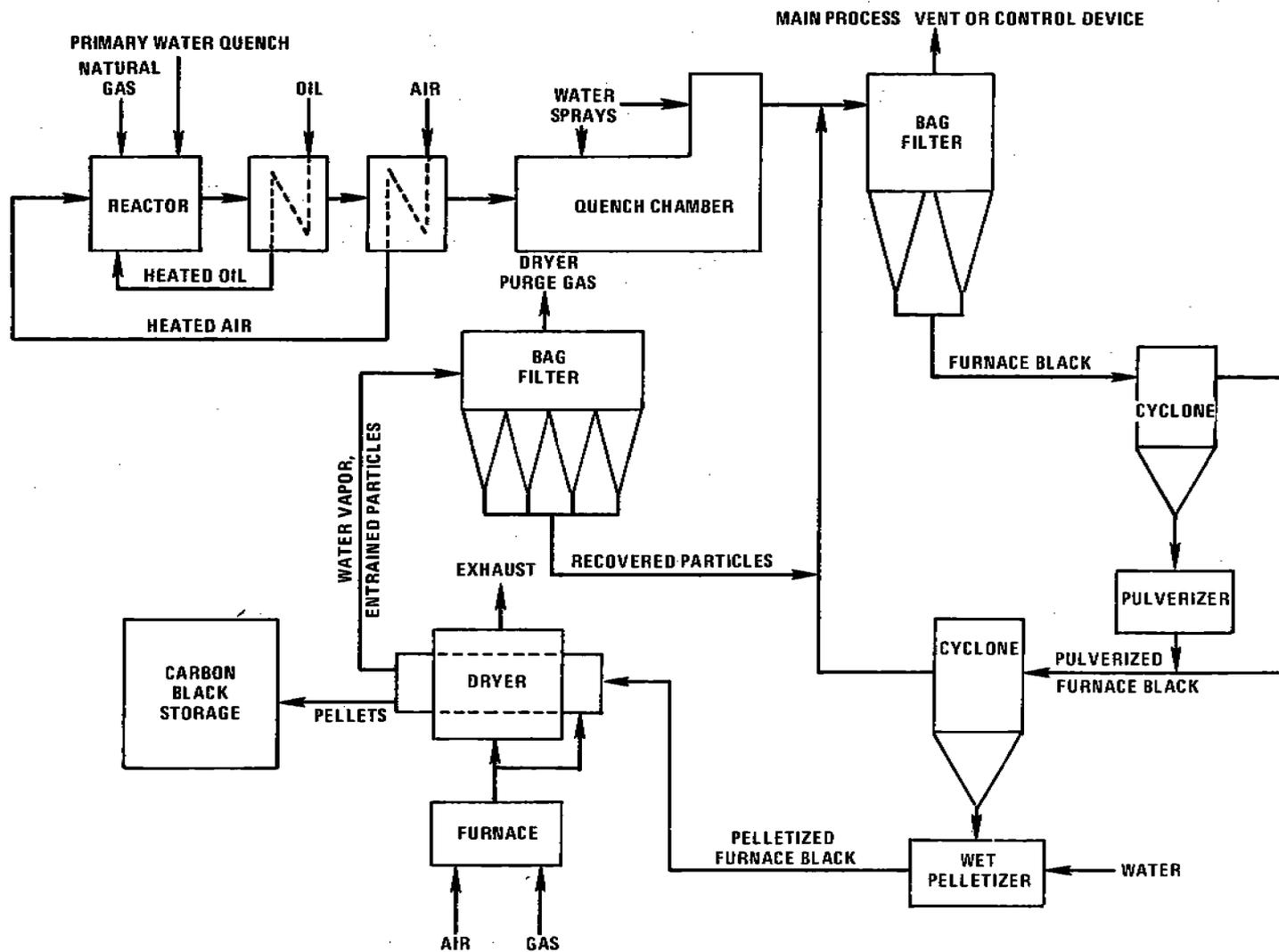


Figure 5.3-1. Simplified flow diagram of carbon black production by the oil-fired furnace process.

coarse particles produced (180- to 470-nm diameter) do not have the strong reinforcing properties required for rubber products.

**5.3.1.3 Channel Process** - In the channel-black process, natural gas is burned with a limited air supply in long, low buildings. The flame from this burning impinges on long steel channel sections that swing continuously over the flame. Carbon black deposited on the channels is scraped off into collecting hoppers. The combustion gases, containing uncollected solid carbon, carbon monoxide, and other combustion products, are then vented directly from the building. Yields from the channel-black process are only 5 percent or less, but very fine particles are produced (10- to 30-nm diameter). Channel-black production has been declining steadily from its peak in the 1940's. Since 1974 no production of channel black has been reported.

### **5.3.2 Emissions and Controls**

Emissions from carbon black manufacture include particulates, sulfur compounds, carbon monoxide, hydrocarbons, and nitrogen oxides. Trace amounts of polynuclear organic matter (POM) are also likely to be emitted. Emissions vary considerably from one process to another. Typical emission factors are given in Table 5.3-1.

The principal source of emissions in the furnace process is the main process vent. The vent stream consists of the reactor effluent plus quench water vapor vented from the carbon-black recovery system. Gaseous emissions vary considerably according to the grade of carbon black being produced. Hydrocarbon and CO emissions tend to be higher for small-particle black production. Sulfur compound emissions are a function of the feed sulfur content. Table 5.3-1 shows the normal emission ranges to be expected from these variations in addition to typical average values. Some particulate emissions may also occur from product transport, drier vents, the bagging and storage area, and spilled and leaked materials. Such emissions are generally negligible, however, because of the high efficiency of collection devices and sealed conveying systems used to prevent product loss.

Particulate emissions from the furnace-black process are controlled by fabric filters that recover the product from process and dryer vents. Particulate emissions control is therefore proportional to the efficiency of the product recovery system. Some producers may use water scrubbers on the dryer vent system.

Gaseous emissions from the furnace process may be controlled by 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 CO, hydrocarbons, and reduced sulfur compounds in the process flue gas. Particulate emissions may also be reduced by combustion of some of the carbon black particles; however, emissions of sulfur dioxide and nitrogen oxides are increased by these combustion devices.

Generally, emissions from the thermal process are negligible. Small amounts of nitrogen oxides and particulates may be emitted during the heating part of the process cycle when furnace stacks are open. Entrainment of carbon particles adhering to the checker brick may occur. Nitrogen oxides may be formed since high temperatures are reached in the furnaces. During the decomposition portion of the production cycle, the process is a closed system and no emissions would occur except through leaks.

Considerable emissions result from the channel process because of low efficiency of the process and the venting of the exhaust gas directly to the atmosphere. Most of the carbon input to the process is lost as CO, CO<sub>2</sub>, hydrocarbons, and particulate.

**Table 5.3-1. EMISSION FACTORS FOR CARBON BLACK MANUFACTURE<sup>a</sup>  
EMISSION FACTOR RATING: B (OIL FURNACE PROCESS)  
C (GAS FURNACE, CHANNEL, THERMAL PROCESSES)**

Process	Particulate		Carbon monoxide		Hydrocarbons <sup>b</sup>		Nitrogen oxides		Hydrogen sulfide <sup>c</sup>		Sulfur oxides <sup>c</sup>	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Oil furnace process <sup>d</sup>												
Uncontrolled	6(2-16) <sup>e</sup>	3(1-8) <sup>e</sup>	2600(1400-3300)	1300(700-1650)	200(60-520)	100(30-260)	0.4	0.2	20S(10S-26S)	10S(5S-13S)	Neg	Neg
With CO boiler	3	1.5	10 <sup>f</sup>	5 <sup>f</sup>	3	1.5	6	3	0.2S	0.1S	40S	20S
With flare	3	1.5	130 <sup>g</sup>	65 <sup>g</sup>	10	5	6	3	0.2S	0.1S	40S	20S
Gas furnace process <sup>h</sup>	10	5	5300(4200-6400)	2650(2100-3200)	1,800	900	-	-	Neg	Neg	Neg	Neg
Channel process <sup>i</sup>	2,300	1,150	33,500	16,750	11,500	5,750	-	-	Neg	Neg	Neg	Neg
Thermal process <sup>j</sup>	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg	Neg

<sup>a</sup>Expressed in terms of pounds per ton and kilograms per metric ton of carbon black product.

<sup>b</sup>As methane. Actual composition of emissions is 50-75% acetylene and the remainder methane.

<sup>c</sup>S is the weight percent sulfur in the feed. Emission factor based on a 50% yield of carbon in the feed to carbon black product and an average 50% conversion of sulfur in the feed to H<sub>2</sub>S.

<sup>d</sup>References 5 and 6.

<sup>e</sup>Based on fabric filter collection efficiency of 99.5 to 99.9%.

<sup>f</sup>Based on over 99% control of CO. Thermal incinerators could also be expected to achieve 99% oxidation of CO. (Reference 6).

<sup>g</sup>Based on 95% oxidation of CO (Reference 6).

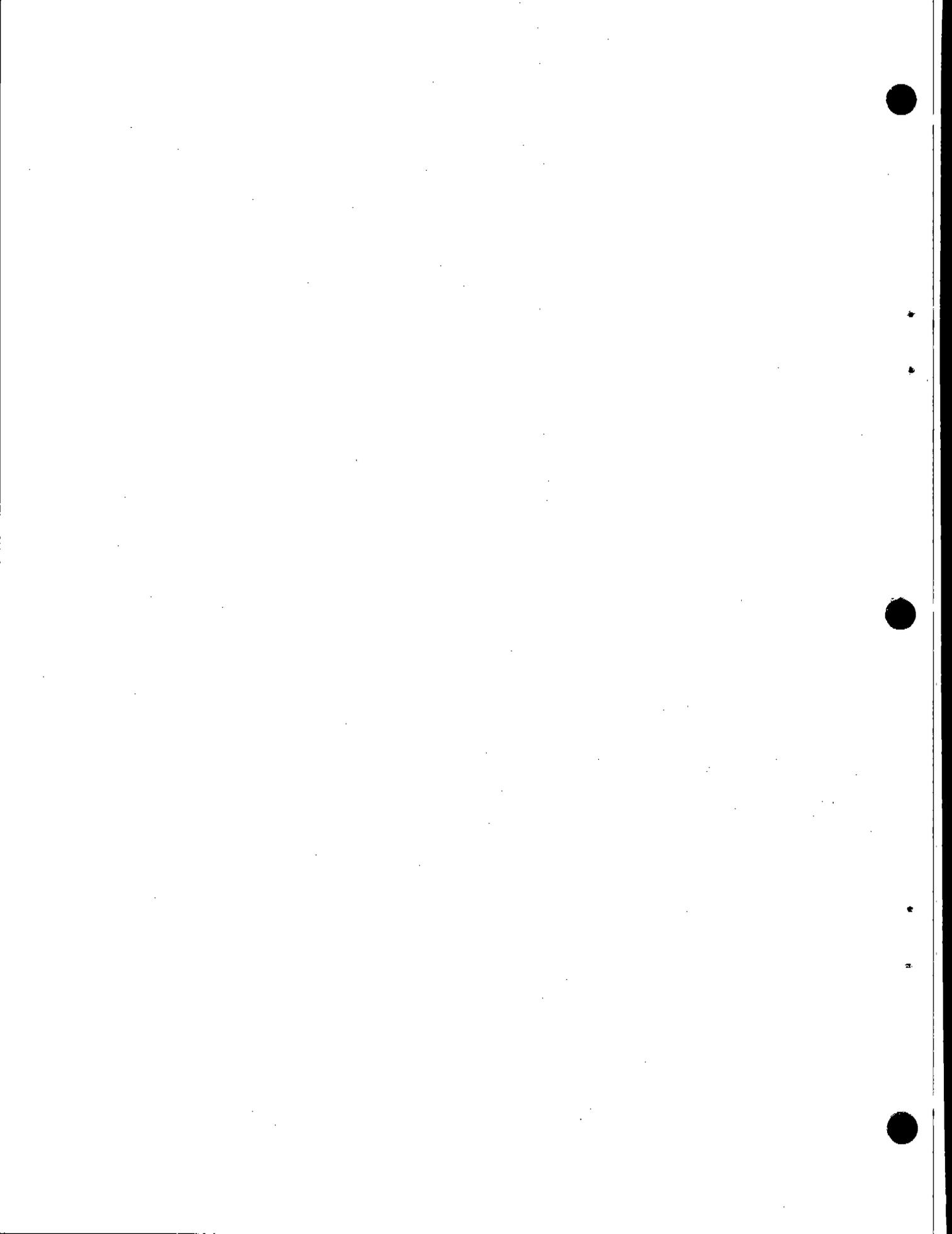
<sup>h</sup>References 1 and 2.

<sup>i</sup>References 1 and 2.

<sup>j</sup>Emissions data are not available, but no significant emissions are believed to occur.

### References for Section 5.3

1. Air Pollutant Emission Factors. Final Report. Resources Research, Incorporated. Reston, Virginia. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.
2. Drogin, I. Carbon Black. J. Air Pol. Control Assoc. 18:216-228, April 1968.
3. Cox, J.T. High Quality, High Yield Carbon Black. Chem. Eng. 57:116-117, June 1950.
4. Reinke, R.A. and T.A. Ruble. Oil Black. Ind. Eng. Chem. 44:685-694, April 1952.
5. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 1: Carbon Black Manufacture by the Furnace Process. Houdry Division, Air Products and Chemicals, Incorporated. Publication Number EPA-450/3-73-006a. June 1974.
6. Hustvedt, Kent C., Leslie B. Evans, and William M. Vatauk. Standards Support and Environmental Impact Statement, An Investigation of the Best Systems of Emission Reduction for Furnace Process Carbon Black Plants in the Carbon Black Industry. U.S. Environmental Protection Agency, Research Triangle Park, N.C. April 1976.
7. Carbon Black (Oil Black). Continental Carbon Company. Hydrocarbon Processing, 52:111. November 1973.



## 5.4 CHARCOAL

### 5.4.1 Process Description<sup>1</sup>

Charcoal is generally manufactured by means of pyrolysis, or destructive distillation, of wood waste from members of the deciduous hardwood species. In this process, the wood is placed in a retort where it is externally heated for about 20 hours at 500 to 700°F (260 to 370°C). Although the retort has air intakes at the bottom, these are only used during start-up and thereafter are closed. The entire distillation cycle takes approximately 24 hours, the last 4 hours being an exothermic reaction. Four units of hardwood are required to produce one unit of charcoal.

### 5.4.2 Emissions and Controls<sup>1</sup>

In the pyrolysis of wood, all the gases, tars, oils, acids, and water are driven off, leaving virtually pure carbon. All of these except the gas, which contains methane, carbon monoxide, carbon dioxide, nitrogen oxides, and aldehydes, are useful by-products if recovered. Unfortunately, economics has rendered the recovery of the distillate by-products unprofitable, and they are generally permitted to be discharged to the atmosphere. If a recovery plant is utilized, the gas is passed through water-cooled condensers. The condensate is then refined while the remaining cool, noncondensable gas is discharged to the atmosphere. Gaseous emissions can be controlled by means of an afterburner because the unrecovered by-products are combustible. If the afterburner operates efficiently, no organic pollutants should escape into the atmosphere. Emission factors for the manufacture of charcoal are shown in Table 5.4-1.

**Table 5.4-1. EMISSION FACTORS FOR CHARCOAL MANUFACTURING<sup>a,d</sup>**  
**EMISSION FACTOR RATING: C**

Pollutant	Type of operation			
	With chemical recovery plant		Without chemical recovery plant	
	lb/ton	kg/MT	lb/ton	kg/MT
Particulate (tar, oil)	—	—	400	200
Carbon monoxide	320 <sup>b</sup>	160 <sup>b</sup>	320 <sup>b</sup>	160 <sup>b</sup>
Hydrocarbons <sup>c</sup>	100 <sup>b</sup>	50 <sup>b</sup>	100 <sup>b</sup>	50 <sup>b</sup>
Crude methanol	—	—	152	76
Acetic acid	—	—	232	116
Other gases (HCHO, N <sub>2</sub> , NO)	60	30	60 <sup>b</sup>	30 <sup>b</sup>

<sup>a</sup>Calculated values based on data in Reference 2.

<sup>b</sup>Emissions are negligible if afterburner is used.

<sup>c</sup>Expressed as methane.

<sup>d</sup>Emission factors expressed in units of tons of charcoal produced.

### References for Section 5.4

1. Air Pollutant Emission Factors. Final Report. Resources Research, Inc. Reston, Va. Prepared for National Air Pollution Control Administration, Durham, N.C., under Contract Number CPA-22-69-119. April 1970.
2. Shreve, R.N. Chemical Process Industries, 3rd Ed. New York, McGraw-Hill Book Company. 1967. p. 619.



5.12.1 General<sup>1</sup>

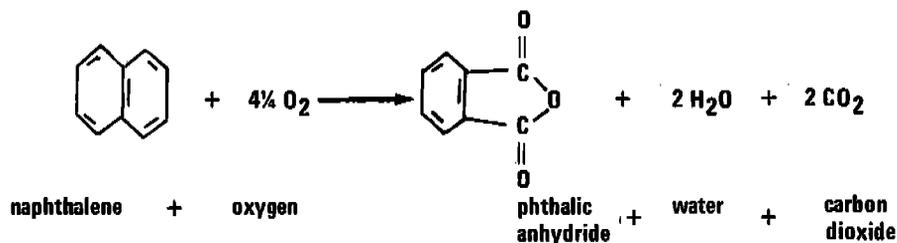
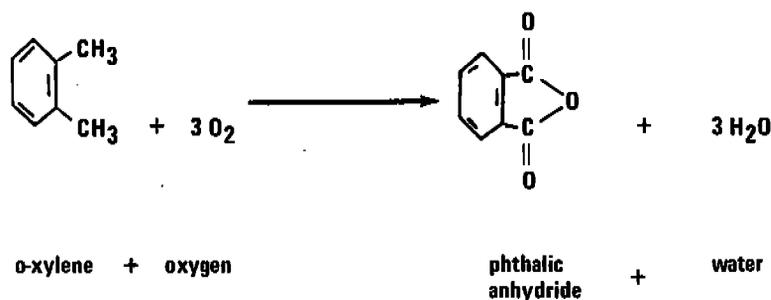
Phthalic anhydride (PAN) production in the United States in 1972 was 0.9 billion pounds per year; this total is estimated to increase to 2.2 billion pounds per year by 1985. Of the current production, 50 percent is used for plasticizers, 25 percent for alkyd resins, 20 percent for unsaturated polyester resins, and 5 percent for miscellaneous and exports. PAN is produced by catalytic oxidation of either ortho-xylene or naphthalene. Since naphthalene is a higher priced feedstock and has a lower feed utilization (about 1.0 lb PAN/lb o-xylene versus 0.97 lb PAN/lb naphthalene), future production growth is predicted to utilize o-xylene. Because emission factors are intended for future as well as present application, this report will focus mainly on PAN production utilizing o-xylene as the main feedstock.

The processes for producing PAN by o-xylene or naphthalene are the same except for reactors, catalyst handling, and recovery facilities required for fluid bed reactors.

In PAN production using o-xylene as the basic feedstock, filtered air is preheated, compressed, and mixed with vaporized o-xylene and fed into the fixed-bed tubular reactors. The reactors contain the catalyst, vanadium pentoxide, and are operated at 650 to 725°F (340 to 385°C). Small amounts of sulfur dioxide are added to the reactor feed to maintain catalyst activity. Exothermic heat is removed by a molten salt bath circulated around the reactor tubes and transferred to a steam generation system.

Naphthalene-based feedstock is made up of vaporized naphthalene and compressed air. It is transferred to the fluidized bed reactor and oxidized in the presence of a catalyst, vanadium pentoxide, at 650 to 725°F (340 to 385°C). Cooling tubes located in the catalyst bed remove the exothermic heat which is used to produce high-pressure steam. The reactor effluent consists of PAN vapors, entrained catalyst, and various by-products and non-reactant gas. The catalyst is removed by filtering and returned to the reactor.

The chemical reactions for air oxidation of o-xylene and naphthalene are as follows.



The reactor effluent containing crude PAN plus products from side reactions and excess oxygen passes to a series of switch condensers where the crude PAN cools and crystallizes. The condensers are alternately cooled and then heated, allowing PAN crystals to form and then melt from the condenser tube fins.

The crude liquid is transferred to a pretreatment section in which phthalic acid is dehydrated to anhydride. Water, maleic anhydride, and benzoic acid are partially evaporated. The liquid then goes to a vacuum distillation section where pure PAN (99.8 wt. percent pure) is recovered. The product can be stored and shipped either as a liquid or a solid (in which case it is dried, flaked, and packaged in multi-wall paper bags). Tanks for holding liquid PAN are kept at 300°F (150°C) and blanketed with dry nitrogen to prevent the entry of oxygen (fire) or water vapor (hydrolysis to phthalic acid).

Maleic anhydride is currently the only by-product being recovered.

Figures 1 and 2 show the process flow for air oxidation of o-xylene and naphthalene, respectively.

### 5.12.2 Emissions and Controls<sup>1</sup>

Emissions from o-xylene and naphthalene storage are small and presently are not controlled.

The major contributor of emissions is the reactor and condenser effluent which is vented from the condenser unit. Particulate, sulfur oxides (for o-xylene-based production), and carbon monoxide make up the emissions, with carbon monoxide comprising over half the total. The most efficient (96 percent) system of control is the combined usage of a water scrubber and thermal incinerator. A thermal incinerator alone is approximately 95 percent efficient in combustion of pollutants for o-xylene-based production, and 80 percent efficient for naphthalene-based production. Thermal incinerators with steam generation show the same efficiencies as thermal incinerators alone. Scrubbers have a 99 percent efficiency in collecting particulates, but are practically ineffective in reducing carbon monoxide emissions. In naphthalene-based production, cyclones can be used to control catalyst dust emissions with 90 to 98 percent efficiency.

Pretreatment and distillation emissions—particulates and hydrocarbons—are normally processed through the water scrubber and/or incinerator used for the main process stream (reactor and condenser) or scrubbers alone, with the same efficiency percentages applying.

Product storage in the liquid phase results in small amounts of gaseous emissions. These gas streams can either be sent to the main process vent gas control devices or first processed through sublimation boxes or devices used to recover escaped PAN. Flaking and bagging emissions are negligible, but can be sent to a cyclone for recovery of PAN dust. Exhaust from the cyclone presents no problem.

Table 5.12-1 gives emission factors for controlled and uncontrolled emissions from the production of PAN.

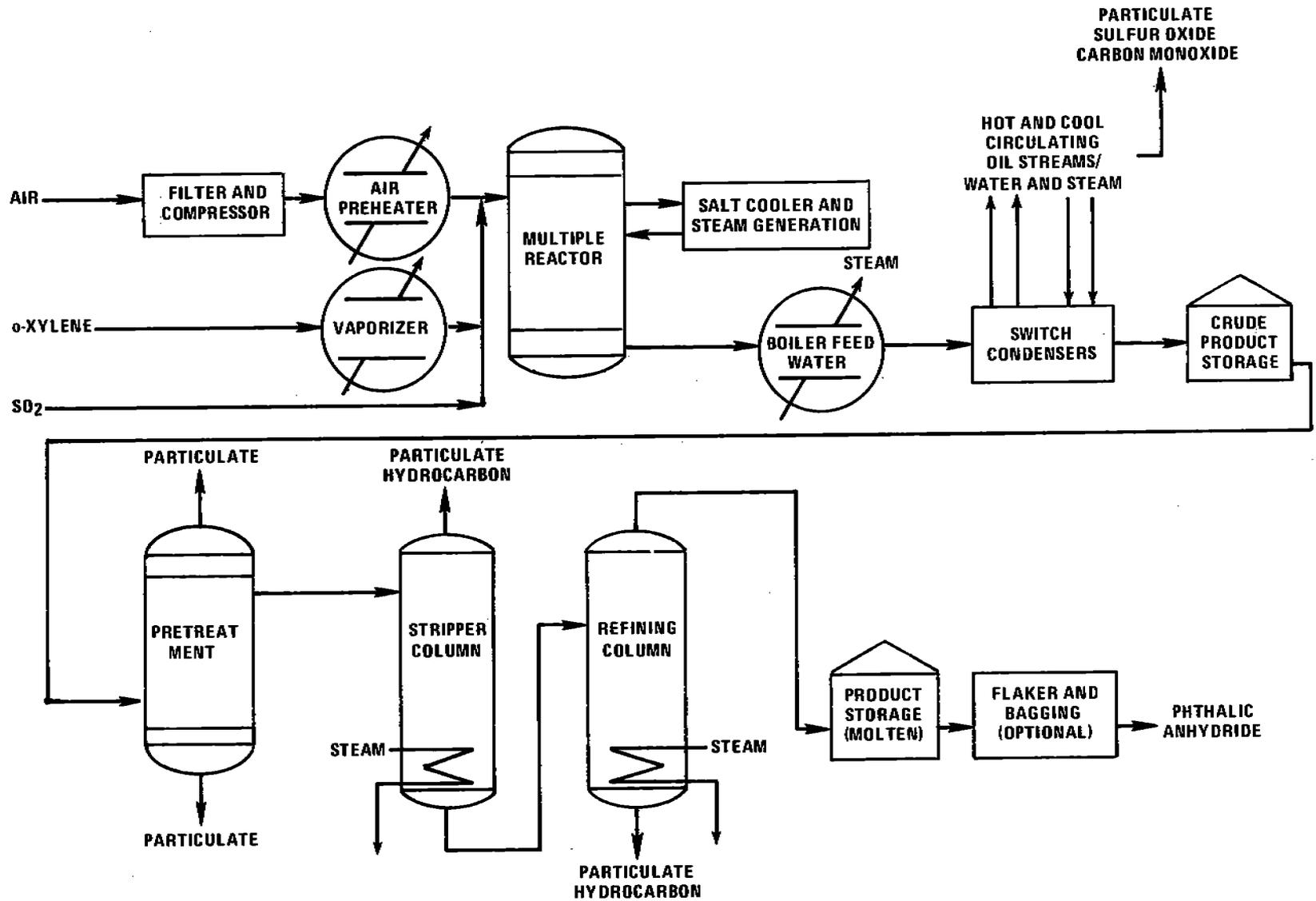


Figure 5.12-1. Flow diagram for phthalic anhydride using o-xylene as basic feedstock.<sup>1</sup>

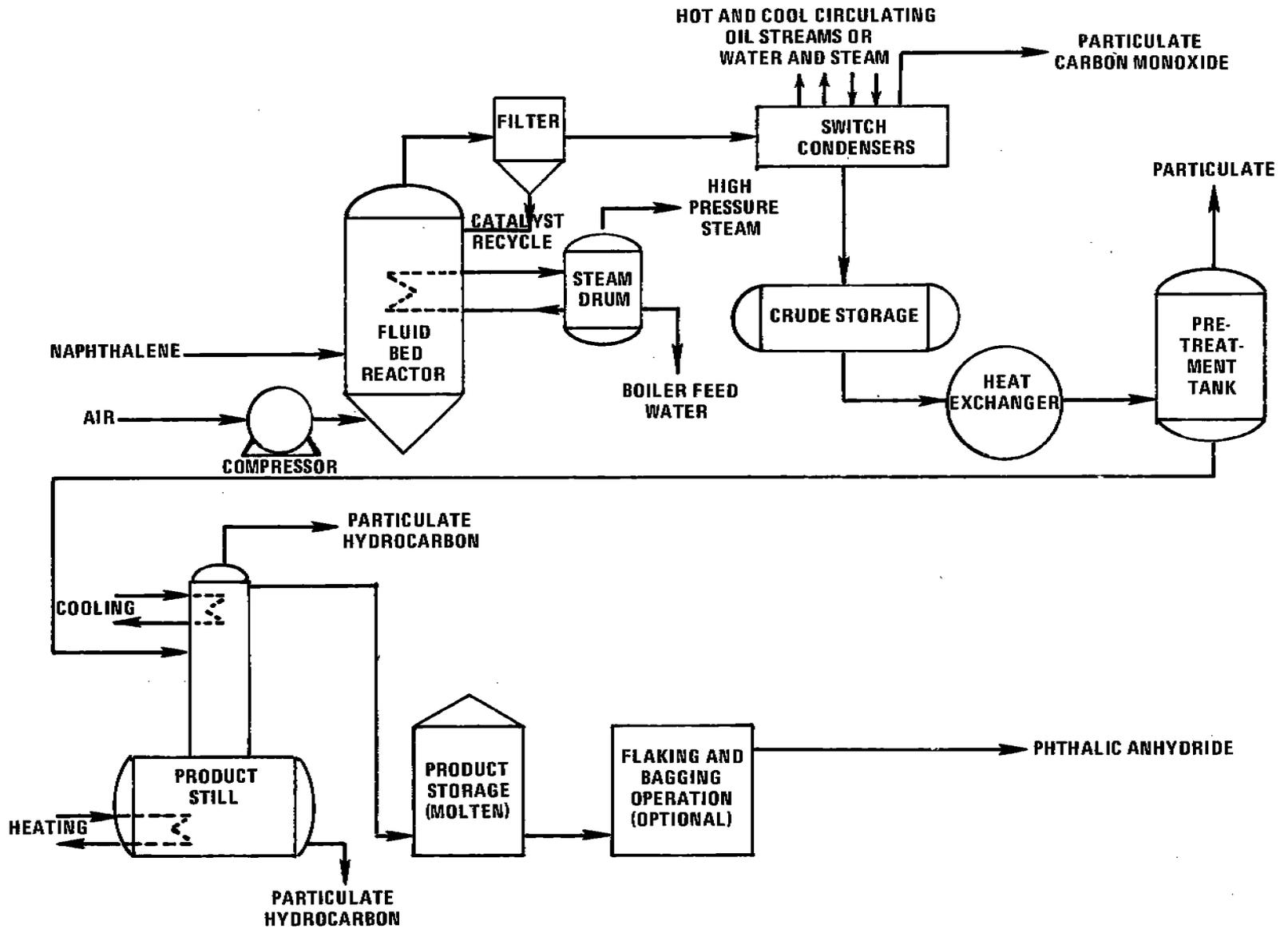


Figure 5.12-2. Flow diagram for phthalic anhydride using naphthalene as basic feedstock.<sup>1</sup>

**Table 5.12-1. EMISSION FACTORS FOR PHTHALIC ANHYDRIDE<sup>1,a</sup>**  
**EMISSION FACTOR RATING: B**

Process	Particulate		SO <sub>x</sub>		HC		CO	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
<b>Oxidation of o-xylene<sup>b</sup></b>								
Main process stream <sup>c</sup>								
Uncontrolled	138 <sup>d</sup>	69 <sup>d</sup>	9.4 <sup>e</sup>	4.7 <sup>e</sup>	0	0	301	151
W/scrubber and thermal incinerator	6	3	9.4	4.7	0	0	12	6
W/thermal incinerator	7	4	9.4	4.7	0	0	15	8
W/incinerator with steam generator	7	4	9.4	4.7	0	0	15	8
<b>Pretreatment</b>								
Uncontrolled	13 <sup>f</sup>	6.4 <sup>f</sup>	0	0	0	0	0	0
W/scrubber and thermal incinerator	0.5	0.3	0	0	0	0	0	0
W/thermal incinerator	0.7	0.4	0	0	0	0	0	0
<b>Distillation</b>								
Uncontrolled	89 <sup>d</sup>	45 <sup>d</sup>	0	0	2.4	1.2	0	0
W/scrubber and thermal incinerator	4	2	0	0	<0.1	<0.1	0	0
W/thermal incinerator	4	2	0	0	0.1	<0.1	0	0
<b>Oxidation of naphthalene<sup>b</sup></b>								
Main process stream <sup>c</sup>								
Uncontrolled	569. <sup>i</sup>	289. <sup>i</sup>	0	0	0	0	100	50
W/thermal incinerator	11	6	0	0	0	0	20	10
W/scrubber	0.6	0.3	0	0	0	0	100	50
<b>Pretreatment</b>								
Uncontrolled	5 <sup>h</sup>	2.5 <sup>h</sup>	0	0	0	0	0	0
W/thermal incinerator	1	0.5	0	0	0	0	0	0
W/scrubber	<0.1	<0.1	0	0	0	0	0	0
<b>Distillation</b>								
Uncontrolled	389	199	0	0	10	5	0	0
W/thermal incinerator	8	4	0	0	2	1	0	0
W/scrubber	0.4	0.2	0	0	0.1	<0.1	0	0

<sup>a</sup>Emission factors are in units of pounds of pollutant per ton (kilogram of pollutant per metric ton) of phthalic anhydride produced.

<sup>b</sup>Control devices listed are those currently being used by phthalic anhydride plants.

<sup>c</sup>Main process stream includes the reactor and multiple switch condensers as vented through the condenser unit.

<sup>d</sup>Particulate consists of phthalic anhydride, maleic anhydride, and benzoic acid.

<sup>e</sup>Emissions change with catalyst age. Value shown corresponds to relatively fresh catalyst. Can be 19 to 25 lb/ton (9.5 to 13 kg/MT) for aged catalyst.

<sup>f</sup>Particulate consists of phthalic anhydride and maleic anhydride.

<sup>g</sup>Particulate consists of phthalic anhydride, maleic anhydride, and naphthaquinone.

<sup>h</sup>Particulate is phthalic anhydride.

<sup>i</sup>Particulate does not include catalyst dust which is controlled by cyclones with an efficiency of 90 to 98 percent.

## Reference for Section 5.12

1. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Vol 7: Phthalic Anhydride Manufacture from Ortho-Xylene. Houdry Division, Air Products and Chemicals, Inc., Marcus Hook, Pa. Prepared for Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-450/3-73-006-g. July 1975.



## 6.4 FEED AND GRAIN MILLS AND ELEVATORS

### 6.4.1 General<sup>1-3</sup>

Grain elevators are buildings in which grains are gathered, stored, and discharged for use, further processing, or shipping. They are classified as "country," "terminal," and "export" elevators, according to their purpose and location. At country elevators, grains are unloaded, weighed, and placed in storage as they are received from farmers residing within about a 20-mile radius of the elevator. In addition, country elevators sometimes dry or clean grain before it is shipped to terminal elevators or processors.

Terminal elevators receive most of their grain from country elevators and ship to processors, other terminals, and exporters. The primary functions of terminal elevators are to store large quantities of grain without deterioration and to dry, clean, sort, and blend different grades of grain to meet buyer specifications.

Export elevators are similar to terminal elevators except that they mainly load grain on ships for export.

Processing of grain in mills and feed plants ranges from very simple mixing steps to complex industrial processes. Included are such diverse processes as: (1) simple mixing operations in feed mills, (2) grain milling in flour mills, (3) solvent extracting in soybean processing plants, and (4) a complex series of processing steps in a corn wet-milling plant.

### 6.4.2 Emissions and Controls

Grain handling, milling, and processing include a variety of operations from the initial receipt of the grain at either a country or terminal elevator to the delivery of a finished product. Flour, livestock feed, soybean oil, and corn syrup are among the products produced from plants in the grain and feed industry. Emissions from the feed and grain industry can be separated into two general areas, those occurring at grain elevators and those occurring at grain processing operations.

**6.4.2.1 Grain Elevators** - Grain elevator emissions can occur from many different operations in the elevator including unloading (receiving), loading (shipping), drying, cleaning, headhouse (legs), tunnel belt, gallery belt, and belt trippers. Emission factors for these operations at terminal, country, and export elevators are presented in Table 6.4-1. All of these emission factors are approximate average values intended to reflect a variety of grain types. Actual emission factors for a specific source may be considerably different, depending on the type of grain, i.e., corn, soybeans, wheat, and other factors such as grain quality.

The emission factors shown in Table 6.4-1 represent the amount of dust generated per ton of grain processed through each of the designated operations (i.e., uncontrolled emission factors). Amounts of grain processed through each of these operations in a given elevator are dependent on such factors as the amount of grain turned (interbin transfer), amount dried, and amount cleaned, etc. Because the amount of grain passing through each operation is often difficult to determine, it may be more useful to express the emission factors in terms of the amount of grain shipped or received, assuming these amounts are about the same over the long term. Emission factors from Table 6.4-1 have been modified accordingly and are shown in Table 6.4-2 along with the appropriate multiplier that was used as representative of typical ratios of throughput at each operation to the amount of grain shipped or received. This ratio is an approximate value based on average values for turning, cleaning, and drying in each

type of elevator. However, because operating practices in individual elevators are different, these ratios, like the basic emission factors themselves, are more valid when applied to a group of elevators rather than individual elevators.

**Table 6.4-1. PARTICULATE EMISSION FACTORS  
FOR UNCONTROLLED GRAIN ELEVATORS  
EMISSION FACTOR RATING: B**

Type of source	Emission factor <sup>a</sup>	
	lb/ton	kg/MT
<b>Terminal elevators</b>		
Unloaded (receiving)	1.0	0.5
Loading (shipping)	0.3	0.2
Removal from bins (tunnel belt)	1.4	1.7
Drying <sup>b</sup>	1.1	0.6
Cleaning <sup>c</sup>	3.0	1.5
Headhouse (legs)	1.5	0.8
Tripper (gallery belt)	1.0	0.5
<b>Country elevators</b>		
Unloading (receiving)	0.6	0.3
Loading (shipping)	0.3	0.2
Removal from bins	1.0	0.5
Drying <sup>b</sup>	0.7	0.4
Cleaning <sup>c</sup>	3.0	1.5
Headhouse (legs)	1.5	0.8
<b>Export elevators</b>		
Unloading (receiving)	1.0	0.5
Loading (shipping)	1.0	0.5
Removal from bins (tunnel belt)	1.4	0.7
Drying <sup>b</sup>	1.1	0.5
Cleaning <sup>c</sup>	3.0	1.5
Headhouse (legs)	1.5	0.8
Tripper (gallery belts)	1.0	0.5

<sup>a</sup>Emission factors are in terms of pounds of dust emitted per ton of grain processed by each operation. Most of the factors for terminal and export elevators are based on Reference 1. Emission factors for drying are based on References 2 and 3. The emission factors for country elevators are based on Reference 1 and specific country elevator test data in References 4 through 9.

<sup>b</sup>Emission factors for drying are based on 1.8 lb/ton for rack dryers and 0.3 lb/ton for column dryers prorated on the basis of distribution of these two types of dryers in each elevator category, as discussed in Reference 3.

<sup>c</sup>Emission factor of 3.0 for cleaning is an average value which may range from <0.5 for wheat up to 6.0 for corn.

The factors in Tables 6.4-1 or 6.4-2 should not be added together in an attempt to obtain a single emission factor value for grain elevators because in most elevators some of the operations are equipped with control devices and some are not. Therefore, any estimation of emissions must be directed to each operation and its associated control device, rather than the elevator as a whole, unless the purpose was to estimate total potential (i.e., uncontrolled) emissions. An example of the use of emission factors in making an emission inventory is contained in Reference 3.

**Table 6.4-2. PARTICULATE EMISSION FACTORS FOR GRAIN ELEVATORS BASED ON AMOUNT OF GRAIN RECEIVED OR SHIPPED<sup>a</sup>**

Type of source	Emission factor, lb/ton processed	x	Typical ratio of tons processed to tons received or shipped <sup>d</sup>	=	Emission factor, lb/ton received or shipped
<b>Terminal elevators</b>					
Unloading (receiving)	1.0		1.0		1.0
Loading (shipping)	0.3		1.0		0.3
Removal from bins (tunnel belt)	1.4		2.0		2.8
Drying <sup>b</sup>	1.1		0.1		0.1
Cleaning <sup>c</sup>	3.0		0.2		0.6
Headhouse (legs)	1.5		3.0		4.5
Tripper (gallery belt)	1.0		1.7		1.7
<b>Country elevators</b>					
Unloading (receiving)	0.6		1.0		0.6
Loading (shipping)	0.3		1.0		0.3
Removal from bins	1.0		2.1		2.1
Drying <sup>b</sup>	0.7		0.3		0.2
Cleaning <sup>c</sup>	3.0		0.1		0.3
Headhouse (legs)	1.5		3.1		4.7
<b>Export elevators</b>					
Unloading (receiving)	1.0		1.0		1.0
Loading (shipping)	1.0		1.0		1.0
Removal from bins (tunnel belt)	1.4		1.2		1.7
Drying <sup>b</sup>	1.1		0.01		0.01
Cleaning <sup>c</sup>	3.0		0.2		0.6
Headhouse (legs)	1.5		2.2		3.3
Tripper (gallery belt)	1.0		1.1		1.1

<sup>a</sup>Assume that over the long term the amount received is approximately equal to amount shipped.

<sup>b</sup>See Note<sup>b</sup> in Table 6.4-1.

<sup>c</sup>See Note<sup>c</sup> in Table 6.4-1.

<sup>d</sup>Ratios shown are average values taken from a survey of many elevators across the U.S.<sup>3</sup> These ratios can be considerably different for any individual elevator or group of elevators in the same locale.

Some of the operations listed in the table, such as the tunnel belt and belt tripper, are internal or in-house dust sources which, if uncontrolled, might show lower than expected atmospheric emissions because of internal settling of dust. The reduction in emissions via internal settling is not known, although it is possible that all of this dust is eventually emitted to the atmosphere due to subsequent external operations, internal ventilation, or other means.

Many elevators utilize control devices on at least some operations. In the past, cyclones have commonly been applied to legs in the headhouse and tunnel belt hooding systems. More recently, fabric filters have been utilized at many elevators on almost all types of operations. Unfortunately, some sources in grain elevators present control problems. Control of loadout operations is difficult because of the problem of containment of the emissions. Probably the most difficult operation to control, because of the large flow rate and high moisture content of the exhaust gases, is the dryers. Screenhouses or continuously vacuumed screen systems are available for reducing dryer emissions and have been applied at several facilities. Detailed descriptions of dust control systems for grain elevator operations are contained in Reference 2.

**6.4.2.2 Grain Processing Operations** - Grain processing operations include many of the operations performed in a grain elevator in addition to milling and processing of the grain. Emission factors for different grain milling and processing operations are presented in Table 6.4-3. Brief discussions of these different operations and the methods used for arriving at the emission factor values shown in Table 6.4-3 are presented below.

**Table 6.4-3. PARTICULATE EMISSION FACTORS  
FOR GRAIN PROCESSING OPERATIONS<sup>1,2,3</sup>  
EMISSION FACTOR RATING: D**

Type of source	Emission factor <sup>a,b</sup> (uncontrolled except where indicated)	
	lb/ton	kg/MT
<b>Feed mills</b>		
Receiving	1.30	0.65
Shipping	0.50	0.25
Handling	3.00	1.50
Grinding	0.10 <sup>c</sup>	0.05 <sup>c</sup>
Pellet coolers	0.10 <sup>c</sup>	0.05 <sup>c</sup>
<b>Wheat mills</b>		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	70.00	35.00
<b>Durum mills</b>		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	-	-
<b>Rye milling</b>		
Receiving	1.00	0.50
Precleaning and handling	5.00	2.50
Cleaning house	-	-
Millhouse	70.00	35.00
<b>Dry corn milling</b>		
Receiving	1.00	0.50
Drying	0.50	0.25
Precleaning and handling	5.00	2.50
Cleaning house	6.00	3.00
Degerming and milling	-	-
<b>Oat milling</b>		
Total	2.50 <sup>d</sup>	1.25 <sup>d</sup>
<b>Rice milling</b>		
Receiving	0.64	0.32
Handling and precleaning	5.00	2.50
Drying	-	-
Cleaning and millhouse	-	-
<b>Soybean mills</b>		
Receiving	1.60	0.80
Handling	5.00	2.50
Cleaning	-	-
Drying	7.20	3.60
Cracking and dehulling	3.30	1.65
Hull grinding	2.00	1.00

Table 6.4-3 (continued). PARTICULATE EMISSION FACTORS  
FOR GRAIN PROCESSING OPERATIONS<sup>1,2,3</sup>  
EMISSION FACTOR RATING: D

Type of source	Emission factor <sup>a,b</sup> (uncontrolled except where indicated)	
	lb/ton	kg/MT
Bean conditioning	0.10	0.05
Flaking	0.57	0.29
Meal dryer	1.50	0.75
Meal cooler	1.80	0.90
Bulk loading	0.27	0.14
Corn wet milling		
Receiving	1.00	0.50
Handling	5.00	2.50
Cleaning	6.00	3.00
Dryers	-	-
Bulk loading	-	-

<sup>a</sup>Emission factors are expressed in terms of pounds of dust emitted per ton of grain entering the plant (i.e., received), which is not necessarily the same as the amount of material processed by each operation.

<sup>b</sup>Blanks indicate insufficient information.

<sup>c</sup>Controlled emission factor (controlled with cyclones).

<sup>d</sup>Controlled emission factor. (This represents several sources in one plant; some controlled with cyclones and others controlled with fabric filters.)

Emission factor data for feed mill operations are sparse. This is partly due to the fact that many ingredients, whole grain and other dusty materials (bran, dehydrated alfalfa, etc.), are received by both truck and rail and several unloading methods are employed. However, because some feed mill operations (handling, shipping, and receiving) are similar to operations in a grain elevator, an emission factor for each of these different operations was estimated on that basis. The remaining operations are based on information in Reference 2.

Three emission areas for wheat mill processing operations are grain receiving and handling, cleaning house, and milling operations. Data from Reference 1 are used to estimate emissions factors for grain receiving and handling. Data for the cleaning house are insufficient to estimate an emission factor, and information contained in Reference 2 is used to estimate the emission factor for milling operations. The large emission factor for the milling operation is somewhat misleading because almost all of the sources involved are equipped with control devices to prevent product losses; fabric filters are widely used for this purpose.

Operations for durum mills and rye milling are similar to those of wheat milling. Therefore, most of these emission factors are assumed equal to those for wheat mill operations.

The grain unloading, handling, and cleaning operations for dry corn milling are similar to those in other grain mills, but the subsequent operations are somewhat different. Also, some drying of corn received at the mill may be necessary prior to storage. An estimate of the emission factor for drying is obtained from Reference 2. Insufficient information is available to estimate emission factors for degerming and milling.

Information necessary to estimate emissions from oat milling is unavailable, and no emission factor for another grain is considered applicable because oats are reported to be dustier than many other grains. The only emission factor data available are for controlled emissions.<sup>2</sup> An overall controlled emission factor of 2.5 lb/ton is calculated from these data.

Emission factors for rice milling are based on those for similar operations in other grain handling facilities. Insufficient information is available to estimate emission factors for drying, cleaning, and mill house operations.

Information contained in Reference 2 is used to estimate emission factors for soybean mills.

Emissions information on corn wet-milling is unavailable in most cases due to the wide variety of products and the diversity of operations. Receiving, handling, and cleaning operations emission factors are assumed to be similar to those for dry corn milling.

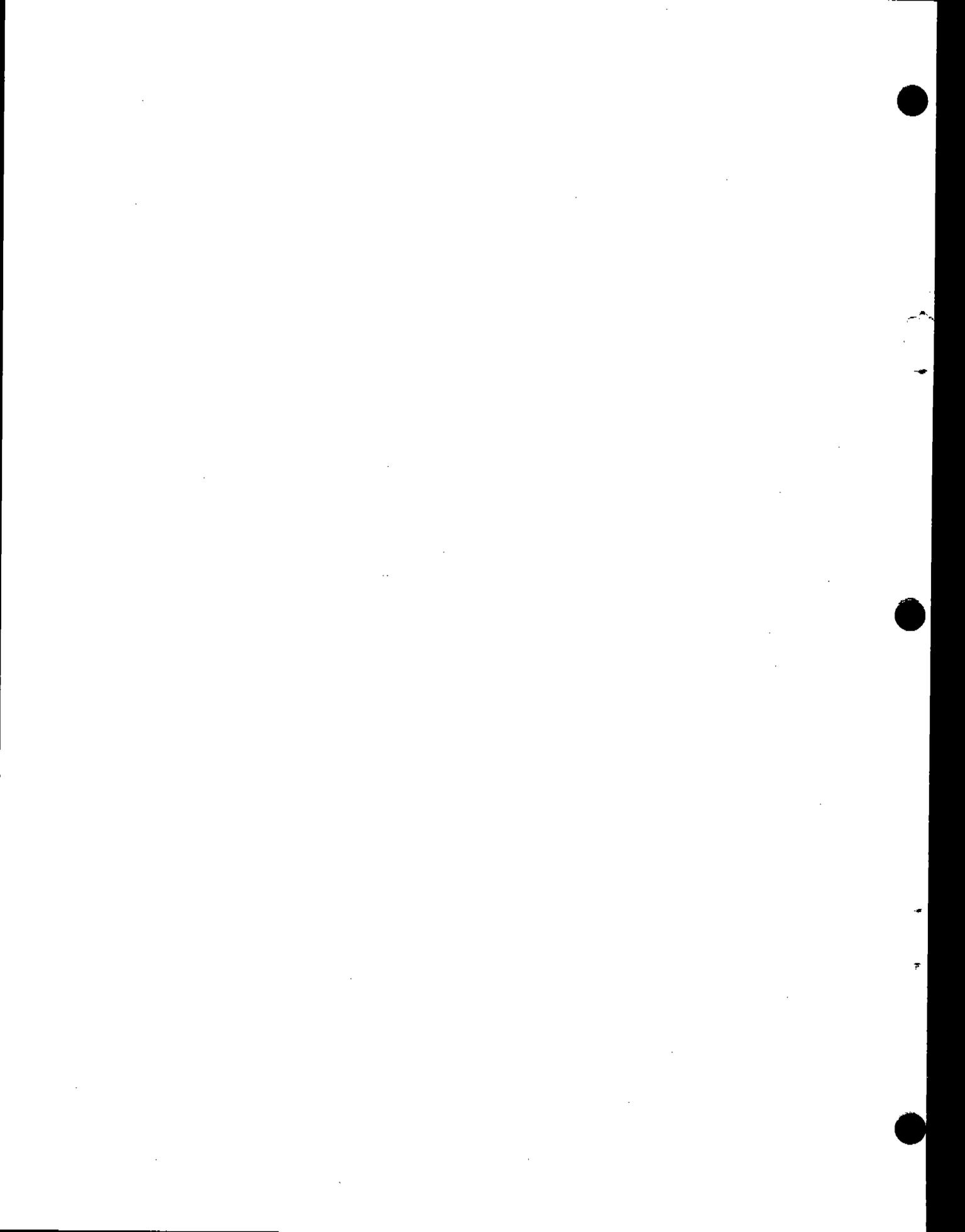
Many of the operations performed in grain milling and processing plants are the same as those in grain elevators, so the control methods are similar. As in the case of grain elevators, these plants often use cyclones or fabric filters to control emissions from the grain handling operations (e.g., unloading, legs, cleaners, etc.). These same devices are also often used to control emissions from other processing operations; a good example of this is the extensive use of fabric filters in flour mills. However, there are also certain operations within some milling operations that are not amenable to use of these devices. Therefore, wet scrubbers have found some application, particularly where the effluent gas stream has a high moisture content. Certain other operations have been found to be especially difficult to control, such as rotary dryers in wet corn mills. Descriptions of the emission control systems that have been applied to operations within the grain milling and processing industries are contained in Reference 2.

This section was prepared for EPA by Midwest Research Institute.<sup>10</sup>

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8. **Belgea, F.J. Grain Handling Dust Collection Systems Evaluation for Farmers Elevator Company, Minot, North Dakota. Report submitted to North Dakota State Department of Health, by Pollution Curbs, Inc. St. Paul, Minnesota. August 28, 1972.**
9. **Belgea, F.J. Cyclone Emission and Efficiency Evaluation. Report submitted to North Dakota State Department of Health on tests at an elevator in Thompson, North Dakota, by Pollution Curbs, Inc. St. Paul, Minnesota. March 10, 1972.**
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## 6.6 FISH PROCESSING

*revised by Susan Sercer*

### 6.6.1 Process Description

Fish processing includes the canning of fish and the manufacturing of by-products such as fish oil and fish meal. The manufacturing of fish oil and fish meal are known as reduction processes. A generalized fish processing operation is presented in Figure 6.6-1.

Two types of canning operations are used. One is the "wet fish" method in which trimmed and eviscerated fish are cooked directly in open cans. The other operation is the "pre-cooked" process in which eviscerated fish are cooked whole and portions are hand selected and packed into cans. The pre-cooked process is used primarily for larger fish such as tuna.

By-product manufacture of rejected whole fish and scrap requires several steps. First, the fish scrap mixture from the canning line is charged to a live steam cooker. After the material leaves the cooker, it is pressed to remove water and oil. The resulting press cake is broken up and dried in a rotary drier.

Two types of driers are used to dry the press cake: direct-fired and steam-tube driers. Direct-fired driers contain a stationary firebox ahead of the rotating section. The hot products of combustion from the firebox are mixed with air and wet meal inside the rotating section of the drier. Exhaust gases are generally vented to a cyclone separator to recover much of the entrained fish meal product. Steam-tube driers contain a cylindrical bank of rotating tubes through which hot, pressurized steam is passed. Heat is indirectly transferred to the meal and the air from the hot tubes. As with direct-fired driers, the exhaust gases are vented to a cyclone for product recovery.

### 6.6.2 Emissions and Controls

Although smoke and dust can be a problem, odors are the most objectionable emissions from fish processing plants. By-product manufacture results in more of these odorous contaminants than cannery operations because of the greater state of decomposition of the materials processed. In general, highly decayed feedstocks produce greater concentrations of odors than do fresh feedstocks.

The largest odor sources are the fish meal driers. Usually, direct-fired driers emit more odors than steam-tube driers. Direct-fired driers will also emit smoke, particularly if the driers are operated under high temperature conditions. Cyclones are frequently employed on drier exhaust gases for product recovery and particulate emission control.

Odorous gases from reduction cookers consist primarily of hydrogen sulfide [ $H_2S$ ] and trimethylamine [ $(CH_3)_3N$ ]. Odors from reduction cookers are emitted in volumes appreciably less than from fish meal driers. There are virtually no particulate emissions from reduction cookers.

Some odors are also produced by the canning processes. Generally, the pre-cooked process emits less odorous gases than the wet-fish process. This is because in the pre-cooked process, the odorous exhaust gases are trapped in the cookers, whereas in the wet-fish process, the steam and odorous offgases are commonly vented directly to the atmosphere.

Fish cannery and fish reduction odors can be controlled with afterburners, chlorinator-scrubbers, and condensers. Afterburners are most effective, providing virtually 100 percent odor control; however they are costly from a fuel-use standpoint. Chlorinator-scrubbers have been found to be 95 to 99 percent effective in controlling odors from cookers and driers. Condensers are the least effective control device. Generally, centrifugal collectors are satisfactory for controlling excessive dust emissions from driers.

Emission factors for fish processing are presented in Table 6.6-1.

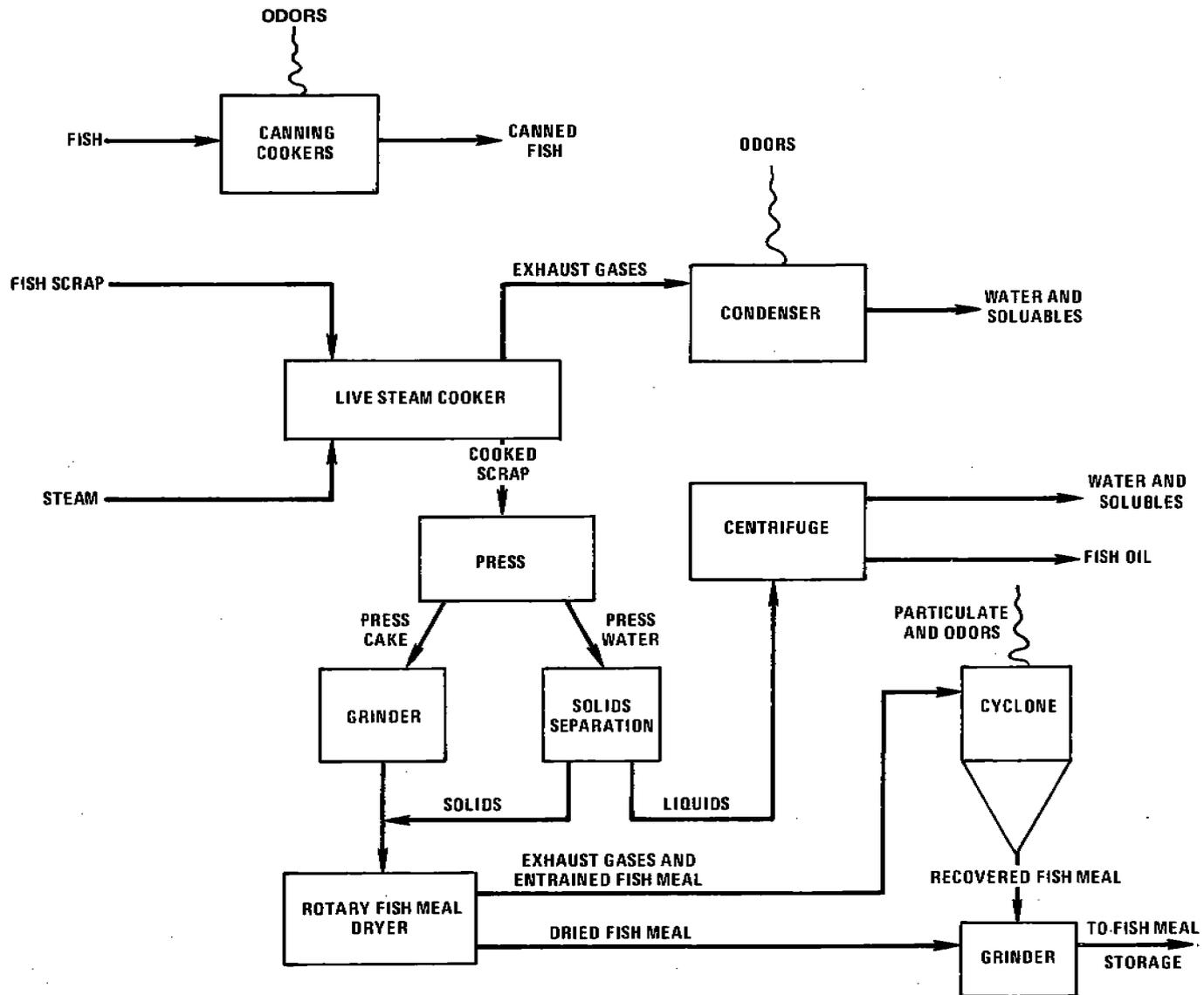


Figure 6.6-1. A generalized fish processing flow diagram.

**Table 6.6-1. EMISSION FACTORS FOR FISH PROCESSING PLANTS**  
**EMISSION FACTOR RATING: C**

Emission source	Particulates		Trimethylamine (CH <sub>3</sub> ) <sub>3</sub> N		Hydrogen sulfide (H <sub>2</sub> S)	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Cookers, canning	Neg. <sup>a</sup>	Neg. <sup>a</sup>	NA <sup>b</sup>	NA <sup>b</sup>	NA <sup>b</sup>	NA <sup>b</sup>
Cookers, fish scrap						
Fresh fish	Neg. <sup>a</sup>	Neg. <sup>a</sup>	0.3 <sup>c</sup>	0.15 <sup>c</sup>	0.01 <sup>c</sup>	0.005 <sup>c</sup>
Stale fish	Neg. <sup>a</sup>	Neg. <sup>a</sup>	3.5 <sup>c</sup>	1.75 <sup>c</sup>	0.2 <sup>c</sup>	0.10 <sup>c</sup>
Dryers	0.1 <sup>d</sup>	0.05 <sup>d</sup>	NA <sup>d</sup>	NA <sup>d</sup>	NA <sup>d</sup>	NA <sup>d</sup>

<sup>a</sup>Reference 1.

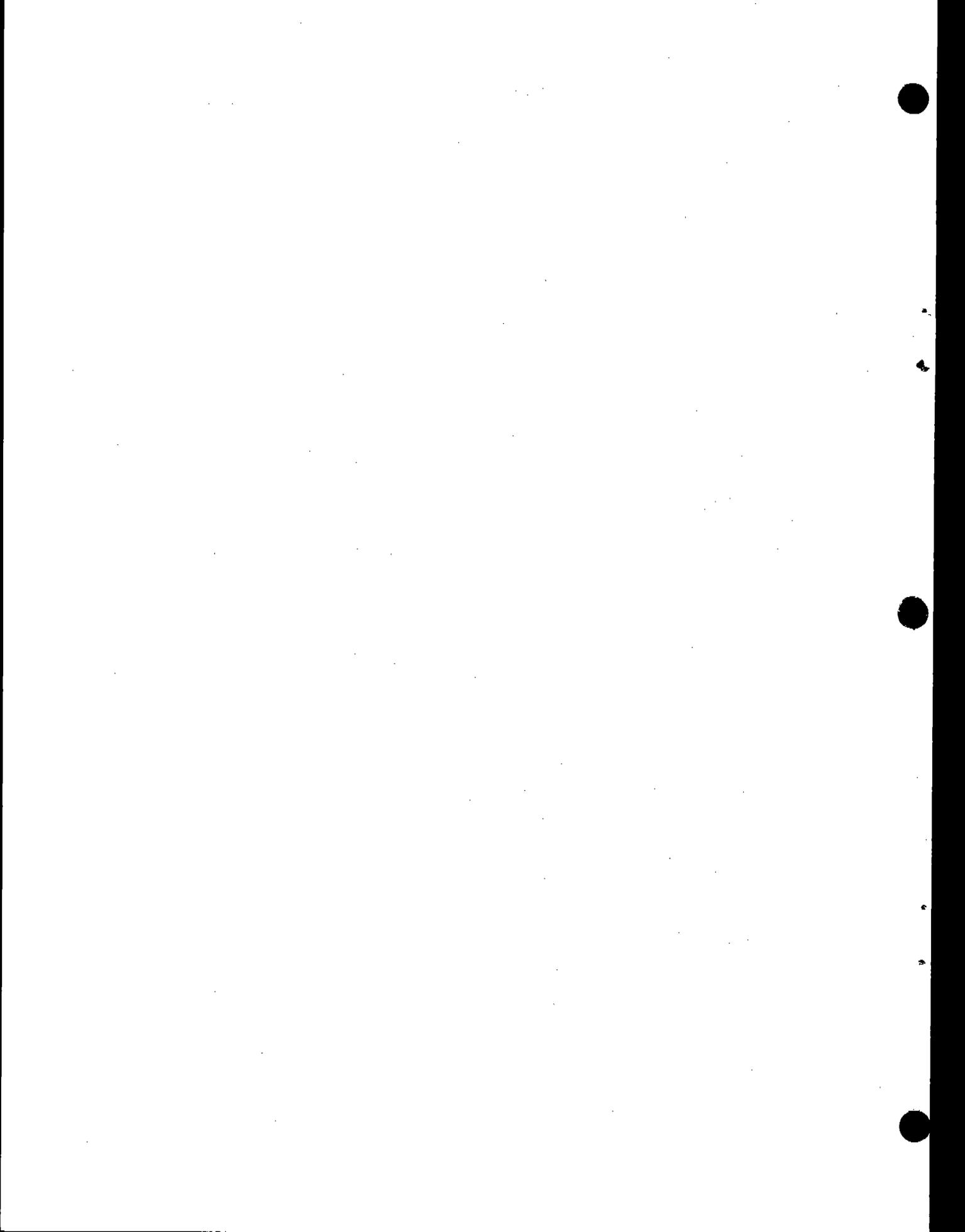
<sup>b</sup>Although it is known that odors are emitted from canning cookers, quantitative estimates are not available.

<sup>c</sup>Reference 2.

<sup>d</sup>Limited data suggest that there is not much difference in particulate emissions between steam tube and direct-fired dryers. Based on reference 1.

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plant in question, and the particulate emission standards in the community, the cement industry generally uses mechanical collectors, electrical precipitators, fabric filter (baghouse) collectors, or combinations of these devices to control emissions.

Table 8.6-1 summarizes emission factors for cement manufacturing and also includes typical control efficiencies of particulate emissions. Table 8.6-2 indicates the particle size distribution for particulate emissions from kilns and cement plants before control systems are applied.

**Table 8.6-1. EMISSION FACTORS FOR CEMENT MANUFACTURING WITHOUT CONTROLS<sup>a,b,c,i</sup>**  
EMISSION FACTOR RATING: B

Pollutant	Dry Process		Wet process	
	Kilns	Dryers, grinders, etc.	Kilns	Dryers, grinders, etc.
Particulate <sup>d</sup>				
lb/ton	245.0	96.0	228.0	32.0
kg/MT	122.0	48.0	114.0	16.0
Sulfur dioxide <sup>e</sup>				
Mineral source <sup>f</sup>				
lb/ton	10.2	-	10.2	-
kg/MT	5.1	-	5.1	-
Gas combustion				
lb/ton	Neg <sup>g</sup>	-	Neg	-
kg/MT	Neg	-	Neg	-
Oil combustion				
lb/ton	4.2S <sup>h</sup>	-	4.2S	-
kg/MT	2.1S	-	2.1S	-
Coal combustion				
lb/ton	6.8S	-	6.8S	-
kg/MT	3.4S	-	3.4S	-
Nitrogen oxides				
lb/ton	2.6	-	2.6	-
kg/MT	1.3	-	1.3	-

<sup>a</sup>One barrel of cement weighs 376 pounds (171 kg).

<sup>b</sup>These emission factors include emissions from fuel combustion, which should not be calculated separately.

<sup>c</sup>References 1 and 2.

<sup>d</sup>Typical collection efficiencies for kilns, dryers, grinders, etc., are: multicyclones, 80 percent; electrostatic precipitators, 95 percent; electrostatic precipitators with multicyclones, 97.5 percent; and fabric filter units, 99.8 percent.

<sup>e</sup>The sulfur dioxide factors presented take into account the reactions with the alkaline dusts when no baghouses are used. With baghouses, approximately 50 percent more SO<sub>2</sub> is removed because of reactions with the alkaline particulate filter cake. Also note that the total SO<sub>2</sub> from the kiln is determined by summing emission contributions from the mineral source and the appropriate fuel.

<sup>f</sup>These emissions are the result of sulfur being present in the raw materials and are thus dependent upon source of the raw materials used. The 10.2 lb/ton (5.1 kg/MT) factors account for part of the available sulfur remaining behind in the product because of its alkaline nature and affinity for SO<sub>2</sub>.

<sup>g</sup>Negligible.

<sup>h</sup>S is the percent sulfur in fuel.

<sup>i</sup>Emission factors expressed in units of tons of cement produced.

**Table 8.6-2. SIZE DISTRIBUTION OF DUST EMITTED  
FROM KILN OPERATIONS  
WITHOUT CONTROLS<sup>1,5</sup>**

Particle size, $\mu\text{m}$	Kiln dust finer than corresponding particle size, %
60	93
50	90
40	84
30	74
20	58
10	38
5	23
1	3

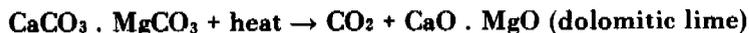
Sulfur dioxide may be generated from the sulfur compounds in the ores as well as from combustion of fuel. The sulfur content of both ores and fuels will vary from plant to plant and with geographic location. The alkaline nature of the cement, however, provides for direct absorption of  $\text{SO}_2$  into the product. The overall control inherent in the process is approximately 75 percent or greater of the available sulfur in ore and fuel if a baghouse that allows the  $\text{SO}_2$  to come in contact with the cement dust is used. Control, of course, will vary according to the alkali and sulfur content of the raw materials and fuel.<sup>6</sup>

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8.15.1 General<sup>1-4</sup>

Lime is the high-temperature product of the calcination of limestone. There are two kinds of lime: high-calcium lime (CaO) and dolomitic lime (CaO · MgO). Lime is manufactured in various kinds of kilns by one of the following reactions:



In some lime plants, the resulting lime is reacted (slaked) with water to form hydrated lime.

The basic processes in the production of lime are (1) quarrying the raw limestone, (2) preparing the limestone for the kilns by crushing and sizing, (3) calcining the limestone, (4) processing the quicklime further by hydrating, and (5) miscellaneous transfer, storage, and handling operations. A generalized material flow diagram for a lime manufacturing plant is given in Figure 8.15-1. Note that some of the operations shown may not be performed in all plants.

The heart of a lime plant is the kiln. The most prevalent type of kiln is the rotary kiln, accounting for about 90 percent of all lime production in the United States. This kiln is a long, cylindrical, slightly inclined, refractory-lined furnace through which the limestone and hot combustion gases pass countercurrently. Coal, oil, and natural gas may all be fired in rotary kilns. Product coolers and kiln-feed preheaters of various types are commonly employed to recover heat from the hot lime product and hot exhaust gases, respectively.

The next most prevalent type of kiln in the United States is the vertical, or shaft, kiln. This kiln can be described as an upright heavy steel cylinder lined with refractory material. The limestone is charged at the top and calcined as it descends slowly to the bottom of the kiln where it is discharged. A primary advantage of vertical kilns over rotary kilns is the higher average fuel efficiency. The primary disadvantages of vertical kilns are their relatively low production rates and the fact that coal cannot be used without degrading the quality of the lime produced. Although still prevalent in Europe, there have been few recent vertical kiln installations in the United States because of the high production requirements of domestic manufacturers.

Other, much less common, kiln types include rotary hearth and fluidized-bed kilns. The rotary hearth kiln, or "calcimatic" kiln, is a circular-shaped kiln with a slowly revolving donut-shaped hearth. In fluidized-bed kilns, finely divided limestone is brought into direct contact with hot combustion air in a turbulent zone, usually above a perforated grate. Dust collection equipment must be installed on fluidized-bed kilns for process economics because of the high lime carryover into the exhaust gases. Both kiln types can achieve high production rates, but neither can operate with coal.

About 10 percent of all lime produced is converted to hydrated (slaked) lime. There are two kinds of hydrators: atmospheric and pressure. Atmospheric hydrators, the most prevalent kind, are used to produce high calcium and normal dolomitic hydrates. Pressure hydrators, on the other hand, are only employed when a completely hydrated dolomitic lime is needed. Atmospheric hydrators operate continuously, whereas pressure hydrators operate in a batch mode. Generally, water sprays or wet scrubbers are employed as an integral part of the hydrating process to prevent product losses. Following hydration, the resulting product may be milled and conveyed to air separators for further drying and for removal of the coarse fractions.

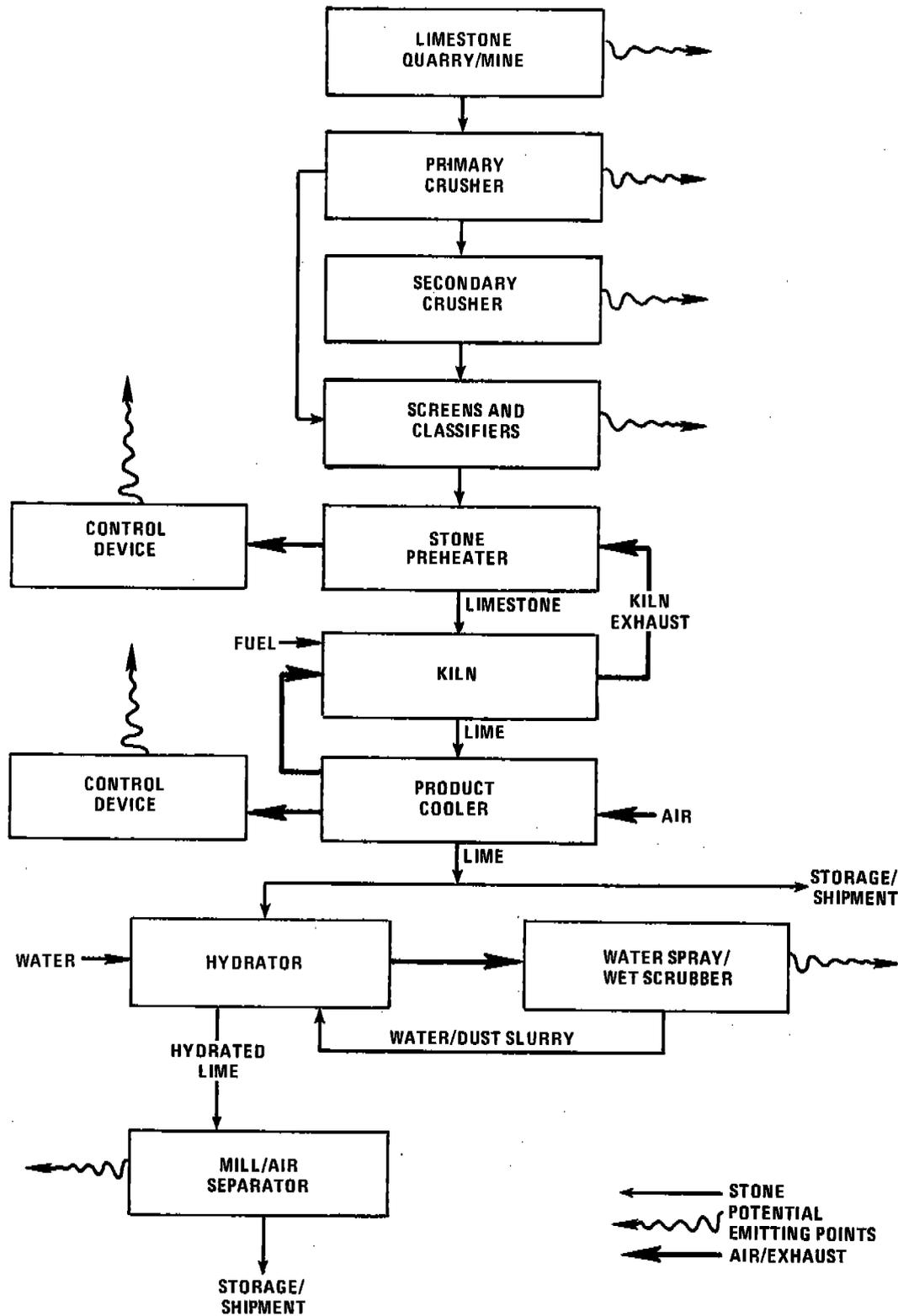


Figure 8.15-1. Generalized lime manufacturing plant.

In the United States, the major use of lime is in chemical and metallurgical applications. Two of the largest uses in these areas are as steel flux and in alkali production. Other lesser uses include construction, refractory, and agricultural applications.

### 8.15.2 Emissions and Controls<sup>3-5</sup>

Potential air pollutant emitting points in lime manufacturing plants are shown in Figure 8.15-1. Particulate is the only pollutant of concern from most of the operations; however, gaseous pollutants are also emitted from kilns.

The largest source of particulate is the kiln. Of the various kiln types in use, fluidized-bed kilns have the highest uncontrolled particulate emissions. This is due primarily to the very small feed size combined with the high air flow through these kilns. Fluidized-bed kilns are well controlled for maximum product recovery. The rotary kiln is second to the fluidized-bed kiln in uncontrolled particulate emissions. This is attributed to the small feed size and relatively high air velocities and dust entrainment caused by the rotating chamber. The rotary hearth, or "calcinatic" kiln ranks third in dust production, primarily because of the larger feed size combined with the fact that the limestone remains in a stationary position relative to the hearth during calcination. The vertical kiln has the lowest uncontrolled dust emissions due to the large lump-size feed and the relatively slow air velocities and slow movement of material through the kiln.

Some sort of particulate control is generally employed on most kilns. Rudimentary fallout chambers and cyclone separators are commonly used for control of the larger particles; fabric and gravel bed filters, wet (commonly venturi) scrubbers, and electrostatic precipitators are employed for secondary control. Table 8.15-1 yields approximate efficiencies of each type of control on the various types of kilns.

Nitrogen oxides, carbon monoxide, and sulfur oxides are all produced in kilns, although the latter are the only gaseous pollutant emitted in significant quantities. Not all of the sulfur in the kiln fuel is emitted as sulfur oxides because some fraction reacts with the materials in the kiln. Some sulfur oxide reduction is also effected by the various equipment used for secondary particulate control. Estimates of the quantities of sulfur oxides emitted from kilns, both before and after controls, are presented in Table 8.15-1.

Hydrator emissions are low because water sprays or wet scrubbers are usually installed for economic reasons to prevent product loss in the exhaust gases. Emissions from pressure hydrators may be higher than from the more common atmospheric hydrators because the exhaust gases are released intermittently over short time intervals, making control more difficult.

Product coolers are emission sources only when some of their exhaust gases are not recycled through the kiln for use as combustion air. The trend is away from the venting of product cooler exhaust, however, to maximize fuel use efficiencies. Cyclones, baghouses, and wet scrubbers have been employed on coolers for particulate control.

Other particulate sources in lime plants include primary and secondary crushers, mills, screens, mechanical and pneumatic transfer operations, storage piles, and unpaved roads. If quarrying is a part of the lime plant operation, particulate may also result from drilling and blasting. Emission factors for some of these operations are presented in Sections 8.20 and 11.2.

Emission factors for lime manufacturing are presented in Table 8.15-1.

**Table 8.15-1. EMISSION FACTORS FOR LIME MANUFACTURING**  
**EMISSION FACTOR RATING: B**

Source	Emissions <sup>a</sup>							
	Particulate		Sulfur dioxide		Nitrogen oxides		Carbon monoxide	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/tr	kg/MT	lb/ton	kg/MT
Crushers, screens, conveyors, storage piles, unpaved roads	b	b	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Rotary kilns								
Uncontrolled <sup>c</sup>	340	170	d	d	3	1.5	2	1
After settling chamber or large diameter cyclone	200	100	d	d	3	1.5	2	1
After multiple cyclones	85 <sup>e</sup>	43 <sup>e</sup>	d	d	3	1.5	2	1
After secondary dust collection <sup>f</sup>	1	0.5	g	g	3	1.5	2	1
Vertical kilns								
Uncontrolled	8	4	NA <sup>h</sup>	NA <sup>h</sup>	NA	NA	NA	NA
Calcimatic kilns <sup>i</sup>								
Uncontrolled	50	25	NA	NA	0.2	0.1	NA	NA
After multiple cyclones	6	3	NA	NA	0.2	0.1	NA	NA
After secondary dust collection <sup>j</sup>	NA	NA	NA	NA	0.2	0.1	NA	NA
Fluidized-bed kilns	NA <sup>k</sup>	NA <sup>k</sup>	NA	NA	NA	NA	NA	NA
Product coolers								
Uncontrolled	40 <sup>l</sup>	20 <sup>l</sup>	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Hydrators	0.1 <sup>m</sup>	0.05 <sup>m</sup>	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.

<sup>a</sup>All emission factors for kilns and coolers are per unit of lime produced. Divide by two to obtain factors per unit of limestone feed to the kiln. Factors for hydrators are per unit of hydrated lime produced. Multiply by 1.25 to obtain factors per unit of lime feed to the hydrator. All emissions data are based on References 4 through 6.

<sup>b</sup>Emission factors for these operations are presented in Sections 8.20 and 11.2.

<sup>c</sup>No particulate control except for settling that may occur in the stack breaching and chimney base.

<sup>d</sup>When low-sulfur (less than 1 percent, by weight) fuels are used, only about 10 percent of the fuel sulfur is emitted as SO<sub>2</sub>. When high-sulfur fuels are used, approximately 50 percent of the fuel sulfur is emitted as SO<sub>2</sub>.

<sup>e</sup>This factor should be used when coal is fired in the kiln. Limited data suggest that when only natural gas or oil is fired, particulate emissions after multiple cyclones may be as low as 20 to 30 lb/ton (10 to 15 kg/MT).

<sup>f</sup>Fabric or gravel bed filters, electrostatic precipitators, or wet (most commonly venturi) scrubbers. Particulate concentrations as low as 0.2 lb/ton (0.1 kg/MT) have been achieved using these devices.

<sup>g</sup>When scrubbers are used, less than 5 percent of the fuel sulfur will be emitted as SO<sub>2</sub>, even with high-sulfur coal. When other secondary collection devices are used, about 20 percent of the fuel sulfur will be emitted as SO<sub>2</sub> with high-sulfur fuels and less than 10 percent with low-sulfur fuels.

<sup>h</sup>Not available.

<sup>i</sup>Calcimatic kilns generally employ stone preheaters. All factors represent emissions after the kiln exhaust passes through a preheater.

<sup>j</sup>Fabric filters and venturi scrubbers have been employed on calcimatic kilns. No data are available on particulate emissions after secondary control.

<sup>k</sup>Fluidized-bed kilns must employ sophisticated dust collection equipment for process economics; hence, particulate emissions will depend on the efficiency of the control equipment installed.

<sup>l</sup>Some or all of the cooler exhaust is typically used in the kiln as combustion air. Emissions will result only from that fraction that is not recycled to the kiln.

<sup>m</sup>This is a typical particulate loading for atmospheric hydrators following water sprays or wet scrubbers. Limited data suggest particulate emissions from pressure hydrators may be approximately 2 lb/ton (1 kg/MT) of hydrate produced, after wet collectors.

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10.1.2.2. Emission and Controls<sup>1-6</sup>—Particulate emissions from the kraft process occur primarily from the recovery furnace, the lime kiln, and the smelt dissolving tank. These emissions consist mainly of sodium salts but include some calcium salts from the lime kiln. They are caused primarily by the carryover of solids plus the sublimation and condensation of the inorganic chemicals.

Particulate control is provided on recovery furnaces in a variety of ways. In mills where either a cyclonic scrubber or cascade evaporator serves as the direct contact evaporator, further control is necessary as these devices are generally only 20 to 50 percent efficient for particulates. Most often in these cases, an electrostatic precipitator is employed after the direct contact evaporator to provide an overall particulate control efficiency of 85 to  $\geq 99$  percent. In a few mills, however, a venturi scrubber is utilized as the direct contact evaporator and simultaneously provides 80 to 90 percent particulate control. In either case auxiliary scrubbers may be included after the precipitator or the venturi scrubber to provide additional control of particulates.

Particulate control on lime kilns is generally accomplished by scrubbers. Smelt dissolving tanks are commonly controlled by mesh pads but employ scrubbers when further control is needed.

The characteristic odor of the kraft mill is caused in large part by the emission of hydrogen sulfide. The major source is the direct contact evaporator in which the sodium sulfide in the black liquor reacts with the carbon dioxide in the furnace exhaust. The lime kiln can also be a potential source as a similar reaction occurs involving residual sodium sulfide in the lime mud. Lesser amounts of hydrogen sulfide are emitted with the noncondensable off-gasses from the digesters and multiple-effect evaporators.

The kraft-process odor also results from an assortment of organic sulfur compounds, all of which have extremely low odor thresholds. Methyl mercaptan and dimethyl sulfide are formed in reactions with the wood component lignin. Dimethyl disulfide is formed through the oxidation of mercaptan groups derived from the lignin. These compounds are emitted from many points within a mill; however, the main sources are the digester/blow tank systems and the direct contact evaporator.

Although odor control devices, per se, are not generally employed in kraft mills, control of reduced sulfur compounds can be accomplished by process modifications and by optimizing operating conditions. For example, black liquor oxidation systems, which oxidize sulfides into less reactive thiosulfates, can considerably reduce odorous sulfur emissions from the direct contact evaporator, although the vent gases from such systems become minor odor sources themselves. Noncondensable odorous gases vented from the digester/blow tank system and multiple-effect evaporators can be destroyed by thermal oxidation, usually by passing them through the lime kiln. Optimum operation of the recovery furnace, by avoiding overloading and by maintaining sufficient oxygen residual and turbulence, significantly reduces emissions of reduced sulfur compounds from this source. In addition, the use of fresh water instead of contaminated condensates in the scrubbers and pulp washers further reduces odorous emissions. The effect of any of these modifications on a given mill's emissions will vary considerably.

Several new mills have incorporated recovery systems that eliminate the conventional direct contact evaporators. In one system, preheated combustion air rather than flue gas provides direct contact evaporation. In the other, the multiple-effect evaporator system is extended to replace the direct contact evaporator altogether. In both of these systems, reduced sulfur emissions from the recovery furnace/direct contact evaporator reportedly can be reduced by more than 95 percent from conventional uncontrolled systems.

Sulfur dioxide emissions result mainly from oxidation of reduced sulfur compounds in the recovery furnace. It is reported that the direct contact evaporator absorbs 50 to 80 percent of these emissions; further scrubbing, if employed, can reduce them another 10 to 20 percent.

Potential sources of carbon monoxide emissions from the kraft process include the recovery furnace and lime kilns. The major cause of carbon monoxide emissions is furnace operation well above rated capacity, making it impossible to maintain oxidizing conditions.

Some nitrogen oxides are also emitted from the recovery furnace and lime kilns although the amounts are relatively small. Indications are that nitrogen oxides emissions from each of these sources are on the order of 1 pound per air-dried ton (0.5 kg/air-dried MT) of pulp produced.<sup>5 6</sup>

A major source of emissions in a kraft mill is the boiler for generating auxiliary steam and power. The fuels used are coal, oil, natural gas, or bark/wood waste. Emission factors for boilers are presented in Chapter 1.

Table 10.1.2-1 presents emission factors for a conventional kraft mill. The most widely used particulate controls devices are shown along with the odor reductions resulting from black liquor oxidation and incineration of noncondensable off-gases.

### 10.1.3 Acid Sulfite Pulping

*by Tom Lahre*

**10.1.3.1 Process Description<sup>14</sup>** - The production of acid sulfite pulp proceeds similarly to kraft pulping except that different chemicals are used in the cooking liquor. In place of the caustic solution used to dissolve the lignin in the wood, sulfurous acid is employed. To buffer the cooking solution, a bisulfite of sodium, magnesium, calcium, or ammonium is used. A simplified flow diagram of a magnesium-base process is shown in Figure 10.1.3-1.

Digestion is carried out under high pressure and high temperature in either batch-mode or continuous digesters in the presence of a sulfurous acid-bisulfite cooking liquor. When cooking is completed, the digester is either discharged at high pressure into a blow pit or its contents are pumped out at a lower pressure into a dump tank. The spent sulfite liquor (also called red liquor) then drains through the bottom of the tank and is either treated and disposed, incinerated, or sent to a plant for recovery of heat and chemicals. The pulp is then washed and processed through screens and centrifuges for removal of knots, bundles of fibers, and other materials. It subsequently may be bleached, pressed, and dried in paper-making operations.

Because of the variety of bases employed in the cooking liquor, numerous schemes for heat and/or chemical recovery have evolved. In calcium-base systems, which are used mostly in older mills, chemical recovery is not practical, and the spent liquor is usually discarded or incinerated. In ammonium-base operations, heat can be recovered from the spent liquor through combustion, but the ammonium base is consumed in the process. In sodium- or magnesium-base operations heat, sulfur, and base recovery are all feasible.

If recovery is practiced, the spent weak red liquor (which contains more than half of the raw materials as dissolved organic solids) is concentrated in a multiple-effect evaporator and direct contact evaporator to 55 to 60 percent solids. Strong liquor is sprayed into a furnace and burned, producing steam for the digesters, evaporators, etc., and to meet the mills power requirements.

When magnesium base liquor is burned, a flue gas is produced from which magnesium oxide is recovered in a multiple cyclone as fine white powder. The magnesium oxide is then water-slaked and used as circulating liquor in a series of venturi scrubbers which are designed to absorb sulfur dioxide from the flue gas and form a bisulfite solution for use in the cook cycle. When sodium-base liquor is burned, the inorganic compounds are recovered as a molten smelt containing sodium sulfide and sodium carbonate. This smelt may be processed further and used to absorb sulfur dioxide from the flue gas and sulfur burner. In some sodium-base mills, however, the smelt may be sold to a nearby kraft mill as raw material for producing green liquor.

Table 10.1.2-1. EMISSION FACTORS FOR SULFATE PULPING<sup>a</sup>  
(unit weights of air-dried unbleached pulp)  
EMISSION FACTOR RATING: A

Source	Type control	Particulates <sup>b</sup>		Sulfur dioxide (SO <sub>2</sub> ) <sup>c</sup>		Carbon monoxide <sup>d</sup>		Hydrogen sulfide(S <sup>=</sup> ) <sup>e</sup>		RSH, RSR, RSSR(S <sup>=</sup> ) <sup>e,f</sup>	
		lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Digester relief and blow tank	Untreated <sup>g</sup>	—	—	—	—	—	—	0.1	0.05	1.5	0.75
Brown stock washers	Untreated	—	—	0.01	0.005	—	—	0.02	0.01	0.2	0.1
Multiple effect evaporators	Untreated <sup>g</sup>	—	—	0.01	0.005	—	—	0.1	0.05	0.4	0.2
Recovery boiler and direct contact evaporator	Untreated <sup>h</sup>	150	75	5	2.5	2 - 60	1 - 30	12 <sup>i</sup>	6 <sup>i</sup>	1 <sup>i</sup>	0.5 <sup>i</sup>
	Venturi scrubber <sup>j</sup>	47	23.5	5	2.5	2 - 60	1 - 30	12 <sup>i</sup>	6 <sup>i</sup>	1 <sup>i</sup>	0.5 <sup>i</sup>
	Electrostatic precipitator	8	4	5	2.5	2 - 60	1 - 30	12 <sup>i</sup>	6 <sup>i</sup>	1 <sup>i</sup>	0.5 <sup>i</sup>
	Auxiliary scrubber	3 - 15 <sup>k</sup>	1.5-7.5 <sup>k</sup>	3	1.5	2 - 60	1 - 30	12 <sup>i</sup>	6 <sup>i</sup>	1 <sup>i</sup>	0.5 <sup>i</sup>
Smelt dissolving tank	Untreated	5	2.5	0.1	0.05	—	—	0.04	0.02	0.4	0.2
	Mesh pad	1	0.5	0.1	0.05	—	—	0.04	0.02	0.4	0.2
Lime kilns	Untreated	45	22.5	0.3	0.15	10	5	0.5	0.25	0.25	0.125
	Scrubber	3	1.5	0.2	0.1	10	5	0.5	0.25	0.25	0.125
Turpentine condenser	Untreated	—	—	—	—	—	—	0.01	0.005	0.5	0.25
Miscellaneous sources <sup>l</sup>	Untreated	—	—	—	—	—	—	—	—	0.5	0.25

<sup>a</sup>For more detailed data on specific types of mills, consult Reference 1.

<sup>b</sup>References 1, 7, 8.

<sup>c</sup>References 1, 7, 9, 10.

<sup>d</sup>References 6, 11. Use higher value for overloaded furnaces.

<sup>e</sup>References 1, 4, 7-10, 12, 13. These reduced sulfur compounds are usually expressed as sulfur.

<sup>f</sup>RSH-methyl mercaptan; RSR-dimethyl sulfide; RSSR-dimethyl disulfide.

<sup>g</sup>If the noncondensable gases from these sources are vented to the lime kiln, recovery furnace, or equivalent, the reduced sulfur compounds are destroyed.

<sup>h</sup>These factors apply when either a cyclonic scrubber or cascade evaporator is used for direct contact evaporation with no further controls.

<sup>i</sup>These reduced sulfur compounds (TRS) are typically reduced by 50 percent when black liquor oxidation is employed but can be cut by 90 to 99 percent when oxidation is complete and the recovery furnace is operated optimally.

<sup>j</sup>These factors apply when a venturi scrubber is used for direct contact evaporation with no further controls.

<sup>k</sup>Use 15(7.5) when the auxiliary scrubber follows a venturi scrubber and 3(1.5) when employed after an electrostatic precipitator.

<sup>l</sup>Includes knotter vents, brownstock seal tanks, etc. When black liquor oxidation is included, a factor of 0.6(0.3) should be used.

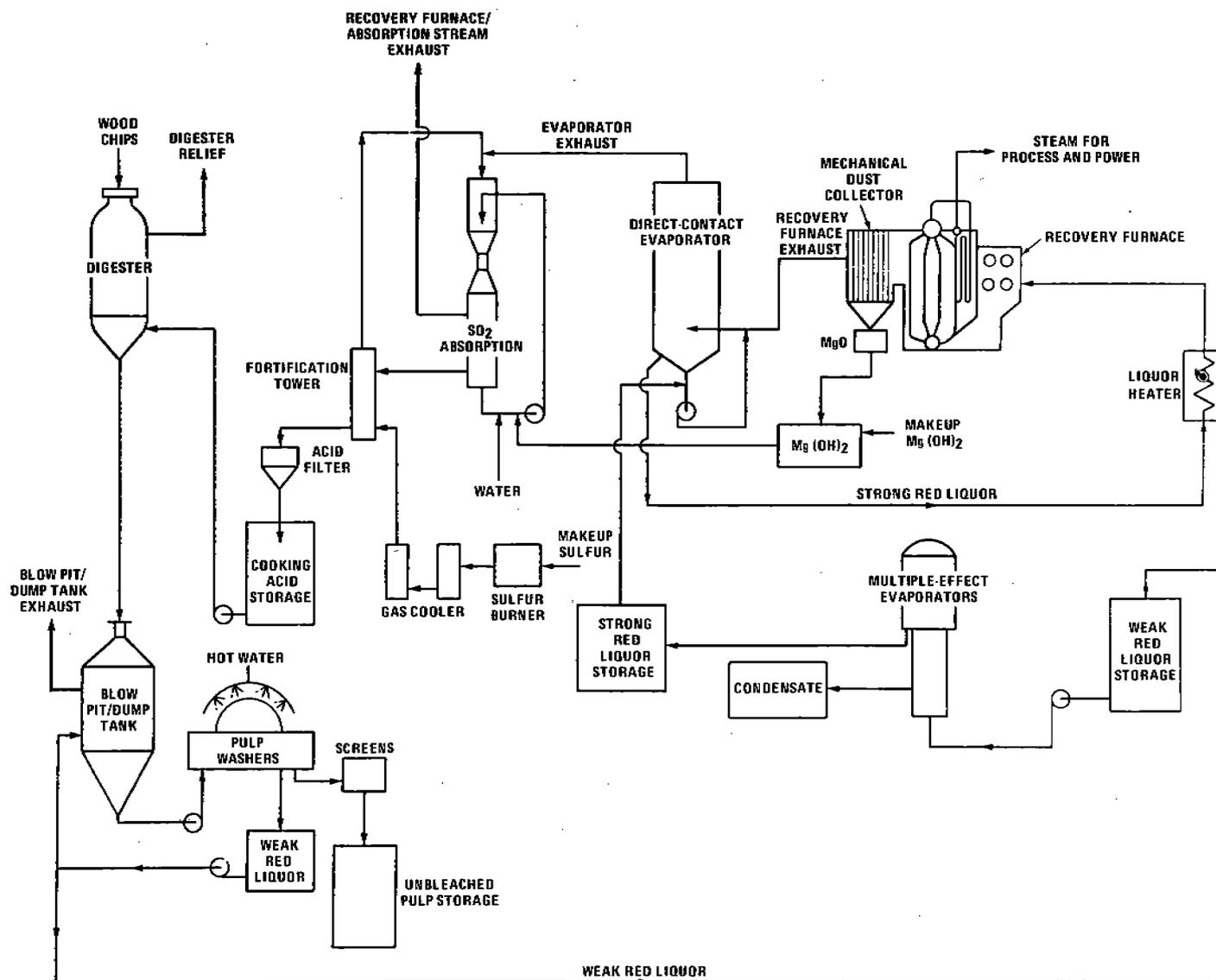


Figure 10.1.3-1. Simplified process flow diagram of magnesium-base process employing chemical and heat recovery.

If recovery is not practiced, an acid plant of sufficient capacity to fulfill the mill's total sulfite requirement is necessary. Normally, sulfur is burned in a rotary or spray burner. The gas produced is then cooled by heat exchangers plus a water spray and then absorbed in a variety of different scrubbers containing either limestone or a solution of the base chemical. Where recovery is practiced, fortification is accomplished similarly, although a much smaller amount of sulfur dioxide must be produced to make up for that lost in the process.

10.1.3.2 Emissions and Controls<sup>14</sup> - Sulfur dioxide is generally considered the major pollutant of concern from sulfite pulp mills. The characteristic "kraft" odor is not emitted because volatile reduced sulfur compounds are not products of the lignin-bisulfite reaction.

One of the major SO<sub>2</sub> sources is the digester and blow pit or dump tank system. Sulfur dioxide is present in the intermittent digester relief gases as well as in the gases given off at the end of the cook when the digester contents are discharged into the blow pit or dump tank. The quantity of sulfur oxide evolved and emitted to the atmosphere in these gas streams depends on the pH of the cooking liquor, the pressure at which the digester contents are discharged, and the effectiveness of the absorption systems employed for SO<sub>2</sub> recovery. Scrubbers can be installed that reduce SO<sub>2</sub> from this source by as much as 99 percent.

Another source of sulfur dioxide emissions is the recovery system. Since magnesium-, sodium-, and ammonium-base recovery systems all utilize absorption systems to recover SO<sub>2</sub> generated in the recovery furnace, acid fortification towers, multiple-effect evaporators, etc., the magnitude of SO<sub>2</sub> emissions depends on the desired efficiency of these systems. Generally, such absorption systems provide better than 95 percent sulfur recovery to minimize sulfur makeup needs.

The various pulp washing, screening, and cleaning operations are also potential sources of SO<sub>2</sub>. These operations are numerous and may account for a significant fraction of a mill's SO<sub>2</sub> emissions if not controlled.

The only significant particulate source in the pulping and recovery process is the absorption system handling the recovery furnace exhaust. Less particulate is generated in ammonium-base systems than magnesium- or sodium-base systems as the combustion productions are mostly nitrogen, water vapor, and sulfur dioxide.

Other major sources of emissions in a sulfite pulp mill include the auxiliary power boilers. Emission factors for these boilers are presented in Chapter 1.

Emission factors for the various sulfite pulping operations are shown in Table 10.1.3-1.

## 10.1.4 Neutral Sulfite Semichemical (NSSC) Pulping

10.1.4.1 Process Description<sup>1,7,15,16</sup> - In this process, the wood chips are cooked in a neutral solution of sodium sulfite and sodium bicarbonate. The sulfite ion reacts with the lignin in the wood, and the sodium bicarbonate acts as a buffer to maintain a neutral solution. The major difference between this process (as well as all semichemical techniques) and the kraft and acid sulfite processes is that only a portion of the lignin is removed during the cook, after which the pulp is further reduced by mechanical disintegration. Because of this, yields as high as 60 to 80 percent can be achieved as opposed to 50 to 55 percent for other chemical processes.

**Table 10.1.3-1. EMISSION FACTORS FOR SULFITE PULPING<sup>a</sup>**

Source	Base	Control	Emission factor <sup>b</sup>				Emission factor rating
			Particulate		Sulfur Dioxide		
			lb/ADUT	kg/ADUMT	lb/ADUT	kg/ADUMT	
Digester/blow pit or dump tank <sup>c</sup>	All	None	Neg <sup>d</sup>	Neg	10-70	5-35	C
	MgO	Process change <sup>e</sup>	Neg	Neg	2-6	1-3	C
	MgO	Scrubber	Neg	Neg	1	0.5	B
	MgO	Process change and scrubber	Neg	Neg	0.2	0.1	B
	MgO	All exhaust vented through recovery system	Neg	Neg	0	0	A
	NH <sub>3</sub>	Process change	Neg	Neg	25	12.5	D
	NH <sub>3</sub>	Process change and scrubber	Neg	Neg	0.4	0.2	B
	Na	Process change and scrubber	Neg	Neg	2	1	C
	Ca	Unknown	Neg	Neg	67	33.5	C
	Recovery system <sup>f</sup>	MgO	Multiclone and venturi scrubbers	2	1	9	4.5
NH <sub>3</sub>		Ammonia absorption and mist eliminator	0.7	0.35	7	3.5	B
Na		Sodium carbonate scrubber	4	2	2	1	C
Acid plant <sup>g</sup>	NH <sub>3</sub>	Scrubber	Neg	Neg	0.3	0.2	C
	Na	Unknown <sup>h</sup>	Neg	Neg	0.2	0.1	D
	Ca	Jenssen scrubber	Neg	Neg	8	4	C
Other sources <sup>i</sup>	All	None	Neg	Neg	12	6	D

<sup>a</sup>All emission factors represent long-term average emissions.

<sup>b</sup>Factors expressed in terms of lb (kg) of pollutant per air dried unbleached ton (MT) of pulp. All factors are based on data in Reference 14.

<sup>c</sup>These factors represent emissions that occur after the cook is completed and when the digester contents are discharged into the blow pit or dump tank. Some relief gases are vented from the digester during the cook cycle, but these are usually transferred to pressure accumulators, and the SO<sub>2</sub> therein is reabsorbed for use in the cooking liquor. These factors represent long-term average emissions; in some mills, the actual emissions will be intermittent and for short time periods.

<sup>d</sup>Negligible emissions.

<sup>e</sup>Process changes may include such measures as raising the pH of the cooking liquor, thereby lowering the free SO<sub>2</sub>, relieving the pressure in the digester before the contents are discharged, and pumping out the digester contents instead of blowing them out.

<sup>f</sup>The recovery system at most mills is a closed system that includes the recovery furnace, direct contact evaporator, multiple-effect evaporator, acid fortification tower, and SO<sub>2</sub> absorption scrubbers. Generally, there will only be one emission point for the entire recovery system. These factors are long-term averages and include the high SO<sub>2</sub> emissions during the periodic purging of the recovery system.

<sup>g</sup>Acid plants are necessary in mills that have no or insufficient recovery systems.

<sup>h</sup>Control is practiced, but type of control is unknown.

<sup>i</sup>Includes miscellaneous pulping operations such as knotters, washers, screens, etc.

The NSSC process varies from mill to mill. Some mills dispose of their spent liquor, some mills recover the cooking chemicals, and some, which are operated in conjunction with kraft mills, mix their spent liquor with the kraft liquor as a source of makeup chemicals. When recovery is practiced, the steps involved parallel those of the sulfite process.

10.1.4.2 Emissions and Controls<sup>1,7,15,16</sup> Particulate emissions are a potential problem only when recovery systems are employed. Mills that do practice recovery, but are not operated in conjunction with kraft operations often utilize fluidized bed reactors to burn their spent liquor. Because the flue gas contains sodium sulfate and sodium carbonate dust, efficient particulate collection may be included to facilitate chemical recovery.

A potential gaseous pollutant is sulfur dioxide. The absorbing towers, digester/blow tank system, and recovery furnace are the main sources of this pollutant with the amounts emitted dependent upon the capability of the scrubbing devices installed for control and recovery.

Hydrogen sulfide can also be emitted from NSSC mills using kraft-type recovery furnaces. The main potential source is the absorbing tower where a significant quantity of hydrogen sulfide is liberated as the cooking liquor is made. Other possible sources include the recovery furnace, depending on the operating conditions maintained, as well as the digester/blow tank system in mills where some green liquor is used in the cooking process. Where green liquor is used, it is also possible that significant quantities of mercaptans will be produced. Hydrogen sulfide emissions can be eliminated if burned to sulfur dioxide prior to entering the absorbing systems.

Because the NSSC process differs greatly from mill to mill, and because of the scarcity of adequate data, no emission factors are presented.

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**APPENDIX B**  
**EMISSION FACTORS**  
**AND**  
**NEW SOURCE PERFORMANCE STANDARDS**  
**FOR STATIONARY SOURCES**

The New Source Performance Standards (NSPS) promulgated by the Environmental Protection Agency for various industrial categories and the page reference in this publication where uncontrolled emission factors for those sources are discussed are presented in Tables B-1 and B-2. Note that, in the case of steam-electric power plants, the NSPS encompass much broader source categories than the corresponding emission factors. In several instances, the NSPS were formulated on different bases than the emission factors (for example, grains per standard cubic foot versus pounds per ton). Non-criteria pollutant standards have not been included in Table B-2. Finally, note that NSPS relating to opacity have been omitted because they cannot (at this time) be directly correlated with emission factors.

Table B-1. PROMULGATED NEW SOURCE PERFORMANCE STANDARDS

Source category and pollutant	New Source Performance Standard (maximum 2-hr average)	AP-42 page reference
Fossil-fuel-fired steam generators with $>63 \times 10^6$ kcal/hr ( $250 \times 10^6$ Btu/hr) of heat input		
Coal-burning plants (excluding lignite)		
Pulverized wet bottom		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.1-3
Sulfur dioxide	2.2 g/10 <sup>6</sup> cal heat input (1.2 lb/10 <sup>6</sup> Btu)	1.1-3
Nitrogen oxides (as NO <sub>2</sub> )	1.26 g/10 <sup>6</sup> cal heat input (0.70 lb/10 <sup>6</sup> Btu)	1.1-3
Pulverized dry bottom		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.1-3
Sulfur dioxide	2.2 g/10 <sup>6</sup> cal heat input (1.2 lb/10 <sup>6</sup> Btu)	1.1-3
Nitrogen oxides (as NO <sub>2</sub> )	1.26 g/10 <sup>6</sup> cal heat input (0.70 lb/10 <sup>6</sup> Btu)	1.1-3
Pulverized cyclone		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.1-3
Sulfur dioxide	2.2 g/10 <sup>6</sup> cal heat input (1.2 lb/10 <sup>6</sup> Btu)	1.1-3
Nitrogen oxides (as NO <sub>2</sub> )	1.26 g/10 <sup>6</sup> cal heat input (0.70 lb/10 <sup>6</sup> Btu)	1.1-3
Spreader stoker		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.1-3
Sulfur dioxide	2.2 g/10 <sup>6</sup> cal heat input (1.2 lb/10 <sup>6</sup> Btu)	1.1-3
Nitrogen oxides (as NO <sub>2</sub> )	1.26 g/10 <sup>6</sup> cal heat input (0.70 lb/10 <sup>6</sup> Btu)	1.1-3
Residual-oil-burning plants		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.3-2
Sulfur dioxide	1.4 g/10 <sup>6</sup> cal heat input (0.80 lb/10 <sup>6</sup> Btu)	1.3-2
Nitrogen oxides (as NO <sub>2</sub> )	0.54 g/10 <sup>6</sup> cal heat input (0.30 lb/10 <sup>6</sup> Btu)	1.3-2
Natural-gas-burning plants		
Particulates	0.18 g/10 <sup>6</sup> cal heat input (0.10 lb/10 <sup>6</sup> Btu)	1.4-2
Nitrogen oxides (as NO <sub>2</sub> )	0.36 g/10 <sup>6</sup> cal heat input (0.20 lb/10 <sup>6</sup> Btu)	1.4-2
Municipal incinerators		
Particulates	0.18 g/Nm <sup>3</sup> (0.08 gr/scf) corrected to 12% CO <sub>2</sub>	2.1-1
Portland cement plants		
Kiln--dry process		
Particulates	0.15 kg/MT (0.30 lb/ton) of feed to kiln	8.6-3

Table B-1. (continued). PROMULGATED NEW SOURCE PERFORMANCE STANDARDS

Source category and pollutant	New Source Performance Standard (maximum 2-hr average)	AP-42 page reference
Kiln-wet process Particulates	0.15 kg/MT (0.30 lb/ton) of feed to kiln	8.6-3
Clinker cooler Particulates	0.050 kg/MT (0.10 lb/ton) of feed to kiln	8.6-4
Nitric acid plants Nitrogen oxides (as NO <sub>2</sub> )	1.5 kg/MT (3.0 lb/ton) of 100% acid produced	5.9-3
Sulfuric acid plants Sulfur dioxide	2.0 kg/MT (4.0 lb/ton) of 100% acid produced	5.17-5
Sulfuric acid mist (as H <sub>2</sub> SO <sub>4</sub> )	0.075 kg/MT (0.15 lb/ton) of 100% acid produced	5.17-7

<sup>a</sup>Title 40 - Protection of Environment, Part 60--Standards of Performance for New Stationary Sources. Federal Register, 36 (247):24876. December 23, 1971



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**TECHNICAL REPORT DATA**  
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16. ABSTRACT

In this supplement for Compilation of Air Pollutant Emission Factors (AP-42) revised and updated emissions data are presented for anthracite coal combustion, fuel oil combustion, bagasse combustion in sugar mills, residential fireplaces, open burning, dry cleaning, storage of petroleum liquids, transportation and marketing of petroleum liquids, adipic acid, carbon black, charcoal, phthalic anhydride, feed and grain mills and elevators, fish processing, portland cement manufacturing, lime manufacturing, and acid sulfite pulping.

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