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CONTROL TECHNIQUES FOR VOLATILE ORGANIC EMISSIONS FROM STATIONARY SOURCES

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LIST OF SYMBOLS

Symbol	Prefix	Multiplication Factor
P	peta	10^{15}
T	tera	10^{12}
G	giga	10^{9}
M	mega	10^{6}
k	kilo	10^{3}
h	hecto	10^{2}
da	deka	10
d	deci	10^{-1}
c	centi	10^{-2}
m	milli	10^{-3}
μ	micro	10^{-6}

Symbol	Meaning
°C	degree celsius
g	gram
J	joule
m	metre
Pa	pascal
s	second
W	watt

SUMMARY

This document constitutes a general reference on the sources of volatile organic emissions, applicable control techniques, and the impacts resulting from control application. It is required through Section 108(b) of the Clean Air Act, as amended, and is intended primarily to be used by State and local air pollution control engineers.

CHARACTERIZATION OF VOLATILE ORGANIC EMISSIONS

For purposes of this document, a volatile organic compound (VOC) is any organic compound that, when released to the atmosphere, can remain long enough to participate in photochemical reactions. The predominant fraction of the VOC burden are compounds which evaporate rapidly at ambient temperatures. Almost all organics which can be considered VOC have vapor pressures greater than 0.1 mm Hg at standard conditions (20°C, 760 mm Hg). Some volatile organics are toxic by themselves and nearly all react photochemically in the atmosphere to produce ozone and other oxidants. Oxidants have been associated with a variety of adverse health and welfare effects. Therefore, volatile organic emissions are an important concern in air pollution control.

The following table gives 1977 estimates of nationwide volatile organic emissions for generalized source categories.

Anthropogenic Sources of Volatile Organics

Source	Estimated Emissions Gg/yr (10^3 ton/yr)
Petroleum Refineries	900 (990)
Storage, Transportation, and Marketing of Petroleum Products	2600 (2860)
Organic Chemical Manufacture	1500 (1650)
Industrial Surface Coating	1900 (2090)
Non-Industrial Surface Coating	500 (550)
Other Solvent Use	5100 (5600)
Other Industrial Processes	1000 (1100)
Miscellaneous Sources	3100 (3400)
Total from Stationary Sources	16,600 (18,300)

Source	Estimated Emissions Gg/yr (10^3 ton/yr)
Highway Vehicles	9350 (10,300)
Off-Highway Vehicles	570 (630)
Rail	140 (150)
Aircraft	300 (330)
Vessels	440 (490)
Total Mobile Sources	10,800 (11,900)
Total Nationwide Emissions	27,400 (30,100)

As can be derived from the table, about 60 percent of volatile organic emissions are from stationary sources and 40 percent from mobile sources. Nationwide emissions have shown only a small decrease from the 1970 estimated level of 29,700 Gg/yr (32.7×10^6 tons/yr).

CONTROL TECHNIQUES

The three methods commonly employed to reduce organic emissions are:

1. Installation of add-on control equipment to recover or destroy off-gas pollutants.
2. Substitution of less photochemically reactive materials.
3. Incorporation of process and/or raw material changes to eliminate or reduce pollutant generation in the process.

Of all add-on control techniques used for volatile organic emissions, five are widely used in a variety of applications. These five are: incineration, adsorption, absorption, condensation, and flaring.

INCINERATION

Incineration is the technique most universally applicable to sources of volatile organics. Incinerators destroy pollutants through thermal or catalytic oxidation and control efficiencies may approach 100 percent. Pollutant streams not capable of sustaining combustion may require additional fuel. Fuel costs can be at least partially offset by employing various methods of heat recovery.

PREFACE

This is the second edition of the department of Health, Education, and Welfare document entitled "Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources (AP-68)." This document was first published in March, 1970 under the National Air Pollution Control Administration. The second edition has been substantially modified from the original and has been retitled "Control Techniques for Volatile Organic Emissions from Stationary Sources."

Radian Corporation prepared this document for the Environmental Protection Agency under EPA contract no. 68-02-2608, Tasks 12 and 23. The EPA Project Officer was D. A. Beck. The Radian Program Manager was E. C. Cavanaugh; the task directors were C. E. Burklin and G. E. Wilkins. Other contributors from Radian were S. Ballard, C. S. Collins, J. Fischer, R. Hearn, P. B. Hulman, P. Jeffcoat, D. C. Jones, W. C. Micheletti, P. J. Murin, and T. B. Parsons.

The document has been reviewed by the Environmental Protection Agency, the National Air Pollution Control Techniques Advisory Committee, and other individuals associated with Federal Agencies and private industry.

Incineration has been successfully applied to aluminum chip dryers, petroleum processing and marketing operations, animal blood dryers, automotive brakeshoe debonding ovens, citrus pulp dryers, coffee roasters, wire enameling ovens, foundry core ovens, meat smokehouses, paint-baking ovens, varnish cookers, paper printing and impregnating installations, pharmaceutical manufacturing plants, sewage disposal plants, chemical processing plants, and textile finishing plants.

ADSORPTION

Control of volatile organics by adsorption is accomplished through use of a highly porous solid material called the adsorbent. Adsorption occurs primarily in two ways: (1) physical adsorption, in which van der Waal's forces attract and hold gas molecules to the adsorbent surface, and (2) chemical adsorption, in which gas molecules are chemically bonded to the adsorbent. Additionally, within the capillaries of the porous solid, surface adsorption is supplemented by capillary condensation. The adsorbent is most commonly regenerated by stripping the organics into a stream of easily condensible gas such as steam.

Activated carbon is a widely used adsorbent for volatile organics control. Carbon adsorption is usually more economical than incineration for the control of organics in concentrations below 100 ppm. Depending on the application, carbon adsorption efficiencies can be well in excess of 90 percent. In addition, this control technique offers recovery of adsorbed organics which can be recycled to the process or used as fuel. Recovery and reuse is gaining importance as the price of petrochemicals rises.

Adsorption has been used successfully in organic chemical processing, varnish manufacture, synthetic rubber manufacture, production of selected rubber products, pharmaceutical processing, graphic arts operations, food production, dry cleaning, synthetic fiber manufacture, and some surface coating operations.

ABSORPTION

Absorption is the process in which pollutants in an exhaust gas are selectively transferred to a liquid solvent. Absorption may be purely physical (organics simply dissolve in the absorbent) or chemical (organics react with the absorbent or with reagents dissolved in the absorbent). The generally low organics concentration of exhaust gases require long contact times and large quantities of absorbent for adequate emissions control. Therefore, absorption is less desirable than adsorption or incineration, unless the absorbent is easily regenerated or can be used as a process make-up stream.

Absorption has been used to control organic vapors and particulates in surface coating operations, waste handling and treatment plants, degreasing operations, asphalt batch plants, ceramic tile manufacturing plants, coffee roasters, chromium-plating units, petroleum coker units, fish meal systems, chemical plants, and varnish and resin cookers.

CONDENSATION

For a two component vapor (where one component can be considered non-condensible), condensation occurs when the partial pressure of the condensible component equals its vapor pressure. Condensers can operate in two ways: (1) at a given temperature, the condenser pressure is increased until one component condenses or (2) at a given pressure, the condenser temperature is reduced until one component condenses. Condensation is usually applied in combination with other air pollution control devices.

Condensers have been used successfully in bulk gasoline terminals, petroleum refining, petrochemical manufacturing, dry cleaning, degreasing, and tar dipping.

FLARING

Flares are external combustors that are usually employed as safety devices to incinerate waste gases from petroleum refining and petrochemical manufacturing. Flares are preferred when disposing of gas streams with sufficient heating value to sustain combustion without supplemental fuel. Gases containing organics are flared if they have little recovery value or contain contaminants that make recovery unprofitable.

Combustion of organics in a well operated flare may be nearly complete. In typical installations, hydrocarbon removal efficiencies of 99 percent have been obtained.

SUBSTITUTION OF LESS PHOTOCHEMICALLY REACTIVE MATERIALS

Another strategy to reduce ambient oxidant concentrations is to use materials that result in emissions of volatile organics with low photochemical reactivity. However, this strategy is no longer recommended because recent research indicates that nearly all volatile organics participate to some extent in photochemical reactions. Of the remaining organics that are only slightly or negligibly reactive, many are inherently toxic and some have been implicated in the destruction of the ozone layer.

PROCESS AND/OR RAW MATERIAL CHANGES

In certain manufacturing or processing operations, it may be possible to effect process or raw material changes that result in lower emission levels. For example, organic emissions from surface coating operations can be significantly reduced by replacing solvent-borne coatings with water-borne, high solids, or powder coatings. There are many other examples of process and material changes. Most improve the efficiency of the operation by improving yield or eliminating the need for add-on control equipment.

CONTROL SYSTEMS FOR INDUSTRIAL PROCESSES

The following table summarizes emission control techniques for major stationary sources of volatile organics.

CONTROL TECHNIQUES SUMMARY

Industry	Emission Sources	Control Techniques
Petroleum and Chemical Process Industries (common sources)	Cooling towers, valves, flanges, pump and compressor seals, pressure relief devices	Proper equipment maintenance, speedy leak repair, good housekeeping programs, leak detection programs
	Compressor engines	Properly adjusted carburetion
	Wastewater drainage and treatment systems	Minimize water contamination, enclose water collection and treatment systems
	Blind changing	Pump out and water flush pipeline before changing, use double block and bleed valves
	Uncontrolled blowdown	Vent to integrated vapor recovery system
Petroleum Refining	Vacuum jets	Vent to blowdown system, incineration
	Air Blowing	Scrubbing, incineration
	Cracking catalyst regeneration	Carbon monoxide waste-heat boiler, incineration in process heater, high temperature operation of regenerator
	Chemical treating	Steam strip spent sweetening solution and incinerate stripped organics, use acid regeneration for acid recovery operations
	Blending operations	Floating roofs on blending tanks, in-line blenders
	Coking	Vent quench stream to blowdown or vapor recovery system
Oil and Gas Production	Process heaters, diesel engines, heater treaters	Proper operation and maintenance
	Miscellaneous process leaks	See "Petroleum and Chemical Process Industries"

CONTROL TECHNIQUES SUMMARY (continued)

Industry	Emission Sources	Control Techniques
Organic Chemicals	Fugitive emissions	See "Petroleum and Chemical Process Industries"
	Process vents	Incineration, scrubbing, adsorption, condensation
Storage Tanks	Fixed roof tanks (low volatility liquids)	Internal floating roofs, vapor recovery systems
	Storage tanks (medium volatility liquids)	Vapor recovery systems, increased internal tank pressure
	Storage tanks (high volatility liquids)	Normally pressure tanks are used, no need for further control
Petroleum Transportation and Marketing Systems	Ship and Barge Terminals	
	a) loading	Slow initial loading, fast bulk loading, and slow final loading; vent vapor at sea; vapor recovery
	b) ballasting	Quick unloading; strip residual product from empty tank; vapor recovery
	Tank truck, rail car, and service station loading	Modified loading techniques, vapor recovery balance system
	Vehicle refueling	"Balance" vapor control, "vacuum assist" vapor control, hybrid system
Polymers	Fugitive emissions, process vents	See Organic Chemicals

CONTROL TECHNIQUES SUMMARY (continued)

Industry	Emission Sources	Control Techniques
Paint, Varnish, and Ink Manufacture	Paint: grinding and thinning operations	Afterburners, condensers, and scrubbers
	Varnish: cooking and thinning	Integral condensers, scrubbers, absorbers, carbon adsorbers, afterburners, reformulation of solvents, sublimation
	Ink: Varnish cooking	Scrubber or condenser followed by afterburner
Surface Coating	Coating application, coating drying	•Add-on controls: carbon adsorbers, incinerators, condensers, scrubbers. •Process and material changes: electrostatic spray coating, electrodeposition, electron beam curing, ultraviolet curing, and coating reformulation.
Rubber and Rubber Products	Synthetic rubber: monomer and solvent recovery, product drying	Incinerators, condensers, and absorbers
	Rubber products: compounding, extrusion, vulcanization	Reformulation, condensers, adsorbers, absorbers, incinerators
	Reclaimed Rubber: reclaimator, devulcanizer	Reclaimator: condensers, scrubbers Devulcanizer: venturi scrubber followed by condenser
Pharmaceuticals	Fermentation: extracting procedures, fermentation, solvent processing and drying	Wet scrubbers, carbon adsorbers, ozonators, incinerators
	Synthesized drugs: distillation, drying, filtration	Incinerators
	Biological Extraction: solvent usage	Incinerators
	Botanical Extractions: solvent usage	Incinerators

CONTROL TECHNIQUES SUMMARY (continued)

Industry	Emission Sources	Control Techniques
Graphic Arts	Solvent losses during drying	Incinerators, adsorbers, use low solvent inks, use waterborne inks
Stationary Fuel Combustion	External and internal combustion devices	Improved operating practice and equipment designs, good maintenance
Metallurgical Coke Plants	•Charging	Sealed charging, staged charging, aspiration by steam jet, wet scrubber
	•Coking cycle	Fill leaks in coke ovens
	•Discharging	Use hood or cover
	•Quenching	Use clean water, use dry quench
Waste Handling and Treatment	Petrochemical waste: blowdown, drainage, process bottoms	Minimize waste generation, enclose wastewater systems, good housekeeping
	Solid waste	Incinerator
Food Processing	Coffee roasting, alcoholic beverages, flavors, fruit and vegetable processing, etc.	Incinerator, carbon adsorption, or spray contact condensers depending on the food produced
Dry Cleaning •Petroleum Solvent-based System	Dryer Filter muck treatment	Good housekeeping, waste solvent treatment, carbon adsorber, incinerator (last two techniques not yet applied by industry)
•Perchloroethylene-based systems	Dryer, filter muck	Good housekeeping, carbon adsorber, use of regenerative filters and muck cookers.

CONTROL TECHNIQUES SUMMARY (continued)

Industry	Emission Sources	Control Techniques
·Fluorocarbon-based systems	Filter solvent; leaks from pumps, valves, and gaskets; cleaning wheel solvent losses	Good housekeeping, refrigeration/ condensation systems, filter drying
Fiber Production	Heating and cooling processes in melt spinning, solvent loss in wet and dry spinning	Carbon adsorber, resin adsorber, incinerator, solvent absorber, refrigeration/condenser, vacuum stripper, good housekeeping
Degreasing and Waste Solvent Disposal	Bath evaporation, carry-out, agitation of bath, waste solvent evaporation	Better equipment design, improved operating practices
Cutback Asphalt	Solvent evaporation from asphalt	Substitute emulsified asphalts for cutback asphalts

1.0 INTRODUCTION

In March 1970 the U.S. Environmental Protection Agency published Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources (AP-68) as one of a series of documents summarizing control techniques information for criteria air pollutants. Section 108 (b) of the Clean Air Act as amended in 1977 instructs the Administrator to review and modify these control techniques documents from time to time as appropriate:

> ". . . the Administrator shall, after consultation with appropriate advisory committees and federal departments and agencies, issue to the States and appropriate air pollution control agencies information on air pollution control techniques, which information shall include data relating to the cost of installation and operation, energy requirements, emission reduction benefits, and environmental impact of the emission control technology. Such information shall include such data as are available on available technology and alternative methods of prevention and control of air pollution. Such information shall also include data on alternative fuels, processes, and operating methods which will result in elimination or significant reduction of emissions."

This document is the prescribed revision, incorporating new information concerning control of hydrocarbons and other vapor phase organics which contribute to the formation of oxidants.

This document is intended primarily as a general reference for state and local air pollution control engineers. It can be used to provide:

(1) basic information on sources of oxidant precursors and control of these sources,
(2) estimates of control costs, and
(3) estimates of emission reductions achievable through control application.

The cost curves presented in the text are the result of averaging costs for differing industrial applications. Therefore, costs derived from these curves are rough estimates. Actual costs for a particular installation may vary.

Because of the general nature of the document, it should not be used as the basis for developing regulations or enforcing them. Additional information for specific industries may be available from EPA's Office of Air Quality Planning and Standards.

The control techniques described in this document represent a broad spectrum of information from many technical fields. The devices, methods, and principles have been developed and used over many years and are constantly being revised and improved. They are recommended as the techniques generally available to control hydrocarbon and organic solvent emissions.

The available control techniques vary in type, application, effectiveness, and cost. The best technique for controlling organic emissions is to design equipment which completely or efficiently utilizes the processed materials. Failing this, control equipment can be used to reduce emissions. Operating principles, design characteristics, advantages, disadvantages, applications, costs, and energy considerations for control equipment and techniques are described in Section 3.0.

A number of industrial processes are described individually in Section 4.0. Emission characteristics for each process are described. The control techniques that can be applied to remove the pollutants from each process are reviewed and compared. The proper choice of a method of controlling emissions from a specific source depends on some factors other than the source characteristics. No attempt is made here to review all possible combinations of control techniques that may be required to completely eliminate a certain emission.

The information included in this document is restricted to stationary sources. Information on control of volatile organic emissions from mobile sources is available from EPA's Office of Mobile Source Air Pollution Control in Washington, D. C.

Naionwide emissions of volatile organics are presented in Section 2.0 together with discussions of photochemical oxidant formation and trends in national air quality. The health effects associated with volatile organics and secondary atmospheric reaction products are considered in Air Quality Criteria for Ozone and Other Photochemical Oxidants which will be published by EPA in April, 1978.

2.0 CHARACTERISTICS OF VOLATILE ORGANIC EMISSIONS

2.1 Definitions

The original AP-68 was titled Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources. Hydrocarbons were defined as compounds containing only the elements hydrogen and carbon. "Organic solvents" was intended to include materials such as diluents and thinners which could contain oxygen, nitrogen, sulfur, and halogens, in addition to carbon and hydrogen.

There are reasons for replacing "Hydrocarbon and Organic Solvents" with "Volatile Organic Emissions" in the title. There has been some confusion in the use of the term "hydrocarbons". In addition to being used in the most literal sense, the term "hydrocarbons" has been used to refer collectively to all organic chemicals. Some organics, which are photochemical oxidant precursors, are not hydrocarbons (in the strictest definition) and are not always used as solvents. Because of possible confusion and in an effort to include all organic emissions which might affect ambient air quality, the new document is titled Control Techniques for Volatile Organic Emissions from Stationary Sources. For purposes of this discussion, organic compounds include all compounds of carbon except carbonates, metallic carbides, carbon monoxide, carbon dioxide, and carbonic acid. A volatile organic compound (VOC) is any organic compound that, when released to the atmosphere, can remain long enough to participate in photochemical reactions. While there is no clear line of demarcation between volatile and nonvolatile organics, the predominant fraction of the VOC burden are compounds which evaporate rapidly at ambient temperatures. Almost all organics which can be considered VOC have vapor pressures greater than 0.1 mm of Hg at standard conditions (20^{o}C and 760 mm Hg).

A complete discussion of the nomenclature of organic compounds is beyond the scope of this work. Brief mention of some of the more common generic names may be beneficial, however. Most common aromatic compounds contain a benzene ring, a six carbon ring with the equivalent of three double bonds in a resonant structure. If the compound is not aromatic, it is said to be aliphatic. Aliphatic hydrocarbons include both saturated and unsaturated compounds. Saturated compounds have all single bonds. Unsaturated compounds have one or more double or triple bonds. Halogenated compounds contain chlorine, fluorine, bromine, or iodine. Alcohols and phenols contain a hydroxyl group (-OH). Ketones and aldehydes contain a carbonyl group ($>C = O$). Acids contain a carboxylic acid group ($-C{\overset{\nearrow O}{\searrow OH}}$). Esters resemble carboxylic acids, having an organic radical, R, substituted for hydrogen ($-C{\overset{\nearrow O}{\searrow OR}}$). The reader may find more detailed information in a reference book.[1]

2.2 Photochemical Reactions

Much research has been conducted concerning the causes and effects of photochemical smog. Investigations have revealed the existence of a complex series of chemical reactions in the atmosphere which cause high levels of photochemical oxidant (mostly NO_2 and ozone with smaller concentrations of peroxyacetyl nitrates and other peroxy compounds). The results are haze, damage to plant and animal life, damage to materials such as rubber, and discomfort and suspected toxic effects for man. Although some volatile organics are inherently toxic, organic emissions are most significant as air pollutants in their role of photochemical oxidant precursors.

A very simple, mechanistic description of the chemical changes taking place in the atmosphere is shown in equations 1 through 4.

$$NO_2 \xrightarrow{\text{Sunlight}} NO + O \qquad (1)$$

$$O + O_2 \xrightarrow{M} O_3 + M \qquad (2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3)$$

$$RO_x + NO \rightarrow NO_2 + RO_y \qquad (4)$$

In these chemical equations M is a third body (usually N_2, O_2, or H_2O) stabilizing the molecule; R is an organic or inorganic radical; $x = 1, 2,$ or 3; and $y = x-1$.

Reactions 1 through 3 are very rapid and their rates are nearly equal. At steady state conditions, ozone and NO are formed and destroyed in equal quantities. An equilibrium equation can be written relating the concentrations of O_3, NO, and NO_2:

$$[O_3] = k \frac{[NO_2]}{[NO]} \qquad (5)$$

This equation shows that any reaction which causes NO to be converted to NO_2 (equation 4) will cause high NO_2 levels and high O_3 levels.

Hydroxyl and peroxy radicals are important atmospheric reactants which convert NO to NO_2. Hydroxyl radicals may react with CO or an organic compound to result in peroxy radicals which, by reacting with NO, cause high levels of NO_2 and O_3. Additionally, some organic compounds (notably aldehydes) can photolyze in the atmosphere to form radicals which participate in atmospheric reactions. Some of the organic radicals formed may react with NO_x to form nitrogenated organic pollutants, such as PAN.

The presence of highly reactive organic radicals can result in high oxidant levels within a few hours. These materials may be carried downwind great distances, increasing oxidant levels downwind at a later time. Recent research indicates that nearly all volatile organics participate, at least to some extent, in photochemical reactions.

Volatile organics or oxidant precursors are emitted to the atmosphere from natural and man-made sources. Globally, natural emissions appear to outweigh anthropogenic emissions. However, it is the high concentration of anthropogenic sources of volatile organics together with NO_x in urban areas which give rise to the oxidant problem. And, transport mechanisms may carry the oxidants formed into rural areas.

It is conceivable that natural phenomena may contribute to high oxidant levels. It has been suggested that terpenes emitted from heavily forested areas might act as precursors reacting with naturally occuring NO_x and that stratospheric ozone intrusions might contribute to oxidant levels. Recent research results do not support these hypotheses, however.[2]

2.3 Sampling and Analytical Methods

The open literature contains much information on sampling and analysis of volatile organic emissions. The following is a brief review of the subject; more detailed information is available.[3-27]

The measurement method chosen must satisfy the intent of the associated emission standard. No single, practical measurement method currently exists that can be generally used to determine organic compound emissions in all situations. Source evaluation by emission measurement (collecting and analyzing samples) can be applied wherever possible. Material balances can sometimes be used to indicate the accuracy of these measurements.

A measurement strategy must address sampling location, sample type, collection method, and analytical method. The location of the sampling point in the sampling plane must be considered.

If no concentration gradient exists, this location is not critical. If there is such a gradient, more exacting methodologies must be used. They may involve traversing (obtaining samples from the centroids of a number of equal areas within the cross-section) or the use of multiple probes or multiorifice probes.

Depending on the requirements of the emission standard, the sample type may be either a grab (instantaneous) sample or an integrated sample. An integrated sample is collected at a rate proportional to the stack flow rate for a specified time period. Other measurements may be necessary to calculate emission rates. If the mass emission rate is to be measured, simultaneous or near simultaneous measurements of stack flow rate and volatile organics concentration are required. Unless the composition of the stack gas mixture is known (air, for example), its molecular weight must be determined. The conditions under which the sample was taken and/or analyzed must be considered when converting reported values to standard conditions.

Several collection methods are particularly suited to volatile organic measurement. The collection methods must be closely coordinated with the analytical methods. In fact, collection methods and analytical methods may best be considered integral parts of the same operation. Adsorption methods may be used to collect organics from a gas stream. Collected organics may be desorbed for analysis with a solvent or heat. Collection and desorption of the entire range of organic compounds can take place on several types of supports.

Another collection method is condensation of organics in a cold trap. Grab samples can be collected with either glass syringes or purge flasks. Collapsible bags have been used to collect integrated gas samples for several years.

Another method of collection is integrated directly with analytical instruments. This technique minimizes the time between collection and analysis. The sample flows from the stack through a sample conditioning (interface) system to the detector. The degree of complexity of an interface system varies. Some simply transport a portion of the stack gas from the stack to the analyzer. Others accomplish cooling or heating, filtering, drying, concentrating or diluting, and reacting the stack gas.

Fugitive emissions sampling is usually conducted by enclosing the source. The enclosure is connected to a pump, flow meter, and pressure measuring device. A grab sample is taken for analysis. Some fugitive emission sources such as open lagoons and API separators cannot practically be enclosed. Fugitive emissions from these sources are generally determined by material balance. A portable hydrocarbon sniffer may be used to determine fugitive emission concentrations at a certain distance from the source.

The analytical methods currently employed for detecting hydrocarbon gases, either directly or indirectly, are limited to infrared spectroscopy, ionization spectroscopy, and mass spectrometry. Infrared analyzers may be used to measure organics directly. They also may be used to measure carbon dioxide produced by oxidation of organics, which can then be translated into an indirect measurement of total hydrocarbons.

Flame ionization detection is another method of organics analysis. FID analyzers are almost universally calibrated in terms of a gas such as methane or hexane and the output read in ppm of carbon measured as methane or hexane.

Gas chromatography is a method useful for analyzing gases for specific organic components or for total organic content. A value for total nonmethane hydrocarbons can be generated chromatographically by summing the individual concentrations as they are revealed by their respective chromatogram peaks. Another approach is to operate the chromatograph in such a manner that all nonmethane hydrocarbons are eluted simultaneously from the column. One peak on the chromatogram then represents total nonmethane hydrocarbons.

Mass spectrometry is a useful analytical method when positive identification of an organic component of a gas stream is necessary. It may be used directly or in conjunction with gas chromatography for ease of interpretation. Components of the gas stream are categorized according to molecular weights. Another method of analysis is known as total organic carbon analysis (TOC). Organic compounds may be converted to CO_2 and then analyzed with a flame ionization detector. This method eliminates response differences due to different types of organic molecules, but it is useful only for liquid samples.

2.4 Emissions and Trends

2.4.1 Emissions Estimates

An extensive list of volatile organics emissions for 1977 is presented in Table 2.4-1 and 2.4-2. These emission figures were gathered by EPA from a number of documents and are presented in metric units and in English units. The numbers are considered representative of typical processes. Emissions from specific installations may vary. More specific information on their use may be found in the body of this report.

2.4.2 Trends

Nationwide volatile organic emissions estimates are presented in Table 2.4-3 for the years 1970-1976. These

TABLE 2.4-1. SOURCES OF VOLATILE ORGANIC COMPOUNDS

Source	Estimated Emissions[a] Gg/yr (10^3 ton/yr)	
PETROLEUM REFINERIES		900 (990)
Refinery Fugitive (leaks)	160 (180)	
Miscellaneous Sources	730 (800)	
a) Process Drains and Waste Water Separators		
b) Vacuum Producing Systems		
c) Process Unit Turnaround		
STORAGE, TRANSPORTATION AND MARKETING OF PETROLEUM PRODUCTS		2600 (2860)
Oil and Gas Production Fields	190 (210)	
Natural Gas and Natural Gasoline Processing Plants	150 (165)	
Gasoline and Crude Oil Storage[b]	900 (990)	
Ship and Barge Transfer of Gasoline and Crude Oil	60 (66)	
Bulk Gasoline Terminals[c]	250 (275)	
Gasoline Bulk Plants[d]	180 (200)	
Service Station Loading (Stage I)	400 (440)	
Service Station Unloading (Stage II)	470 (520)	
ORGANIC CHEMICAL MANUFACTURE[e]		1500 (1650)
Process Streams	450 (500)	
Storage and Handling	300 (330)	
Waste Disposal	150 (165)	
Fugitive (leaks)	600 (660)	
INDUSTRIAL PROCESSES		1000 (1100)
Paint Manufacture	24 (26)	
Vegetable Oil Processing	15 (16)	
Pharmaceutical Manufacture	50 (55)	
Rubber Products Manufacture	140 (150)	
Plastic Products Manufacture	no estimates available	
Textile Polymers Manufacture	no estimates available	
Others	750 (825)	

TABLE 2.4-1 (Continued)

Source	Estimated Emissions[a] Gg/yr (10^3 ton/yr)	
INDUSTRIAL SURFACE COATING		1900 (2090)
Large Appliances	42 (46)	
Magnet Wire	10 (11)	
Automobiles	90 (100)	
Can	140 (150)	
Metal Coils	30 (33)	
Paper	390 (430)	
Fabric	100 (110)	
Metal Furniture	90 (99)	
Wood Furniture	230 (250)	
Flat Wood Products	84 (92)	
Other Metal Products	230 (250)	
Others	310 (340)	
NON-INDUSTRIAL SURFACE COATING		500 (550)
Architectural Coatings	320 (350)	
Auto Refinishing	160 (175)	
OTHER SOLVENT USE		5100 (5600)
Degreasing	680 (750)	
Dry Cleaning	230 (250)	
Graphic Arts	380 (420)	
Adhesives	210 (230)	
Cutback Asphalt Paving	660 (730)	
Other Solvent Use	2900 (3200)	
OTHER MISCELLANEOUS SOURCES		3100 (3400)
Fuel Combustion	1300 (1400)	
Forest, Agricultural, and Other Open Burning	1000 (1100)	
Solid Waste Disposal	800 (880)	
TOTAL VOLATILE ORGANIC EMISSIONS FROM STATIONARY SOURCES		16,600 (18,300)

TABLE 2.4-1 (Continued)

Source	Estimated Emissions[a] Gg/yr (10^3 ton/yr)	
MOBILE SOURCES		10,800 (11,900)
Highway Vehicles	9350 (10,300)	
Off-Highway Vehicles	570 (630)	
Rail	140 (150)	
Aircraft	300 (330)	
Vessels	440 (490)	
TOTAL VOLATILE ORGANIC EMISSIONS FROM MOBILE SOURCES		10,800 (11,900)
TOTAL VOLATILE ORGANIC EMISSIONS		27,400 (30,100)

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[a] EPA Estimates for 1977 (Gg = 10^3 MT).

[b] Gasoline and Crude Oil Storage - includes all storage facilities except those at service stations and bulk plants. Storage tank emission tests were in progress as this document was printed. These emission estimates may change as more data become available.

[c] Bulk Terminals - emissions from loading tank trucks and rail cars.

[d] Bulk Plants - emissions from storage and transfer.

[e] Organic Chemical Manufacturing - see Table 2 for product specific emissions.

TABLE 2.4-2. CHEMICAL MANUFACTURING SOURCES OF VOLATILE ORGANIC EMISSIONS

Source	Estimated Emissions[a] Gg/yr (10^3 tons/yr)
Process Streams	450 (500)
Storage and Handling	300 (330)
Waste Disposal	150 (160)
Fugitive (leaks)	600 (660)
	1500 (1650)
<u>Major Chemical Products</u>[b]	
Acrylonitrile	69 (76)
Ethylene Oxide	42 (46)
Ethylene Dichloride	34 (38)
Dimethyl Terephthalate	33 (37)
Vinyl Chloride	18 (20)
Ethylene	16 (18)
Propylene Oxide	16 (18)
Ethylbenzene	16 (17)
Methyl Methacrylate	15 (16)
Formaldehyde	12 (13)
Methanol	12 (13)
Maleic Anhydride	11 (12)
Terephthalic Acid	9 (10)
Acetic Acid	9 (10)

TABLE 2.4-2. (Continued)

Major Chemical Products[b]	Estimated Emissions[a] Gg/yr (10^3 tons/yr)
Cyclohexane	7 (8)
Acetic Anhydride	7 (8)
Vinyl Acetate	6 (7)
Carbon Tetrachloride	6 (7)
Butadiene	5 (5)
Phenol	5 (5)
Acetone	5 (5)
Cyclohexanol/Cyclohexanone	5 (5)
Chloroprene	5 (5)
Ethylene Glycol	5 (5)
Acrylic Acid	5 (5)

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[a] EPA estimates for 1977.

[b] EPA estimates. These numbers include only process stream emissions and in-process storage and handling emissions. Waste disposal, fugitive, and out-of-process storage and handling emissions are not included.

estimates were made by EPA for internally consistent sets of figures based on current emission factors. The trends indicated by these numbers should, therefore, represent real trends and not differences in data handling or analysis.

TABLE 2.4-3. SUMMARY OF NATIONAL EMISSION ESTIMATES, 1970-1976[28]

National Volatile Organic* Emissions		
Year	Tg/yr	(10^6 tons/year)
1970	29.7	(32.7)
1971	29.3	(32.2)
1972	29.7	(32.7)
1973	29.8	(32.8)
1974	28.6	(31.5)
1975	26.2	(28.8)
1976	27.9	(30.7)

*The term "hydrocarbon" is used in the reference cited. It is a misnomer. The numbers actually reflect volatile organic emissions.

Although the nationwide estimates of volatile organic emissions show only a small overall decrease, there are some specific areas in which reduced volatile organic emissions have contributed to reduced oxidant levels and improved air quality. Air quality data collected from 1965-1974 in the Los Angeles Basin area showed a considerable reduction in the percentage of days the 1-hour primary health standard for oxidant was violated. Also, the average duration of violation of the oxidant standard was shortened. Improvements in air quality are attributed to fewer days of stagnant meteorological conditions as well as to reduced hydrocarbon emissions. Table 2.4-5 is a quantitative summary of the trend in oxidant standard violations in the Los Angeles Basin. These data indicate that in areas where stringent volatile organic controls are practiced, volatile organics emissions and oxidant levels may be reduced. More detailed information concerning oxidant trends may be found in the EPA document, Air Quality Criteria for Ozone and Other Photochemical Oxidants.[31]

TABLE 2.4-5. VIOLATIONS OF NAAQS FOR OXIDANT FROM 1965 TO 1975 IN LOS ANGELES AIR BASIN [30]

Index	1965 and 1966	1967 and 1968	1969 and 1970	1971 and 1972	1973 and 1974
Avg No. of days per year exceeding 160 μg/m^3 (8pphm)	186	162	144	109	105
Avg daily duration,[a] hr	5.1	4.8	4.6	3.8	4.3
Avg No. of days per year exceeding 320 μg/m^3 (16 pphm)	70	59	45	26	26
Avg daily duration,[b] hr	3.1	3.1	2.8	2.1	2.9

[a] The average daily duration is the average number of hours per day above the oxidant NAAQS.

[b] The average daily duration is the average number of hours per day the oxidant level was twice the NAAQS.

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3.0 CONTROL TECHNOLOGIES AND EQUIPMENT

The three methods employed commercially to control emissions of volatile organic compounds are as follows:

1. installation of control equipment to recover or destroy the organic vapors,
2. substitution of less photochemically reactive materials in the process, and
3. incorporation of process and material changes that reduce or eliminate vapor emissions.

Five major techniques for the first method are: incineration, adsorption, absorption, condensation, and flaring which are discussed in Section 3.1 through 3.5. Operating characteristics of each technology are explained, and the primary areas of application are indicated. Where possible, representative capital and annualized costs are provided, along with energy requirements and the environmental impact of each technology.

Section 3.6 describes the other two methods, substitution of less reactive materials and incorporation of process changes that reduce emissions.

3.1 Incineration

Incineration is the control technology most universally applicable to sources of volatile organics. Because of its need for supplemental fuel, incineration is most useful when the heat developed during combustion can be recovered and used to offset other plant energy needs.

Afterburners, also called vapor incinerators, are devices in which dilute concentrations of organic vapors are burned with additional fuel. In contrast, flares are used for safety reasons to dispose of rich waste gases, i.e., those having sufficient heating value to burn without additional fuel. Flares are discussed in Section 3.5.

Afterburners oxidize organic emissions either by direct-flame (thermal) incineration or by catalytic oxidation. Under proper conditions, the firebox of a process heater or boiler may also be used as an afterburner.

3.1.1 Equipment and Operating Principles

3.1.1.1 Thermal Afterburners

For combustion of organic vapors and liquids, the concentrations of vapor and air must be within the limits of flammability, termed the upper and lower explosive limits (UEL and LEL). These limits differ for various hydrocarbon compounds. However, for many volatile organics, the UEL is between 8 and 10 volume percent and the LEL between 1 and 2 volume percent. When concentrations of combustibles are less than the LEL, supplemental heat is required to initiate combustion.

An efficient thermal afterburner design must provide for 1) an adequate dwell or residence time for completion of the combustion process, 2) sufficiently high temperature in the afterburner for the complete oxidation of the combustibles, and 3) adequate velocities to insure good mixing without quenching combustion. Most designs also provide contact between the combustible gases and the burner flame.

Burner type and arrangement affect combustion rates and residence time. The more thorough the contact of flame with the waste organics, the shorter the time required for complete combustion. Burner placement depends not only on the burner type, but also on the design requirement for intimate contact of the combustible gases with the burner flame. Maximum efficiency occurs when all of the combustible matter passes through the burner. Multijet and mixing-plate burners provide the most effective flame contact.

If combustion is inhibited by insufficient temperature, insufficient residence time, or poor mixing, then carbon monoxide, aldehydes, and other products of incomplete combustion may result. Maintaining high turbulence or injecting steam promotes the intimate contact necessary for complete combustion.

In thermal afterburners, the organic vapor stream is delivered to the refractory-lined burner area by either the process exhaust system or by a blower. The combustible gases are mixed thoroughly with the burner flames in the upstream part of the chamber and then pass through the remaining part of the chamber where the combustion process is completed. The overall residence time of the gases flowing through the afterburner varies with the type of effluent and the method of incineration. Residence time is on the order of 0.3 to 0.6 seconds at 540 to 820°C (1000-1500°F). Table 3.1-1 reports recommended temperature ranges for afterburners which clean waste gases from various manufacturing operations. Afterburners are more efficient at higher temperatures.

Natural gas, LPG, and distillate and residual fuel oils are used to fuel afterburners. Oil flames are longer than gas flames and thus require longer fireboxes. The combustion of

TABLE 3.1-1. RECOMMENDED AFTERBURNER OPERATING TEMPERATURES[1]

Operation	Recommended Temperature	
Carpet laminating	1200-1400°F	(650-760°C)
Core oven	1400°F	(760°C)
Cloth carbonization	1800°F	(980°C)
Deep fat fryers	1200°F	(650°C)
General opacity problems	1200-1400°F	(650-760°C)
Oil and grease smoke	1200-1400°F	(650-760°C)
Paint bake ovens	1200-1500°F	(650-820°C)
Pipe wrapping	1400°F	(760°C)
Rendering operations	1200°F	(650°C)
Smokehouse	1200°F	(650°C)
Solvent control	1300-1500°F	(700-820°C)
Varnish cookers	1200°F	(650°C)
Vinyl plastisol curing	1200-1400°F	(650-760°C)

fuel oils produces sulfur oxides and particulates which may cause corrosion and soot accumulation on afterburner internals and heat transfer surfaces.

Heat recovery from the hot cleaned gases offers a way to reduce the afterburner energy requirements at the expense of increased equipment costs. The simplest application is to use the hot cleaned gases exiting the afterburner to preheat cooler process gases entering the afterburner. This arrangement is termed primary heat recovery. In designing heat recovery systems, consideration should be given to potential safety problems. Explosions or fires may occur in the heat exchanger from process upsets or from accumulation of flammable liquids or dust in the exchanger.

Secondary heat recovery uses exhaust from the primary heat exchanger to supply heat elsewhere in the plant. Secondary heat recovery can effect major energy economies when used to supply steam, hot water, or process heat to facilities located near the incinerator. Optimum application occurs when heat utilizing equipment is operated on the same schedule as the afterburner. Figures 3.1-1 to 3.1-5 illustrate afterburner configurations with and without primary and/or secondary heat exchange.[2]

3.1.1.2 Catalytic Afterburners

A catalyst is a substance that changes the rate of a chemical reaction without being permanently altered. When the preheated gas stream is passed through a catalytic afterburner the catalyst bed initiates and promotes oxidation. By using a catalyst the combustion reaction occurs at a significantly lower temperature than that of direct flame combustion; however, care must be taken to assure that combustion is complete. Catalytic

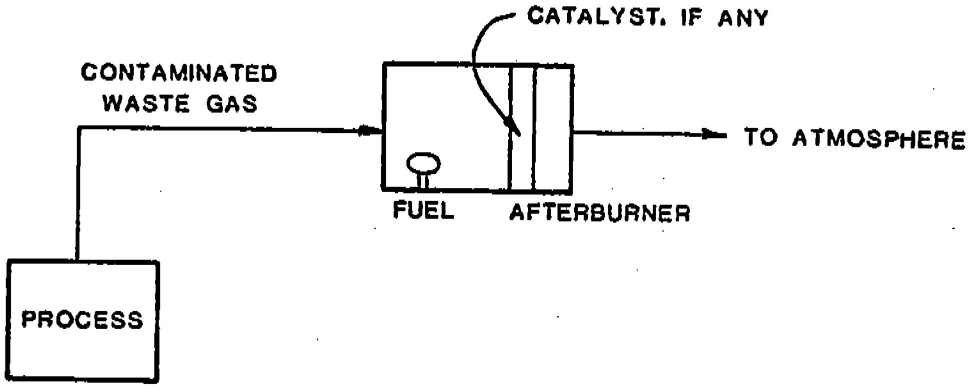

Figure 3.1-1. Afterburner Configuration for Operation without Heat Recovery

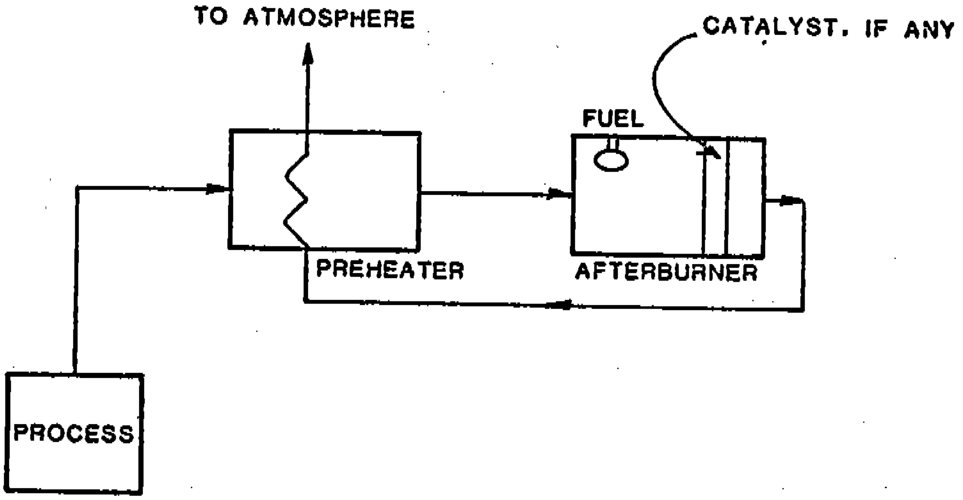

Figure 3.1-2. Afterburner Configuration for Operation with Primary Heat Recovery

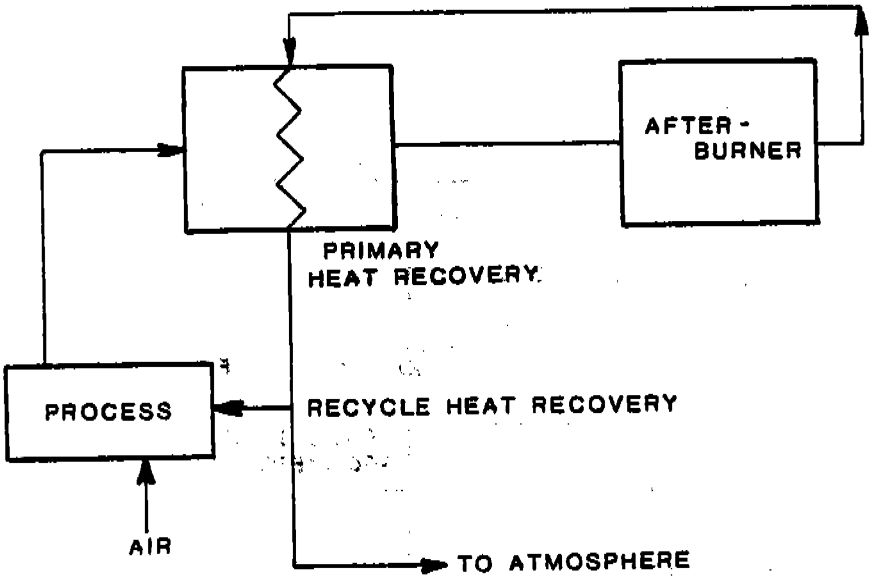

Figure 3.1-3. Afterburner Configuration with Primary Heat Recovery and Direct Recycle Heat Recovery

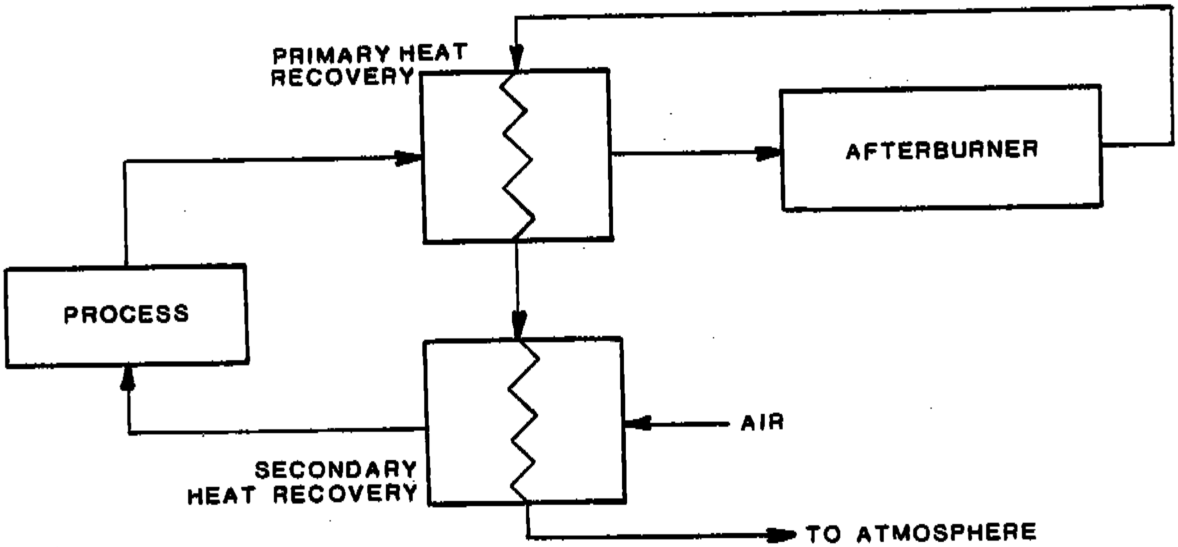

Figure 3.1-4. Afterburners Configuration with Primary and Secondary Heat Recovery

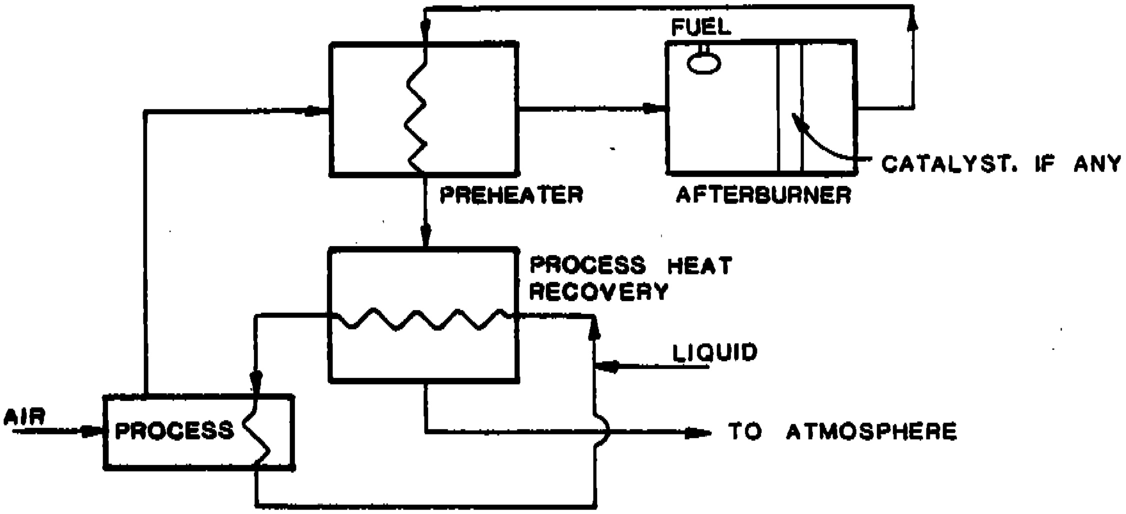

Figure 3.1-5. Afterburner Configuration for Operation with Primary and Liquid Medium Secondary Heat Recovery

afterburners offer the advantage of lower fuel costs in some applications; however, the fuel savings diminish as primary and secondary heat recovery are added to thermal afterburners. Construction materials costs may also be lower because of the reduced temperatures.

Combustion catalysts include platinum, platinum alloys, copper chromite, copper oxide, chromium, manganese, nickel, and cobalt. These are deposited in thin layers on an inert substrate. Available substrate shapes include rods, honeycombs, and ribbons designed to provide catalyst surface area.

For a catalyst to be effective, "active sites" upon which the organic gas molecules can react must be accessible. The buildup of condensed polymerized material or particulates prevents contact between active sites and the gases ("deactivation"). A catalyst can be "reactivated" by removing the coating; cleaning methods vary with the catalyst. Deactivation also occurs through reaction of the catalyst metal with phosphorous, bismuth, arsenic, antimony, mercury, lead, zinc or tin. Gas streams containing these elements are best treated by thermal incineration. Sulfur and halogens are also "poisonous" to the catalyst, but their effects are reversible.

Catalyst material can be lost from the support by erosion and attrition and by vaporization at high temperatures. To protect the catalyst from overheating, volatile organic concentrations are usually limited to 25 percent of the lower flammability limit. Most combustion catalysts cannot be operated at temperatures greater than 540-650°C (1000-1200°F).

3.1.1.3 Boilers Used as Afterburners

Fireboxes of boilers and fired heaters can be potential afterburners if the temperature, turbulence, and flame contact are adequate to burn the combustible contaminants. If the waste volatile organics have appreciable heating value, the firebox must be specially designed to take advantage of this heat potential; such units are known as waste heat boilers. If the heat content of the waste gas is low, common steam and hot water heaters and boilers are used.

Successful adaptation of boilers for use as afterburners is not common. The primary function of a boiler is to supply steam or hot water. Its use as an air pollution control unit may interfere with that function.

Satisfactory use of boilers as afterburners is possible only if the following conditions exist:

1. the boiler operates when the pollution source is operated,
2. temperature, turbulence, and residence time within the firebox are sufficient for complete combustion,
3. the air contaminants are wholly combustible (otherwise, boiler efficiency and steam generation may be reduced from deposits on the process heater internals), and
4. the products of combustion are compatible with the boiler construction materials.

3.1.2 Control Efficiencies

Properly designed and operated thermal afterburners usually achieve organic vapor removal efficiencies in excess of 95 percent. Overall efficiency:

- increases with operating temperature
- increases with flame contact
- increases with residence time (for times less than 1 second).

The efficiency of catalytic afterburners depends on catalyst type and surface area, gas velocity through the catalyst, oxygen concentration, operating temperature, and the nature and concentration of waste gas. Catalyst activity begins to decrease as soon as the afterburner is operated. Catalyst life varies from 1 to 5 years. Compensation for the decline in catalyst efficiency can be made by overdesigning the amount of catalyst in the original charge, or by raising the temperature of entering gases.

3.1.3 Applications

Incineration is applicable to almost all volatile organic emission sources including solvent operations and operations performed in ovens, dryers, and kilns. Successful combustion control devices have been applied to aluminum chip dryers, petroleum processing and marketing operations, animal blood dryers, automotive brakeshoe debonding ovens, citrus pulp dryers, coffee roasters, wire enameling ovens, foundry core ovens, meat smokehouses, paint-baking ovens, varnish cookers, paper printing and impregnating installations, pharmaceutical manufacturing plants, sewage disposal plants, chemical processing plants, and textile finishing plants. In many of these operations, the afterburners reduce the amount of particulate matter as well as the organic vapors present in the gas stream.

A new application of an old principle has been reported to provide efficient volatile organic compound (VOC) destruction at low fuel cost. For many years glass furnaces have used heat recovered from a ceramic heat storage mass (brick checker work). Now an afterburner for VOC control has been combined with packed beds of a heat storage medium to substantially reduce fuel cost. Effective heat recovery can range to over 90% with only a pilot flame being required for the burner. The resulting flue gas will be relatively cool and will have used only a small amount of oxygen from the flue gas. Thus, the cleaned flue gas could be directly recycled into ovens with additional fuel savings being realized.[3] Figure 3.1-6 illustrates the operation of such a system.

It may be unwise to attempt control of organic vapors containing halogens, sulfur, or nitrogen solely by combustion. The combustion products of such materials are usually less desirable because of toxic and/or corrosive properties. A secondary control system such as a scrubber may be required in series with the afterburner to remove these contaminants.

3.1.4 Incineration Costs

Capital costs for catalytic and thermal afterburners vary with:

- the nature of contaminants in the waste gas
- the concentration of organics in the gas

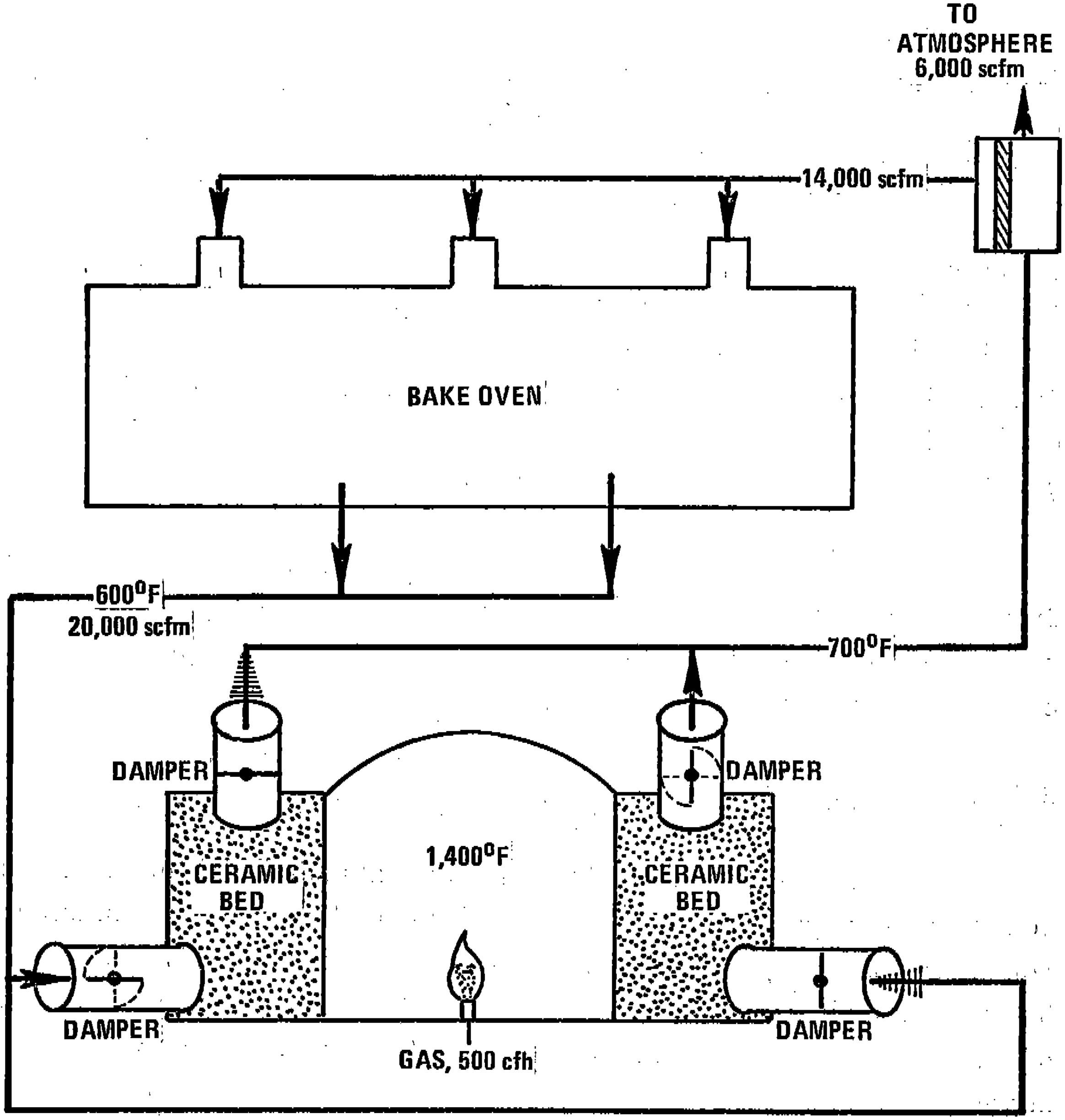

Figure 3.1-6. Ceramic bed regenerative type incineration and heat recovery system.

- the gas volume flow rate
- the fuel used for afterburner operation
- package or custom designs
- the degree of heat recovery
- the designed residence time.

Curves relating capital and annualized costs to gas volumes treated are presented in Sections 3.1.4.1 and 3.1.4.2.

Incineration of some substances requires absorption equipment. Capital and operating costs for incineration of organic streams containing halogens, sulfur, or nitrogen may be 3 to 5 times more than direct incineration without absorption. Increased costs are due to the use of expensive contruction materials necessary to handle the corrosive nature of the off gases. These costs are not considered in this document.

The parameters used to develop costs are summarized in Table 3.1-2. Additional information regarding afterburner costs is provided in Reference 4. Additional graphs covering other conditions are included in this document.

3.1.4.1 Capital Costs

Capital cost estimates are intended to represent the total investment required to purchase and install a particular control system. Afterburner capital costs include costs of the basic equipment, and auxiliary equipment (i.e., fans, piping, hooding), equipment installation, and interest charges on the investment during construction. Capital costs for catalytic and thermal afterburners are shown in Figures 3.1-7 to 3.1-9 as a function of the contaminated gas flow rate.[5] The capital cost

TABLE 3.1-2. TECHNICAL ASSUMPTIONS USED IN DEVELOPING COST ESTIMATES FOR CATALYTIC AND THERMAL AFTERBURNERS[6,7]

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1. Thermal afterburners designed for both oil and natural gas operation; catalytic afterburners designed for natural gas and propane operation.
2. Catalytic afterburners capable of 427°C (800°F) operation at low pollutant concentrations, 650°C (1200°F) at higher concentrations.
3. Equal weight percent hexane and benzene in air.
4. Afterburner operates 5840 hr/year.
5. Catalyst lifetime of 3 years.
6. 816°C (1500°F) operation in thermal afterburner with a residence time of 0.5 seconds.
7. Primary heat recovery efficiency of 35%, secondary heat recovery efficiency of 55%.
8. Outdoor rooftop installation requiring structural steel.
9. Gas inlet temperature of 150°C (300°F).
10. Materials to be combusted and combustion products are non-corrosive.

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of afterburners with primary heat recovery is roughly 20 to 25 percent more than for afterburners without primary heat recovery. Similarly, afterburners with primary and secondary heat recovery cost 20 to 25 percent more than afterburners with primary heat recovery only. Thermal afterburners have lower capital costs than catalytic afterburners for treatment of large gas flows and for treatment of higher organics concentrations.

The capital costs in Figures 3.1-7 to 3.1-9 are representative of installations easily retrofitted with afterburners. New installation costs should be similar. Difficult retrofits or installations requiring corrosion resistant materials may cost up to two times the values depicted in the figures.

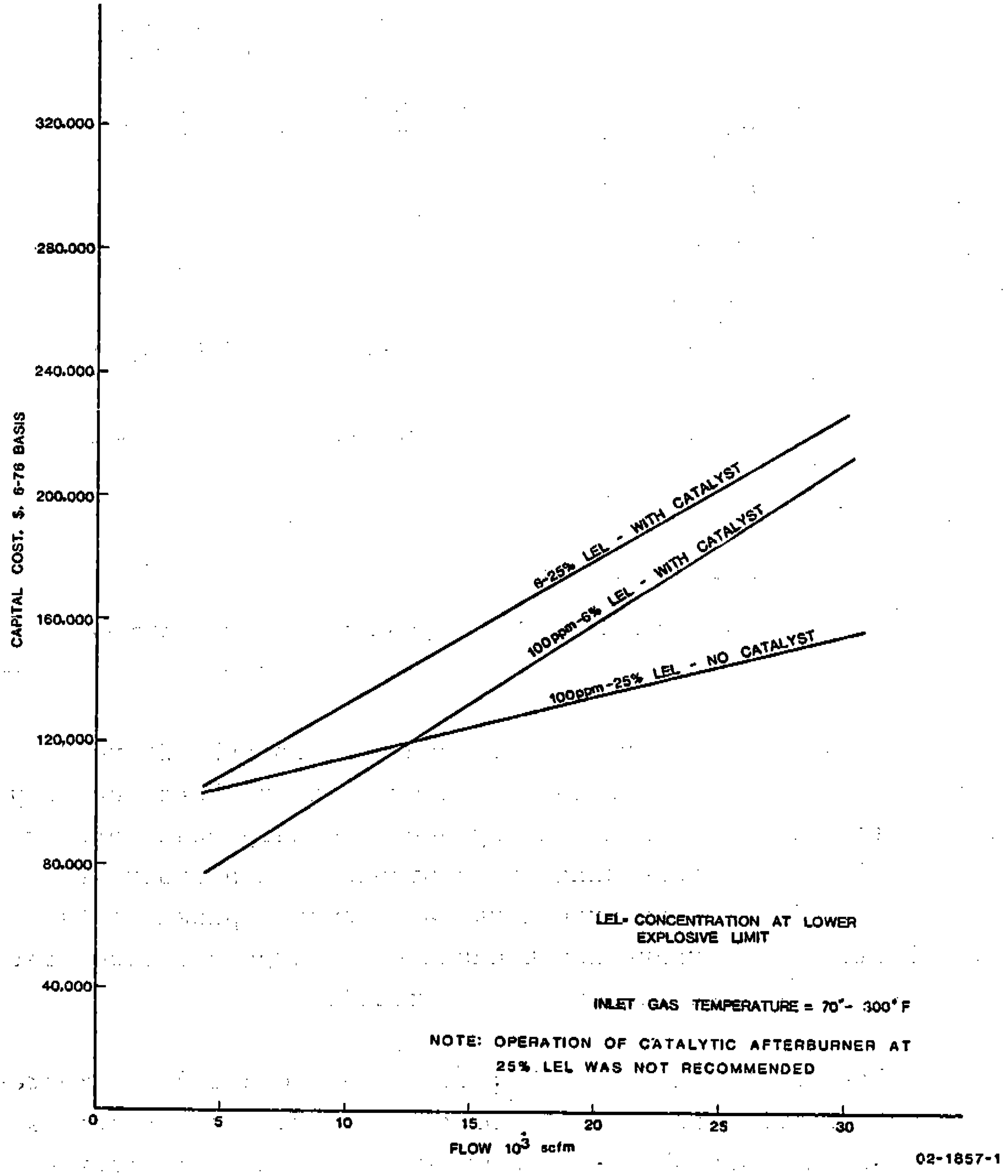

Figure 3.1-7. Capital Costs for Cayalytic and Thermal Afterburners Without Primary Heat Recovery

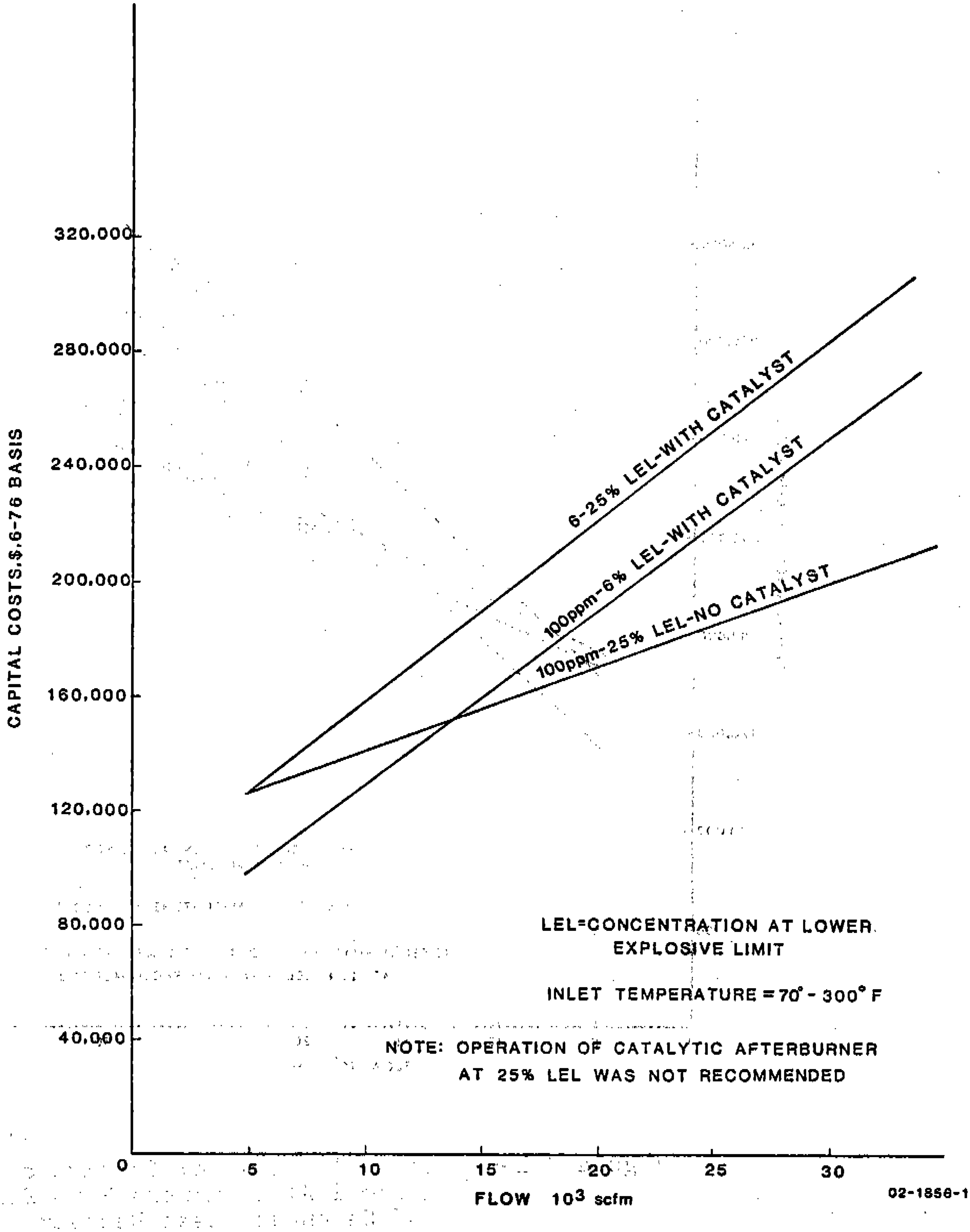

Figure 3.1-8. Capital Costs for Catalytic and Thermal Afterburners With Heat Recovery

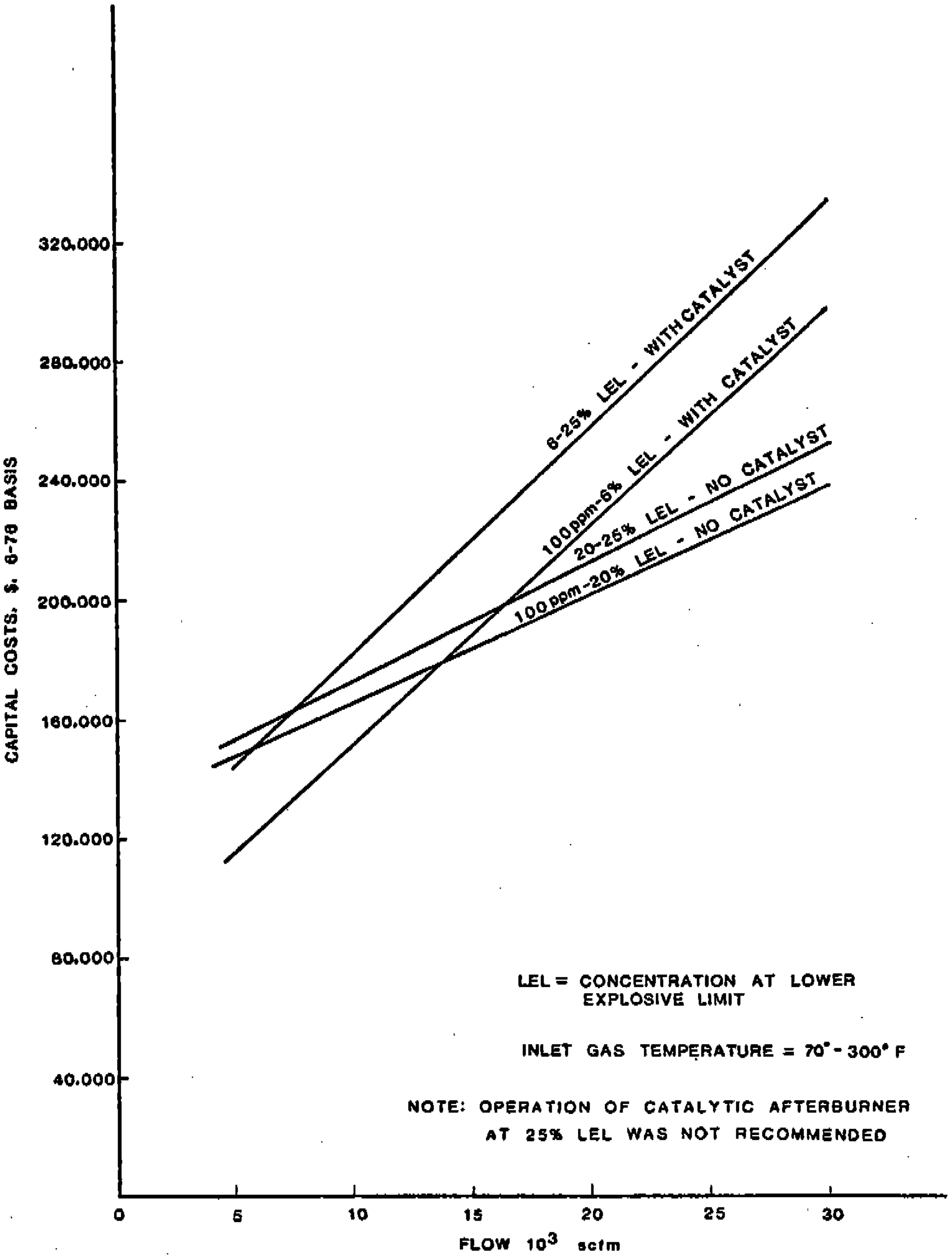

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Figure 3.1-9. Capital Costs for Catalytic and Thermal Afterburners With Primary and Secondary Heat Recovery

3.1.4.2 Annualized Costs

Annualized costs include labor and maintenance costs, utilities and materials costs, and capital related charges (depreciation, taxes, interest, and insurance). Annualized costs for catalytic and thermal afterburners are shown in Figures 3.1-10 through 3.1-12 for three heat recovery configurations.[8] Parameters used in developing the costs estimates are footnoted in Table 3.1-3.

As illustrated in Figures 3.1-10 through 3.1-12, heat recovery significantly reduces the annualized costs of afterburners. Primary heat recovery reduces the annualized costs by reducing the afterburner fuel requirements. Secondary heat recovery reduces the annualized costs by producing credits for heat used elsewhere in the process. Both cost reductions must be balanced against increased capital charges associated with the heat exchange equipment. The annualized costs for afterburners correspond to new installations or to existing installations with minimum retrofit costs.

Annualized cost components for a catalytic afterburner with primary heat recovery are reported in Table 3.1-3. Afterburner installations without heat recovery have higher utilities costs and lower capital charges. Installations with both primary and secondary heat recovery have lower utilities costs and higher capital charges. Lower gas inlet temperatures or lower organics concentrations result in higher annualized costs (from increased fuel requirements). Thermal afterburners have greater utilities costs, but avoid catalyst replacement costs. Fuel expenses for thermal afterburners are typically a function of the heating value of organics in the gas stream, fuel costs, heat recovery and operating schedule. Catalytic incineration

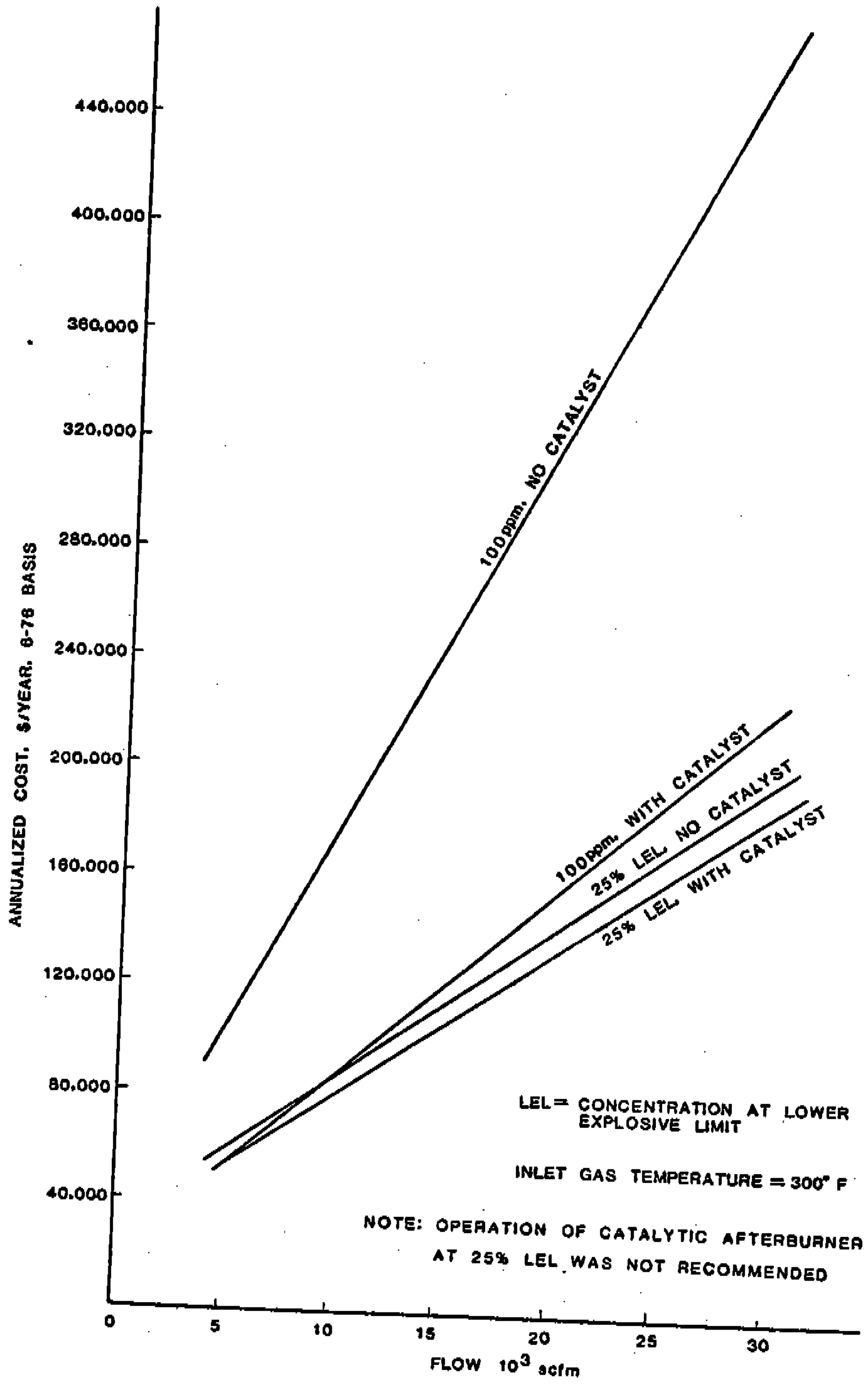

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Figure 3.1-10. Annualized Costs of Afterburners Without Heat Recovery

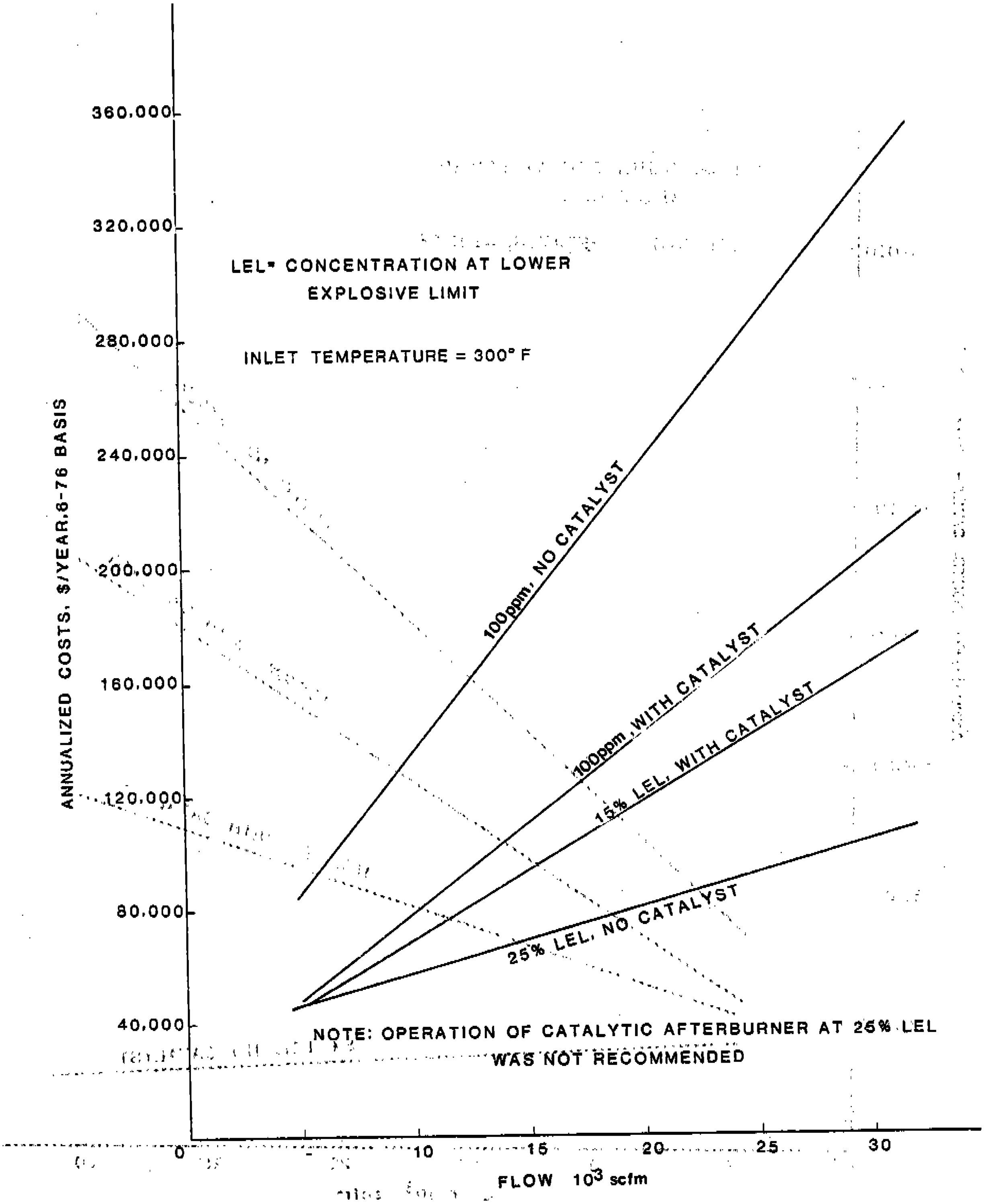

Figure 3.1-11. Annualized Costs of Afterburners With Primary Heat Recovery

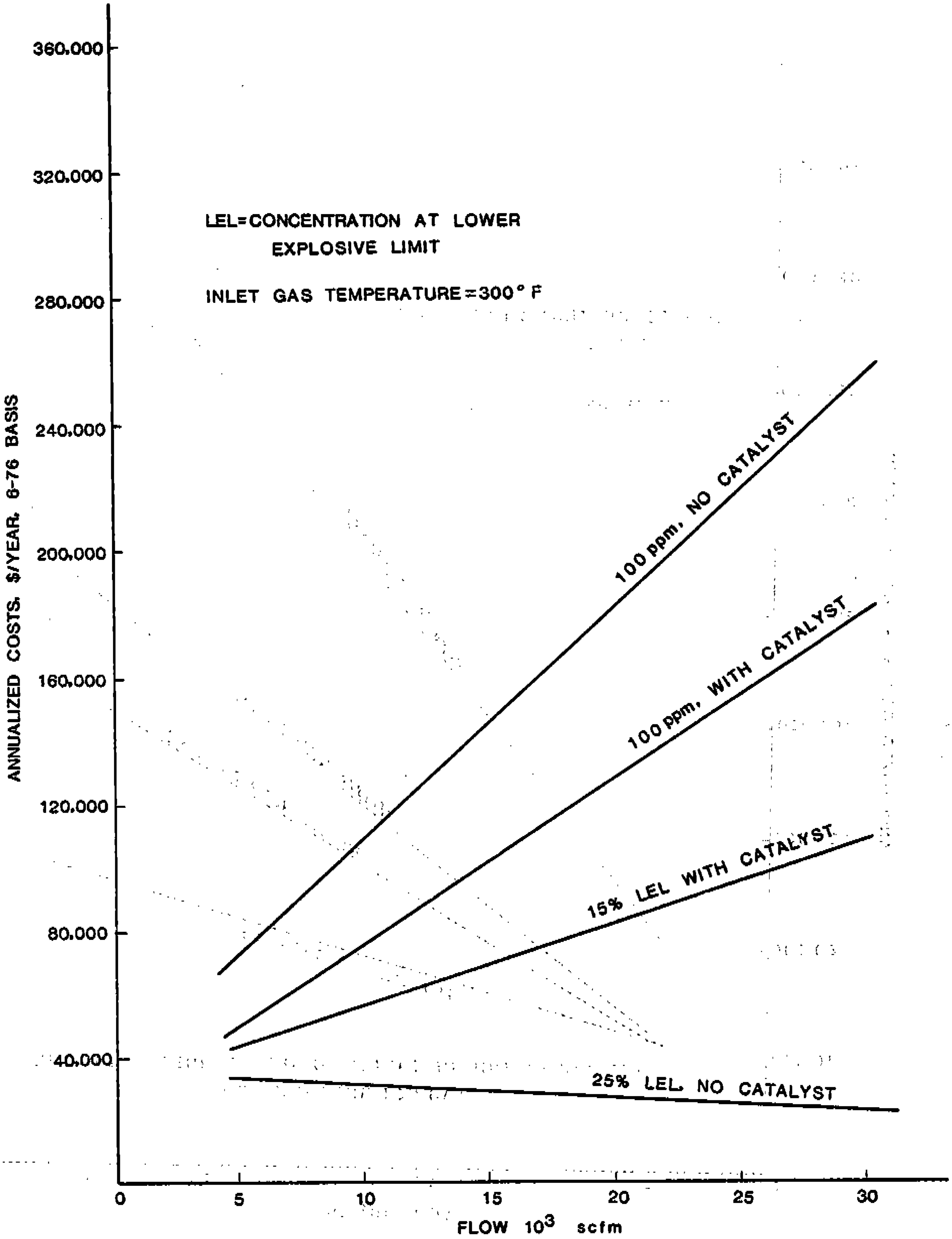

Figure 3.1-12. Annualized Costs of Afterburners With Primary and Secondary Heat Recovery

TABLE 3.1-3. TYPICAL COMPONENTS OF ANNUALIZED COSTS FOR CATALYTIC AFTERBURNERS[9]

Gas Stream Characteristics

Flow	15,000 scfm (7 m^3/s)
Concentration	15% LEL
Inlet Temperature	300°F (150°C)

Component	Cost
Direct Operating Costs	
Utilities	\$ 20,000[a]
Direct Labor	3,000[b]
Maintenance	7,800[c]
Annualized catalyst replacement	19,800[d]
Capital Charges	41,000[e]
Total	\$ 91,600

---

[a] Fuel at \$1.56/GJ (\$1.65/10^6 Btu), electricity at \$9.17/GJ (\$0.033/kWh).

[b] Labor at \$8.25/man-hour.

[c] Maintenance as percent of capital cost: 4%.

[d] Three-year catalyst life

[e] Capital charges include as a percent of capital cost: depreciation, 13%; taxes, insurance and administrative overhead, 4%.

can result in savings of about 40-60% in fuel costs as compared to thermal afterburners.

3.1.5 Incineration Energy Requirements

The energy requirement for a typical afterburner system includes supplemental fuel and electricity. The fuel may be either natural or produced fuel gas, LPG, distillate fuel oil, or residual fuel oil and is burned to heat the process gas to the proper combustion temperature. A temperature of 590-680°C (1100-1250°F) is necessary to combust 90 percent of the organics in the waste stream.[10] Electricity is necessary for powering a fan which conveys process gas to the afterburner. Figures 3.1-13 through 3.1-15 show energy requirements for afterburners using three different heat recovery configurations at varying organic vapor concentrations. Catalytic and non-catalytic operations are included. The bases for the data are listed in Table 3.1-3.

In general, afterburner supplemental fuel requirements depend on the organic content of the process gas stream, waste stream temperature, incineration temperature required, and type of heat recovery employed.

A great deal of the sensible heat in the incinerator exhaust stream can be recovered. This heat can be used to preheat the process gas, thus reducing the amount of fuel to be burned. This is called primary heat recovery. The supplemental fuel requirement can be reduced to zero under proper conditions of preheating. This can be accomplished with moderate concentrations of organic compounds in the stream (>25% LEL). Secondary heat recovery is the use of a portion of the waste heat elsewhere in the process, thereby saving on other utilities.

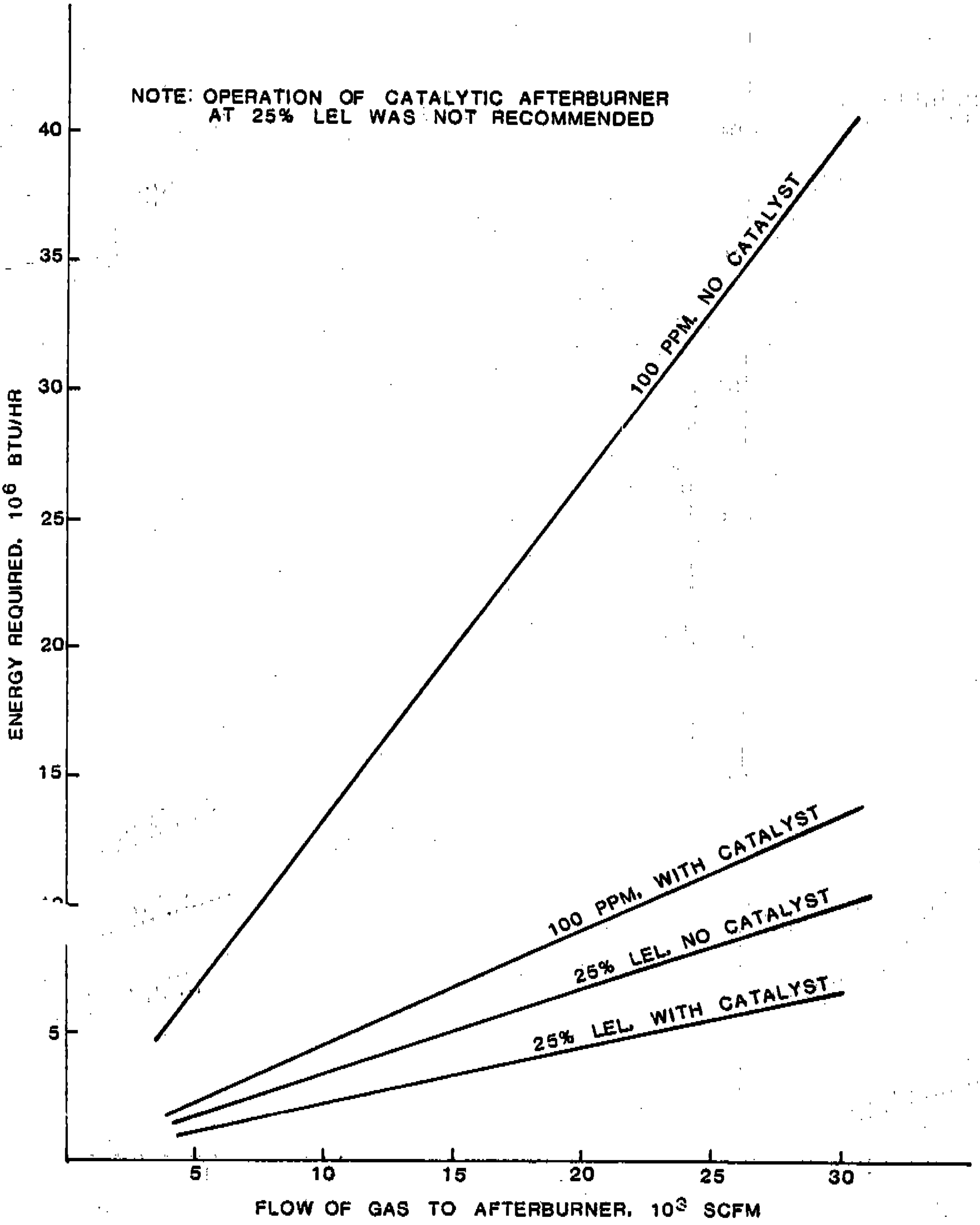

Figure 3.1-13. Energy Requirements of Afterburners Without Heat Recovery

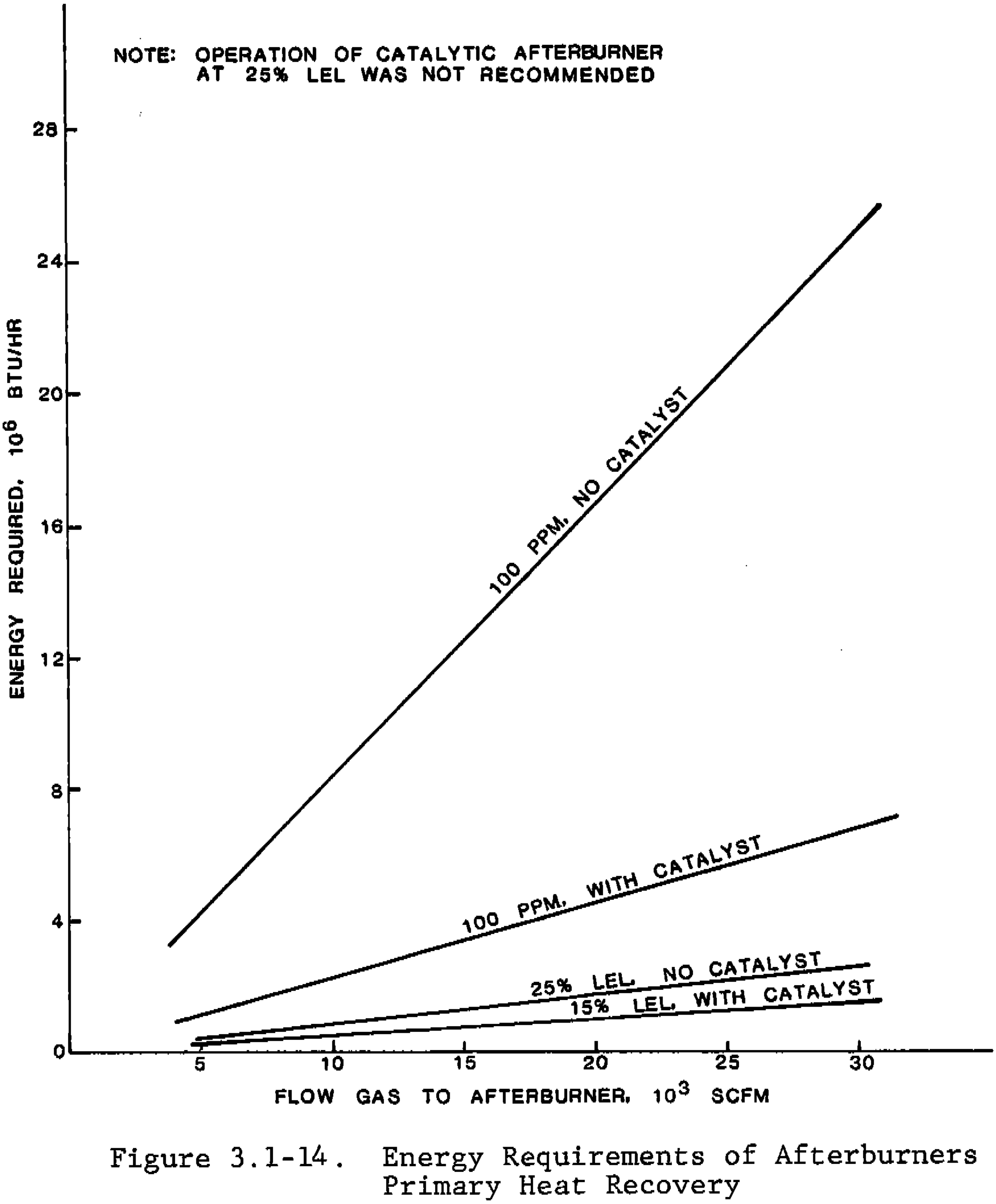

Figure 3.1-14. Energy Requirements of Afterburners With Primary Heat Recovery

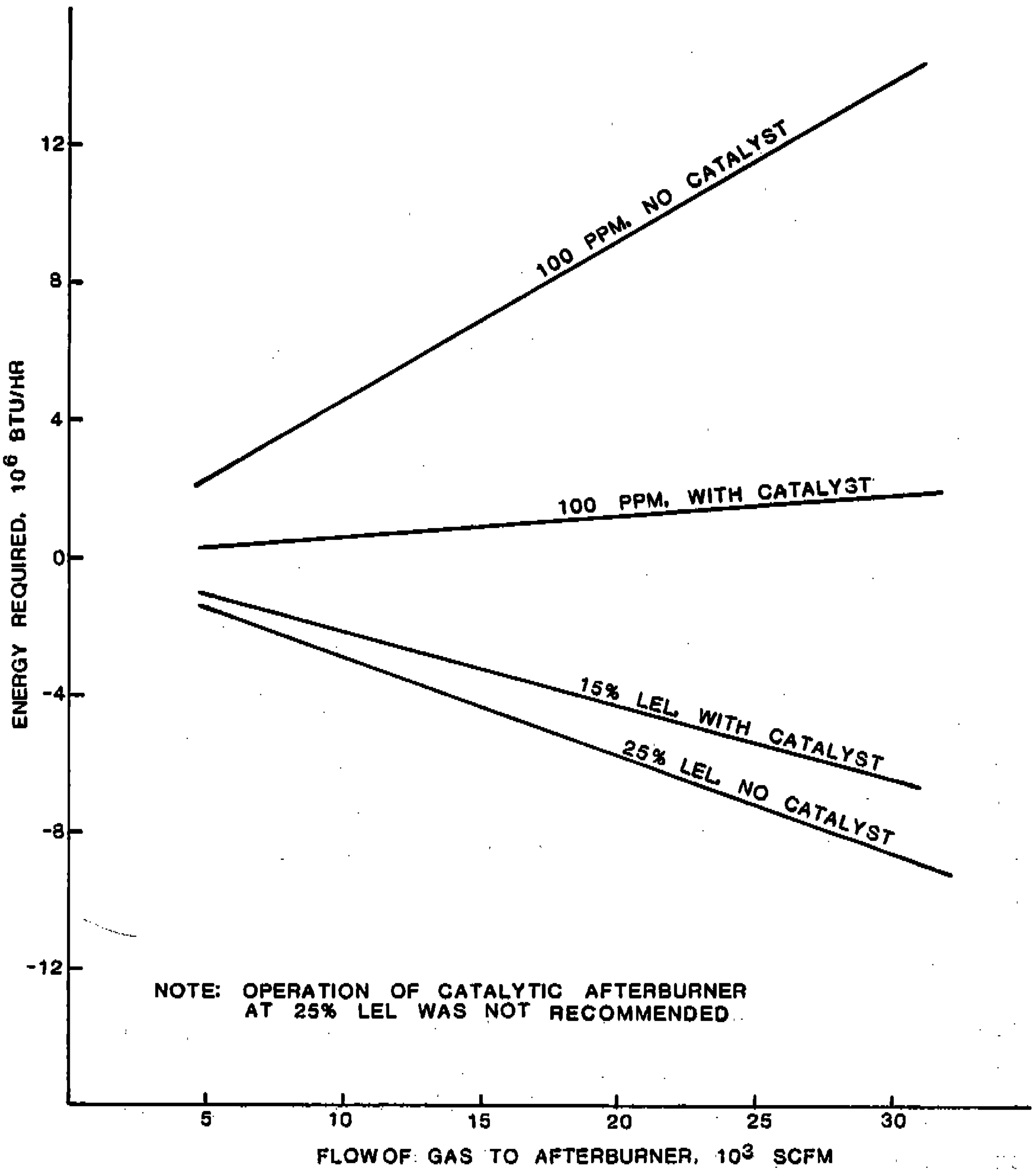

Figure 3.1-15. Energy Requirements of Afterburners With Primary and Secondary Heat Recovery

It is even possible with secondary heat recovery to realize a net gain in energy. The economic savings from the recovered energy may offset the higher capital costs associated with the heat recovery option.

Catalytic afterburners require less energy than thermal afterburners. Supplemental fuel requirements are diminished, as clearly shown in the example in Figures 3.1-13 through 3.1-15. In this example the gases were heated to 1400°F (760°C) with no catalyst and only 600°F (316°C) with catalyst present to promote oxidation.

Electricity usually represents only a small portion of the total energy consumed in operating an afterburner. This power is needed to convey either or both the combustion air and the process gas to the combustion chamber. If the pressure of both streams is adequate, no electricity is necessary, but this means additional energy is spent elsewhere in the process.

3.1.6 Environmental Impact of Incineration

Possible adverse environmental effects must be considered in choosing thermal or catalytic incineration as a means of controlling volatile organic vapor emissions. The benefits of incineration must be weighed against the adverse effects of implementing this control method.

The process stream, fuel gas, or fuel oil to be combusted in an incinerator may contain sulfur compounds. Oxidation of these compounds will produce varying amounts of sulfur oxides which are then released to the atmosphere. For an afterburner combusting a 15% LEL gas stream containing no appreciable sulfur compounds with No. 2 fuel oil, SO_2 emissions are approximately 50 ppm.[11,12]

In addition, nitrogen-containing compounds may be oxidized to NO_x, increasing pollution emissions. Due to the abundance of nitrogen in air, no nitrogen compounds need be found in the fuel or VOC stream to produce NO_x emissions. NO_x emissions will result from all combustion processes. The estimated NO_x concentration for effluent from natural gas-fired, non-catalytic afterburners is 40 to 50 ppm.[13]

Incineration of any halogen-containing compound will cause acid formation, which is undesirable. A scrubber following the incinerator may be required to prevent acid gas discharge.

In catalytic incineration, the regeneration or replacement of the catalyst can present a secondary pollution problem. When the catalyst needs to be completely replaced, the used catalyst is treated as solid waste, and an acceptable means for disposal must be found. If the catalyst can be reused, the suggested cleaning or reactivation process, usually supplied by the manufacturer, requires provisions for proper disposal of any waste material.

3.2 Adsorption

Adsorption is the process by which components of a gas are retained on the surface of granular solids. The solids adsorbent particles are highly porous and have a very large surface-to-volume ratio. Gas molecules penetrate pores of the material and contact the large surface area available for adsorption. Organic vapors retained on the adsorbent are subsequently desorbed. Both the vapors and the adsorbent are recovered and may be reused.

Complete package adsorption systems are available from a number of manufacturers. The economic feasibility of organic vapor emission control by adsorption depends on the value of solvent recovered from the adsorbent and the cost of removing adsorbed organics from the adsorbent bed.

3.2.1 Equipment and Operating Principles

Adsorption occurs primarily through two mechanisms: 1) physical adsorption, in which van der Waals' forces attract and hold gas molecules to the adsorbent surface, and 2) chemical adsorption, in which gas molecules are chemically bonded to the adsorbent. On a smooth surface, van der Waals' adsorption produces a layer of gas molecules not more than several molecules thick. Within the capillaries of a porous solid, however, this surface adsorption is supplemented by capillary condensation. The combination of capillary condensation and molecular attraction substantially increases the total amount of vapors adsorbed. Chemical adsorption, or chemisorption, produces an adsorbed gas layer only one molecule thick. Both chemisorption and physical adsorption are exothermic processes; the heat released from adsorption is on the order of 10 kcal/g-mole.

Adsorption of a vapor occurs in two stages. Initially, adsorption is rapid and removes essentially all of the pollutant from the gas stream. After some period of usage, the adsorbent will begin to remove vapors with less than 100 percent efficiency. Eventually, the adsorbent will become saturated with the pollutant vapors and the inlet organic concentration will equal the outlet concentration. The point at which removal efficiency first diminishes to less than 100 percent is called the "breakpoint". Economic and/or design considerations usually require the adsorbent to be regenerated or replaced soon after the breakpoint is reached.

If the gas or vapors to be adsorbed consist of several compounds, the adsorption of the various components is not uniform. Generally, components are adsorbed in an approximate inverse relationship to their relative volatilities. Initially the vapors are equally adsorbed. As the amount of the higher-boiling constituent retained in the bed increases, the more volatile component desorbs. The displacement of the lower-boiling component by the higher-boiling component is repeated for each of the vapors in the mixture. The adsorption cycle should be ended when the breakpoint for adsorption of the most volatile component is reached.

After completion of the adsorption cycle, the used adsorbent may be either regenerated or replaced. Regenerative systems reactivate the adsorbent while recovering the desorbed vapors for reuse or disposal. Nonregenerative systems usually return the used adsorbent to the vendor for regeneration.

Adsorbers can have fixed, moving, or fluidized beds, which can be set vertically or horizontally. A typical two-unit fixed-bed adsorber system is shown in Figure 3.2-1. One adsorber cleanses the vapor-laden stream while the other is undergoing regeneration. The adsorbent is most commonly regenerated by stripping the organic vapors into a stream of an easily condensible gas such as steam. The steam and pollutant vapors are then routed to a condenser, after which they can be separated by gravity decantation or by distillation. Alternately, the steam and organic vapors may be directly incinerated. While steam stripping is fairly common, it does require the use of expensive corrosion-resistant construction materials.

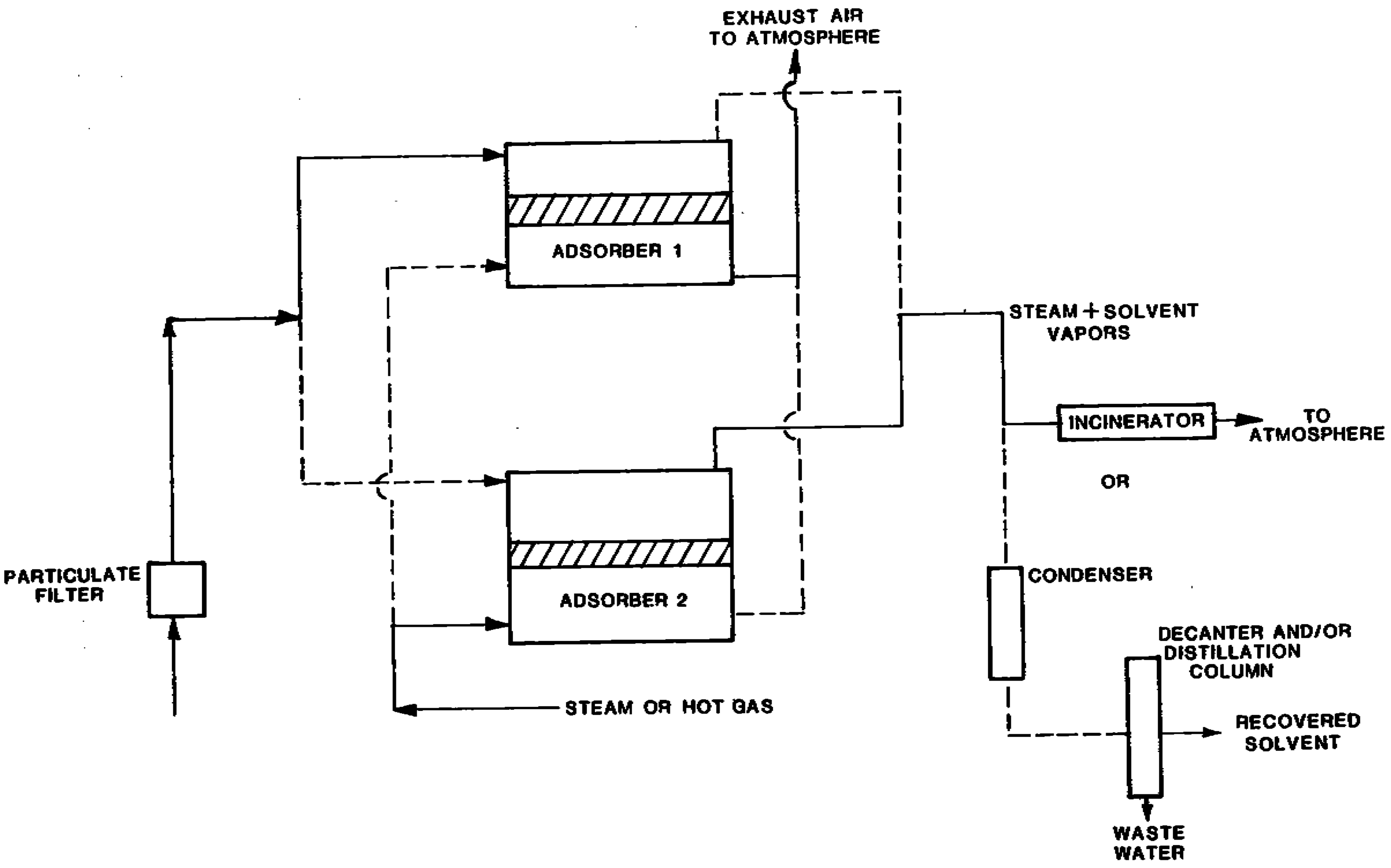

FIGURE 3.2-1 A TWO-UNIT FIXED BED ADSORBER

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Although two-unit adsorber systems have been proven efficient, a three-unit adsorber system may be desirable. The third unit would allow a freshly regenerated bed to cool after steam stripping. A cool bed would prevent the decomposition and/or partial oxidation that may occur when organic vapors contact a hot freshly regenerated bed.

The simplest equipment for a fixed-bed adsorber is a vertical cylindrical vessel fitted with perforated screens that support the adsorbent. Another type of fixed-bed arrangement is in the shape of a cone. The cone shape allows more surface area for gas contact and accommodates higher gas flow rates at lower pressure drops than a flat bed.

Moving bed adsorbers actually move the adsorbent into and out of the adsorption zone. Because of the continuous regeneration capability of a moving bed, a more efficient utilization of the adsorbent is possible than with stationary bed systems. Disadvantages include wear on moving parts, attrition of the adsorbent, and lower steam utilization efficiency caused by shorter beds.

The fluidized-bed adsorber contains a number of shallow fluidized beds of activated adsorbent. The air/solvent vapors flow upward through the beds and fluidize the solids. Solvent-free air is discharged into the atmosphere through dust collectors at the top of the adsorber vessel. Because regenerated adsorbent can be metered into the adsorber, a very high loading of solvent on adsorbent can be maintained. The steam requirements for regeneration are reduced by the high solvent loading.

3.2.2 Applications

The preferential adsorption characteristics and physical properties of industrial adsorbents determine the applications for each type. Soda lime alone or combined with activated carbon has been used to chemisorb vapors such as ethanoic acid, acetonitrile, acrylonitrile, allyl chloride, and vinyl propyl disulfide. Some physical adsorbents are impregnated with chemically-reactive compounds that react with vapor molecules after physical adsorption has occurred. Pollutant vapors removed by impregnated adsorbents include ethylene, organic acids, mercaptans, olefins, phosgene, and thiophenol. Chemisorption has had only limited use in organic vapor control.

Physical adsorbents can remove organic solvents, impurities, and water vapor from gas streams, but each has a particular affinity for either polar or nonpolar compounds. Polar adsorbents such as silica gel and activated alumina are poor adsorbents for the control of organic emissions because of their strong affinity for water. Activated carbon is the most widely used nonpolar adsorbent, selectively adsorbing organic vapors from gases even in the presence of water. A list of vapors that can be adsorbed by activated carbon is presented in Table 3.2-1. Molecular sieves are also classed as physical adsorbents. Like silica gel and alumina, their strong affinity for water greatly limits their use for control of organic vapor emissions.

Alternative regeneration arrangements are desirable in certain control applications. If the adsorbed solvent has no value, if the solvent is soluble in water, or if the solvent has only small amounts of halogen, nitrogen, or sulfur compounds, then air or inert gas may be considered for use as regenerant instead of low pressure steam. High-boiling solvents may require the use of superheated steam for efficient desorption. Alternative resorb systems include:[14]

TABLE 3.2-1. REPRESENTATIVE GASES AND VAPORS SELECTIVELY ADSORBED BY ACTIVATED CARBON

1. acetaldehyde
2. acetone
3. benzene
4. isobutane
5. normal butane
6. normal butene
7. butyne
8. carbon dioxide
9. carbon disulfide
10. carbon tetrachloride
11. carbonyl sulfide
12. chloroform
13. cumene
14. cyclohexane
15. cyclohexanone
16. cyclopentadiene
17. dichloroethane
18. dichloroethylene
19. dimethyl formamide
20. ethane
21. ethanol
22. ethyl acetate
23. ethyl chloride
24. ethyl mercaptan
25. ethylene
26. ethylene oxide
27. freon 12
28. heptane
29. normal hexane
30. hexanol
31. hydrogen cyanide
32. hydrogen sulfide
33. isopentane
34. isoprene (methyl butadiene 1,3)
35. isovaleric acid
36. simulated kerosene ($C_{14}H_{30}$)
37. methane
38. methyl ethyl ketone
39. methyl mercaptan
40. mineral spirits
41. neopentane
42. normal pentane
43. perchloroethylene
44. propane
45. propylene
46. propyl mercaptan
47. pyridine
48. tetrahydrofuran
49. tetrahydrothiamine
50. toluene
51. trichloroethylene
52. vinyl chloride
53. meta-xylene

1. Heated air or inert gas regeneration of the primary bed followed by a second adsorption with steam regeneration of the second bed

2. Heated air or inert gas regeneration followed by solvent condensation at lowered temperature with recycle of non-condensibles through adsorbent bed

3. Regeneration by pressure reduction.

Concentrations of organics greater than 25 percent of the lower explosive limit are undesirable because the heat released by adsorption may raise the temperature of the carbon bed high enough to cause carbon combustion. For safe and efficient operation, the inlet gas temperature is limited to less than 100°F (40°C) and the organics concentration to less than 25 percent of the lower explosive limit.

Processes that can be controlled by adsorption include dry cleaning; degreasing; paint spraying; tank dipping; solvent extracting; metal foil coating; fabric impregnation; and manufacturing of plastics, chemicals, pharmaceuticals, rubber, linoleum, and transparent wrapping. In the manufacture of paints and varnishes, fouling of the adsorbent with paint solids can occur. Scrubbing with water to remove the paint solids and condensibles from the adsorbent is required.

3.2.3 Adsorption Costs

Purchase costs for adsorption systems vary with:

- the nature of contaminants in the waste gas

- the concentrations of organics in the gas
- the adsorbent
- the regeneration technique
- the type of adsorber
- the gas volume flow rate.

Cost curves relating capital and annualized costs to gas volumes treated are presented in Sections 3.2.3.1 and 3.2.3.2.[15] All costs are indexed to June 1976.

The parameters assumed in specifying the adsorber design are summarized in Table 3.2-2. Additional information regarding carbon adsorption system costs can be found in Reference 4.

3.2.3.1 Capital Costs

Adsorption capital costs include costs of the basic equipment, auxiliary equipment, equipment installation, and interest charges on investment during construction. The capital costs for a fixed-bed adsorber system with recovery of desorbed vapors are shown in Figure 3.2-2.

Costs for moving and fluidized bed adsorbers are slightly lower than those for fixed-bed systems. The cost advantages arise from a reduction in the physical size of fluidized bed adsorbers. Adsorbent attrition losses and the subsequent need for adsorber effluent filtration are drawbacks to this design.

Organic vapors selected for cost presentations in this section can be considered easily adsorbed and desorbed on

TABLE 3.2-2. TECHNICAL ASSUMPTIONS USED IN DEVELOPING COST ESTIMATES FOR REGENERATIVE CARBON ADSORPTION SYSTEMS WITH RECOVERY OF DESORBED VAPORS[16,17]

1. Equal percentages of benzene and hexane by weight in air
2. Activated carbon with useful life of 5 years
3. Dual fixed-bed adsorber operates at 40°C (100°F)
4. Inlet gas at 77°C (170°F)
5. No water soluble compounds contained in the air stream[a]
6. No particulates contained in the entering air stream
7. Steam regeneration and solvent recovery by condenser/decanter
8. Adsorber operates 5840 hr/yr

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[a] Most organic compounds have sufficient water solubility to contaminate the water from steam desorption. This waste water may have to be treated before discharge. The wastewater treatment costs should be considered where applicable. They were unavailable for this report.

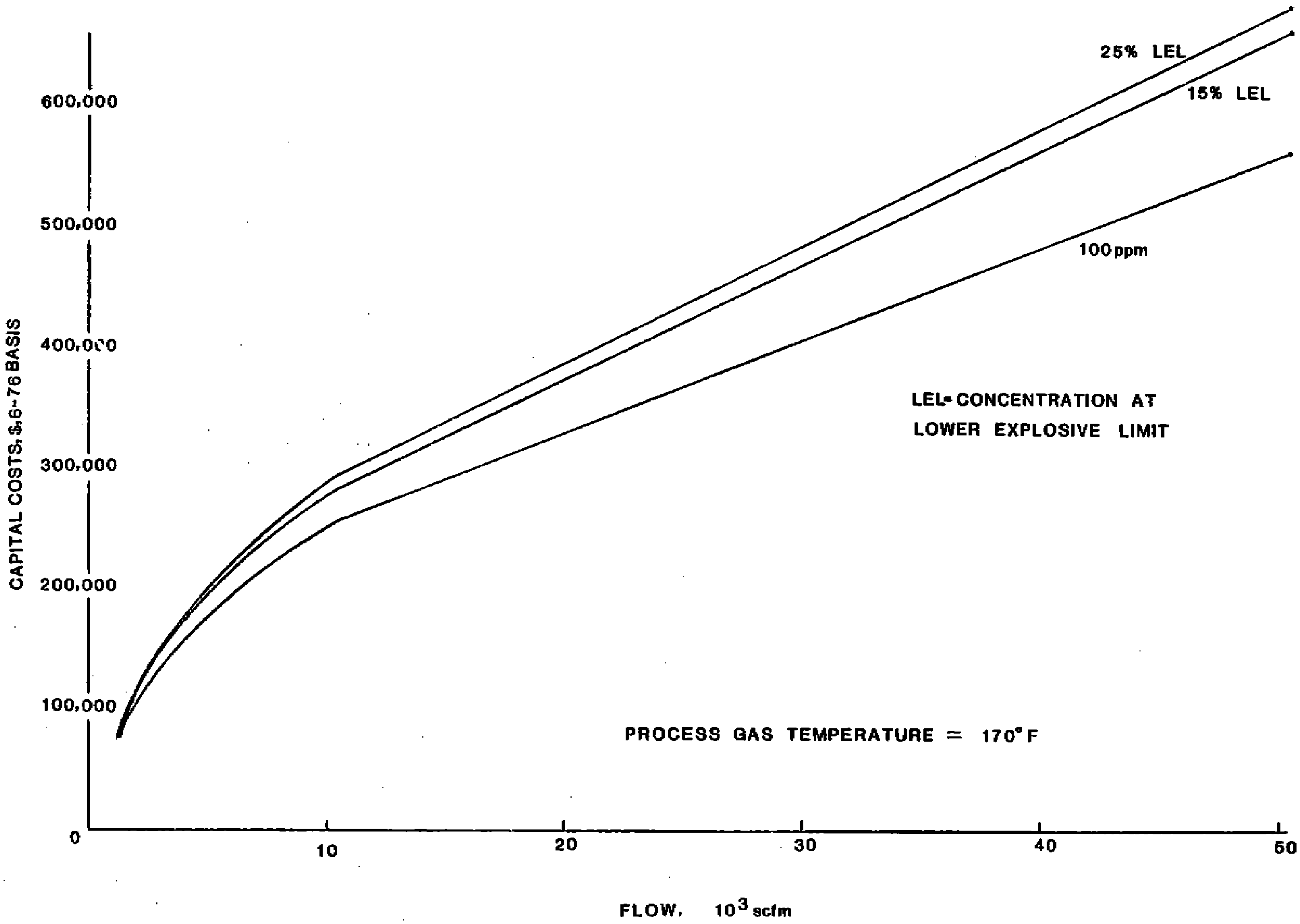

Figure 3.2-2. Adsorption Capital Costs

activated carbon. System cost for other organics will be dependent on adsorption characteristics of the vapors to be controlled. When organics are desorbed from the carbon bed by steam stripping, distillation and water-treatment equipment are required to recover the organics. An alternative to recovery is the addition of an incinerator for combustion of the desorbed effluent during stripping. Capital costs for adsorption-incineration systems with no heat recovery are approximately 20-30 percent higher than adsorption recovery systems handling comparable flows.[18]

The capital costs provided in Figure 3.2-2 are representative of new installations or easy retrofits. Difficult retrofits may cost twice these reported values.

3.2.3.2 Annualized Costs

Annualized costs include labor and maintenance costs, utilities and materials costs, capital related charges, and credits for chemical (solvent) recovery. The annualized adsorption costs presented in Figure 3.2-3 include recovery credits at fuel value \$1.56/GJ (\$1.65/10^6 Btu) and at market value (benzene @ \$.20/liter (\$.75/gal), hexane @ \$.12/liter (\$.47/gal). Other costing assumptions are summarized in the footnotes in Table 3.2-3. When recovered organics are credited at their market values, the adsorption operation shows a capital return. Reuse of the recovered organics, however, is not usually practical when more than one solvent is recovered. Product separation may be too costly to warrant the organic compounds' reuse in the process.

If it is not economically desirable to recover the organic vapors, the desorbed vapors can be incinerated.

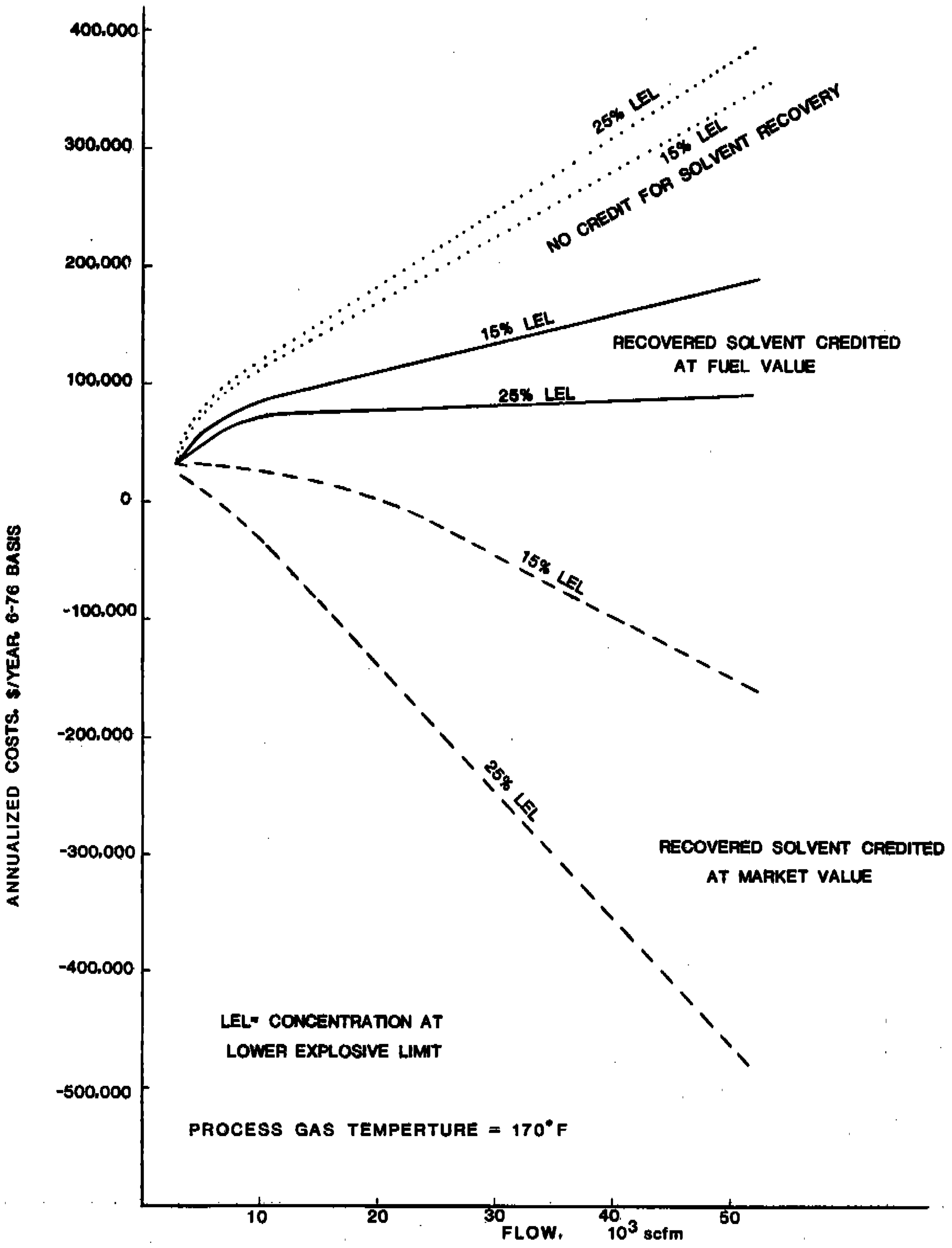

Figure 3-2.3. Annualized Adsorption Costs

TABLE 3.2-3. TYPICAL COMPONENTS OF ANNUALIZED COSTS FOR CARBON ADSORPTION SYSTEMS[19]

Configuration	1. Dual fixed-bed adsorber operating at 100°F (38°C) 2. Solvent recovery with condenser and decanter

Gas Stream Characteristics

Flow	20,000 scfm (9.4 m^3/s)
Concentration	25% LEL
Process Gas Temperature	170°F (77°C)

Component	Annual Cost
Direct Operating Costs	
Utilities	\$ 48,700[a]
Direct Labor	3,000[b]
Maintenance	15,400[c]
Carbon Replacement	11,500[d]
Capital Charges	80,850[e]
Recovery (Credits)	(297,000)[f]
Total Net Annualized Costs (Credits)	(137,500)[g]

[a] Cooling water at \$.045/1000 gal (\$0.012/m^3), steam at \$2/1000 lb (\$0.53/m^3), electricity at \$.033/kwh (\$9.17/GJ).

[b] Labor at \$8.25/hr.

[c] Maintenance as 4% of the capital cost.

[d] Carbon at \$0.72/lb (\$1.58/kg.) with 20% of carbon replenished each year.

[e] Capital charges include as percent of capital cost: depreciation, 12%; taxes, insurance, and overhead, 4%; interest, 5%

[f] Benzene credited at \$.75/gal, hexane at \$.47/gal.

[g] Net costs calculated as capital charges + direct operating costs - recovery credits.

Annualized costs for the adsorption-incineration system are comparable to those for the adsorption-recovery system except that no credit is allowed for organics recovery. Allowances for chemical recovery at fuel or market values give a significant advantage to the recovery system. Processes employing adsorption with incineration cannot be justified on economic grounds under any circumstances that allow normal incinerator operations.

Annualized cost components for a carbon adsorption system are reported in Table 3.2-3. Steam requirements are significantly larger for organics that are difficult to desorb from the adsorbent. Cooling water requirements are dependent on the temperature of the incoming gas stream, and on the condensation temperature of the organic vapors. Power costs for moving and fluidized bed adsorbers are smaller than those for fixed-bed adsorbers. Adsorbent replacement requirements will vary with the system's applications, with an average five year bed life assumed for carbon.

3.2.3.3 Comparison to Incineration

Carbon adsorption is usually more economical than incineration for the control of organics in concentrations below 100 ppm. Carbon adsorption is applicable to sources which do not contain particulates, water-soluble compounds, or compounds which are not difficult to adsorb or desorb. Incineration with primary heat recovery is more economical at high organics concentrations unless the recovered solvent is valuable and can be credited at market value.[20]

3.2.4 Adsorption Energy Requirement

The energy required for an adsorption system includes a supply of steam or air for regeneration and electricity to pump cooling water and to power a process gas blower. Figure 3.2-4 illustrates energy requirements as a function of the flow rate of gas treated for a typical dual fixed-bed adsorber operating at 100°F (38°C).[21] Table 3.2-3 contains process characteristics for this example.

Adsorber energy requirements are dependent on flow rate, exit temperature of the gas from the process, the nature of the chemical being adsorbed (ease of desorption), the concentration of organic vapors in the process gas, and downstream processing such as solvent recovery or thermal incineration.

When steam is used to desorb the organic vapors from the adsorption bed, the majority of the total energy required is for the production of this steam. The amount of steam needed is approximately 3 lb steam/lb (3 kg/kg) organic vapor adsorbed.[22] Steam regeneration has the advantage of leaving the bed wet; thus, some cooling of the gas can be accomplished. The alternative to steam regeneration is non-condensible gas regeneration. Energy requirements for this system are for heating and transporting the non-condensible gas, usually air.

Waste gases existing the process are usually hotter than the optimum adsorption temperature. Energy in the form of a cooling water system is needed to cool this waste gas stream. In the example in Figure 3.2-4 cooling water requirements were approximately 3 gallons per hour/SCFM (400 liters per hour/Nm^3 per minute).[23]

A blower is used to overcome the pressure drop encountered by the gas moving through the adsorption bed. The only requirement for the blower is electrical power. The amount of electricity consumed depends upon the type and configuration of the packing.

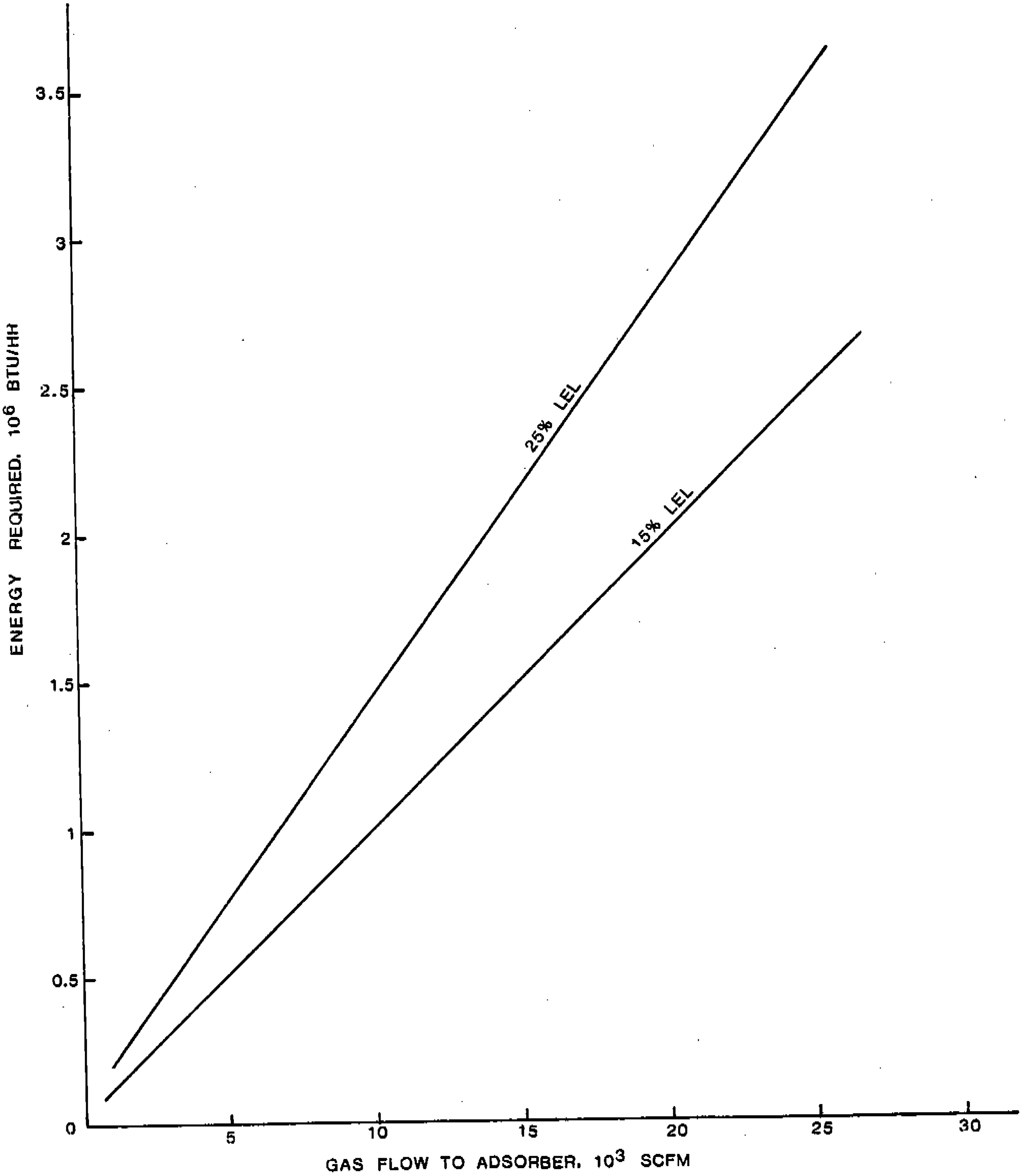

Figure 3.2-4. Energy Requirement for Adsorption-Solvent Recovery System

If a non-condensible gas is used for regeneration, the organics can be removed by incineration, condensation, or secondary adsorption. Utility requirements for an entire adsorber system are dependent on which technique is used as final treatment.

3.2.5 Environmental Impact of Adsorption

There will be some secondary pollution from an adsorption system, including both air and water pollution. Loss of organic solvent with wastewater, oxidation product emissions with incineration, and solid waste disposal are possible results depending upon the type of adsorption system utilized.

If a steam desorption cycle is used and the recoverable organic solvents are soluble in water, then some form of water treatment or separation process is required to minimize the organic concentration of the wastewater. Table 3.2-3 lists the process characteristics for an adsorber system removing hexane and benzene vapors at 25% of the LEL from a process gas stream. Some of the organic material will be soluble in the water and will remain in the waste stream. The steam condensate would contain approximately six percent benzene and one percent hexane.[24] This stream would become a plant emission unless a secondary control method were applied.

Incineration can be used to destroy the exit stream from the adsorber whether steam or hot air is used to desorb the vapors. The type and amount of emission are very dependent on the nature of the exit stream as noted in Section 3.1.6.

Some process streams contain particulates which will plug the void spaces in the adsorbent bed and render it ineffective much sooner than normal. This problem is solved by precleaning the gas feed stream. However, an effective means for disposing of the particulates must then be found. The disposal of spent adsorbent is also an environmental concern, but this may be necessary only once in three to five years.

3.3 Absorption

Absorption is the process in which certain constituents of a gas stream are selectively transferred to a liquid solvent. Absorption may be purely physical, in which the solute simply dissolves in the absorbent, or chemical, in which the solute chemically reacts with the absorbent or with reagents dissolved in the absorbent.

The generally low concentrations of exhausted organics require long contact times and large quantities of absorbent for adequate emissions control. Absorption is, therefore, less desirable than adsorption or incineration, unless the absorbent is easily regenerated or the solution can be used as a process make-up stream. Absorption may be best suited for use in conjunction with other control methods such as incineration or adsorption to achieve the prescribed degree of emissions removal.

3.3.1 Equipment and Operating Principals

The desirability of an absorption process for use as an emission control method depends on the ease with which organic vapors are removed by a readily available absorbent. In general, absorption is most efficient under the following conditions:[25]

1. the organic vapors are quite soluble in the absorbent

2. the absorbent is relatively nonvolatile
3. the absorbent is noncorrosive
4. the absorbent is inexpensive and readily available
5. the absorbent has low viscosity
6. the solvent is nontoxic, nonflammable, chemically stable, and has a low freezing point.

The organic-laden absorbent stream may be stripped of organic compounds and recycled. Some absorbent will be lost with the stripped organics and must be replaced. Alternately, the spent absorbent stream may be used as a product or intermediate compound in chemical manufacture.

The rate of mass transfer between the gas and the absorbent is largely determined by the amount of surface area available for absorption. Other factors governing the absorption rate, such as the solubility of the gas in the absorbent and the degree of chemical reaction, are characteristic of the constituents involved and are independent of the equipment used.

Gas absorption equipment must be designed to provide adequate contact between the gas and the absorbent liquid to permit interphase diffusion of the organic vapors. Contact is provided by several types of equipment: plate towers, packed towers, spray towers, and venturi scrubbers. Plate towers employ stepwise contact. Several plates or trays are arranged so that the gas is dispersed through a layer of liquid on each plate, as shown in Figure 3.3-1.[26] Each plate can be modeled as a separate stage; the number of required plates is determined by the difficulty of the mass transfer operation and the desired degree of absorption.

Packed towers are filled with a packing material having a large surface-to-volume ratio. The packing is wetted by the absorbent to provide a large liquid film surface area for continuous contacting of the gases (Figure 3.3-2).[27] Usually, the flow through plate and packed towers is countercurrent. Liquid is introduced at the top and trickles down through the packing or across the plates. Gas is introduced at the bottom and passes upward. This results in the highest possible transfer efficiency. As the organic concentration in the gas stream decreases and the gas rises through the tower, there is constantly fresher absorbent available for contact. This produces (maximum average) driving force for the absorption process throughout the entire column.

Spray towers dispense the liquid absorbent in a spray and pass the gas through the spray (Figure 3.3-3). Venturi scrubbers contact the gas and the absorbent in the throat of a venturi nozzle (Figure 3.3-4). The gas-liquid mixture then enters an entrainment separator, where centrifugal force separates the liquid droplets from the gas.

Packed and spray towers introduce lower pressure losses than tray towers. Spray towers have the advantage of providing particulate removal without plugging; however, they provide the least effective mass transfer capability. Their use has been restricted to applications requiring only limited removal of highly soluble gases.

Venturi scrubbers are highly efficient for particulate removal. They are preferred when removing a highly soluble gas

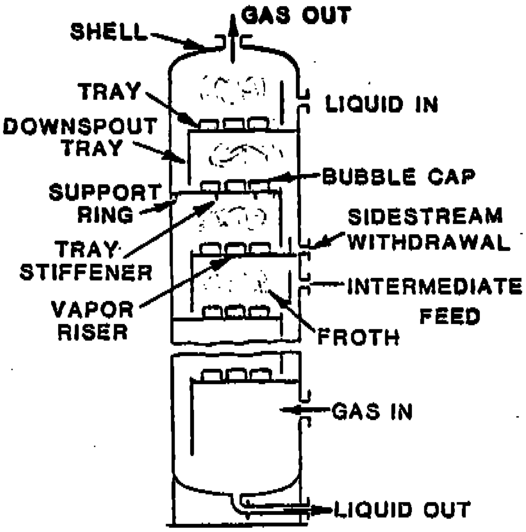

Figure 3.3-1. Schematic diagram of a bubble-cap tray (Courtesy of McGraw-Hill Book Co.).

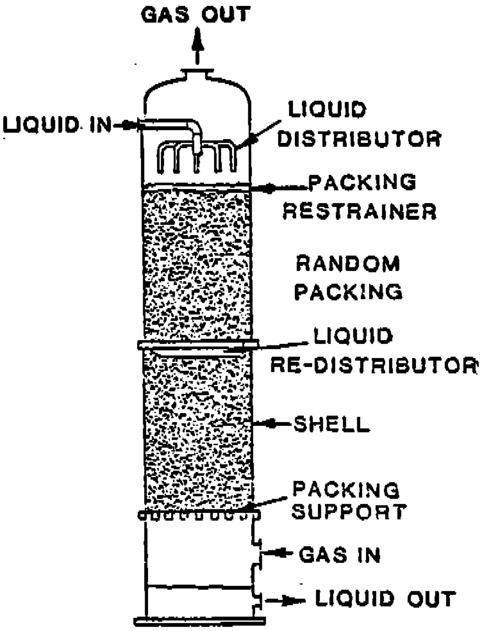

Figure 3.3-2. Packed tower. (Courtesy of McGraw-Hill Book Co.)

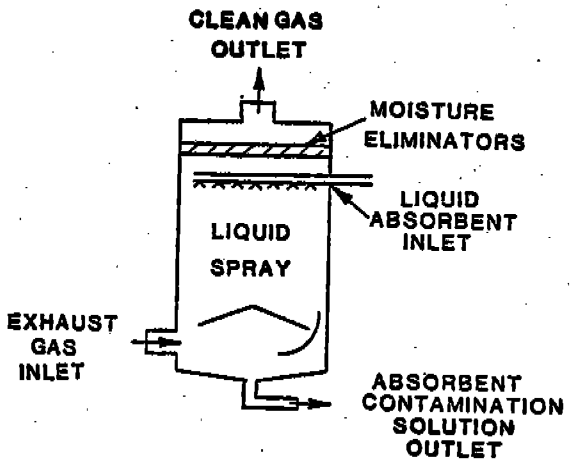

Figure 3.3-3 Spray tower.

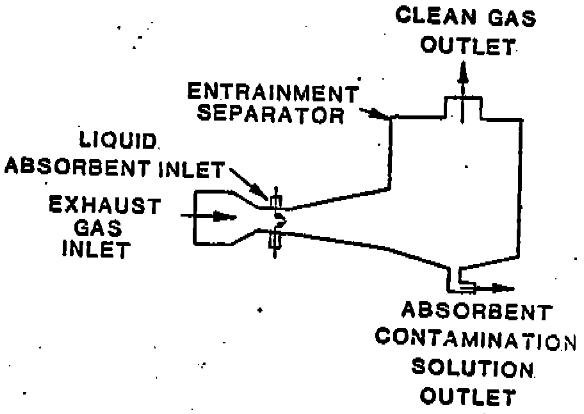

Figure 3.3-4 Venturi scrubber.

from a dirty gas stream. A major disadvantage of venturi units is the high pressure drop associated with their operating velocities. Consequently, the power requirements for the operation of venturi scrubbers are large.[28]

Since spray towers and venturi absorbers have only limited application for gas absorption, the choice of equipment is usually between a packed tower and a plate tower. Conditions for which one contractor type is preferred over the other are reported in Table 3.3-1.

TABLE 3.3-1. COMPARISON OF PACKED AND PLATE TOWERS[29]

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1. Packed towers are less expensive than plate towers when materials of construction must be corrosion resistant.
2. Packed towers have smaller pressure drops than plate towers designed for the same throughput.
3. Packed towers are preferred for foamy liquids.
4. Packed towers usually have a smaller liquid holdup than plate towers.
5. Plate towers are preferred when the liquid contains suspended solids since plate towers are more easily cleaned.
6. Plate towers are preferred for larger installations because they minimize channeling and reduce tower height.
7. Plate towers are more suitable when the process involves appreciable temperature variation, since expansions and contractions due to temperature changes may crush the tower packing.
8. Plate towers are preferred when heat must be removed, because cooling coils are more easily installed.
9. Packed towers are preferred in sizes up to 2 feet in diameter if other conditions are nearly equal.

3.3.2 Applications

Although absorption has been used primarily to control inorganic rather than organic vapors, it has been used to control organic vapors and particulate matter in surface coating operations, waste handling and treatment plants, degreasing operations, asphalt batch plants, ceramic tile manufacture plants, coffee roasters, chromium-plating units, petroleum coker units, fish meal systems, smoke generators, and varnish and resin cookers. The organic vapors removed are usually alcohols, ketones, amines, glycols, aldehydes, phenols, organic acids, and certain light hydrocarbons. Commonly used absorbents for organic vapors are water, mineral oil, nonvolatile hydrocarbon oils, and aqueous solutions of oxidizing agents, sodium carbonate, or sodium hydroxide.

3.3.3 Absorption Costs

Absorption costs vary widely and depend on the following factors:

- the type of absorber
- the kind of contacting media (*e.g.*, the use of ceramic berl saddles in a packed bed absorber)
- the nature and amounts of organic vapors in the gas
- the absorbent used
- the application of regeneration techniques
- the value of recovered organics or of the absorbent-dissolved organics solution

- the design removal efficiency
- the gas volume flow rate.

Cost curves relating capital and annualized costs to gas volumes treated are presented in Sections 3.3.3.1 and 3.3.3.2.

3.3.3.1 Capital Costs

Capital costs for a packed tower absorber are depicted graphically in Figure 3.3-5.[30] These costs include the cost of the basic equipment, the cost of any auxiliary equipment, and the costs associated with equipment installation and site preparation. Corrosive properties of certain organic streams require special construction materials which increase capital costs. It is emphasized that costs provided in Figure 3.3-5 are for illustrative purposes only. Each particular application of an absorption system will require an engineering analysis of performance requirements and gas stream characteristics before costs can be estimated.

Absorption systems using absorbents with poor absorption capabilities for organic vapors would have larger capital costs associated with the need for larger absorption towers. Regenerative absorption systems also have increased capital costs because of additional equipment needed for absorbent regeneration.

The costs shown in Figure 3.3-5 are representative of new installations. Retrofits may cost up to two times the reported values.

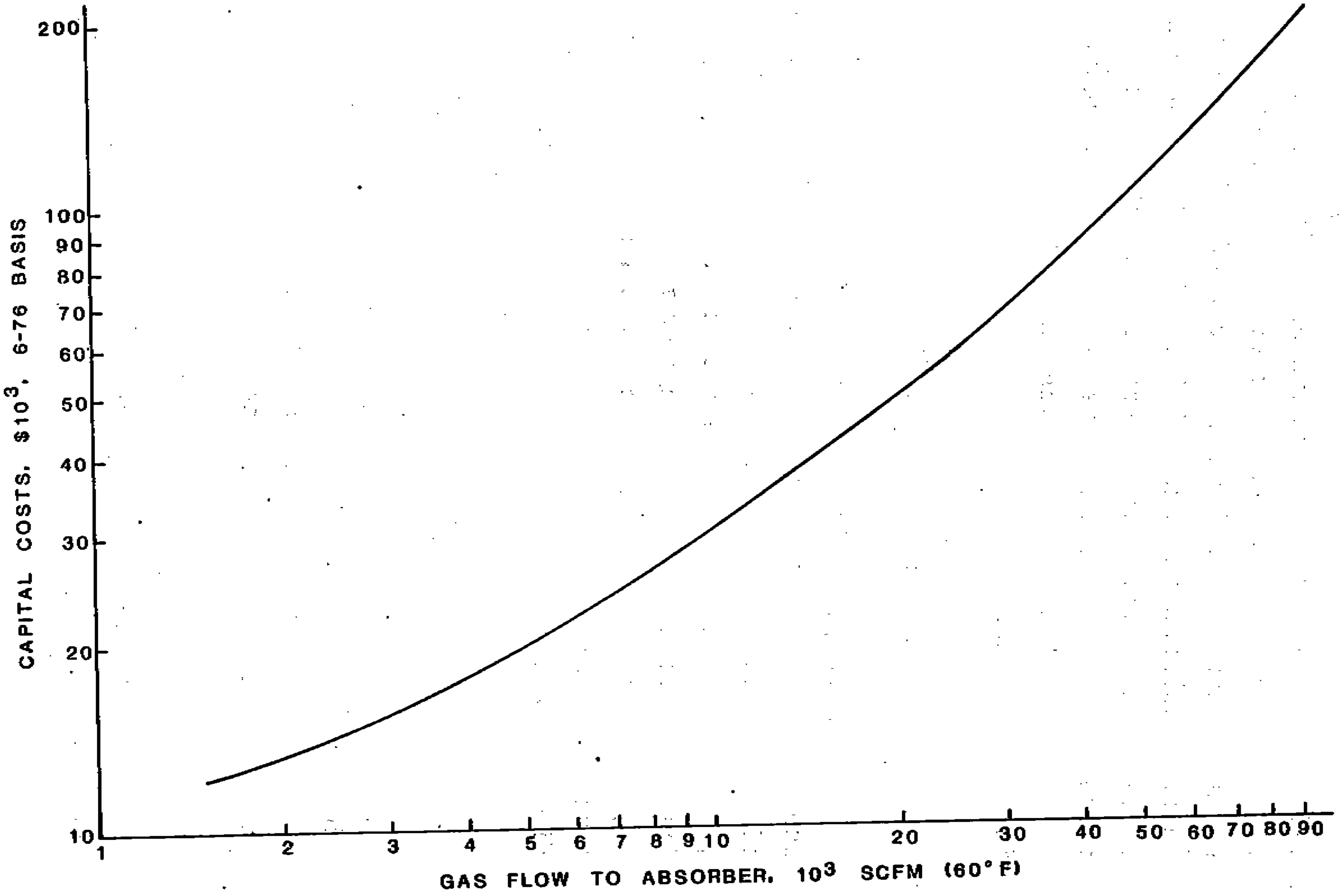

Figure 3.3-5. Capital Costs for Packed Tower Absorbers (New Installations)

3.3.3.2 Annualized Costs

Annualized costs for a cross-flow packed scrubber are presented in Figure 3.3-6.[31] Utilities include power costs for the recirculating pump and fan. Process water costs are small in this case since recirculation is assumed. Treatment costs, although not included in Figure 3.3-6, should be taken into consideration when evaluating absorption system costs. Maintenance costs appear to average five percent of the capital investment. Relatively low capital investments for absorption systems help minimize capital charges.

3.3.4 Absorption Energy Requirement

The energy required for absorbers will vary greatly depending upon the particular configuration used. The energy required in a typical absorber system is for pumps, cooling water system, blowers, and a source of heat if absorbent regeneration is desired. Variables involved in energy consumption by an absorber system are the concentration of organic vapors in the gas, the amount of absorbent, the gas flow rate, and the type of regeneration. The energy required for a typical cross-flow packed scrubber operation as a function of gas flow rate is shown in Figure 3.3-7.[32]

A source of power, either electricity or steam, is needed for a charge pump to keep fresh absorbent in contact with the gas. If a stripper (regenerator) is part of the system, circulating pumps are necessary to keep the entire system operating in steady state.

Electricity is also needed to power a cooling water system necessary for removing heat from the absorbent and the effluent gas stream.

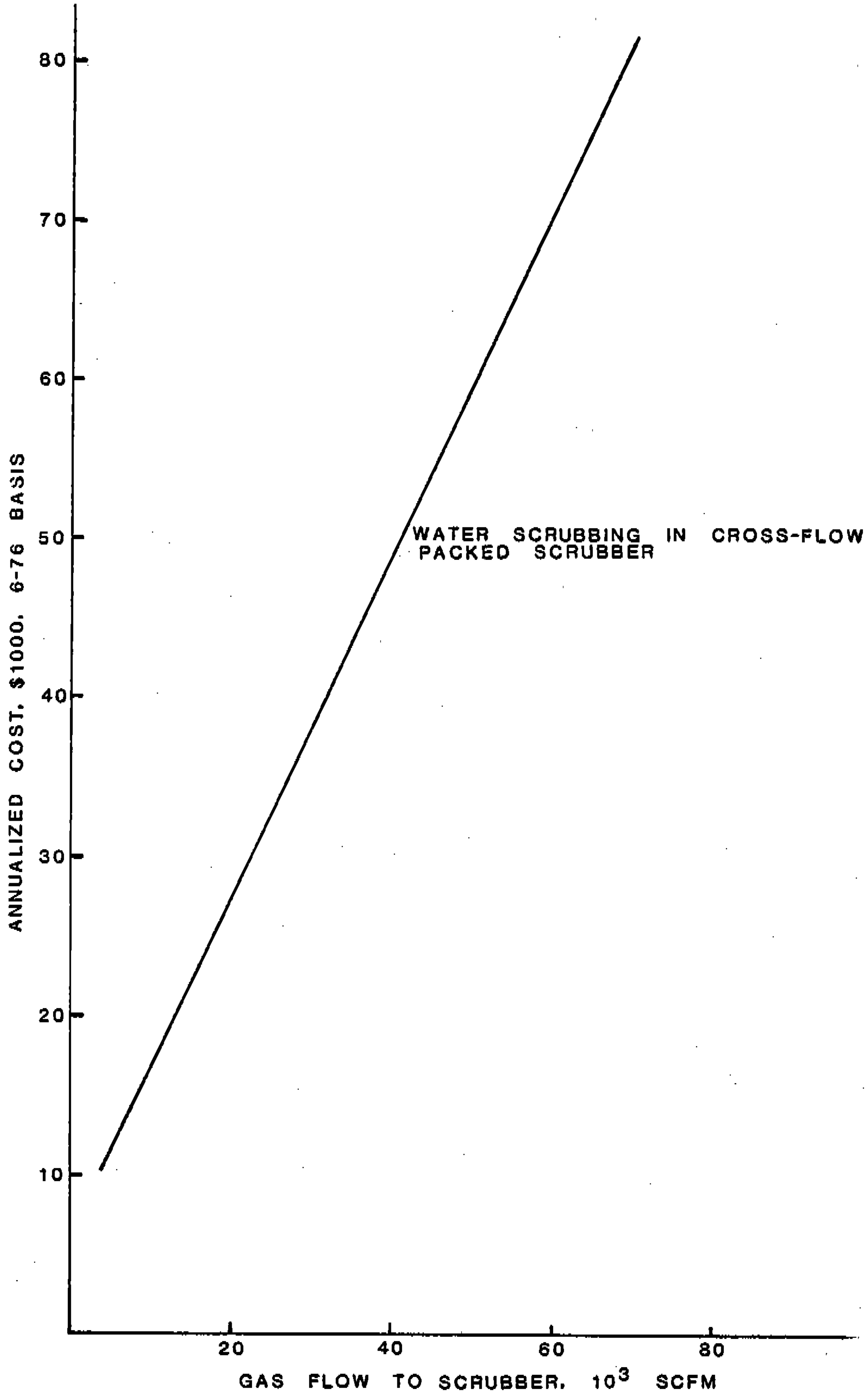

Figure 3.3-6. Annualized Costs for a Cross-flow Packed Scrubber

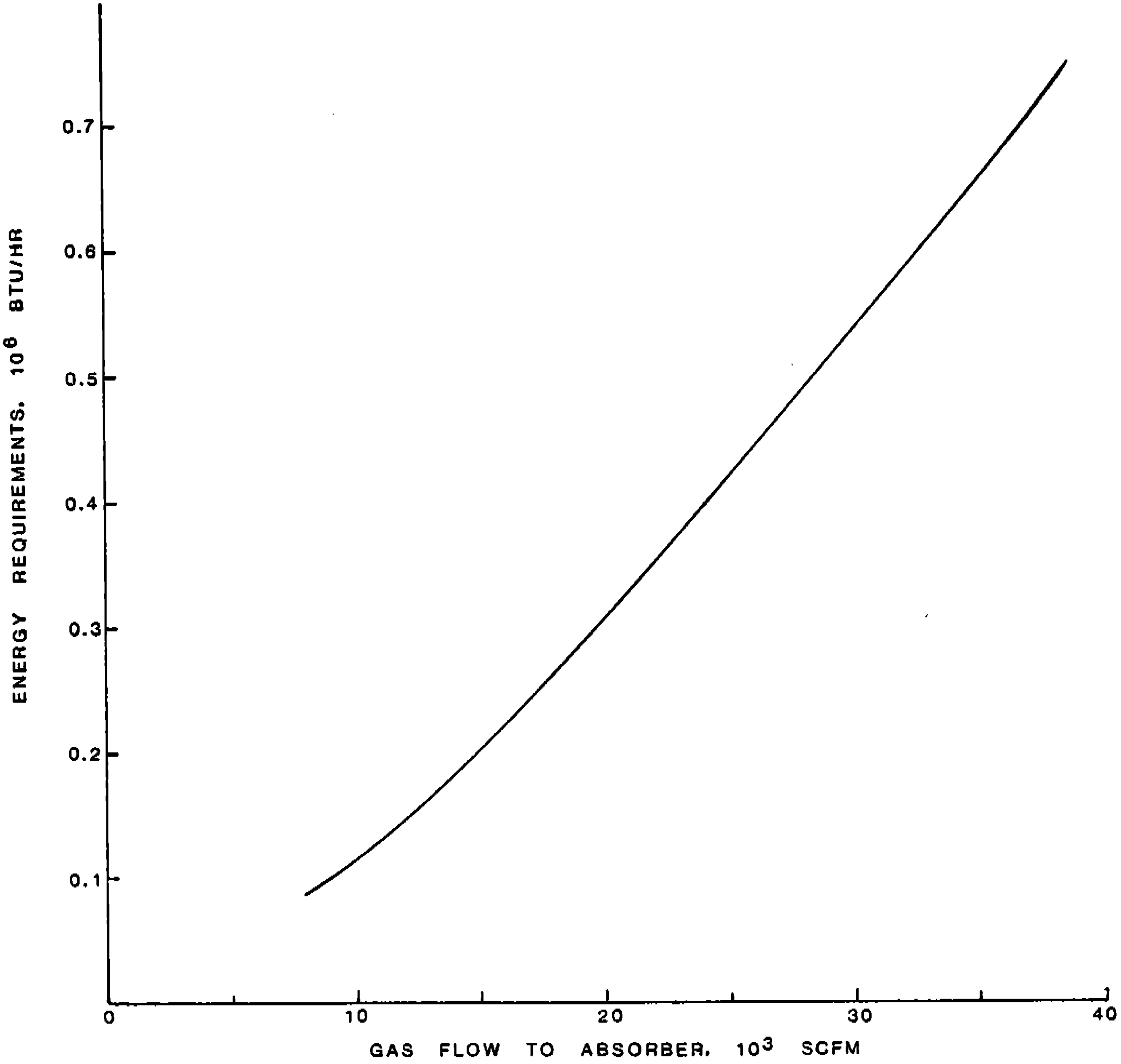

Figure 3.3-7. Energy Requirements for a Typical Cross-flow Packed Scrubber Operation

In order to overcome pressure drop through the absorber configuration, a fan or blower is required for the process gas stream. Pressure drop varies widely with the type of absorber equipment used. The pressure drop through a packed or spray tower is not significant compared with the pressure drop encountered in a Venturi scrubber. The energy requirements for operation of a Venturi scrubber are relatively large.[33]

3.3.5 Environmental Impact of Absorption

Adverse environmental effects resulting from the operation of an absorber include improper disposal of the organic-laden liquid effluent, undesired emissions from the incineration of the regenerated waste gas, loss of absorbent to the atmosphere, and increased water usage.

The liquid effluent from an absorber can frequently be used elsewhere in the process. When this is not possible, the non-regenerated absorbent effluent should be treated to provide good water quality. Such treatment may include a physical separation process (decanting or distilling) or a chemical treating operation.

Regeneration consists of heating the liquid effluent stream to reduce the solubility of the absorbed organics and separate them from the absorbent. These concentrated organics can then be oxidized in an afterburner. Emissions of SO_x, NO_x, and other incomplete oxidation products may be a result, depending on the nature of the regenerated gas stream.

The control of one type of volatile organic emission can result in the emission of another at an even greater rate when liquid absorption is employed. For example, vapors of trichloroethylene can be substantially reduced in an air stream by absorption in a lean mineral oil; however, at ambient temperature the air stream leaving the absorber might contain 120 ppm mineral oil.[34]

An add-on water scrubbing system will usually mean only a minimal increase in the throughput to the existing water treatment facilities in a plant.

3.4 Condensation

Condensation is usually applied in combination with other air pollution control systems. Condensers located upstream of afterburners, carbon beds, or absorbers can reduce the total load entering the more expensive control equipment. When used alone as in gasoline vapor control in bulk terminals, refrigeration is the usual means of achieving the low temperatures necessary for condensation. This is the best application for the principle of condensation.

3.4.1 Equipment and Operating Principles

In a two-component vapor (where one component can be considered non-condensible), condensation occurs when the partial pressure of the condensible component equals the component's vapor pressure. There are two ways to obtain condensation. First, at a given temperature, the system pressure may be increased until the partial pressure of the condensible component equals its vapor pressure. Alternately, at a fixed pressure, the temperature of the gaseous mixture may be reduced until the vapor pressure of the condensible component equals its partial pressure. As the temperature is further reduced, condensation continues such that the partial pressure is always equal to the vapor pressure. While condensation by increasing pressure is possible, in practice, condensation is achieved mainly through removal of heat from the vapor. Some components in multicomponent condensation may dissolve in the condensate even though their boiling points are below the exit temperature of the condenser.

Condensers employ several methods for cooling the vapor. In surface condensers, the coolant does not contact the vapors or condensate; condensation occurs on a wall separating the coolant and the vapor. In contact condensers, the coolant, vapors, and condensate are intimately mixed.

Most surface condensers are common shell-and-tube heat exchangers. The coolant usually flows through the tubes and the vapor condenses on the outside tube surface. The condensed vapor forms a film on the cool tube and drains away to storage or disposal. Air-cooled condensers are usually constructed with extended surface fins; the vapor condenses inside the finned tubes.

Contact condensers usually cool the vapor by spraying an ambient temperature or slightly chilled liquid directly into the gas stream. Contact condensers also act as scrubbers in removing vapors which normally might not be condensed. The condensed vapor and water mixture is then usually treated and discarded as waste. Equipment used for contact condensation includes simple spray towers, high velocity jets, and barometric condensers.

Contact condensers are, in general, less expensive, more flexible and more efficient in removing organic vapors than surface condensers. On the other hand, surface condensers may recover marketable condensate and minimize waste disposal problems. Often condensate from contact condensers cannot be reused and may require significant wastewater treatment prior to disposal. Surface condensers must be equipped with more auxiliary equipment and have greater maintenance requirements.

3.4.2 Applications

Condensation processes with significant refrigeration requirements are being used for the recovery of gasoline vapors at bulk gasoline terminals. In some installations, gasoline vapors are compressed and then refrigerated to obtain condensation. Other installations omit compression and simply refrigerate the vapors to temperatures approaching -73°C (-100°F). Removal efficiencies depend on the hydrocarbon concentration of the inlet vapors, but are greater than 96% for the removal of saturated hydrocarbons. Similar systems have been proposed for marine petroleum terminals.

Condensers have been used successfully (usually with additional control equipment) in controlling organic emissions from petroleum refining and petrochemical manufacturing, drycleaning, degreasing, and tar dipping. Even when used as the primary control equipment, condensers are usually followed by a secondary air pollution control system (such as an afterburner) which treats the non-condensible gases and achieves a high degree of overall efficiency. Condensation is sometimes practical in the surface coating industry when large concentrations of relatively nonflammable materials are present.

3.4.3 Condensation Costs

The costs for shell-and-tube surface condensers depend on the following:

- the nature and concentrations of the vapors in the waste gas
- the mean temperature difference between gas and coolant
- the nature of the coolant
- the desired degree of condensate subcooling
- the presence of non-condensible gases in the waste gas
- the buildup of particulate matter on heat exchange surfaces.

In general, capital costs for surface condensers are greater than the corresponding costs for contact condensers. Preliminary cost estimates can be made after the necessary heat exchange area is determined from the factors listed above.

Costs for contact condensers used for organic emissions control also depend on the factors given above. In addition, the cost for treatment of the organics-coolant effluent must be included.

Condensers have been most widely applied as preliminary or auxiliary equipment for other control devices (*e.g.*, as part of the regeneration step in carbon absorbers). One important application as primary control equipment is at bulk gasoline terminals as vapor recovery units. Annualized and capital costs for refrigeration vapor recovery units have been developed by the EPA in a draft document on the control of

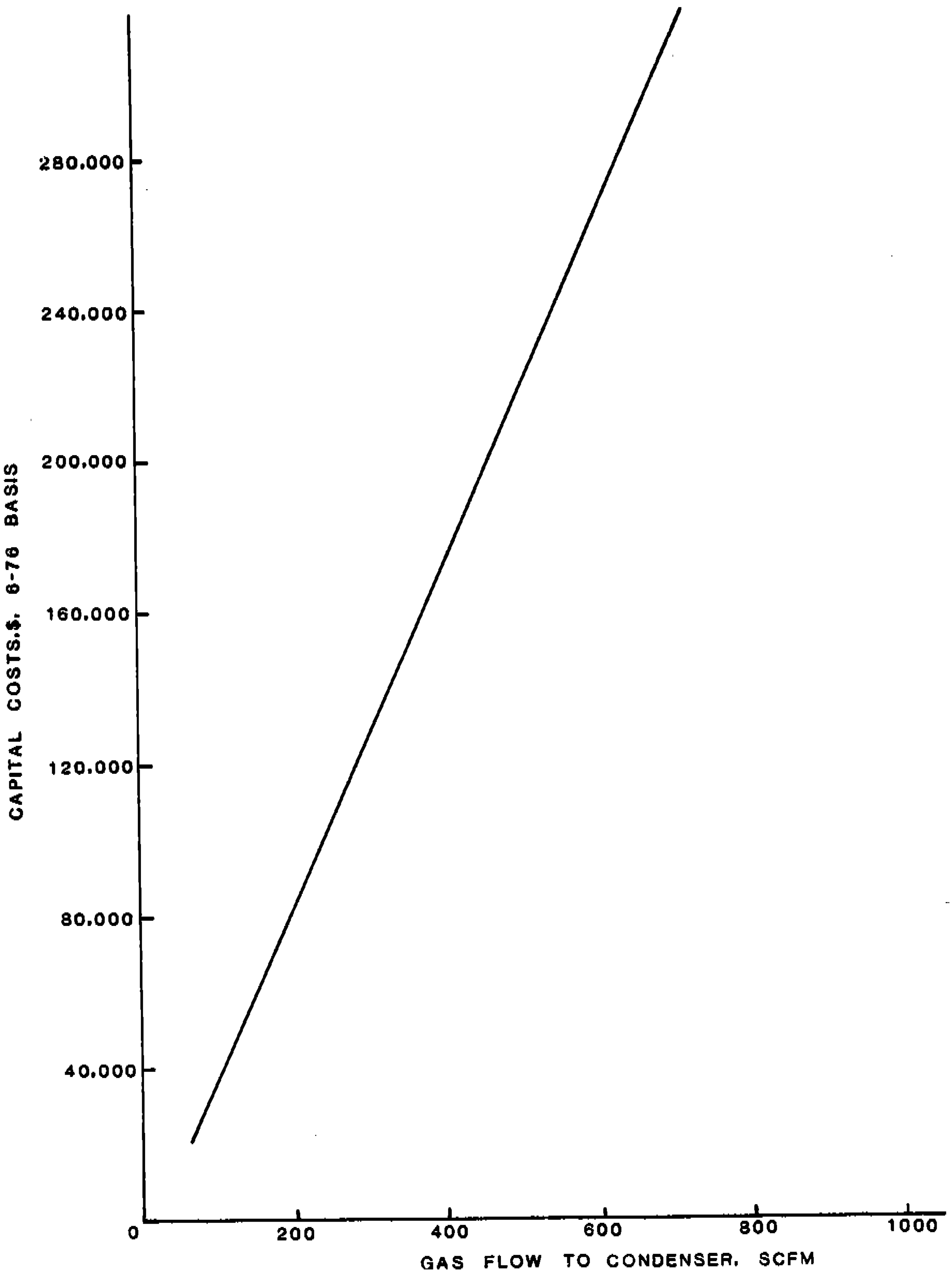

Figure 3.4-1. Capital Costs for Refrigeration Vapor Recovery Units

hydrocarbons from tank truck loading terminals.[35] These costs are shown in Figures 3.4-1 and 3.4-2 as a function of the hydrocarbon vapor flow rate. All costs are indexed to June 1976.

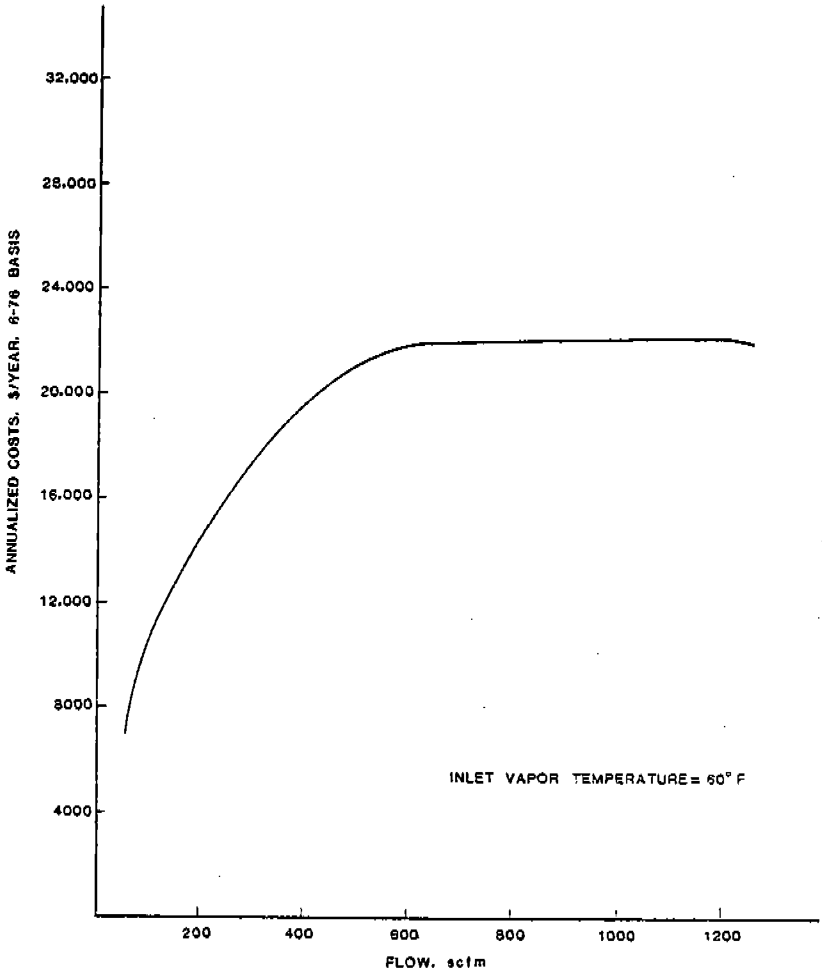

Figure 3.4-2. Annualized costs for refrigeration vapor recovery units.

Capital cost estimates are intended to represent the total investment required to purchase and install a refrigeration unit. New installations are assumed, but retrofitting at existing installations is expected to be only slightly higher.

An example of annualized cost components for a refrigeration vapor recovery unit is shown in Table 3.4-1.

TABLE 3.4-1. COMPONENTS OF ANNUALIZED COSTS FOR A REFRIGERATION VAPOR RECOVERY UNIT[36]

Gas Stream Characteristics	
Flow	420 scfm (12 m^3/min)
Concentration	20% (by vol.) hydrocarbons
Inlet Temperature	60°F (16°C)
Direct Operating Costs	
Utilities	\$ 6,000[a]
Maintenance	5,300[b]
Capital Charges	30,000[c]
Gasoline Recovery (Credit)	(21,400)[d]
Net Annualized Costs	19,900[e]

[a] Electricity @ \$.04/kWh (\$11.11/GJ).

[b] Maintenance as 3% of the capital costs.

[c] Calculated @ 10% for 15 years plus 4% for taxes, insurance, and administration.

[d] Gasoline valued at \$.40/gal (\$.10/ℓ) F.O.B. terminal before tax.

[e] Computed as operating costs + capital charges - gasoline recovery credits

Utilities costs will vary depending on the inlet concentration of the hydrocarbon vapors. Gasoline credits help offset about 35-75% of the annualized expenses. At higher flow rates, gasoline credits appear to offset operating expenses and capital charges, resulting in a net savings by recovering the vapors.

In general, condensation systems are uneconomical as the sole means of emission control unless the gas contains high concentrations of valuable organic vapors which can be recovered from the gas stream.

3.4.4 Condensation Energy Requirements

The amount and type of energy required for a condenser will depend primarily on the type of condensation system employed. The different configurations and their energy requirements vary greatly from one system to another. In general, condensation systems consist of a cooling system and a means for transporting the different streams.

A contact condenser requires energy in the form of cold liquid supply, injection pumps, and a blower to move the gas through the condensation zone. The condensate and coolant are usually not recovered due to the prohibitive costs, but a surface condenser can easily recover marketable condensate without costly separation processes. A surface condenser requires energy for a cooling water system or a forced convection air cooler.

Figure 3.4-3 is a plot of the energy requirements as a function of vapor flow rate for a refrigeration condenser system used for the recovery of gasoline vapors at a bulk terminal.[37] Characteristics and bases for this system are found in Table 3.4-1. Electricity is used to power the refrigeration unit which provides the cooling in this example. A refrigerator can be used alone or in conjunction with a compressor to facilitate condensation. The type of equipment chosen for a refrigeration unit depends on the concentration of organic vapors in the gas stream, the physical properties of the vapors, and the flow rate of the gas stream.

If the organic vapors are recovered, some energy credit can partially offset the energy required to effect the condensation. This is especially true if the condensate can be used as fuel or if the energy required to produce the organic compound is very high.

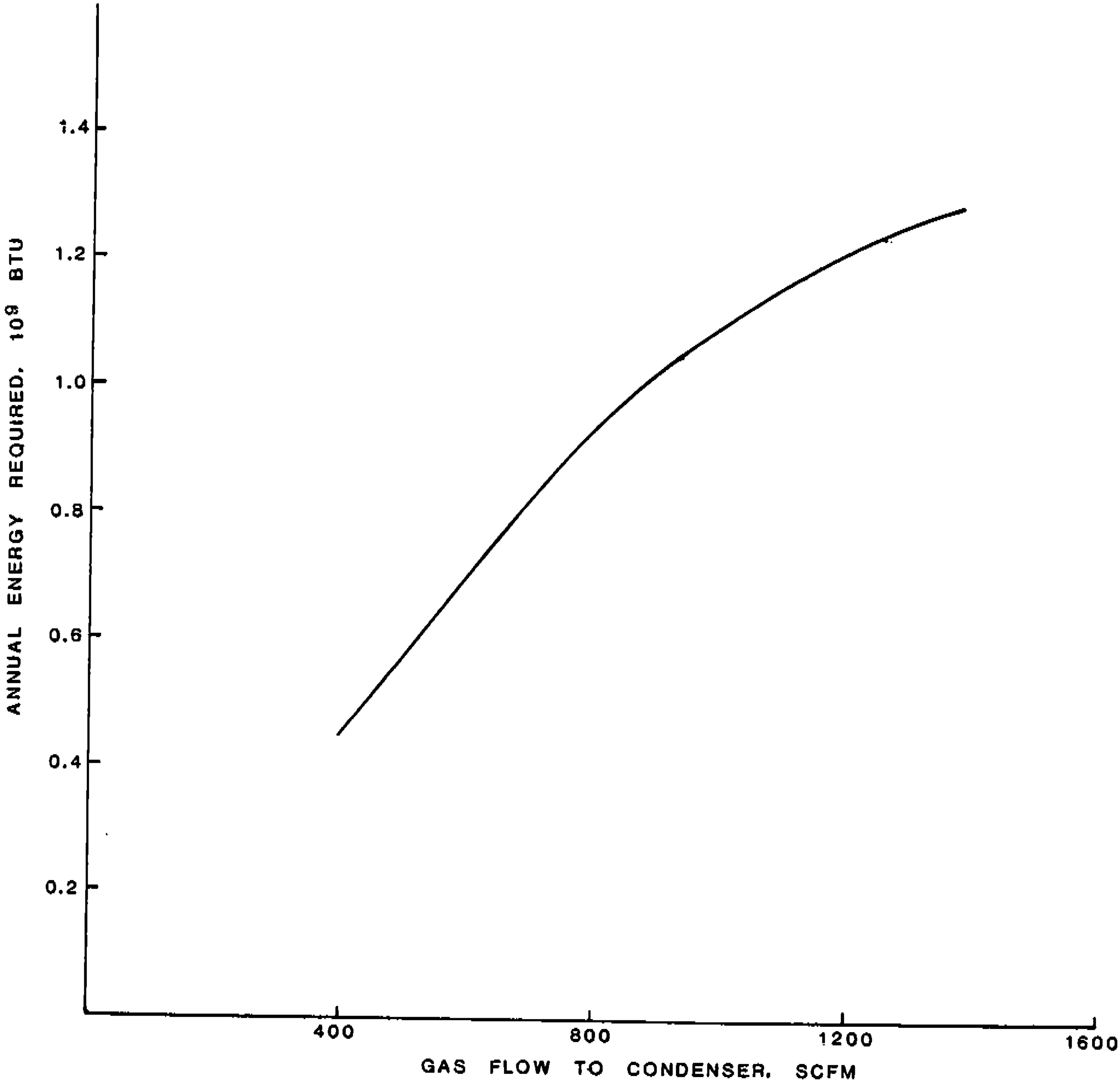

Figure 3.4-3. Energy Required for a Refrigeration Condenser (Gasoline Vapor Recovery System at a Bulk Terminal)

Condensation is rarely used as the sole means for controlling organic vapors. The total energy requirement for a system involving condensation must allow for the energy associated with a secondary air pollution control system, such as an afterburner.

3.4.5 Environmental Impact of Condensers

A condenser will create few secondary environmental problems when the condensation process is considered by itself. Problems that do arise include disposal of non-condensibles in surface condensers and refrigeration systems, and the need for proper treatment of the liquid effluent in contact condenser systems. Condensation is rarely used alone as a control method; therefore, it is imperative that all associated equipment produce effluent streams of sound environmental quality.

The non-condensible gas effluent from surface condensers is either vented to the atmosphere or further processed (e.g., via incineration), depending on the effluent composition. The coolant never contacts the vapors or condensate in a surface condenser; therefore, the recovered organic compounds are usually reusable. The condensate might not be saved if more than one compound is condensed and separation is costly. Proper treatment of the condensate is then imperative before final disposal. This also applies for the recovery of volatile organic emissions by refrigeration.

In contact condensation, the condensate is contaminated with the coolant liquid. The usual procedure is treatment of the waste stream and disposal. The amount of organic material entrained in the existing wastewater will depend on the extent of treatment.

3.5 Flaring

Flares are most commonly used as safety devices to incinerate waste gases from petroleum refining and petrochemical manufacturing operations. Flares are preferred when disposing of gas streams with sufficient heat value to attain the combustion temperature without the use of supplemental fuel. Flares are also preferred when disposing of gases with little recovery value, or for gases containing contaminants that make recovery unprofitable.

3.5.1 Equipment and Operating Principles

3.5.1.1 Operating Characteristics

Complete combustion of organic gases and vapors can be achieved if 1) the gas has sufficient heat value to attain the minimum temperature necessary for combustion, 2) adequate combustion air is supplied, and 3) the gas and air are adequately mixed. An insufficient air supply produces a smokey flame. Within the reducing atmosphere of the smoke, hydrocarbons can crack to elemental hydrogen and carbon or can react to form polymers. Side reactions become more pronounced as the molecular weight and unsaturation of the inlet gas increase. Olefins, diolefins, and aromatics characteristically burn with smokey, sooty flames as compared with paraffins and naphthenes. A smokeless flame can be obtained when an adequate amount of combustion air is mixed with the gas so that it combusts completely and rapidly before any side reactions can occur.

Combustion of organics in a well-operated flare may be nearly complete. In typical installations hydrocarbon removal efficiencies of 99% have been obtained. Not all of the hydrocarbons are completely oxidized to carbon dioxide and water. As much as 10% of the combustion products may be carbon monoxide.[38]

Firing of the flare can produce temperatures which favor the formation of nitrogen oxides. Other air contaminants emitted from flares vary with the composition of gases burned. Sulfur dioxide is produced from the combustion of sulfur compounds such as hydrogen sulfide. Burning hydrogen sulfide can create enough sulfur dioxide to cause crop damage or local nuisance in some instances. However, for emergency conditions, discharge of a stream containing hydrogen sulfide to an elevated flare may be safer than venting or incineration at a low elevation.

Materials that cause health hazards or nuisances should not be combusted in flares. Compounds such as mercaptans or chlorinated hydrocarbons require special combustion devices with chemical treatment of the gas or the combustion products.

3.5.1.2 Types of Flares

There are, in general, three types of flares for the disposal of waste gases: elevated flares, ground-level flares, and burning pits.

Burning pits are reserved for extremely large gas flows caused by catastrophic emergencies in which the capacity of the primary smokeless flares is exceeded. Ordinarily, the main gas header to the flare system has a water seal bypass to a burning pit. Excessive pressure in the header blows the water seal and vents the vapors and gases to the burning pit for combustion.

Smokeless combustion can be obtained in an elevated flare by the injection of an inert gas into the combustion zone to provide turbulence and inject air. The most commonly used air-injecting material for an elevated flare is steam. Three main types of steam-injected elevated flares are in use. These types vary in the manner in which the steam is injected into the combustion area.

In the first type, steam is injected by several small jets placed concentrically around the flare tip. The jets are installed at an angle and cause the steam to discharge in a converging pattern immediately above the flare tip.

A second type has a flare tip with no obstruction to flow. The flare tip is the same diameter as the stack. The steam is injected by a single nozzle located concentrically within the burner tip. In this type of flare, the steam is premixed with the gas before ignition and discharge.

A third type is equipped with a flare tip that promotes turbulence by causing the gases to flow through several tangential openings. A steam ring at the top of the stack has numerous equally spaced holes for injecting steam into the gas stream.

Most modern refinery and petrochemical plant flares have a tip with three locations for steam injection. The steam rates to the three different locations at the flare tip are controlled by three different regulator valves.

Steam injection provides the following benefits:

1. energy available at relatively low cost can be used to inject air and provide turbulence within the flame

2. steam and/or water react with the gas to form oxygenated compounds that burn readily at relatively low temperatures

3. steam retards polymerization by reducing the partial pressure of the fuel.

The injection of steam into a flare can be controlled either manually or automatically. In some installations, the steam is supplied at maximum rates, and manual throttling of the steam is required for a particular gas flow rate. For the best combustion with minimum steam consumption, instrumentation should be provided which automatically controls the steam rate based on the gas flow rate.

Ground-level flares are usually enclosed and are used primarily where noise or light would be objectionable. A ground-level flare is usually designed for daily process needs with the high flows during major emergencies routed to an accompanying elevated flare. Ground-level flares are of four principal types: horizontal venturi, water injection, multijet, and vertical venturi.

A horizontal venturi flare system utilizes groups of standard venturi burners. In this type of burner, the gas pressure inspires combustion air for smokeless operation.

A water-injection flare consists of a single burner with a water spray ring around the burner nozzle. Air is drawn in as a result of the spray action and the water vapor provides for the smokeless combustion of gases. Water is not as effective as steam for controlling smoke with high gas-flow rates, unsaturated materials, or wet gases.

A multijet ground flare uses two sets of burners, one for normal gas release rates and both for higher flaring rates.

A vertical, venturi ground flare also uses commercial-type venturi burners. This type of flare is suitable for relatively small flows of gas at a constant rate.

3.5.2 Applications and Costs

Flares are usually unsuitable for the treatment of dilute gas streams because the costs of supplemental fuel needed to attain the minimum combustion temperature are prohibitive. Unlike afterburners, flares have no heat recovery capability that could produce credits for heat generated from combustion. Flares are also generally less effective than other devices in controlling organic vapors. While nearly all of the hydrocarbon pollutants are combusted, considerable quantities of carbon monoxide may be produced.

Elevated flare equipment costs vary considerably because of the disporportionate costs for auxiliary and control equipment and the relatively low costs of the flare stack and burner. As a result, equipment costs are rarely dependent on the gas flow rate. Typical installed costs range from $30,000 to about $100,000. Figure 3.5-1 represents estimates of installed cost for a typical elevated flare in the petrochemical industry.[39] Low level flares are approximately ten times more expensive for similar capacity ranges.[40]

Operating costs are determined chiefly by fuel costs and by steam required for smokeless flaring. On the basis of 40 cents per 10 million Btu's of fuel, typical refinery elevated flare stack operating costs (2-foot diameter stack) are about $2000 per year.[41] The cost of operating large elevated flares can be considerably greater than this number.

Figures 3.5-2 and 3.5-3 represent estimates of capital and annualized costs for an enclosed ground-level flare handling small volumes of gasoline vapors from tank truck loading operations at gasoline bulk terminals.[42] Capital costs for enclosed

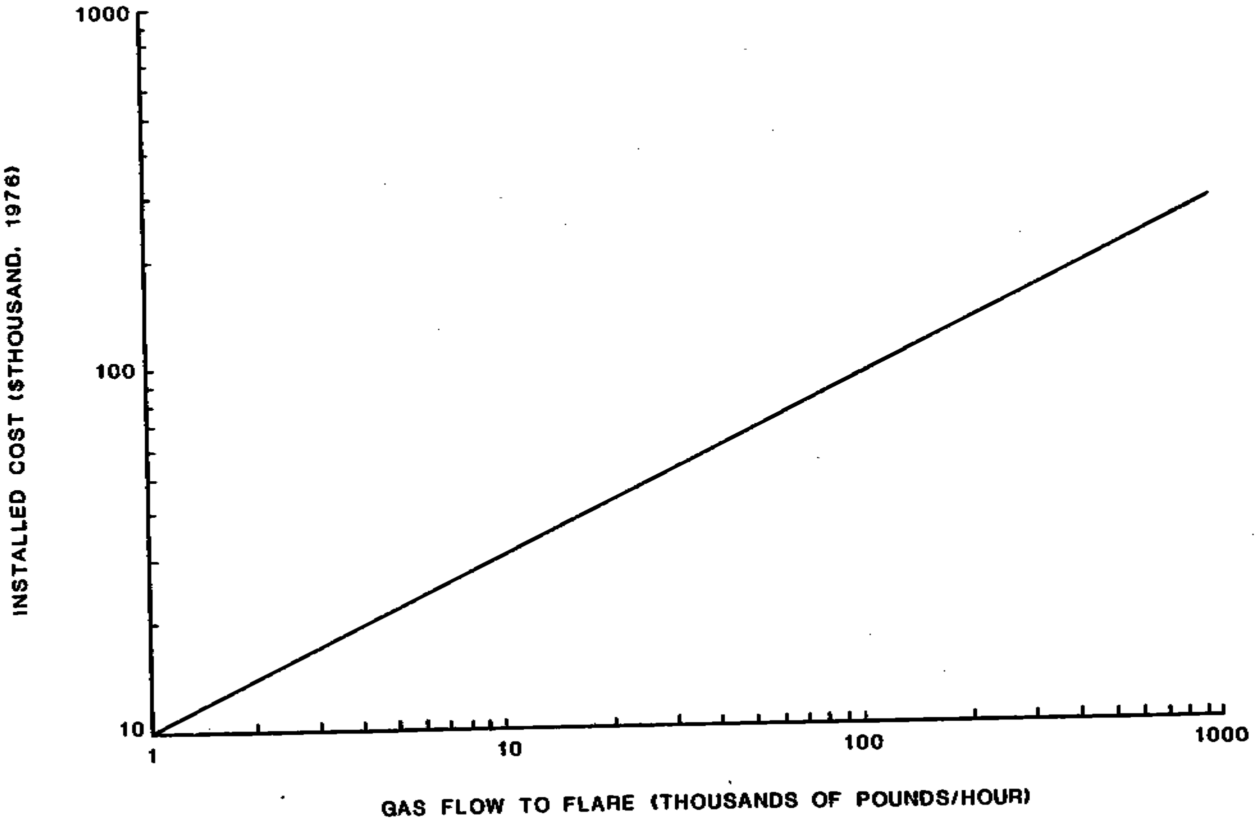

Figure 3.5-1. Installed cost of typical petrochemical elevated flare.

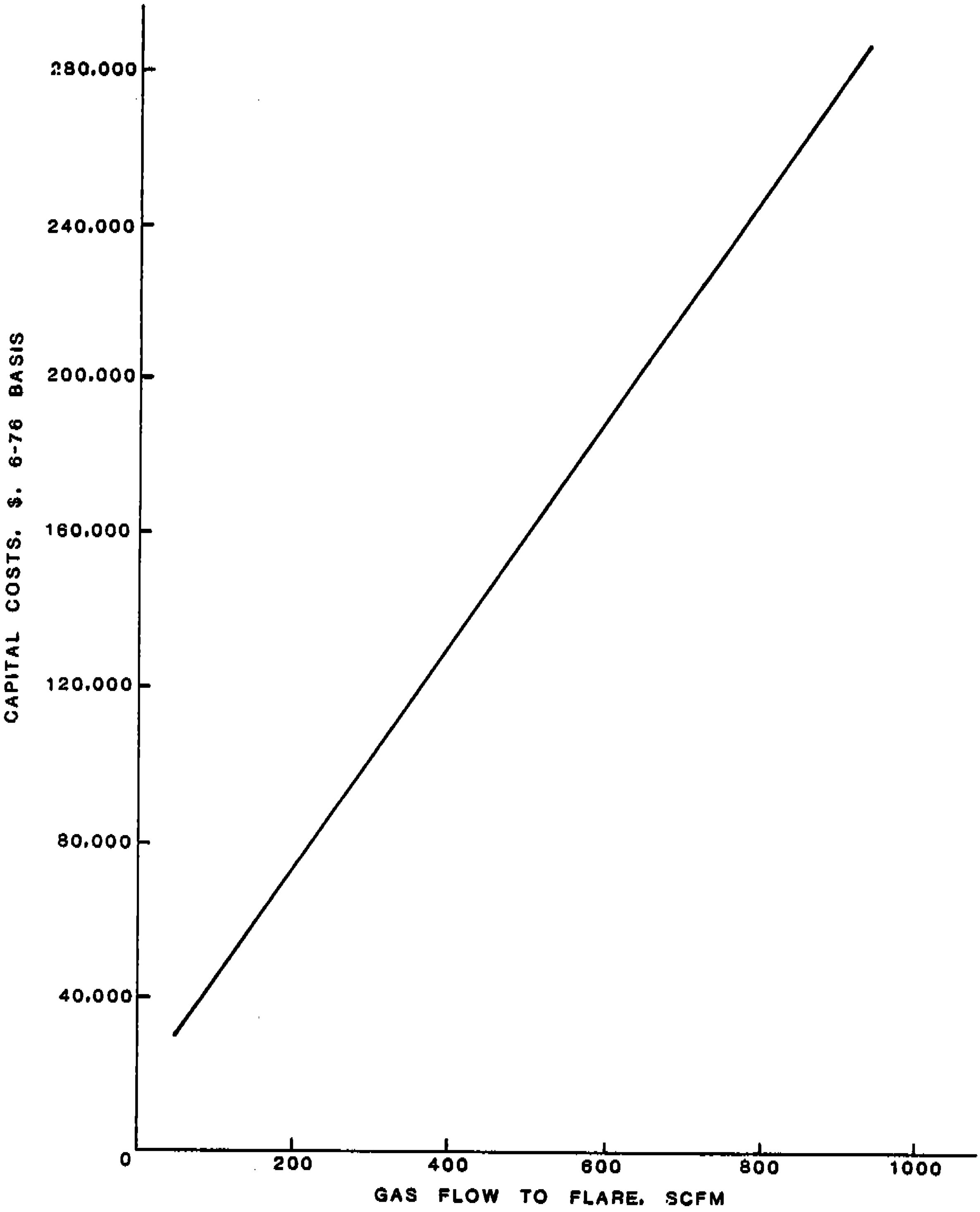

Figure 3.5-2. Capital Costs for an Enclosed Ground-level Flare (Vapors from Tank Truck Loading Operations at a Bulk Terminal)

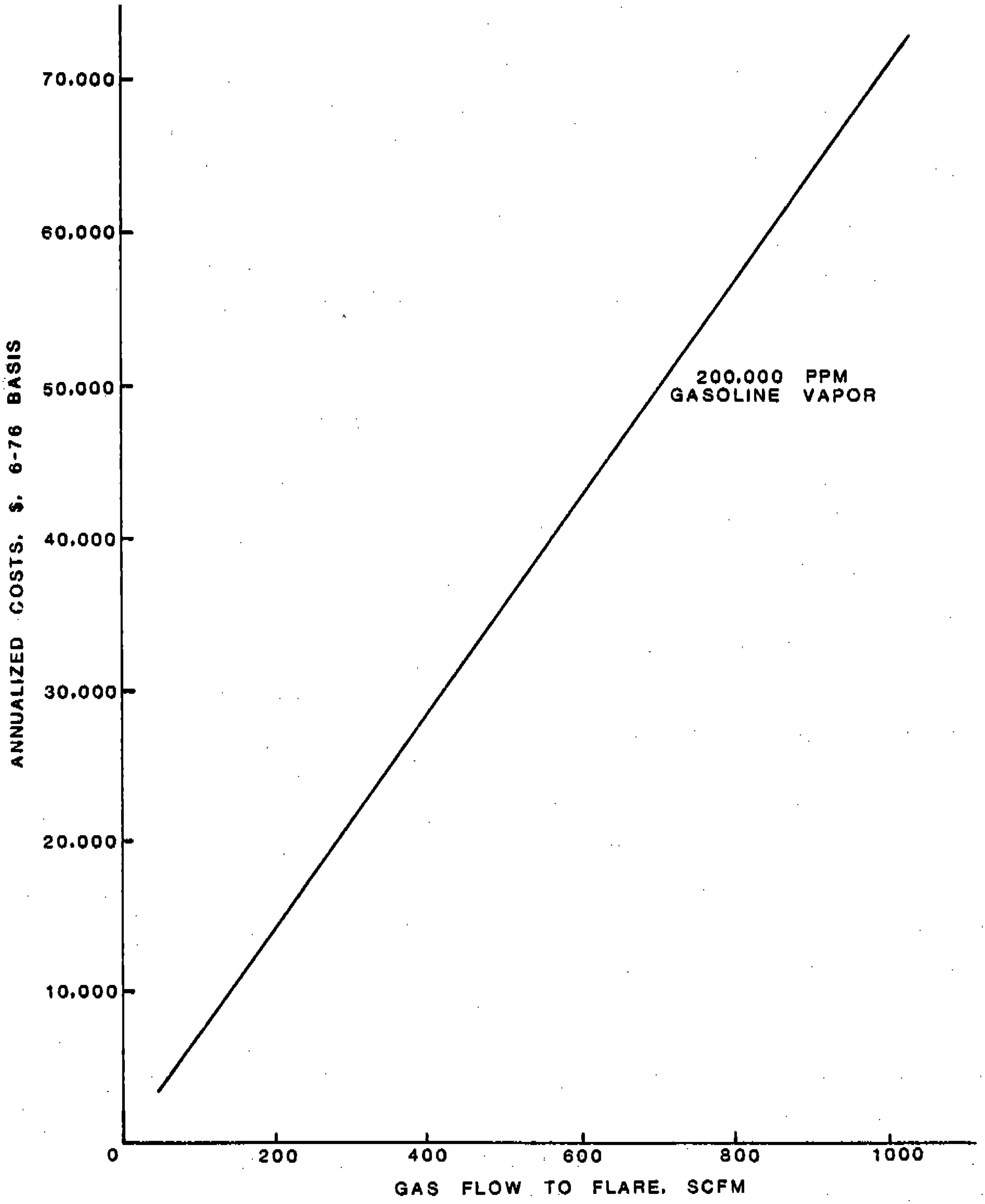

Figure 3.5-3. Annualized Costs for an Enclosed Ground-level Flare (Vapors from Tank Truck Loading Operations at a Bulk Terminal)

flares are greater than elevated flares for comparable flow rates; however, enclosed flares afford better emission control and greater safety for the application mentioned.

Annualized costs are minimized in this example since hydrocarbon concentrations are sufficient to support combustion without supplemental fuel. A pilot is required to ensure ignition. Maintenance costs average about two percent of capital costs. Power costs are associated with a blower that supplies combustion air to the burners and a purging system that prevents the flare from starting when explosive mixtures are present.

3.5.3 Energy Requirement for Flares

Smokeless operation of a flare usually requires a supply of steam or air because very few organic compounds burn smokelessly without steam or air injection. The purpose of energy input to a flare is to maintain efficient operation, since flares usually do not need any additional fuel to support the combustion of the waste stream. Other possible energy requirements may be power for a vapor purging system which prevents explosive mixtures in flare stacks and fuel for a gas pilot. Additional fuel will be required if dilute gas streams are to be flared; however, gas streams with low heating value are better suited to disposal by direct incineration.[43]

A forced draft flare is used for special purposes, and its energy requirement includes electricity for a blower to provide the flare tip with combustion air. A ground level flare normally uses a natural draft air supply, and steam is seldom necessary for smokeless operation.[44]

Figure 3.5-4 displays the energy requirement for a low capacity, enclosed, ground-level flare. Included in the

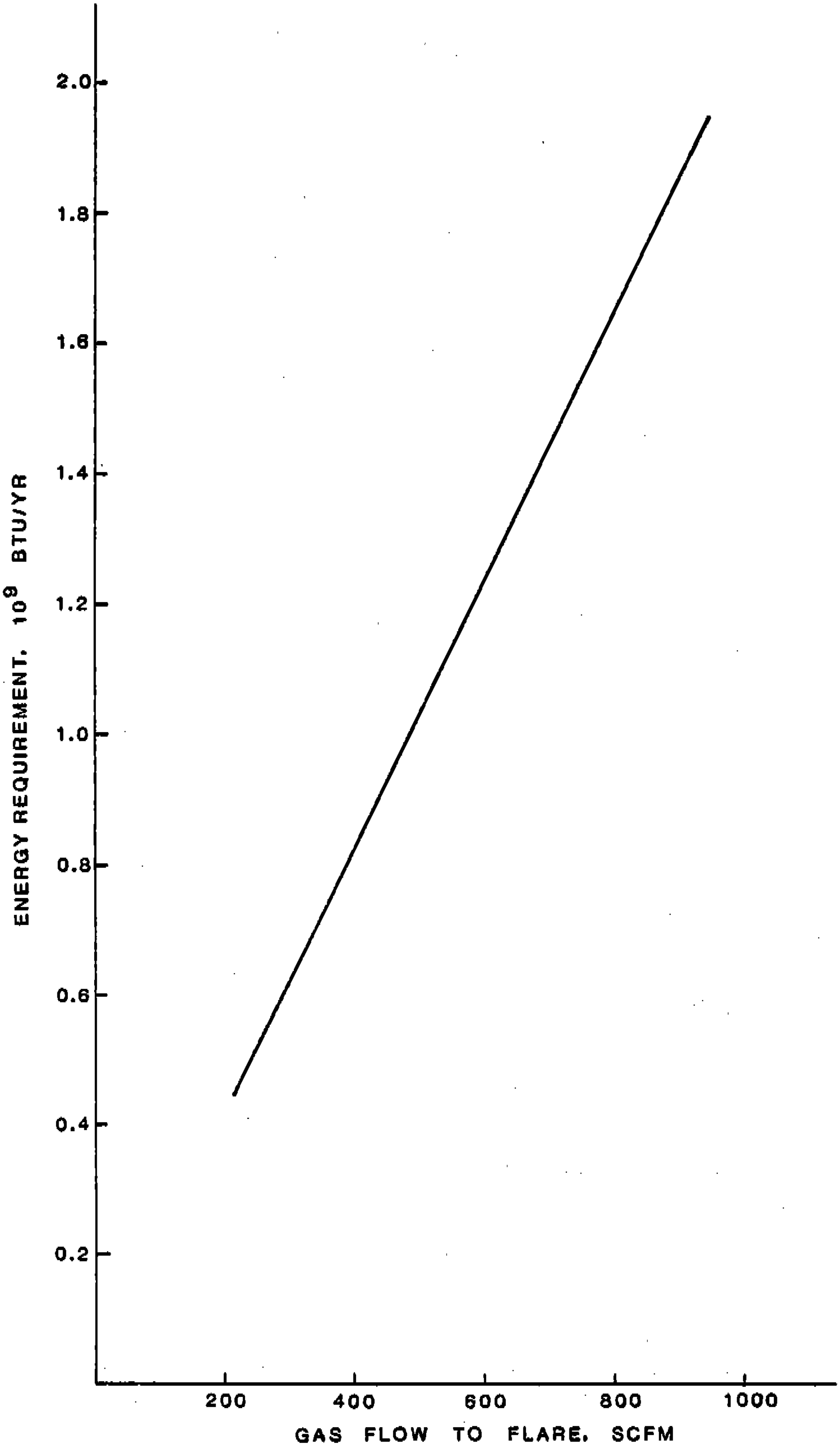

Figure 3.5-4. Energy Requirements for a Low Capacity, Enclosed, Ground-level Flare

energy consumption for this example is a combustion air blower and a vapor purging system.[45]

Since flares are used for emergency operation and as safety devices, it is difficult to predict energy requirements for one single flare, especially one with a large capacity. Smooth and efficient operation of the process is the best guarantee of minimizing energy consumption of a flare system.

3.5.4 Environmental Impact of Flaring

The operation of a flare affects the environment in the following areas: chemical and oxidation emissions, particulate emissions, thermal and visible radiation, and noise. Elevated flares are primarily intended for plant emergencies and are inherently not as efficient in the above areas as new, enclosed, ground-level flares.

Chemical emissions are the direct result of incomplete combustion of the volatile organics contained in the waste gas stream. Carbon monoxide and partially oxidized hydrocarbons such as aldehydes are known to be products of elevated flares. Because of lower design velocities, emission of unburned hydrocarbons is much lower in an enclosed, ground-level flare.[46]

Sulfur compounds, nitrogen compounds, and other undesirable chemicals are also completely oxidized and emitted to the atmosphere. In particular, hydrogen sulfide streams are often routed to flares and burned. SO_x emissions from refinery flares average 27 $lb/10^3$ bbl refinery feed (77 $kg/10^3m^3$).[47]

NO_x emissions from flares are also common due to direct contact of nitrogen with oxygen at the flame temperature.

But NO_x emissions from elevated flares using steam to inject air are lower than for gas-fired burners due to the lower flame temperature. A typical emission rate for a flare system in a petroleum refinery is 19 lb $NO_x/10^3$ bbl refinery feed (54 kg $NO_x/10^3m^3$ refinery feed).[48]

Air must be well mixed with the gas at the point of combustion in a flare or soot will escape from the flare. A smokeless flame is attained when an adequate amount of air is kept well mixed at the point of combustion. This is usually accomplished by injecting steam to provide the needed turbulence.

Other undesirable emissions include thermal and visible radiation. Steam injection can reduce thermal radiation by lowering the flame temperature. Luminosity cannot be completely reduced, but enclosing a ground level flare is desirable, especially in populated areas.

Low frequency combustion noise and high frequency jet noise in flares is an environmental problem for elevated flares in populated areas. The jet noise is not a problem with ground-level flares, and the combustion noise is reduced significantly.[49]

3.6 Other Control Methods

In many instances, the emission of chemically reactive organic vapors may be completely avoided. Compounds of low photochemical reactivity can sometimes be substituted for highly-reactive compounds currently in use. While the total organic emissions would not decrease and could increase, the substitution of nonreactive or less reactive organic compounds could reduce urban photochemical oxidant formation. Few volatile organic compounds are of such low photochemical reactivity that they can be ignored in oxidant control programs.

The most efficient technique for controlling organic emissions is to design processes which produce little or no pollution. Improved operating and maintenance procedures can sometimes substantially reduce or eliminate organic emissions. New process technologies can reduce organic emissions by avoiding inefficient or poorly controlled operations.

3.6.1 Substitution of Less Photochemically Reactive Materials

Most air pollution control strategies applicable to stationary sources of volatile organic compounds (VOC) are patterned after Rule 66 of the Los Angeles County Air Pollution Control District (presently Regulation 442 of the Southern California Air Pollution Control District). Rule 66 and similar regulations incorporate two basic strategies to reduce ambient oxidant concentrations: selective substitution of less photochemically reactive materials, and positive reduction schemes for the destruction or recovery of organic vapors.

Of the small number of VOC which have only negligible photochemical reactivity, several are suspected of posing threats to human health. Only those compounds listed in Table 3.6-1 have been recommended for exclusion from oxidant control under State Implementation Plan regulations. Methylene chloride, benzene, benzaldehyde, acetonitrile, chloroform, carbon tetrachloride, ethylene dichloride, and ethylene dibromide are also only slightly photochemically reactive. However, all except benzaldehyde are possible carcinogens, teratogens, or mutagens. Benzaldehyde forms a strong eye irritant when irradiated. It is not appropriate to encourage or support increased utilization of these compounds.

TABLE 3.6-1. NONTOXIC VOLATILE ORGANIC COMPOUNDS OF NEGLIGIBLE PHOTOCHEMICAL REACTIVITY[50]

Methane
Ethane
1-1-1 Trichloroethane (Methyl Chloroform)
Trichloro-trifluoroethane (Freon 113)

The volatile organic compounds listed in Table 3.6-2 yield significant oxidant only during multiday stagnations. Perchloroethylene, the principal solvent employed in the dry cleaning industry is also of low reactivity. It was not included in Table 3.6-2 because of its suspected adverse health effects.

TABLE 3.6-2. VOLATILE ORGANIC COMPOUNDS OF LOW PHOTOCHEMICAL REACTIVITY[51]

Propane	Tertiary Alkyl Alcohols
Acetone	Methyl Acetate
Methyl Ethyl Ketone	Phenyl Acetate
Methanol	Ethyl Amines
Isopropanol	Acetylene
Methyl Benzoate	N,N-dimethyl Formamide

Most volatile organic compounds are significantly more reactive than the VOC listed in Table 3.6-2.

3.6.2 Process Operation and Material Changes

Process operation and material changes are the most diverse options available for control of organic emissions. In general, there are three types of possible changes: 1) material substitutions, in which alternate materials are used in the process or products of the process are reformulated; 2) process changes, in which certain operations of the process are modified, and 3) housekeeping and maintenance procedure changes. Each type of change is best illustrated by examples.

Material substitutions are intended to reduce volatile organic emissions by replacing materials used in the process with less volatile or nonreactive compounds. For example, organic emissions from surface coating operations can be significantly reduced by replacing conventional organic solvent-borne coatings with water-borne, high solids, or powder coatings. Water-borne coatings can be applied with most of the same methods used for organic solvent-borne coatings. Water-borne spray coating solvent contains 20 to 30% organic solvent; thus, volatile organic emissions cannot be completely eliminated.

Process changes reduce organic vapor emissions by using raw materials more effectively. For example, organic emissions from surface coating can be reduced by adopting more efficient coating application methods or by changing curing techniques. Electrostatic spray coating, electron beam curing, and ultraviolet curing reduce emissions by limiting solvent contact with air. Most uses of electron beam and ultraviolet curing are still in the developmental stage.[52]

Improved maintenance procedures and "good housekeeping" reduce volatile organic emissions by preventing leaks and spillage and by improving produce yield. For example, emissions from process heaters and steam boilers can be minimized by maintaining the fuel-to-air ratio at the optimum level. Vapor leaks from pumps and valves can be reduced by increasing routine maintenance and inspections. Conscientious preventive maintenance can minimize fugitive emissions from process and auxiliary equipment.

3.7 References

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4.0 CONTROL SYSTEMS FOR INDUSTRIAL PROCESSES

This section describes volatile organic emissions and control technology for 18 industrial operations. Processing methods and equipment are described in enough detail to indicate how emissions are produced. Emission quantities and compositions are described. Currently applied control technology and other applicable control methods are discussed. The efficiency of current and potential control methods is addressed. General discussions of energy requirements, costs, and environmental impacts of control methods are covered in Section 3.0. Information for specific processes, when available, is presented in this section.

The 18 operations described in this section are not the only sources of volatile organic emissions. They are the sources for which information is available. Some are described more completely than others. The extent of coverage depends on the availability of information for each operation.

The first section, 4.1, describes emission sources common to the petroleum and chemical processing industries. The following 18 sections, 4.2. through 4.19, are separate discussions of each class of industrial operations. References are given at the end of each section.

4.1 Emission Sources Common to the Petroleum and Chemical Process Industries

Petroleum and Chemical Process Industries (PCPI) include oil and gas production, gas processing, oil refining, and organic chemicals processing. There are several sources of volatile organic emissions found in all areas of the PCPI. Typical examples are listed in Table 4.1-1. Most emissions are the result of accidents, poor planning, inadequate maintenance, or simply normal leakages.

TABLE 4.1-1. EMISSION SOURCES COMMON TO THE PETROLEUM AND CHEMICAL PROCESS INDUSTRIES

Storage Tanks[a]
Wastewater Treatment[b]
Cooling Towers
Compressor Engines
Stationary Fuel Combustion
Valves
Flanges and Other Connecting Devices
Pump and Compressor Seals
Pressure Relief Devices
Drains, Sumps, Hot Wells
Blind Changing
Sampling
Uncontrolled Blowdown

[a] Discussed in Section 4.5

[b] Discussed in Section 4.15.

Refineries and Organic Chemical Plants

Volatile organic emission rates vary greatly among refineries and chemical plants. These variations are caused by differences in feedstocks, products, processing complexity, and applications of control measures. In general, any hydrocarbon found in a process stream can be emitted from one or more of the common sources. The two largest sources are storage and fugitive leaks.

Oil and Gas Production/Gas Processing

Emissions from oil and gas production usually contain saturated, lower molecular weight hydrocarbons. Fugitive losses account for most of the hydrocarbon emissions. One study estimated that 89% of the hydrocarbon emissions at an oil production facility were due to leaks.[1] Gas losses of 0.22% of the gas produced are attributed to wellsite leaks.[2] Natural gas production has an especially high fugitive emission potential because of high pressures, the corrosiveness of hydrogen sulfide and water, and the gaseous nature of the products. Since most installations are in remote locations maintenance is sometimes infrequent. Natural gas processing plants are essentially miniature refineries, but they have a lower fugitive emission potential because they employ simpler process schemes and lower processing temperatures.

Two other common sources that have slightly more significance for oil and gas production than for oil or chemical processing are internal combustion engines and flares. Natural gas production requires numerous compression steps. Many of the field compressors use internal combustion engines. Also, uncontrolled blowdown and flaring of gases is practiced more in oil production than in the other operations. Excess gas produced with the oil is often unneeded onsite and uneconomical to transport. It is usually disposed of by venting or flaring.

Each of the thirteen emission sources listed in Table 4.1-1 is described separately in the following Sections 4.1.1 through 4.1.13. Emission characteristics; control technology; and cost, energy, and environmental impacts of controls are described. References are given in Section 4.1.14.

4.1.1 Storage Tanks

Various types of tanks are used for the storage of products and feedstocks in every area of the PCPI. Emissions from storage tanks are discussed in Section 4.5.

4.1.2 Wastewater Treatment

Wastewater treatment facilities exist in all phases of oil, gas, and chemical production and processing. They are discussed in Section 4.15.

4.1.3 Cooling Towers

Petroleum refineries, chemical plants, and gas processing plants use large quantities of water for cooling. Before the water can be reused, the heat (abosrbed in heat exchangers) must be removed. This is usually accomplished by allowing the water to cascade through a cooling tower, where it is contacted countercurrently with a stream of air. Evaporation removes sensible heat from the water, and warm, wet air leaves the top of the tower. The cooled water collects in an open basin at the bottom, from which it is recirculated through the process water system.

4.1.3.1 Emission Characteristics

During processing, volatile organics may leak into the cooling water system. These organics may then be stripped by air in the cooling tower and emitted at the top of the tower and from the basin. Emissions can include any organic processed within the plant. Hydrocarbon emissions from cooling towers in petroleum refineries have been estimated to be 700 mg/m^3 of cooling water (6 lb/10^6 gal water). It is emphasized that these emissions vary widely.

4.1.3.2 Control Technology

Cooling tower emissions can be best controlled at the point where they enter the cooling water, at the leaking heat exchangers. Hence, systems for detection of contamination in water, proper exchanger maintenance, speedy repair of leaks, and good housekeeping programs, in general, are necessary to minimize the emissions occurring at the cooling tower.

4.1.3.3 Cost, Energy, and Environmental Impacts of Controls

Maintenance and good housekeeping are already performed in many plants. Costs are the cost of labor for inspection and the cost of materials for repairs or maintenance. Credits are received for product recovery and improved process operations. Increased plant safety is an additional benefit.

Minimal energy is expended for inspection or maintenance. An indirect energy credit is received in the form of recovered organic products. The net result is a positive energy impact.

Costs for monitoring equipment to detect organic contamination in water range between \$3500 and \$10,000.[4] Energy requirements should be minimal.

No secondary environmental impact will be produced by the above control methods.

4.1.4 Compressor Engines

Many older refineries, organic chemical plants, gas processing plants, and gas producing fields use internal combustion engines fired with natural gas or low molecular weight refinery gas to run high-pressure compressors. The largest numbers are found in gas production/processing operations.

Internal combustion engines are less reliable and harder to maintain than those driven by steam or electricity.[5] Future use of internal combustion engines will probably decline because of problems with the cost and availability of natural gas as well as environmental regulations.

4.1.4.1 Emission Characteristics

Internal combustion engines have inherently high volatile organic emissions. Volatile organic emissions from internal combustion engines fired with refinery fuel gas are approximately 220 mg/m^3 fuel (1.4 lbs/10^3 scf fuel).[6] Further discussion is found in Section 4.13 on combustion sources.

4.1.4.2 Control Technology

The major means of controlling emissions from this source is carburetion adjustments similar to those applied to automobile engines for emission control. Further discussion of combustion source controls is given in Section 4.13.

4.1.4.3 Cost, Energy and Environmental Impact of Controls

Proper carburetion adjustment will maximize fuel combustion efficiency. Maintenance costs may be more than compensated by savings in fuel consumption. Further discussion of energy, costs and environmental impact for combustion source controls is provided in Section 4.13.

4.1.5 Stationary Fuel Combustion

Heat is produced for use in many phases of the PCPI by combustion of fuel. Process heaters and steam boilers can be found in chemical plants, gas processing plants, and refineries. They are discussed in Section 4.2 (Petroleum Refineries). Heater-treaters are used to aid in oil-water separations in field production operations and are described in Section 4.3.

4.1.6 Pipeline Valves

Large numbers of pipeline valves are associated with every type of equipment used in the PCPI. Although many types exist, they perform one of three functions:

- On/off flow control and throttling,
- flowrate control (control valves), or
- flow direction control (check valves).

Almost all check valves are enclosed within the process piping, but their top access connections to working parts may be sources of fugitive emissions. All other valves consist of internal parts connected to an external actuator by means of a stem. A packing is used to prevent process fluid from escaping from the valve. On/off and throttling valves are actuated by the operation of a handwheel or crank. Control valves are automatically operated, often by air pressure.

4.1.6.1 Emission Characteristics

Under the influence of heat, pressure, vibration, friction, and corrosion, leaks can develop in the packing surrounding the stem. Liquid leaks drop to the ground or nearest surface and vaporize at a rate dependent upon volatility and ambient conditions. The average leak rate from valves is 0.07 kg/day-valve (0.15 lb/day-valve). The factor expressed in terms of refinery throughput is 0.08 kg/10^3 liters refinery feed (28 lb/10^3 bbl refinery feed).[7] The valves tested had very diverse rates of leakage.

4.1.6.2 Control Technology

Emissions originating from product leaks at valves can be controlled only by regular inspection and prompt maintenance of valve packing boxes. Because of its dependence on the nature of the products handled, the degree of maintenance, and the characteristics of the equipment, the level of emission reduction achievable by such programs is difficult to estimate.

4.1.6.3 Cost, Energy, and Environmental Impact of Controls

Inspection and maintenance of valve packing boxes are routinely performed by many industries. A discussion of maintenance and good housekeeping is provided in Section 4.1.3.3.

No secondary environmental impact will be produced by these control methods.

4.1.7 Flanges and Other Connecting Devices

Process piping can be joined to process vessels and equipment or to other lengths of piping in as many as 17 different ways.[8] There are, however, three principal types of joints found in petroleum and chemical operations:

- threaded fittings,
- flanges, and
- welds.

Threaded fittings are connecting devices into which threaded lengths of pipe are screwed. They are most commonly used for pipes of 5 cm (2 inch) diameter or smaller. Threaded joints are more common in field production operations than in processing plants.

Flanges are removable connections consisting of circular discs (faces) attached to the outer circumference of pipe ends. A gasket forms the seal between the pipe ends and is held in place by bolts connecting the two flange faces. Flanges are the most common connecting devices used in refineries and chemical plants.

Welds are employed to connect pieces of pipe when disassembly will not be needed. Welding produces a seal almost as strong as the pipe itself and is desirable wherever practical.

4.1.7.1 Emission Characteristics

The influences of heat, pressure, vibration, friction, and corrosion can cause leakage in connectors. Of the three kinds of connectors described, threaded fittings that have been frequently assembled and disassembled are most prone to leaks. Welds are virtually leakproof because they are rigid connections less susceptible to the effects of vibration, etc., that disturb the original seal. Flanges can leak if the gasket material is damaged or the flange is not aligned properly or because of seal deformation due to thermal stresses on the piping system. However, in a study of oil refineries in California, flanges were found to be a negligible source of emissions.

4.1.7.2 Control Technology

Emissions from product leaks at flanges and threaded fittings can be controlled by regular inspection and prompt maintenance.

4.1.7.3 Cost, Energy, and Environmental Impact of Controls

Inspection and maintenance of flanges and threaded fittings are routinely performed by many industries. A discussion of maintenance and good housekeeping is provided in Section 4.1.3.3.

No secondary environmental impacts will be produced by these controls.

4.1.8 Pump and Compressor Seals

Pumps and compressors can leak at the point of contact between the moving shaft and the stationary casing. If volatile, the leaked product will evaporate to the atmosphere. Examples of nonleaking pumps are completely enclosed or "canned" pumps in which there are no seals, diaphragm pumps in which a flexible diaphragm prevents the product from contacting the working parts of the pump, and pumps with magneto-magnet drivers and no seals.

The most common types of pumps used in the PCPI are centrifugal and reciprocating pumps. The seals normally used on them are mechanical or packed. Packed seals consist of a fibrous packing between the shaft and casing wall. Mechanical seals consist of two plates situated perpendicular to the shaft and forced tightly together. One plate is attached to the shaft and one is attached to the casing. Packed seals can be used on reciprocating or rotating shafts; mechanical seals are for rotating shafts only.

4.1.8.1 Emission Characteristics

A study of Los Angeles County refineries found centrifugal pumps with packed seals lost 2.2 kg of hydrocarbons/day-seal (4.8 lbs/day-seal), centrifugal pumps with mechanical seals lost 1.4 kg/day-seal (3.2 lbs of hydrocarbons/day-seal), reciprocating pumps with packed seals lost 2.3 kg hydrocarbons/day-seal (5.4 lbs of hydrocarbons/day-seal), and compressors lost 4.1 kg/day-seal (8.5 lbs of hydrocarbons/day-seal). On an overall refinery basis, these hydrocarbon emissions amount to 50 g/m^3 (17 lb/1000 bbl) refinery feed for pumps and 14 g/m^3 (5 lb/1000 bbl) refinery feed for compressors.[9] Pump seals are one of the principal sources of emissions in oil production operations. They contributed 68% of the hydrocarbons emitted from one California oilfield.[10]

4.1.8.2 Control Technology

Both packed and mechanical seals inherently leak but emissions from centrifugal pumps can be reduced 33% by replacing packed seals with mechanical seals. Emissions from dual mechanical seals can be eliminated by using a circulating, inert fluid between the two seals at a pressure higher than that on the process fluid side of the pump; thus, any leakage is of inert fluid into the process stream. According to several oil producers, the highest temperatures in which mechanical seals can be used ranges from 210-330°C (410-608°F). Emissions from reciprocating pumps can be controlled by installation of dual packed seals with provisions to vent the volatile vapors that leak past the first seal into a vapor recovery system.

As mentioned previously, diaphragm, canned, and magnet-drive pumps are not subject to leaks. In a few circumstances, installation of one of these pump types can be a cost-effective means of eliminating emissions.

Emissions from any kind of pump or compressor seal can be minimized by frequent inspection and corrective maintenance.

4.1.8.3 Cost, Energy, and Environmental Impact of Controls

According to a recent estimate, the cost for installing a mechanical seal on an existing pump, including a cooler, labor, and materials, is about $2000-2500.[11] The cost will be lower if a cooler is not required. Current trends indicate that mechanical seals are becoming more economical as a result of a huge increase in sales volume and greater standardization of sizes.[12] Total costs for a plant are hard to predict, since the number of pumps for which a changeover is indicated will vary from plant to plant. Some of the capital cost will be compensated by a cost benefit from product recovery.

No cost information for dual seals is available from the sources consulted. A price comparison of the different types of pumps is difficult. The suitability of a pump will vary according to the specific application.

No secondary environmental impact will be produced by these controls.

4.1.9 Pressure Relief Devices

The build-up of dangerously high pressures in process units and storage vessels is avoided by use of pressure relief devices. These include pressure relief valves (liquid), safety valves (gas), and safety hatches (gas). The main difference between liquid and gas service valves is that liquid valves open in proportion to the amount of excess pressure applied, while safety valves pop fully open whenever the set pressure is exceeded. The valves discharge to a blowdown system, a vapor recovery system, or the atmosphere.

4.1.9.1 Emission Characteristics

Fugitive emissions from pressure relief devices occur when a valve not vented to an enclosed system seats improperly due to damage, wear, or corrosion of the seat or gasket. Therefore, emissions are very dependent on the frequency and quality of maintenance. Surveys indicate hydrocarbon leaks from relief valves on refinery process vessels average 1.3 kg/day-valve (2.9 lb/day-valve). Leaks from relief valves on pressure storage tanks average 0.3 kg/day-valve (0.6 lb/day-valve). The storage tanks had a higher incidence of leaks than the process vessels. The average total quantity of volatile organics leaked from refinery relief valves was 1.1 kg/day-valve (2.4 lb/day-valve).[13]

4.1.9.2 Control Technology

Emissions from pressure relief devices can be controlled by manifolding to a vapor control device or a blowdown system.[14] For valves where it is not desirable, because of convenience or safety aspects, to discharge into a closed system, flanged blanks called rupture discs can be installed before the valve. Rupture discs prevent the pressure relief valve from leaking and protect the valve seat from corrosive environments.[15] Care must be taken in the selection and use of rupture discs because they can affect the operation of the relief device they are supposed to protect. Monitoring and proper maintenance are also important control techniques.

4.1.9.3 Cost, Energy, and Environmental Impact of Controls

Blowdown systems are discussed in Section 4.1.13. Installation costs will depend on the length of piping required to connect the system.

According to estimates by one oil producer, cost of rupture disks in 1975 in a refinery was \$1000-1500 per installation.[16] Total costs for a plant will vary depending on the number of installations. Some portion of the capital cost will be compensated by a cost benefit from product recovery.

The only secondary environmental impact will be associated with a blowdown system, as discussed in Section 4.1.13. Flaring products containing sulfur may produce SO_x emissions. Flaring also has the potential to produce CO and NO_x emissions.

4.1.10 Wastewater Drainage System

A refinery or chemical plant wastewater system treats water from a number of sources. Aqueous waste streams include cooling water, process water and steam condensates, storm runoff, blowdown water, sanitary wastes, and ship ballast water. These streams are usually segregated into separate flow channels. Organics can enter these aqueous streams through leaks in process units, spills, sampling, blind changing, and turnarounds.

4.1.10.1 Emission Characteristics

Every element of the drainage system that handles organics-contaminated wastewater is a fugitive emissions source.

Organics can evaporate from the large surface areas present in the drainage ditches, oily water sumps, oil-water separators, and open basins. Manholes on the sewer boxes also allow organics to escape. Every organic processed by the plant is a potential source of fugitive emissions from the wastewater drainage system.

4.1.10.2 Control Technology

Emissions from wastewater drainage systems can be reduced through minimizing the contamination of water with organics and by enclosing some of the wastewater collection and treatment systems. Proper inspection and maintenance is necessary to minimize organics contamination of the water. Manhole covers can be installed on all sewer and junction boxes. In some cases it may be practical to vent enclosed systems to vapor recovery units. Whenever systems are enclosed, care would have to be taken to avoid risk of explosion.

4.1.10.3 Cost, Energy, and Environmental Impact of Controls

Costs for enclosing a wastewater system will be site specific. Retrofitting in older plants might require extensive modifications. In some cases, all existing facilities may have to be replaced.

The buildup of explosive concentrations in a covered system must be avoided. It may be necessary to vent to a blowdown system, as discussed in Section 4.1.13. Vapor recovery units, if used, will provide a cost benefit from product recovery. Flaring of material containing sulfur may produce SO_x emissions. Flaring also has the potential to produce CO and NO_x emissions.

Oily wastewater treatment is discussed further in Section 4.2.3.

4.1.11 Blind Changing

Process plant operations sometimes require that a pipeline be used for more than one product. To prevent leakage and contamination of a particular product, other product-connecting or product-feeding lines are customarily "blinded off." Blinding a line involves inserting a flat solid plate between two flanges of a pipe connection. Spillage of product can occur when the blind is inserted or withdrawn.

4.1.11.1 Emission Characteristics

The magnitude of emissions from product spillage during blind changing is a function of the spilled product's vapor pressure, type of ground surface, distance to the nearest drain, and amount of liquid spilled. A survey of refineries in Los Angeles County[17] determined that in 1958 hydrocarbon emissions from blind changing varied greatly. A two-month log of emissions there indicated an average emission rate of 1.0 g/m^3 (0.29 $lb/10^3$ bbl) of feed.[18]

4.1.11.2 Control Technology

The most prevalent form of control is the double block and bleed valve. This replaces the blind and does not allow product spillage. Any bleed valve effluent is sent to oily wastewater treatment. This technology is currently in use in many U.S. refineries and chemical plants.

Frequently, double block and bleed valves are not suitable substitutes for blinds. If blinds must be used, emissions from changing of the blinds can be minimized by pumping out the pipeline and then flushing the line with water before breaking the flange. Spillage can also be minimized by the use of special "line" blinds in place of the common "slip" blind. The survey of Los Angeles County refineries indicated that spillage from line blinds was 40% of the spillage for slip blinds. In addition, combinations of line blinds in conjunction with gate valves allow changing of line blinds while the pipeline is under pressure.[19]

4.1.11.3 Cost, Energy and Environmental Impact of Controls

Cost information for double block and bleed valves or "line" blinds is unavailable in the consulted literature. No energy is required for either control technique. Oily wastewater treatment is discussed in Section 4.2.3. Product recovery from separators and/or vapor recovery units provides a cost credit and an indirect energy credit.

Many plants already pump out and flush pipelines before changing blinds. Cost are the cost of labor and the capital cost for pumps and associated collection equipment. Energy is required for pump operation. At least a portion of the costs and energy requirement is compensated by credits from recovered products. This control technique may also be justifiable in terms of plant safety.

Water used to flush pipelines may be heavily contaminated with organics. It must be sent to the plant wastewater system before disposal (see Sections 4.1.10 and 4.2.3). Large volumes of water may overload a plant's system and result in pollution of plant effluent water.

4.1.12 Sampling

The operation of process units is constantly checked by routine analysis of feedstocks and products. Samples are usually collected by opening a small valve on a sample line and collecting a certain volume of the liquid. In large chemical plants and refineries there are hundreds of sampling points throughout the installation.

4.1.12.1 Emission Characteristics

One of the greatest emission sources during sampling is line flushings or purgings. Since the sample tap is used frequently, it is generally located conveniently at ground level. This often necessitates use of a long sampling line. To obtain a sample representative of current operations, the operator must flush out the volume of the sample line before filling his sample container. Liquid line flushings are often collected in an open bucket; gas purges are vented to the atmosphere. There is ample time for evaporation of the volatile components from the liquid material before it is dumped.

In plants manufacturing hazardous chemicals, closed loop sampling is employed. In this method, sample taps are placed across a pump or other source of pressure drop. This allows the flushing stream to return to the process.

Studies in oil refineries have found that hydrocarbon emissions from excessive purging of sampling lines can amount to 140-280 g/m^3 (50-100 $lbs/10^3$ bbl) of refinery feed,[20] but generally average 6.6 g/m^3 (2.3 $lbs/10^3$ bbl) of refinery feed.[21]

4.1.12.2 Control Technology

One means for controlling the emissions generated by purging sampling lines is the installation of drains and flushing facilities at each sample point. Conscious efforts to avoid excessive sampling in addition to flushing sample purges into the drain have a significant impact on the emissions from sampling operations. Closed loop sampling is a technique that could be applied to all aspects of the PCPI, as it is in hazardous chemicals manufacture.

4.1.12.3 Cost, Energy, and Environmental Impact of Controls

Costs for the installation of drains and flushing facilities will be site specific. Cost information for closed-loop sampling is unavailable from the sources consulted. Energy requirements will be minimal. For either system, costs and energy are at least partially compensated by credits from product recovery. Recovery is better from closed-loop sampling than from wastewater treatment of sampling line purges.

If wastewater is adequately treated, there will be no environmental impact from these controls.

4.1.13 Uncontrolled Blowdown Systems

A blowdown system is a set of relief devices, piping, and/or vessels used to discharge or collect gaseous and liquid material released during process upsets or turnarounds. In uncontrolled blowdown systems, gases and vapors are vented unburned into the atmosphere. Uncontrolled venting is more common in oil and gas production operations because of the lack of need for excess gas at oil wells, or because of the remoteness of the production site. One estimate states that 20% of the vented production gas is vented without burning.[22]

4.1.13.1 Emission Characteristics

Emissions from uncontrolled refinery blowdown systems have been estimated to be as much as 1.66 kg/m^3 (580 lb hydrocarbon/10^3 bbl) feed.[23] Because blowdown systems receive material from all processing units within the plant, any volatile hydrocarbons found in the process streams could be emitted from the blowdown system. Those from production and gas processing operations are primarily lower molecular weight, saturated hydrocarbons.

4.1.13.2 Control Technology

Blowdown emissions can be effectively controlled by venting into an integrated vapor-liquid recovery system. All units and equipment subject to shutdown, upsets, emergency venting, and purging are manifolded into a multi-pressure collection system for flaring or reprocessing. Discharges into the collection system are segregated according to their operating pressures. A series of flash drums and condensers arranged in descending pressures separates the blowdown into vapor pressure cuts. Such an extensive system might be impractical for some facilities such as offshore production locations where space is very limited. Emissions from controlled blowdown systems have been estimated to be 2.0 g/m^3 of refinery capacity (0.8 lb/10^3 bbl).[24]

4.1.13.3 Cost, Energy, and Environmental Impact of Controls

Condensers and flares are discussed in Sections 3.4 and 3.5. Vapor recovery may also be based on adsorption or absorption, as discussed in Sections 3.2 and 3.3. Energy requirements and costs will be site specific. Smokeless flares will require extra energy for the production of steam (about 1.3 MJ/kg or 560 Btu/lb of organic flared).[25]

Controls for a blowdown system are already employed in several refineries. For these applications they may be justifiable for the cost credit and indirect energy credit from product recovery or for plant safety. This may not be true for other industries in the PCPI or small refineries with less product to recover.

Flaring of any material containing sulfur may produce emissions of SO_x. Flaring also has the potential to produce CO and NO_x emissions.

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4.2 Petroleum Refining

The petroleum refining industry converts crude oil into more than 2500 refined products including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry. Petroleum refinery activities start with crude storage at the refinery, include all petroleum handling and refining operations, and terminate with storage of the refined products at the refinery.

The petroleum refining industry employs a wide variety of processes for the conversion of crude oil to finished petroleum products. The processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 4.2-1 shows the general arrangement used by U.S. refineries for major refinery processes. Few, if any, refineries employ all these processes.

In general, refinery processes and operations can be divided into five categories: separation processes, conversion processes, treating processes, product handling, and auxiliary facilities. The processes comprising each of these categories are presented in the following sections.

Petroleum Separation Processes

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using atmospheric distillation, vacuum distillation, and light ends recovery. Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons

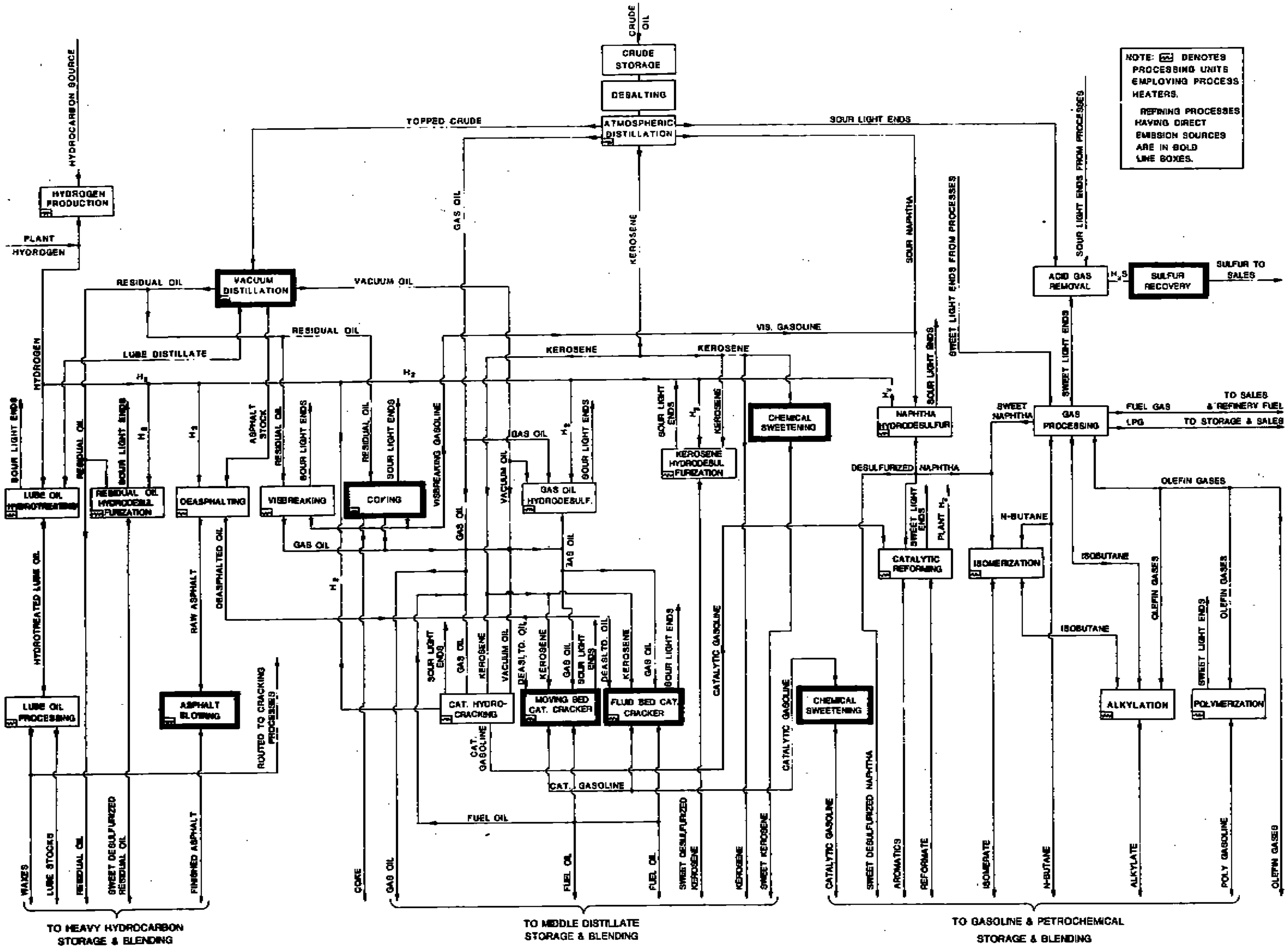

Figure 4.2-1. Schematic of a typical integrated petroleum refinery.

plus small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes use distillation, stripping, and absorption to separate these crude oil constituents into common boiling point fractions.

Petroleum Conversion Processes

Product demand and economic considerations require that less valuable components of crude oil be converted to more valuable products using cracking, reforming and alkylation processes. To meet the demands for high octane gasoline, jet fuel, and diesel fuel, low value residual and fuel oil components are often converted to gasoline and lighter fractions.

Petroleum Treating Processes

Petroleum treating processes convert olefins and diolefins to saturated hydrocarbons, separate fractions for further processing, and remove objectionable elements. Treating also includes gasoline treating processes such as caustic washing, acid treating, copper sweetening, hydrogen treating, etc. Objectional elements removed from petroleum liquids include sulfur, nitrogen, oxygen, halides, and metals. Separation includes aromatics extraction, deasphalting, dewaxing, and deoiling.

Feedstock and Product Handling

The refinery feedstock and product handling operations consist of storage, blending, loading, and unloading activities. All feedstocks entering the refinery and all products leaving the refinery are subject to the refinery handling operations.

Auxiliary Facilities

Auxiliary facilities include a wide assortment of processes and equipment which are not directly involved in the refining of crude oil, but which perform functions vital to the operation of the refinery. These include boilers, wastewater treatment, hydrogen plants, sulfur recovery units, and cooling towers. Products from auxiliary facilities (clean water, steam, process heat, etc.) are required by the majority of refinery process units.

Emission Sources

Sources of hydrocarbon emissions found in petroleum refineries are listed in Table 4.2-1. Included in this table are sources common to the petroleum and chemical industry. These are discussed in Section 4.1. Control methods and cost, energy, and environmental impact of control are presented in the following Section 4.2.1 through 4.2.13.

4.2.1 Pressure Relief Systems

Pressure relief systems are common to many operations in the petroleum and chemical industries, and are presented as a common source of emissions in Section 4.1.9.

4.2.2 Blowdown Systems

Blowdown systems are found in many phases of the petroleum and chemical industries, and are described in Section 4.1.13.

TABLE 4.2-1. HYDROCARBON EMISSION SOURCES FOUND IN PETROLEUM REFINERIES

Pressure Relief Systems[a]
Blowdown Systems[a]
Oil-Water Effluent Systems
Pumps and Compressors[a]
Pipeline Valves and Flanges[a]
Vacuum Jets
Air Blowing
Cracking Catalyst Regeneration
Boilers and Process Heaters
Chemical Treating
Compressor Engines[a]
Miscellaneous Catalyst Regeneration
Blending
Coking
Cooling Towers[a]
Compressor Engines
Drains, Sumps, Hot Wells[a]
Blind Changing[a]
Sampling[a]
Storage[b]

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[a] See Section 4.1

[b] See Section 4.5

4.2.3 Oil-Water Effluent Systems

Oil-water effluent systems found in refineries include drainage systems and primary wastewater treatment facilities. This section deals only with the primary treatment of oily wastewaters; drainage systems are discussed in Section 4.1. Oil-water separation equipment includes API separators, corrugated plate interceptors, flocculation units, and dissolved air flotation (DAF) units.

The API separator is one of the major units employed for separation of oil from refinery wastewater. It is simply a gravity settling device in which oil is skimmed from the liquid surface and suspended solids are removed from the bottom. Separation efficiency can vary from 50 to 100% depending on the physical characteristics of the oil. Corrugated plate interceptors (CPI) operate on the principle that the controlling parameter for oil-water separation is the surface area per unit flow. CPI equipment provides surface area for oil-water contact with parallel plates of corrugated material. The CPI design generally provides better separation capability in a smaller space than the API separator.[1]

Flocculation is a technique in which oil and organic particles in wastewater are agglomerated by flocculating agents in order to improve settling characteristics. Two common flocculants are alum and polyelectrolytes. Polyelectrolytes are polar, synthetic, water soluble organic polymers of high molecular weight.[2] While flocculation gives excellent removal of oil and the added advantage of removal of other particulates, it also involves higher capital and operating costs than the CPI unit or API unit.[3]

Air flotation is a waste treatment process in which air is dissolved into the water to aid in oil-water separation. In some units, air is induced into the waste by surface agitation or transfer from vessel to vessel through venturis. In others, air under pressure (approximately 0.28 MPa or 40 psig) is dissolved in the wastewater. When the pressure is released, millions of fine air bubbles less than 100 μm (0.004 in.) in diameter attach themselves to the oil, causing it to rise to the surface for removal.

4.2.3.1 Emission Characteristics

Emissions from oil-water effluent systems primarily result from the evaporation of volatiles from liquid surfaces open to the atmosphere. Such surfaces exist in uncovered API separators, corrugated plate interceptors, and DAF units. Those separators with a fixed roof and vapor space are also subject to leaks at sampling and maintenance hatches and vents. Floating roof-equipped separators can also leak around hatches and vents, as well as around the roof seal, but the lack of a vapor space eliminates much of the emission potential.

Studies of refineries in Los Angeles County indicate that hydrocarbon emissions from sumps, drains, and API separators range from 30 g/m^3 to 600 g/m^3 capacity (10-200 lb/1000 bbl capacity), with an average emission rate of 2700 kg/day (3 tons/day).[4] A 1972 estimate set average nationwide emissions of hydrocarbons from refinery wastewater systems at 0.3 kg/m^3 refinery feed (105 lb/1000 bbl).[5] These emissions can contain any volatile hydrocarbon processed in the refinery.

4.2.3.2 Control Technology

The primary methods of controlling emissions from oil-water effluent systems are minimization of the quantity of oil leaked to the systems and enclosure of all system components. The benefits of the first method are obvious. Enclosure of system components can be accomplished by using floating roofs. Another method is to vent fixed-roof units to blowdown or vapor recovery systems. Another technique that has received limited application is floating an insulating material such as fiberglass foam slabs on the surface of the oil.

Hydrocarbon emissions from API separators can be reduced to 3 g/m^3 capacity (0.01 lb/bbl) by use of floating roofs on API separators.[6] A reduction in emissions to approximately 7 kg/m^3 (23.3 lb/bbl, 2 vol%) has been achieved by the insulation technique.[7] Floating roofs are recommended over fixed roofs because they do not have a vapor space in which explosive mixtures can form.

4.2.3.3 Cost, Energy, and Environmental Impact of Controls

Costs for installing floating roofs, including labor and materials, usually are more than compensated by the cost benefit from product recovery. However, in some cases an existing separator cannot be covered effectively and a new facility would have to be built to accommodate the floating roof. Table 4.2-2 lists capital and annual costs for the installation of floating roofs on API separators in three different size refineries.

TABLE 4.2-2. TYPICAL COSTS FOR FLOATING ROOFS ON API SEPARATORS[a, 8]

Refinery Size	Capital Costs ($)	Annual Costs ($/Yr)[b]
1,590 m^3/s day (10,000 bbl/s day)	27,800	-6,670
9,840 m^3/s day (61,900 bbl/s day)	82,800	-65,830
31,800 m^3/s day (200,000 bbl/s day)	167,300	-240,710

[a] Costs are based on several assumptions. See original reference for bases of estimates.

[b] Negative signs indicate that savings from the recovered product exceed the annual cost.

Installation of fixed roofs was estimated to cost about \$135.00/m^2 (\$12.5/ft^2), including labor and materials. The capital cost is about \$62,800 for a typical 16000 m^3/day (100,000 bbl/day) refinery.[9] This estimate does not include the cost of a vapor recovery system. General discussions of costs for vapor recovery and blowdown systems are provided in Section 3.0 and 4.1.13. As with floating roofs, a cost credit is produced by product recovery. Specific information is not available in the consulted literature.

There is no energy required for the use of floating roofs. Fixed roofs, however, require energy for the operation of associated vapor recovery or blowdown systems. General discussions of these energy requirements are presented in Sections 3.0 and 4.1.13. For both types of roofs, an indirect energy credit will be provided by recovery product.

The use of floating roofs produces no secondary environmental impact. Use of fixed roofs may result in SO_x emissions if any organic materials containing sulfur are flared in blowdown systems or fuel gas systems and incineration in furnaces, waste heat boilers, or incinerators. Vapor recovery units recover condensible hydrocarbon vapors and return them to process streams. Incineration is accomplished by catalytic or direct flame combustion.

Oily condensate emissions can be eliminated by use of mechanical vacuum pumps or surface condensers which discharge to a closed drainage system. Neither of these alternate vacuum systems, however, are effective at reducing non-condensibles emissions.

Both noncondensibles and oily condensate can be minimized by the installation of a lean-oil absorption unit between the vacuum tower and the first stage vacuum jet.[12] The rich oil effluent is used as charge stock and is not regenerated.

The maximum degree of control attainable for the hydrocarbon vapors from vacuum jets equipped with barometric condensers is effectively 100%.[13]

4.2.6.3 Cost, Energy, and Environmental Impact of Controls

The cost for controls will vary widely depending on the quantity of vapor produced and the maximum summer water temperature. A water quench with higher temperature water will result in richer vapors. According to API, costs for installation of a lean-oil absorption unit are only justifiable for treating streams containing large quantities of non-condensibles.[14]

General discussions of incineration and vapor recovery are presented in Section 3.0. Costs for one installation, including a compressor, piping to the nearest firebox, and a suitable burner, amounted to approximately $50,000. Costs for a condensate receiver for a surface condenser were not included. The system was designed to handle 1 Mg/hr (2,200 lbs/hr) of non-condensibles from a vacuum distillation column treating 6,200 m^3/sday (39,000 bbls/sday).[15] The energy requirement for a compressor will be more than compensated by the energy gained from the incineration of recovered vapors.[16]

Incineration of any material containing sulfur may produce SO_x emissions. Incineration also has the potential to produce CO and NO_x emissions.

4.2.7 Air Blowing

There are currently two refinery processes in which air is blown through petroleum products. These are brightening (moisture removal) of gas oil products (diesel fuels, furnace oil) and air oxidation of asphalt. Gas oil brightening is a physical stripping of moisture from the petroleum liquid; asphalt blowing is a high temperature oxidation process. Both produce an exhaust air containing hydrocarbons and aerosols.

Air blowing of gas oils is accomplished in standard packed towers or vessels. The air is blown countercurrent to the oil and strips the moisture from it. Operating temperatures are usually low to minimize hydrocarbon vaporization and to prevent product oxidation or degradation. The exhaust air stream contains primarily the lighter hydrocarbon components of the gas oil.

Asphalt blowing processes oxidize residual oils (asphalts containing polycyclic aromatics) in order to increase their melting temperature and hardness. Both batch and continuous processes are employed. Fresh feed and recycle are heated to approximately 260°C (500°F) and charged to a vertical vessel. Pressurized, preheated air (200-310°C or 390-590°F) is charged into the bottom of the vessel through a sparger. The reaction is exothermic, and quench steam is sometimes required for temperature control. In some cases, ferric chloride or phosphorus pentoxide is used as a catalyst to increase reaction rate and impart special characteristics to the asphalt.

4.2.7.1 Emission Characteristics

The quantity of hydrocarbon emissions from asphalt-blowing units should be relatively small since the asphalt is distilled at high temperatures before reaching the air-blowing process. Available data indicate that uncontrolled emissions amount to 30 g/kg of alphalt (60 lb/ton), which represents 2-4% of the asphalt charged.[17] The production of asphalt in this manner is limited; therefore, the total emission for the U.S. is considered minor. The operating conditions are favorable for the production of extremely undesirable polynuclear aromatics.

4.2.7.2 Control Technology

Emissions from air blowing can be reduced by vapor scrubbing, incineration, or a combination of both. These are most often found on asphalt-blowing units. Air-blown brightening units have been replaced in many refineries with packed vessels containing solid absorbents.[18] These have no potential for hydrocarbon emissions other than fugitive emissions.

Vapor scrubbers condense steam, aerosols, and essentially all of the hydrocarbon vapors. A disadvantage in water scrubbing is the high volume ratio of water-to-exhaust gas required to remove the hydrocarbons. Values as high as 13.4 dm^3/Nm^3 (100 gal/1000 scf) have been reported.[19]

When an adequate water supply is not available or when condensate handling may result in hydrocarbon emissions, incineration of the vapors by direct flame contact may be used. Incineration may be accomplished in process heaters, boilers or fume burners. Flame temperatures in these devices should be maintained in the range of 680-840 C (1250-1550 F).[20]

Hydrocarbon emissions from a controlled asphalt-blowing unit are negligible.[21]

4.2.7.3 Cost, Energy, and Environmental Impact of Controls

A general discussion of vapor scrubbing is presented in Section 3.0. Specific energy and cost information is unavailable.

According to a 1973 API estimate, costs for installation of an incineration system, including a vapor compressor, piping to an existing firebox, and a suitable burner, amount to approximately $20,000. This system will handle emissions from asphalt production of 16 m^3 (100 bbls)/12 hour day. Energy required for compressor operation will at least in part be compensated by energy gained from incineration of recovered fuel.

A secondary environmental impact may be produced by vapor scrubbing. Additional contamination of wastewater streams will increase the chances of volatile organic emissions from the wastewater treatment system (see Sections 4.1.10 and 4.2.3). Contaminants may be discharged with the plant water effluent stream if the treatment system does not have sufficient capacity to handle the large volumes of scrubbing water.

Incineration of organic material containing sulfur may produce SO_x emission. Incineration may also produce CO and NO_x emissions.

4.2.8 Cracking Catalyst Regeneration

Catalytic cracking uses heat, pressure, and a catalyst to convert heavy oils into lighter products. Product distributions favor the more valuable gasoline and distillate blending components. All of the catalytic cracking processes currently in use can be classified as either fluidized bed or moving bed units.

Fluidized bed catalytic cracking (FCC) uses a catalyst in the form of very fine particles which behave as a fluid when a gas is blown through them. Fresh feed is preheated in a process heater and introduced into the bottom of a verticle transfer line (riser) with hot regenerated catalyst. Most of the cracking reactions take place in the riser as the catalyst and oil mixture flow upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionator for separation.

The spent catalyst falls to the bottom of the reactor, is steam stripped to remove absorbed hydrocarbons as it exits the reactor bottom and is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. The catalyst is mixed with fresh hydrocarbon feed and recycled.

In the moving bed catalytic cracking (TCC) process catalyst beads (5.0 mm, 0.2 in.) flow by gravity into the top of the reactor where they contact a mixed phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section. The catalyst is steam stripped to remove any absorbed hydrocarbons and falls into the regenerator where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases, mixed with fresh hydrocarbon feed, and recycled.

4.2.8.1 Emission Characteristics

The combustion rate in catalyst regenerators is controlled by limiting the air to the regenerator. This causes partial oxidation, leaving CO and some unburned hydrocarbons in the regenerator flue gas.

Regenerator flue gas contains from 100-1500 ppm of hydrocarbons[22] depending on characteristics of the charge and the type of catalytic cracker. Hydrocarbon emissions from FCC regenerators average 630 g/m^3 fresh cat cracker feed (220 lbs/1000 bbl) and hydrocarbon emissions from TCC regenerators average 250 g/m^3 fresh cat cracker feed (87 lbs/1000 bbl).[23] In 1968, the estimated hydrocarbon emissions from FCC regenerators were 130 Gg/yr (143,000 tons/yr) and from TCC regenerators were 9.1 Gg/yr (10,000 tons/yr).[24]

4.2.8.2 Control Technology

There are three major control measures applicable to the reduction of hydrocarbon emissions in the flue gas of catalyst regenerators. The first of these is incineration in a carbon monoxide waste-heat boiler. By incinerating regenerator flue gas in CO boilers, the hydrocarbon emissions are reduced and valuable thermal energy is recovered from the flue gas. Recent oil company figures indicate that CO boilers lower hydrocarbon emissions in the regenerator off gas to values ranging from 0 to 57 g/m^3 (0-20 lbs/1000 bbl) of feed.[25]

TCC regenerators produce significantly less flue gas than FCC regenerators and may not justify using a CO boiler. A second control measure applicable to the flue gas from TCC catalyst regenerators is incineration in a process heater box or smokeless flares. Hydrocarbon emissions in regenerator flue gas are reduced to negligible quantities by incineration in heater fire boxes and smokeless flares.

The newest method of control is high temperature operation of the regenerator itself. Newer designs operate at 760°C+ (1400°F) with a slight excess of air, converting 98+% of the CO to CO_2 and completely oxidizing all hydrocarbons.[26,27] However, high temperature operation is not a widely available option for existing units. Existing regenerators often cannot withstand the high temperatures necessary to burn off the coke unless they have been originally designed to do so.

4.2.8.3 Cost, Energy, and Environmental Impact of Controls

Controls for volatile organic emissions from catalyst regeneration are the same as those used for control of CO emissions. If CO emissions are controlled, no extra energy or costs will be required for volatile organics control.

CO boilers have been installed in many refineries as energy recovery devices. A typical CO boiler will recover approximately 396 MJ/m^3 (60 M Btu/bbl) of FCC fresh feed.[28] In all but small refineries, costs of CO boilers are more than compensated by the fuel savings from heat recovery. A comparison of capital and annual costs for installation of a CO boiler is presented in Table 4.2-3.

Flares can be used in small refineries where CO boilers are uneconomical. Although there would be no cost benefit from energy recovery, as in a CO boiler, costs to construct an elevated flare are considerably less. General discussions of energy requirements and costs for flares are presented in Section 3.5

High temperature regeneration has also been developed by the industry as a method for energy recovery. At a higher temperature, a greater portion of coke deposits are burned off the catalyst. This provides extra sensible heat that can be recovered by waste heat boilers. It also improves the operating efficiency of the catalytic cracking unit, resulting in an indirect energy credit from increased yield. The total energy credit from the operation of a typical high temperature regenerator is about 395 MJ/m^3 (59.8 MBtu/bbl) of FCC fresh feed.[30] Increased metallurgy costs for a high temperature catalyst regenerator (for materials that can withstand the higher temperature) are at least partially balanced by the cost benefit from increased yield.[31] Elimination of the need to construct a CO boiler is an indirect cost benefit.

The control methods all involve oxidation (combustion) of organic materials. Any material containing sulfur may result in emissions of SO_x. Combustion may also produce NO_x emissions.

4.2.9 Boilers and Process Heaters

Most refineries utilize steam boilers to supply their process and utility steam requirements. Equipment requiring

TABLE 4.2-3. TYPICAL COSTS FOR CO BOILERS[a], [29]

Type of Installation	Refinery Size	Catalytic Cracker Size	Capital Cost($)	Annual Cost ($/Yr)[b]
Retrofit	1,590 m^3/sday (10,000 bbl/sday)	493 m^3/sday (3,100 bbl/sday)	920,000	56,210
New	NA[c]	4,930 m^3/sday (31,000 bbl/sday)	3,070,000	-1,267,600
Retrofit	NA[c]	4,930 m^3/sday (31,000 bbl/sday)	3,680,000	-1,086,600
Retrofit	9,840 m^3/sday (61,900 bbl/sday)	3,050 m^3/sday (19,200 bbl/sday)	2,760,000	- 526,600
Retrofit	31,800 m^3/sday (200,000 bbl/sday)	9,860 m^3/sday (62,000 bbl/sday)	5,570,000	-2,702,000

[a] Costs are based on several assumptions. See original reference for basis of estimates.

[b] Negative signs indicate that savings from recovered heat exceed the annual cost.

[c] NA indicates that information was not available.

large amounts of process steam includes light ends strippers, vacuum steam ejectors, process heat exchangers, and reactors. The steam demand for a typical gasoline refinery is approximately 114 kg/m^3 (40 lb/bbl) of refinery feed. This steam demand requires a boiler size of 0.35 GJ/m^3 (53 MBtu/bbl) of refinery feed.

Process heaters are used extensively in refining operations to heat and thermally crack feed streams prior to separation and treating processes. They are the largest combustion source of hydrocarbon emissions in refineries. The total process heater demand for a modern refinery is approximately 1.79 GJ/m^3 (270 MBtu/bbl) of refinery feed.[32] However, the process heater demand for older, less efficient refineries may reach 4 GJ/m^3 (600 MBtu/bbl) of refinery feed.[33]

4.2.9.1 Emission Characteristics

Refinery boilers and heaters are fired with the most available fuel, usually purchased natural gas and refinery fuel gas. Sometimes, however, residual fuel oil is used. A refinery survey in California reported the emissions listed in Table 4.2-4.[34] The heating values of the fuels are included.[35] In addition, refinery carbon monoxide boilers are partially fired with catalyst regenerator flue gas as a means of controlling carbon monoxide and recovering the heating value of carbon monoxide. The hydrocarbon emissions from burning catalyst regenerator flue gas are not significantly different from those of burning refinery fuel gas.

TABLE 4.2-4. HYDROCARBON EMISSIONS FROM REFINERY BOILERS AND HEATERS[36]

Fuel	Hydrocarbon Emissions	Heating Value
Refinery fuel gas	480 mg/Nm^3 (0.03 lb/10^3 scf)	39.1 MJ/Nm^3 (1050 Btu/scf)
Distillate fuel oil	0.4 kg/m^3 (140 lb/10^3 bbl)	39 GJ/m^3 (5.9x10^6 Btu/bbl)
Residual fuel oil	0.4 kg/m^3 (140 lb/10^3 bbl)	42 GJ/m^3 (6.3x10^6 Btu/bbl)

Because of the increasing cost of gas and fuel, refineries in the future may elect to fire process heaters with unrefined vacuum residual, which is a lower grade of fuel. Vacuum residual may produce slightly greater hydrocarbon, SO_x, and NO_x emissions than refined fuel oils.

4.2.9.2 Control Technology

Hydrocarbon emissions from process heaters and steam boilers can be minimized by adjusting the fuel to air ratio for optimum fuel combustion. To insure that optimum combustion conditions are maintained, some refineries have installed oxygen analyzers and smoke alarms on heater and boiler stacks.[37] Adequate residence time, high temperatures, and turbulence are essential for complete combustion.

4.2.9.3 Cost, Energy, and Environmental Impact of Controls

Costs for oxygen analyzers and smoke alarms are unavailable from the sources consulted. Optimum combustion conditions will yield maximum fuel efficiencies. Costs for monitoring equipment will at least in part be compensated by the cost benefit from savings in fuel.

No secondary environmental impact will be produced by these controls.

4.2.10 Chemical Treating

Chemical treating processes convert olefins and diolefins to saturated hydrocarbons and remove objectionable elements from petroleum products and feedstocks. Objectionable elements removed include sulfur (mercaptans), nitrogen, oxygen, halides, and metals. The processes can be classified as sweetening, acid/caustic treating, and solvent treating. The process selected for a given application depends on the material to be treated and the specifications to be met.

Sweetening

Chemical sweetening is used to remove mercaptans from such hydrocarbons as naphthas, gasolines, distillates, kerosene, and crude oil. Two kinds of sweetening are used, extractive sweetening and oxidative sweetening. In extractive sweetening processes, aqueous NaOH or KOH solutions extract the sulfur by forming sulfides. The solutions can be regenerated by steam blowing (reconversion to hydroxides and mercaptans) or by steam-air blowing (conversion to hydroxides and disulfides). Sometimes spent treating solutions are disposed of rather than regenerated. Disposal is often preceeded by inert-gas stripping of the solution for trace hydrocarbon removal.

Oxidative sweetening converts mercaptans to disulfides which remain in the hydrocarbon stock. There are a variety of catalytic processes for oxidative sweetening. Catalysts include copper chloride, sodium sulfide/lead oxide, sodium hydroxide, and various organic inhibitors. Air is used as the oxidizing agent, and air blowing is used to regenerate many of the catalyst solutions.

Acid/Caustic Treating

Hydrocarbon streams are treated with acid to remove aromatics, attack olefins, remove sulfur, and dissolve resinous or asphaltic substances and nitrogenous bases. The two most common treating agents are sulfuric acid and acetic anhydride. The hydrocarbon is contacted with the acid and mixed thoroughly to form an emulsion. The emulsion is then allowed to settle and break into two phases by coalescence, sometimes aided by electrostatic precipitation. Air blowing may be employed for agitation.

The use of sulfuric acid results in a hydrocarbon/ acid sludge. The sludge is removed by clay filtration. The sludge is often incinerated and the resultant SO_2 is used to produce more sulfuric acid. Another method of acid recovery is the hydrolysis-concentration process. Hot gases from the combustion of oil or gas are bubbled through the sludge, volatilizing much of the hydrocarbon diluent and concentrating the acid. The acid is then cooled for reuse or sale. The off gases pass through a mist eliminator and are discharged to the atmosphere.

Caustic is also used to remove organic acids and as a neutralizer following acid treatment. The treating process involves emulsification and separation, as in acid treating. Treatment is often followed by a water wash. When used in a sweetening agent, caustic can be regenerated as previously described.

Solvent Treating

Solvent treating processes are applied primarily to the extraction of undesirable components from lubricating oils. They are also used to separate petroleum fractions and to remove impurities from gas oils. Undesirable components removed include unstable, acidic, or organometallic compounds of nitrogen and sulfur.

Solvent and oil are contacted in a countercurrent continuous extractor. The raffinate and extract streams are steam-stripped to produce refined oil and finished extract streams. The solvent is separated from the oil and water by settling or stripping and returned to the contactor.

4.2.10.1 Emission Characteristics

There are varied sources of hydrocarbon emissions from chemical treating processes. Hydrocarbon emissions are generated whenever sweetening processes are accompanied by air blowing for oxidation and regeneration. The stripping of hydrocarbons from spent caustic with an inert gas is a potential emissions source. If the acid concentration process is used in conjunction with acid treating, both SO_2 and hydrocarbons can be emitted with the exhaust gases. Solvent treating emissions are in the form of evaporative losses that occur when the distillate product is in contact with the atmosphere.

4.2.10.2 Control Technology

Control of emissions from the air blowing regeneration of spent chemical sweetening solutions can be accomplished by steam stripping the spent sweetening solution to recover hydrocarbons prior to the air blowing step. The gaseous effluent from air blowing can then be incinerated to remove residual hydrocarbons.

Emissions from the inert gas stripping of spent caustic can be prevented by venting the gases to a flare or furnace firebox.

Hydrocarbons escaping from acid recovery operations can be eliminated by using acid regeneration. Regeneration involves sludge incineration to product SO_2 followed by standard H_2SO_4 production. If the acid concentration process is used, the off gases from the demister can be vented to caustic scrubbers for SO_2 and odorant removal, followed by incineration in a firebox or flare.

4.2.10.3 Cost, Energy, and Environmental Impact of Controls

General discussions of energy and cost requirements for incineration, absorption (steam stripping), and flaring are presented in Sections 3.1, 3.3, and 3.5. No specific energy or cost information is available. Energy and cost information for acid regeneration is also unavailable from the sources consulted.

Combustion of organics containing sulfur may produce SO_x emissions. Steam stripping produces wastewater which must be handled in the wastewater treatment system (see Sections 4.1.10 and 4.2.3).

4.2.11 Miscellaneous Catalyst Regeneration

Unlike cracking catalysts which are regenerated continuously, other refinery catalysts are only regenerated periodically. A steam and air mixture is introduced to the catalyst bed, causing combustion of the coke deposits. Hydrodesulfurization, hydrocracking, reforming, and isomerization units all require periodic catalyst regeneration.[38]

4.2.11.1 Emission Characteristics

The combustion of deposited impurities may produce emissions similar to FCC catalyst regeneration, mainly CO and unoxidized hydrocarbons. The emissions from catalyst regeneration are not significant because of the infrequent occurrence of regeneration operations.

4.2.11.2 Control Technology

The principal control measure for hydrocarbons in catalyst regeneration flue gas is incineration in a heater firebox or a smoke plume burner. These devices reduce hydrocarbon emissions to negligible quantities. Use of these control processes is not widespread, however, because of the lack of significance of this emissions source.

4.2.11.3 Cost, Energy, and Environmental Impact of Controls

General discussions of energy and cost requirements for incineration methods are provided in Section 3.1.

Incineration of organics containing sulfur may produce SO_x emissions. Incineration also has the potential to produce CO and NO_x emissions.

4.2.12 Blending Operations

Refinery blending operations involve the mixing of various components to achieve a product of desired characteristics. The most common blending operation in petroleum refining is the final step in gasoline manufacturing. Gasoline components such as catalytic gasoline, reformate, alkylate, isomerate, butane, lead, and dye are mixed in proportions required to meet gasoline-marketing specifications.

There are two methods of blending, batch and in-line. Batch blending is accomplished in a blending tank (or tanks) into which each component is added individually. Mixing is continued until a homogeneous mixture of the desired properties is produced. The final blend is routed to storage tanks to await transfer out of the refinery or pumped directly to transportation facilities.

Agitation in the blending tank is accomplished either by an external circulation loop (or loops) or by internal propellers powered by external motors. The propeller shafts are sealed in the same ways as rotating pump shafts. A special case is the blending of butane into gasoline, wherein liquid butane is sometimes charged through a sparger ring in the bottom of the blending tank.

In-line blending can be either partial or continuous. Partial in-line blending involves simultaneous combination of stock components in a mixing manifold. Final additions and adjustments are made downstream or in a storage tank.

Continuous in-line blending involves continuous and simultaneous blending of all stock components and additives in a mixing manifold. Each component stream is controlled automatically by a feedback control loop; the entire control system is often under computer guidance. There is no blending tank, and storage capacity is often minimized by direct discharge of blended products to transportation facilities or pipeline.

4.2.12.1 Emission Characteristics

Agitation in batch blending operations increases the evaporation of lighter components. Thus, fugitive losses from batch blending tanks are generally greater than those from similar quiescent storage tanks.

Emissions from in-line blending are limited to fugitive leaks from valves and flanges.

4.2.12.2 Control Technology

Control technology for batch blending operations includes floating roofs on blending tanks and replacement of batch operations by in-line blenders. Further discussion of storage tank emission prevention is presented in Section 4.5.

The introduction of in-line blending facilities will reduce emissions. Prevention of hydrocarbon leaks from in-line blending systems can be reduced by proper inspection and maintenance of valve stem seals, flange gaskets, and pump seals.

4.2.12.3 Cost, Energy, and Environmental Impact of Controls

In-line blending facilities are not usually economical for small refineries; larger refineries usually already have in-line blending. Specific energy cost and information is unavailable.

Storage tanks are discussed in Section 4.5. Valves, flanges, and pump seals are discussed in Sections 4.1.6, 4.1.7, and 4.1.8.

No secondary environmental impact will be caused by these control methods.

4.2.13 Coking

Coking is a thermal cracking process which is used to convert low value residual fuel oil to higher value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked at high temperature and atmospheric pressure. Products are petroleum coke, gas oils and lighter petroleum stocks. Delayed coking is the most widely used coking process today.

In the delayed coking process heated charge stock is fed into the bottom section of a fractionator where light ends are stripped from the feed. The remaining feed is combined with recycle from the coke drum and is rapidly heated in the coking heater to a temperature of 480-590°C (900-1100°F). Steam injection is used to control heater velocities. The vapor-liquid from the heater is converted to coke in a coke drum which provides the proper residence time, pressure, and temperature for coking. Vapors from the top of the drum return to the fractionator where the thermal cracking products are recovered. When the onstream coke drum has been filled to the proper capacity with coke, it is taken offstream and quenched/purged with steam. The drum is opened when the temperature reaches the desired level, and the coke is cut with high-pressure water.

4.2.13.1 Emission Characteristics

When the coke drum is opened large quantities of steam and hydrocarbons may be released to the atmosphere. More steam may be produced by vaporization of the cutting water and by release of pockets of trapped steam/hydrocarbon vapors from cutting operations. The hydrocarbons may include polynuclear aromatics and other hazardous compounds, as conditions within the coker are favorable for their production.

4.2.13.2 Control Technology

Hydrocarbon emissions from coking operations can be minimized by venting the quenching stream to a vapor recovery or blowdown system. Once the drum cools to 100°C (212°F), the steam purge can be replaced by a water flood. Allowing further cooling to approximately ambient temperature will minimize steam and hydrocarbon vaporization and escape when the drum is opened.

4.2.13.3 Cost, Energy, and Environmental Impact of Controls

The various methods of vapor recovery are discussed in Section 3.0. Blowdown systems are discussed in Section 4.1.13. No specific information is available.

Flaring of organics containing sulfur in a blowdown system may produce SO_x emissions. Flaring also may produce CO and NO_x emissions.

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4.3 Oil and Gas Production

Both oil wells and gas wells may produce appreciable quantities of oil, gas, and water or brine. In fact, about one sixth of the marketed natural gas is produced along with crude oil.[1] Wells are classified as oil wells or gas wells according to the ratio of oil to gas produced. For example, Texas law defines an oil well as "...any well which produces one (1) barrel or more of crude petroleum oil to each one hundred thousand (100,000) cubic feet of natural gas."[2]

Although offshore and onshore production are alike in many ways, there are distinct differences. Offshore production operations have the added complications of space limitations, greater capital expenditures, limited modes of access to facilities, and the generally hostile environment surrounding the fixed or floating platforms on which the work must be done. Because of adverse conditions and the possibility of catastrophic failure, offshore platforms are usually equipped with sophisticated safety devices and manned by crews well trained for emergency situations. In offshore production a centralized processing platform may serve several wells in the same area (as with onshore production) or the entire production may be shipped ashore by barge or pipeline for processing.

Oil Production

The production and processing of oil for transport to petroleum refineries involves recovery of well fluids, processing for free gas separation, water separation, and storage. The three methods of bringing the oil to the surface are natural flow, gas lifting (injection of gas into the flowing column), and mechanical lifting (using subsurface pumps of either a plunger or centrifugal type). The oil from several wellheads is brought together by a pipe gathering system into a central collection manifold. If the wells are not at equal pressures or are producing heavy crudes, then the gathering system must provide for pressure reduction or heating, respectively.

Processing the well stream requires separation of crude oil, gas and water. Oil and gas separations are normally classified into either one, two or three pressure stages. The number of stages depends on the pressure of the incoming gas/oil mixture; the higher the pressure, the greater the number of stages. Horizontal separators are usually used for high pressure, high gas-to-oil ratios; while vertical separators are used for lower pressure separation. A separator can be either two-phase (oil and gas) or three-phase (oil, gas and water). For three-phase separation, a lower section of the two-phase separators is modified for three-phase operations. Recovered gas may require sweetening and/or purification at a gas treating plant. In remote areas, gas may be reinjected; if volumes are small or noncommercial, it may be flared. It can also be used for lease fuel.

Separation of crude oil and free water (usually waste brine) is accomplished by gravity separation using either a three-phase separator, free water knockout, wash tank or settling tank. Remaining water forms an emulsion which must be broken down in a dehydration plant. The four methods used in dehydrating emulsions are heating, chemical treating, electrical coalescing, and extended gravity settling. Residence times are usually on the order of 20 minutes.[3] The recovered water may be treated and used for repressuring, or it may be returned to an abandoned formation for disposal. Additional water treatment may be needed if it is disposed above ground.

Crude oil in the production field is most commonly stored in both bolted and welded steel tanks, usually vertical with a fixed roof. Floating roofs are seldom used in the production field.[4] In addition the natural gas liquids processed from the separated gas stream can be stored in high pressure horizontal cylinders or spheres and under pressure in caverns in the earth's crust. If the pressure is reduced, the chilled liquids may be stored in lighter, insulated vessels above ground or in frozen earth pits.

Gas Production

There are two types of gas fields. One is the "dry" gas field in which no hydrocarbons heavier than methane and ethane are produced and the only processing required is dehydration and acid-gas removal. The other type is the "wet" or "condensate" field where a relatively heavy hydrocarbon condensate is usually produced with the gas. Besides acid-gas removal and dehydration, separation of these heavier hydrocarbons is a necessary step in achieving acceptable natural gas specifications.[5]

There are over twenty methods available for the removal of acid gas constituents such as carbon dioxide and hydrogen sulfide. Two of the more commonly used methods are absorption with aqueous solutions of ethanolamines or alkali carbonates, and dry bed adsorption with molecular sieves. In the solution system, the amine or carbonate solution flow countercurrent to the sour natural gas in a packed or tray tower. Effluents are sweet gas which is sent to a dehydration unit and H_2S rich absorbent which is regenerated by heating, pressure reduction or inert gas stripping. Molecular sieves can be used for the removal of all polar contaminants present in the gas, including sulfur- and oxygen-bearing compounds and water vapor.

Dehydration is accomplished by either adsorption with a dry desiccant (activated alumina, silica gel or molecular sieves) or absorption with a glycol solution (diethylene glycol or triethylene glycol). Both systems provide for adsorbent/absorbent regeneration and represent proven gas dehydration technologies. This operation would complete the processing of gas produced from a dry field. However for gas produced from a condensate field, a third step is required to remove the heavy hydrocarbons.

Several processes are currently used for the removal of heavy hydrocarbons from natural gas. These processes usually involve various combinations of absorption, refrigeration, compression, adsorption, factionation, cryogenic separation, and turbo-expansion. Separation may occur between methane and ethane or ethane and propane. The heavier hydrocarbons are recovered as product streams.

4.3.1. Emission Characteristics

Hydrocarbon emissions from the production and on-site processing of crude oil and natural gas can occur from a number of sources. For the most part, these emissions consist chiefly of the lighter saturated hydrocarbons and the major contributors are process equipment and storage vessels (see Section 4.4, Storage Tanks). Table 4.3-1 is a hydrocarbon emission summary for crude oil and natural gas production.

Oil Production

The evaporative losses in production of crude oil result in the emission of low molecular weight saturated hydrocarbons. Emission estimates for venting and flaring based on 1972 data are 1.42 km^3/yr (50 billion ft^3/yr) or 6.2 Gg/day (6,800 tons/day).[8]

TABLE 4.3-1. HYDROCARBON EMISSIONS FROM OIL AND GAS PRODUCTION[6,7]

Source	Continuous or Intermittent	Disposition	Comments
Oil and Gas Separation	Intermittent	Vented or Flared	During upsets, or in remote, low production areas
Oil, Condensate Storage	Intermittent	Atmosphere	Leaks and ruptures
Natural Gas Separation	Intermittent	Atmosphere	Leaks and ruptures in plant and lines; kept to a minimum by preventive maintenance
Natural Gas Liquids Recovery	Intermittent	Market (LPG, LNG)	Occur in absorber and absorber refrigeration
Gas Dehydration	Intermittent	Atmosphere	Occurs during glycol regenerator overloading; can be recovered in inlet liquid scrubber
	Continuous	Waste Pit	Free liquids, H_2O, and hydrocarbons from inlet scrubber
Heaters and Boilers	Continuous	Atmosphere	Combustion Exhaust
Compressors and Pumps	Continuous	Atmosphere	Leaks from mechanical seals and packing glands
Effluent Sumps	Continuous	Atmosphere	Evaporation

Major sources of these hydrocarbon emissions include evaporation from brine pits and tanks, improper flaring, and leaks. Typical hydrocarbon emission factors for these operations and others are given in Table 4.3-2.

For every volume of oil extracted, an additional two to three volumes of waste brine are produced. Waste brine may contain some residual oil and usually has a concentration of dissolved solids seven times that of seawater. The most common method of disposal is reinjection, although approximately 28% is dumped in rivers, unlined pits, non-potable water sites, and approved disposal sites. All discharges into marine waters must be approved by state and federal authorities. Some treated effluent is used for livestock and irrigation. The open disposal methods allow free evaporation of hydrocarbons. Waste water separators may be used, but they also produce hydrocarbon emissions. For offshore production, the water is either cleaned before discharge into the sea or pumped into tankers or pipelines for treatment onshore.[12]

Leaks can represent another significant source of hydrocarbon emissions and are discussed in Section 4.1.

Natural Gas Production

Natural gas is composed of methane with decreasing amounts of ethane, propane, and heavier hydrocarbons. Removal of these heavier components is a necessary step in producing natural gas for pipeline sales. Hydrocarbon emissions from natural gas processing are mainly fugitive in nature and result from leaks in pumps, valves, compressors, and other machinery. These losses have been estimated at 3.0 g/normal m^3 (190 $lb/10^6$ standard ft^3) of natural gas processed or approximately 6.28 Gg/day (6,920

TABLE 4.3-2. TYPICAL HYDROCARBON EMISSION FACTORS FOR CRUDE OIL PRODUCTION[9,10,11]

	$kg/10^6\ m^3$ fuel	($lb/10^6\ ft^3$ fuel)
Heater Treater	0.128	(8)
	$kg/10^3\ m^3$ crude	($lb/10^3$ bbl crude)
Heater Treater - Combustion Emissions[a]	(0.325)	(0.114)
Steam Injection - Steam Generator Combustion Emissions[b]		
50% Brine with Oil	19.4	(6.8)
Water Flooding - Diesel Engine Exhaust[c]	326	(114)
Vapor Recovery System	Neg.	Neg.
Wastewater Separators	22.6	(7.9)
Pumps	211	(73.8)
Compressors	10.9	(3.8)
Relief Valves	22.6	(7.9)
Pipeline Valves	33.1	(11.6)
Diesel Pump for Water Flooding	20.3	(7.1)
Miscellaneous Flaring and Fires	2.17	(0.76)
Storage Tanks	11.1	(3.9)

[a] Based on heat requirement on 1 MG/m^3 (15,000 Btu/bbl) natural gas fired.

[b] Burning produced oil.

[c] Includes emissions calculated from aldehyde emission factors.

short tons/day) in 1973.[13] Hydrocarbon emissions can occur at any point in the system which is open to the atmosphere. Typical hydrocarbon emission factors for natural gas production are given in Table 4.3-3. These emissions are about 89% methane. They contain no significant amounts of H_2.

TABLE 4.3-3. TYPICAL HYDROCARBON EMISSION FACTORS FOR NATURAL GAS PRODUCTION[14]

	mg/m^3	$(lb/10^6 ft^3)$
Gas Well Compressor	0.64	(0.04)
Acid Gas Removal Unit	0.10	(0.006)
Glycol Dehydration	0.03	(0.002)
Refrigerated Absorption	0.32	(0.02)
Flare	0.13	(0.008)

4.3.2 Control Technology

There are three sources of hydrocarbon emissions in the production of crude oil and natural gas: combustion of a fuel, evaporation of a volatile liquid hydrocarbon, and miscellaneous process leaks. Control techniques for emissions from evaporation and leaks are described in Sections 4.1 and 4.5. Techniques for the control of emissions from combustion are described below and in Sections 4.1 and 4.13.

Combustion sources include process heaters, diesel engines, and heater treaters. Proper application, installation, operation, and maintenance of combustion equipment represents the most practical means of lowering combustion emissions. Hydrocarbon emissions resulting from combustion exhaust can also be significantly reduced by substitution of clean burning natural gas for distillate or diesel oil as fuel. In the case of heater treaters, other possible alternatives to accomplish oil-water separation without combustion are chemical destabilization, electrical coalescence, and gravitational settling. It is noted, however, that these alternatives are not always applicable.

4.3.3 Cost, Energy, and Environmental Impact of Controls

Cost, energy, and environmental impact of controls for oil and gas production are given in Sections 4.1, 4.5, and 4.13.

4.3.4 References

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4.4 Organic Chemicals

The organic chemical processing industries (OCPI) convert hydrocarbons obtained mainly from petroleum, coal, and natural gas into synthetic intermediates and products. During 1974 nearly 64 Tg (1.4×10^{11} lb) of chemicals with a value of approximately 7 billion dollars were produced in the United States.[1] Table 4.4-1 is a list of the synthetic organic chemicals with the highest production volume in 1976. The primary raw materials for this industry are ethylene, propylene, butylenes, benzene, toluene, xylene, natural gas, and natural gas liquids.

Organic pollutants may be emitted to the atmosphere from organic chemical processing in various ways. Vented gases from various processing operations may contain organic compounds. Vents are required for removal of by-products or inerts and for pressure control during plant upsets. Other sources of hydrocarbons include evaporation from storage tanks, loading and unloading facilities, sampling, spillage, processing equipment leakage, barometric condensers, cooling towers, equipment blowdown, and miscellaneous sources.

The volatile organics in vent streams can be controlled by conventional methods of controlling organic atmospheric pollutants from stationary sources, i.e.,combustion, condensation, adsorption, absorption, and process modifications. These controls can be used to achieve as much as 90 to 100 percent removal efficiency. In most cases, study is required to determine the economically feasible reduction potentials for specific processes.

Descriptions of the production of several organic chemicals are included in the following Sections 4.4.1 - 4.4.8.

TABLE 4.4-1. THE MOST SIGNIFICANT SYNTHETIC ORGANIC CHEMICALS BY PRODUCTION VOLUME IN 1976[2]

Chemical	Production	
	Tg	(10^9 lb)
Ethylene Dichloride	3.60	7.92
Urea	3.50	7.72
Styrene	2.86	6.30
Methanol	2.83	6.24
Ethylbenzene	2.78	6.13
Vinyl Chloride	2.62	5.77
Formaldehyde (37% by weight)	2.55	5.62
Terephthalic Acid	2.29	5.05
Hydrochloric Acid	2.21	4.86
Ethylene Oxide	1.90	4.18
Ethylene Glycol	1.53	3.36
Butadiene (1,3-)	1.48	3.25
p-Xylene	1.45	3.20
Cumene	1.22	2.69
Acetic Acid	1.10	2.43
Phenol	0.99	2.18
Cyclohexane	0.99	2.18
Acetone	0.87	1.92
Propylene Oxide	0.82	1.80
Isopropyl Alcohol	0.78	1.72

The organic chemicals chosen have been the subject of industry surveys and reports. They are only a few of many significant chemical processes, however. Their inclusion indicates only that hydrocarbon emissions and controls have been studied and characterized for these processes. Most emissions data from the referenced reports are several years old. It is believed that current emissions are lower, due to increased usage of controls and improved processing methods. There is additional work in progress directed at better characterization of organic chemical emissions and their control.

The following descriptions concentrate on the major process emissions. Fugitive, storage, loading and unloading emissions are discussed in Sections 4.1, 4.5, and 4.6, respectively. Flow sheets included show only the major process streams and no auxiliary equipment.

Costs, energy requirements, and environmental impacts of the major control technologies for volatile organic chemicals are included in Section 3 of this report. Costs and energy requirements developed for specific organic chemical production processes are included in the following discussions when they were available. In addition, comments on possible environmental problems encountered with the use of control devices are made. The data are very specific, however, and are not meant to be applied to other industries. All cost estimates and energy requirements are based on assumptions; the references cited should be consulted for the bases of the estimates.

4.4.1 Acrylonitrile by Propylene Ammoxidation

Acrylonitrile is produced in the U.S. by the Sohio fluid bed catalytic process. Figure 4.4-1 is a simplified flow sheet of the process. Air, ammonia, and propylene are fed to a

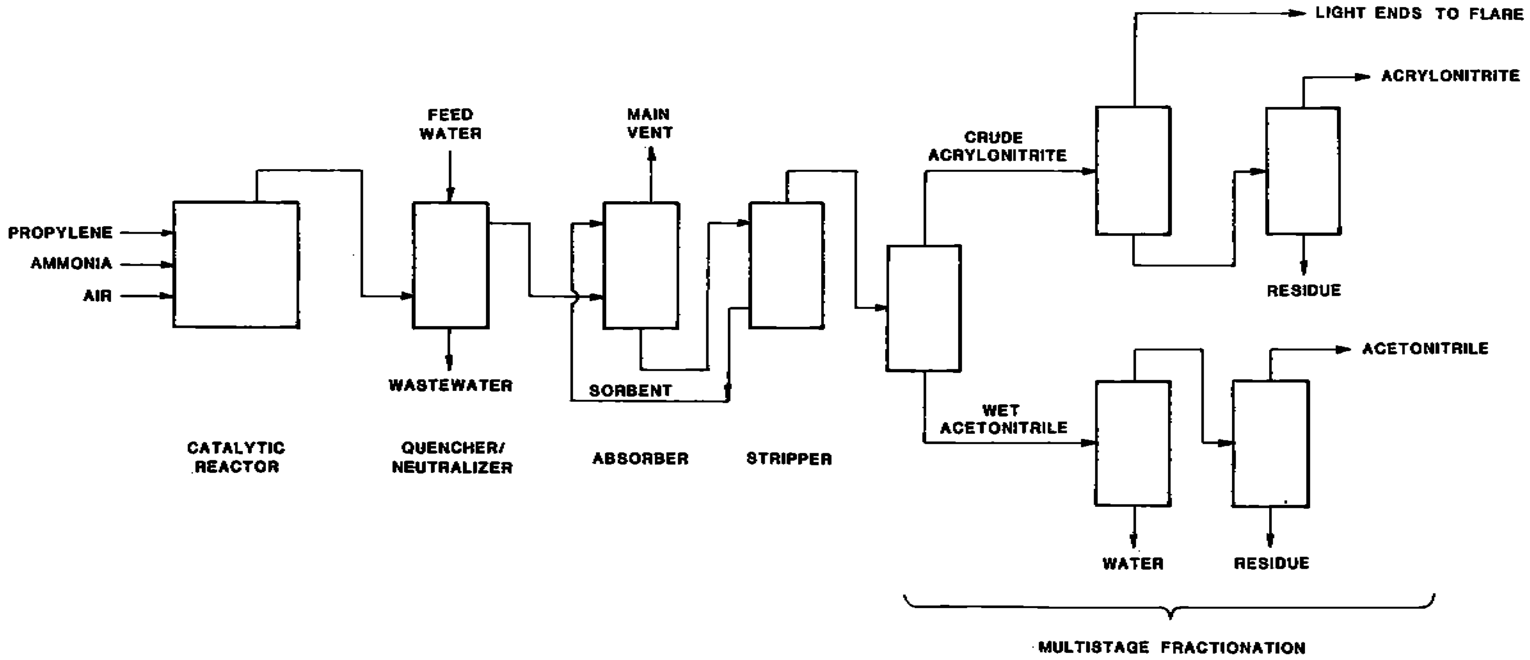


Figure 4.4-1. Flow diagram for the Sohio process for acrylonitrile production.

reactor at 140-310 kPa (5-30 psig) and 420-530°C (780-980°F) to form acrylonitrile by ammoxidation. The chemical reaction may be represented by the equation shown below.

$$2CH_2{=}CH{-}CH_3 + 2NH_3 + 3O_2 \rightarrow 2CH_2{=}CH{-}CN + 6H_2O$$

No recycle is required, as the reaction is virtually complete. The reactor effluent is sent to a water quench tower in which acid is added to neutralize the remaining ammonia. Reaction products are recovered in a water absorber-stripper system. Acrylonitrile is then separated from by-products in a series of distillations. The first fractionation of crude acrylonitrile usually removes HCN as an overhead stream. The acrylonitrile is then dried and purified to 99+% in further distillation steps. The wet acetonitrile is subjected to extractive distillation using water as the extractive solvent.

By-product streams may be processed to recover high purity HCN and acetonitrile for sales. The by-product streams which are not sold are incinerated. The amounts incinerated are determined by market demand; excess by-product is incinerated. Currently, two acrylonitrile producers market or have plans to market acetonitrile. All of the producers market HCN. Fifth percent of the HCN is sold; forty percent is incinerated.[3]

Aqueous wastes from the quench tower and from the extractive distillation of acetonitrile are sent to a settling pond prior to disposal by deep well injection.

There have recently been two catalysts in use: Catalyst 21 and Catalyst 41. Although the yields are about the same for the two catalyst systems, Catalyst 41 provides for better utilization of ammonia and requires less oxygen. All acrylonitrile producers have switched to Catalyst 41 or are in the process of switching.

4.4.1.1 Emission Characteristics

Hydrocarbon and organic chemical emissions may be encountered at the absorber vent, at the fractionation column vents, at the settling pond, at the incinerator stack, and at storage tank vents. The estimated total volatile organic emissions from acrylonitrile plants in the U.S. are presented in Table 4.4-2.

TABLE 4.4-2. ESTIMATED VOLATILE ORGANIC EMISSIONS FROM ACRYLONITRILE PRODUCTION[4]

	Emissions		
Catalyst system	kg/kg acrylonitrile	Mg/yr	(10^6 lbs/yr)[a]
Catalyst 21	0.1650	$82.3x10^3$	(181.5)
Catalyst 41	0.1071	$53x10^3$	(117.8)

[a] Assuming 499 Gg/yr ($1.1x10^9$ lb/yr) production

The primary gaseous air emission occurs at the absorber vent. Incinerators have been installed on this vent stream in at least two plants. Table 4.4-3 contains a typical absorber vent gas composition for a 90 Gg/yr ($200x10^6$ lbs/yr) acrylonitrile plant. Table 4.4-4 is a list of emission factors for absorber vent emissions.

The fractionation column vent stream contains some nitriles. These gases are usually incinerated. The vent stream flow rate is small.

TABLE 4.4-3. TYPICAL ABSORBER VENT GAS COMPOSITION FOR A 90 Gg/yr (200x10^{6} lb/yr) ACRYLONITRILE PLANT USING CATALYST 41[5]

Component	Average Flow Rate	
	kg/hr	(lb/hr)
Carbon dioxide	3,784	(8,342)
Carbon monoxide	1,359	(2,996)
Ammonia		
Propylene	426	(939)
Propane	676	(1,491)
Hydrocyanic acid	5.4	(12)
Acrylonitrile	2.7	(6)
Acetonitrile	73	(160)
Nitrogen and argon	73,789	(162,677)
Oxygen	876	(1,931)
Water	7,799	(17,195)
NO$_x$	.45	(1)
	88,790	(195,750)

TABLE 4.4-4. EMISSION FACTORS FOR ABSORBER VENT GAS FROM ACRYLONITRILE PRODUCTION USING CATALYST 41[6]

Component	Emission factor[a] (g/kg, lb/1000 lb)
Nitrogen	5,865
Oxygen	103
Carbon dioxide	185
Carbon monoxide	79.3
C$_3$-Hydrocarbons	55.0
Acrylonitrile	0.039
Acetonitrile	0.625
Hydrogen cyanide	0.275

[a] Emission factors based on actual field sampling

Storage losses are another source of hydrocarbon and organic chemical emissions. Acrylonitrile and acetonitrile have vapor pressures in the range of 21-35 kPa (3-5 psi) at ambient temperature. The storage tanks may be vented to the atmosphere, but in some cases recovery systems are employed for safety reasons. The propylene is stored in sealed pressure storage tanks equipped with relief valves that discharge to a flare. Noncondensibles and some HCN from HCN tanks are also vented to a flare. Section 4.5 describes emissions from storage tanks.

Results of field sampling indicate negligible volatile organic emissions from incinerator stacks in acrylonitrile plants.

Liquid wastes are held in a settling pond before they are disposed of in injection wells. Organic chemicals in the wastes are emitted to the atmosphere.

4.4.1.2 Control Technology

The absorber vent gas emissions may be controlled with a combustion device such as a CO boiler, thermal incinerator, catalytic incinerator, or flare. Catalytic incinerators and combined liquid-gaseous incinerators are in operation.

Organic emissions in fractionation column vent gases may also be controlled by combustion. Flaring is the generally accepted procedure in this case because the volume is small. Indications are that this control method is practiced widely in the industry. It is estimated that more than 90 percent of the combustibles are burned by flaring.[7]

Emissions from the settling pond are reduced by covering the surface with a high molecular weight oil.[8]

For control technology for storage tank emissions see Section 4.5.

4.4.1.3 Cost, Energy, and Environmental Impact of Controls

Although discussions of energy requirements, environmental impacts, and cost data for the combustion devices mentioned are located in Section 3, energy and cost data for this specific process are included in Table 4.4-5. The data were developed for a typical acrylonitrile plant producing 90 Gg/yr (200 x 10^6 lb/yr) in 1973. Energy requirements and costs for adding lube oil to a pond are probably minimal.

Combustion of nitriles and HCN by flaring may result in emissions of NO_x. If supplemental fuel contains sulfur compounds, SO_2 emissions may also result. The lube oil layer used as a control method for hydrocarbon emissions from the storage pond contributes some volatile organic emissions. The net result is a decrease in the total organic emissions from the pond and a change in the composition of emissions.

4.4.2 Formaldehyde from Methanol with Silver Catalyst

Formaldehyde is manufactured by two processes. One employs a silver catalyst and the other a mixed metal oxide catalyst. The mixed catalyst process is discussed in the next section. The overall reaction for making formaldehyde from

TABLE 4.4-5. ENERGY AND COST DATA FOR CONTROL OF EMISSIONS FROM ACRYLONITRILE PRODUCTION[a, 9]

		Energy Requirements		
Waste Stream	Control Technique	Fuel	Electricity	Annualized[b] Cost (1973)
Absorber vent 21.4 m^3/s (45,370 scfm)	Afterburners generating steam	1.31 PJ/yr (1.24×10^{12} Btu/yr)		$355,400/yr
	Thermal incinerator	1.69 PJ/yr (1.60×10^{12} Btu/yr)	1.5 TJ/yr (430,000 kWh/yr)	$135,900/yr
	Thermal incinerator plus afterburner generating steam	1.69 PJ/yr (1.60×10^{12} Btu/yr)	1.5 TJ/yr (430,000 kWh/yr)	$116,600[c]/yr
	Flare	1.55 PJ/yr (1.47×10^{12} Btu/yr)		$619,500/yr
Product fractionation vent 0.033 m^3/s (70 scfm)	Flare	9.24 TJ/yr (8.75×10^{9} Btu/yr)		$20,500/yr
By-product Disposal 2.15 Mg/hr (4743 lb/hr)	thermal incinerator	5.3 TJ/yr (5.0×10^{9} Btu/yr)	0.86 TJ/yr (240,000 kWh/yr)	$70,700[d]/yr
HCN storage tank vent 0.120 m^3/s (255 scfm)	Flare	3.2 TJ/yr (3.0×10^{9} Btu/yr)		$6,400/yr

[a] Estimates for 90 Gg/yr (200 MM lb/yr) acrylonitrile production.

[b] Cost estimates are based on several assumptions. See original references. These costs are based on 1973 dollars and conditions. Current costs may be as much as 3 times those given.

[c] Assuming steam produced can be used.

[d] Includes excess capacity for all waste water streams.

methanol with a silver catalyst is shown in the following chemical equation.

$$2CH_3OH + \frac{1}{2}O_2 \rightarrow 2CH_2O + H_2 + H_2O$$

Figure 4.4-2 is a simplified flow diagram of the silver catalyst process.

The feedstocks are prepared before they are introduced into the reactors. Air is washed with caustic to remove CO_2 and sulfur compounds and heated to about 80°C (180°F). Fresh and recycle methanol are combined, vaporized, and superheated to about 70-80°C (160-180°F). The treated air and vaporized methanol are combined and sent to a battery of catalytic reactors. Some plants use a feed vs. effluent heat exchanger as the next step. Otherwise, effluent gases go directly to the primary absorber, a packed tower. The sorbent is an aqueous solution of formaldehyde and methanol, part of which is recycled. The other portion goes to an intermediate storage facility. Noncondensibles and uncondensed vapors are sent to a secondary absorber using distilled water as a sorbent. The resulting solution of formaldehyde and methanol is used as makeup for the primary absorber. Noncondensibles and associated vapors (methanol, formaldehyde, methyl formate, methylal, CO) from the secondary absorber are vented overhead. The methanol and formaldehyde solution resulting from the primary absorber is fractionated to yield 99+% methanol and a 37% (weight) solution of formaldehyde containing less than 1% methanol. The formaldehyde product may undergo additional treatment to remove formic acid and to prevent polymerization during storage.

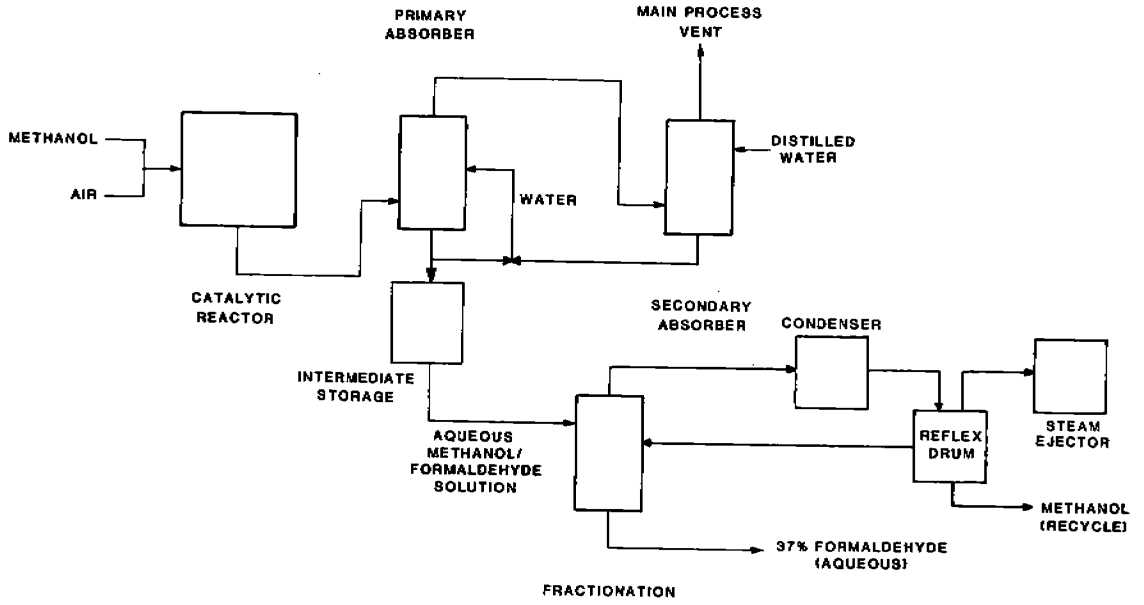


Figure 4.4-2. Flow diagram for silver catalyst process for formaldehyde production.

4.4.2.1 Emission Characteristics

Volatile organic emissions from silver process formaldehyde plants are estimated to be 0.004 kg/kg (0.004 lb/lb) of 37% formaldehyde. For an annual production rate of 2.68 Tg (3x10^6 lb) this amounts to 11 Gg/yr (24x10^6 lb/yr).[10] The main source of volatile organic emissions is the absorber vent. Another identified source is the ejector exhaust from the fractionation column. A typical absorber vent gas is presented in Table 4.4-6. Storage emissions are reported to be low.[11]

TABLE 4.4-6. TYPICAL ABSORBER VENT GAS COMPOSITION FOR A 45 Gg/YR (100 MM lb/yr)[a] SILVER CATALYST PROCESS FORMALDEHYDE PLANT[12]

Component	Composition mole %	Flowrate	
		kg/hr	(lb/hr)
Formaldehyde	0.07	3	(7)
Methanol	0.28	14	(31)
Hydrogen	17.72	56	(123)
Carbon dioxide	3.69	253	(558)
Carbon monoxide	0.66	29	(64)
Oxygen	0.35	17	(38)
Nitrogen	74.35	3,242	(7,147)
Water	2.88	81	(178)
TOTAL	100.00	3,695	(8,146)

[a] 37% Formaldehyde solution

4.4.2.2 Control Technology

The use of a mist eliminator on the secondary absorber effluent is standard practice in the industry. The majority of U.S. plants do not employ additional controls. Combustion devices (thermal incinerators and boilers) are used by a few producers. Combustion efficiencies are estimated at 99+%.[13]

Several other devices are available for controlling absorber vent losses. Plume burners are applicable, but they control only 90% of CO and volatile organics. Water scrubbers share the disadvantage of low control efficiency, and they have the additional problem of causing a potential water pollution problem. Catalytic incinerators are also applicable although they have not been demonstrated. They are estimated to have efficiencies similar to thermal incinerators.[14]

In plants operating fractionation columns at reduced pressures, a vent stream is emitted through a steam vacuum ejector or pump. Water scrubbing is practiced by at least one plant to control hydrocarbon emissions from this source. Removal efficiency is in the range of 79-97 percent.[15] Another plant reportedly recycles the vent gases to the fractionation column, and a small purge stream is probably required. A condenser is used as a control device in one plant.

4.4.2.3 Cost, Energy, and Environmental Impact of Controls

General cost, energy, and environmental impact information is located in Section 3 for incinerators, boilers, condensers, absorbers, and flares. In addition to this general data some specific cost and energy data for control techniques are presented in Table 4.4-7 for a 45 Gg/yr (100 x 10^6 lb/yr) formaldehyde plant employing a silver catalyst in 1973.

Combustion control methods involve the potential for NO_x and CO formation and release to the atmosphere. Additionally, if supplemental fuel contains sulfur, SO_2 emissions will also result. Water scrubbers, as mentioned above, are a potential source of wastewater pollution.

TABLE 4.4-7. ENERGY AND COST DATA FOR CONTROL OF VOLATILE ORGANIC EMISSIONS FROM METHANOL PRODUCTION USING A SILVER CATALYST[a,b,16]

Waste Stream	Control Technique	Energy Requirements Fuel	Energy Requirements Electricity	Annualized[c] Cost (1973)
Absorber vent gas 1.02 m^3/s (2170 scfm)	Water scrubber[c]			\$8,200/yr
	Thermal incinerator	1.32 TJ/yr (1250×10^6 Btu/yr)	0.11 TJ/yr (30,000 kWh/yr)	\$10,100/yr
	Catalytic incinerator	1.06 TJ/yr (1000×10^6 Btu/yr)	0.11 TJ/yr (30,000 kWh/yr)	\$14,100/yr
	Plume burner	1.85 TJ/yr (1750×10^6 Btu/yr)		\$ 6,800/yr
	Steam boiler	-34.3 TJ/yr ($-32{,}500 \times 10^6$ Btu/yr)	0.36 TJ/yr (100,000 kWh/yr)	-\$ 3,100/yr
Fractionator vent gas 0.422 m^3/s (894 scfm)	Total recycle			\$ 2,100/yr
	Water scrubber[d]			> \$ 2,100/yr

---

[a] Estimates are for a typical 45 Gg/yr (100 MM lb/yr) plant.

[b] 1973 dollars.

[c] Costs are based on several assumptions. See original reference. Costs are based on 1973 dollars and conditions. Current costs may be significantly higher.

[d] Does not include water treatment requirements.

4.4.3 Formaldehyde from Methanol with Mixed Catalyst

The reaction for making formaldehyde from methanol using the mixed metal oxide catalyst is shown in the following chemical equation.

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O$$

Methanol is mixed with air and recycled vent gas and heated to 105-177°C (220-350°F). The reaction takes place in the presence of a mixed oxide catalyst at temperatures between 343°C and 427°C (650°F and 800°F). The heat of reaction is removed by circulating coolant. A heat exchanger cools the effluent gases to 105°C (220°F) before they are quenched in the absorber. Water is used as a sorbent to form a 37-53 percent solution. Part of the noncondensibles are vented from the top of the absorber, and the remaining portion is recycled. Figure 4.4-3 is a simplified flowsheet of the mixed oxide catalyst process.

4.4.3.1 Emission Characteristics

Volatile organic emissions from the process are estimated to be 0.0149 kg/kg (0.0149 lb/lb) of 37% formaldehyde. This amounts to a total emission rate of about 11.7 Gg/yr (25.7×10^6 lb/yr), based on 785 Gg/yr ($1{,}729 \times 10^6$ lb/yr) mixed metal oxide process capacity.[17]

The primary source of volatile organic emissions in a mixed oxide catalyst formaldehyde plant is the absorber vent. The amount of emissions is highly dependent on recycle ratio. Absorber vent gas compositions for recycle and nonrecycle operations are presented in Table 4.4-8.

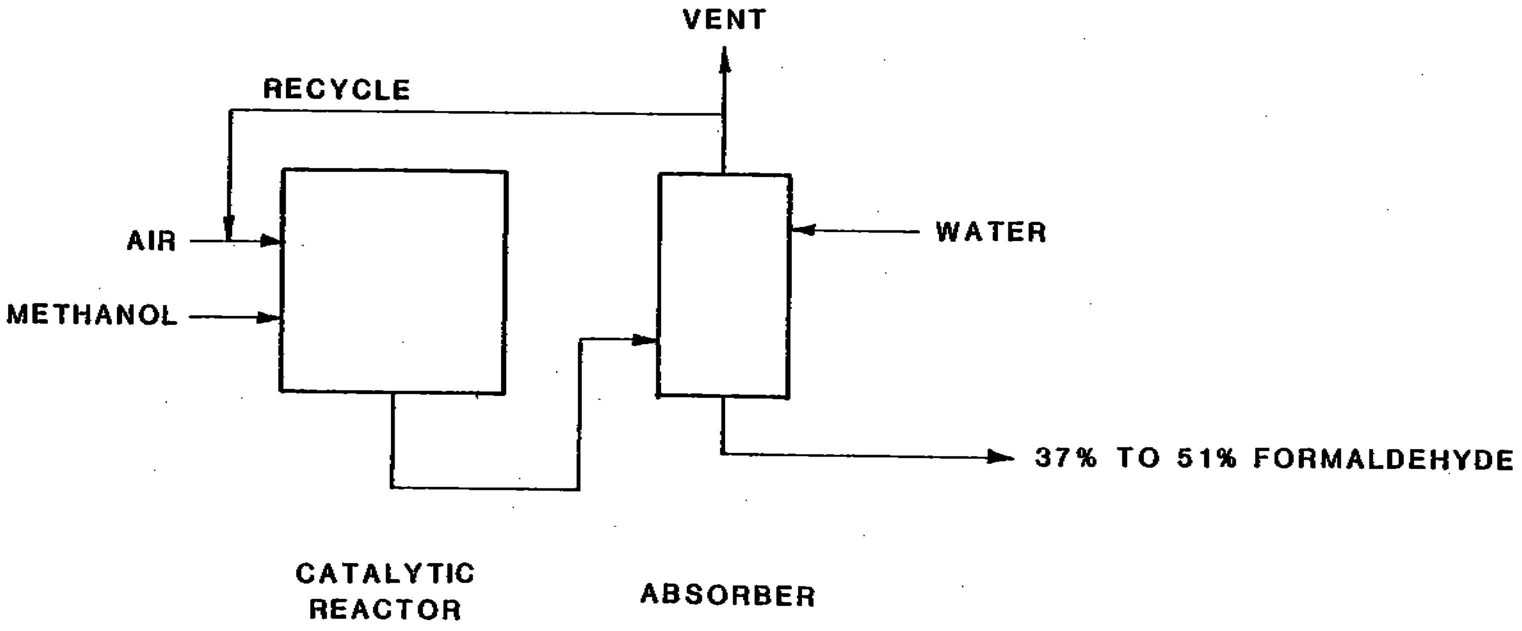


Figure 4.4-3. Flow diagram for mixed catalyst process for formaldehyde production.

TABLE 4.4-8. TYPICAL ABSORBER VENT GAS COMPOSITION FOR A 45 Gg/YR (100 X 10^6 lb/yr)[a] FORMALDEHYDE PLANT USING MIXED OXIDE CATALYST[18]

Component	Composition (vol%)		Flowrate Recycle	
	Non-recycle	Recycle	kg/hr	(lb/hr)
Formaldehyde	0.01-1.0	0.03-0.15	2.3	(5)
Methanol	0-0.7	0.05-0.2	9.5	(21)
Dimethyl ether	0.05-2.5	0-0.53	4.5	(10)
Oxygen	18.5-19.6	5.3-18.1	606	(1,336)
Nitrogen	75.1-77.0	73.9-89.2	5,893	(12,994)
Carbon dioxide	2.2-4.0	0.03-0.9	10	(22)
Carbon monoxide		0.28-1.9	68	(151)
Water	0.7-2.24	5.1	195	(429)
Total			6,788	(14,968)

[a] 37% solution

A vent on the reactor cooling system has been reported as a source of volatile organic emissions in some plants. Volatile organic emissions from this source are less than 0.002 kg/kg (0.002 lb/lb) formaldehyde (37%).[19]

Most of the storage tanks employed in formaldehyde facilities vent directly to the atmosphere. Emissions from this source are said to be low, however.[20]

4.4.3.2 Control Technology

Industrywide utilization of recycling has resulted in significant reductions in volatile organic emissions from this process. In addition to this process modification, mist eliminators are employed in some absorbers. Water scrubbers were reported in at least one plant on the absorber vent and on the storage tank vents. Water scrubbing is about 99% efficient on the tank vents, while it is only 66% efficient when used on the absorber vent. The low scrubbing efficiency for the absorber vent is due to the presence of dimethyl ether, which is relatively insoluble in water. Combustion devices (thermal incinerators, catalytic incinerators, flares) could be applied for further emission reductions. Thermal and catalytic incinerators have estimated efficiencies of 99+%, while flares have estimated removal efficiencies of about 90%.[21]

4.4.3.3 Cost, Energy, and Environmental Impact of Controls

General discussions are included in Section 3 for energy requirements, costs, and environmental impacts for absorbers, incinerators, and flares. Some cost data and energy requirements for control devices applied in a typical 45 Gg/yr (100 MM lb/yr) formaldehyde plant in 1973 are listed in Table 4.4-9 also.

Combustion may produce NO_x and CO emissions. If supplemental fuel contains sulfur, SO_2 emissions will also result. Water scrubbing has the disadvantage of creating a potential wastewater problem.

4.4.4 Ethylene Oxide

Ethylene oxide is produced in the direct oxidation process by reacting air or oxygen and ethylene in the presence of a silver catalyst. The reaction is shown in the following chemical equation.

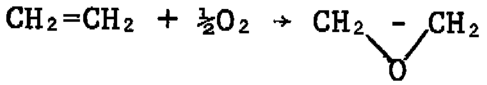


TABLE 4.4-9. ENERGY AND COST DATA FOR CONTROLLING VOLATILE ORGANIC EMISSIONS FROM FORMALDEHYDE PRODUCTION WITH MIXED OXIDE CATALYST[a,b,22]

Waste Stream	Flow Rate	Control Technique	Energy Requirements		Annualized[c] Cost (1973)
			Fuel	Electricity	
Absorber vent gas	2.26 m^3/s (4790 scfm)	Thermal incinerator (no heat recovery)	68 TJ/yr (64,000x10^6 Btu/yr)	0.144 TJ/yr (40,000 kWh/yr)	\$36,600/yr
	2.26 m^3/s (4790 scfm)	Thermal incinerator (40% heat recovery)	40 TJ/yr (38,000x10^6 Btu/yr)	0.144 TJ/yr (40,000 kWh/yr)	\$29,600/yr
	2.02 m^3/s (4270 scfm)	Catalytic incinerator	42 TJ/yr (40,000x10^6 Btu/yr)	0.144 TJ/yr (40,000 kWh/yr)	\$26,700/yr
	2.02 m^3/s (4270 scfm)	Flare	68 TJ/yr (64,000x10^6 Btu/yr)		\$31,700/yr
	1.60 m^3/s (3385 scfm)	Water scrubber			\$19,900/yr[d]

[a] For a typical formaldehyde plant producing 45 Gg/yr (100 x 10^6 lb/yr) with mixed oxide catalyst.

[b] 1973 dollars.

[c] Costs are based on several assumptions. See original reference. Costs are based on 1973 dollars and conditions. Current costs may be significantly higher.

[d] Does not include water treatment requirements.

CO_2 and H_2O are by-products formed by oxidation of the ethylene oxide product and by oxidation of ethylene directly. Most of the installations use air as the source of oxygen, but there is a trend toward using pure oxygen. The two processes are similar.

In the air based process, ethylene, air, small amounts of oxidation inhibitors, and recycle gas are fed to a primary reactor packed with silver catalyst. Temperature control is provided by circulating heat transfer fluid. Effluent gas from the primary reactor is cooled and compressed before it enters the primary absorber which uses water as a sorbent. Unabsorbed gas passes overhead. Part of the gas is recycled to the reactor, but the major part goes to a secondary reactor and another absorber. Overhead gases from this secondary absorber may be vented directly to the atmosphere; however, the trend is toward catalytic incineration. The gases from the incineration may be used to drive an air compressor. The water solutions from both absorbers are pumped to a steam stripper. Ethylene oxide is then purified by fractionation. Purified ethylene oxide is stored under nitrogen or under refrigeration. Bottoms from the fractionation are sent to waste disposal (see Section 4.15). Figure 4.4-4a is a simplified flow chart of the air-based process.

Process flows for the oxygen process are very similar to the air oxidation process. A simple flow chart is included in Figure 4.4-4b. There are some important differences, however. There is usually only a primary reactor and absorber. Conversion of ethylene per pass is low, so that a larger recycle stream is required. A CO_2 absorber is required on a portion of the recycle stream to control CO_2 buildup.

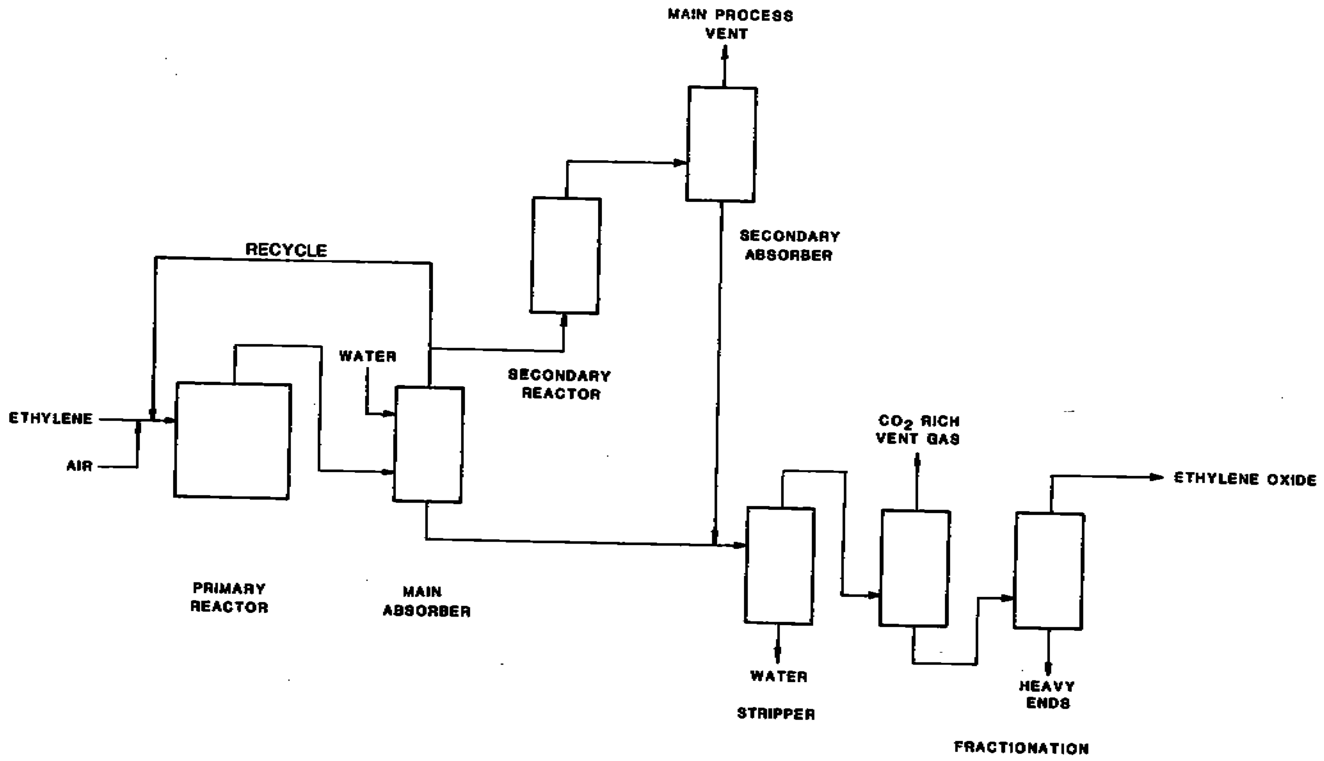


Figure 4.4-4a. Flow diagram for the production of ethylene oxide by oxidation of ethylene with air.

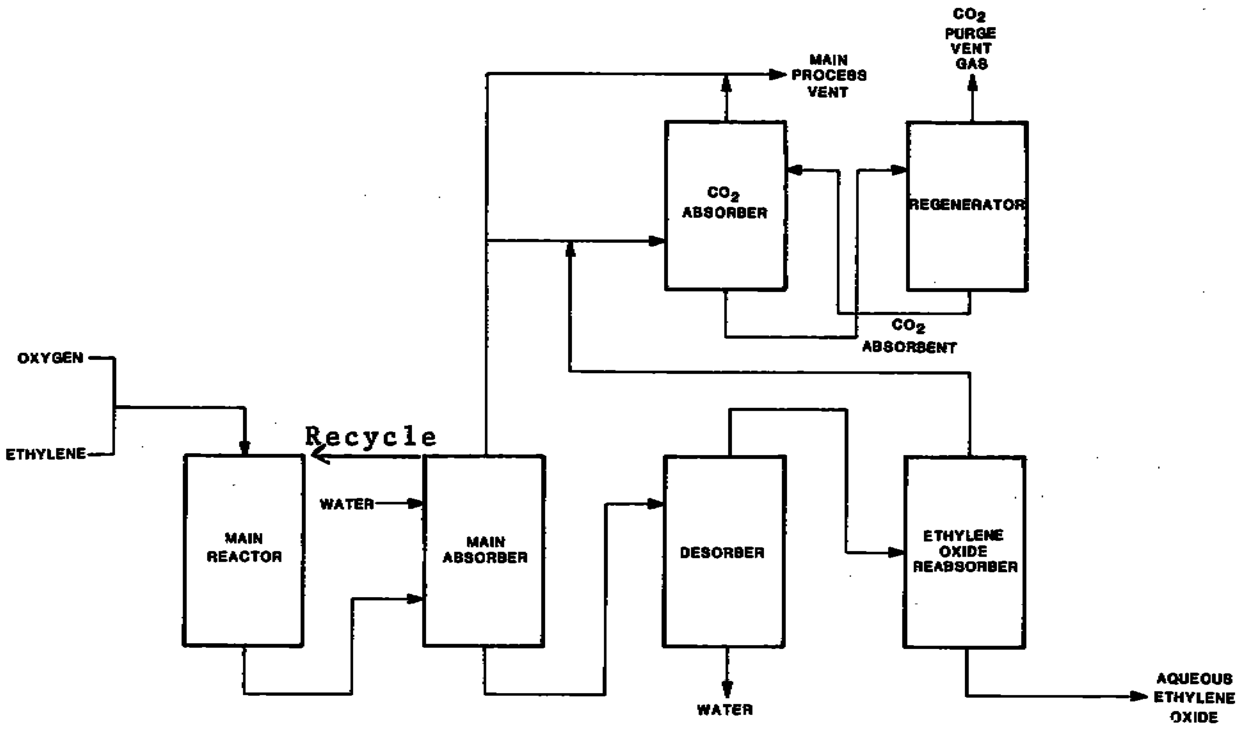


Figure 4.4-4b. Flow diagram for the production of ethylene oxide by oxidation with oxygen.

4.4.4.1 Emission Characteristics

Estimated average volatile organic emissions from ethylene oxide manufacture are 0.02048 kg/kg (0.02048 lb/lb) ethylene oxide produced. Total volatile organic emissions from ethylene oxide manufacture are about 39 Gg/yr (86x10^6 lb/yr), based on 1.9 Tg/yr (4,191x10^6 lb/yr) ethylene oxide produced in 172.[23] Emissions are produced at the secondary absorber vent and at the fractionation tower vent. In plants using pure oxygen, emission sources are the absorber vent and the CO_2 absorption system. The composition of the vent gas from the secondary absorber in plants using air is shown in Table 4.4-10. Although the concentration of volatile organics is low, the flow rate is high, resulting in significant amounts of hydrocarbon emissions from this vent.

TABLE 4.4-10. TYPICAL COMPOSITION OF VENT GAS FROM SECONDARY ABSORBER IN AN AIR-BASED ETHYLENE OXIDE PLANT[a,b][24]

Component	Composition (mol %)	Composition Average (mol %)	Average flow rate[c] (kg/hr)	Average flow rate[c] (lb/hr)
Nitrogen	80-90	86.7	59,629	131,460
Oxygen	0.5-4.5	2.9	2,278	5,024
Methane	0-0.9	0.0	0	0
Ethane	0-0.1	0.1	68	150
Ethylene	TR-2.3	1.6	1,105	2,436
Ethylene oxide	0-0.01	0.01	8	17
Carbon dioxide	0-10	8.7	8,973	19,782
Total		100.0	72,061	158,869

[a] dry basis

[b] 90 Gg/yr (200x10^6 lb/yr) ethylene oxide plant using air feed

[c] 32,402 scfm

A typical composition of the overhead vent stream from the fractionation tower in plants using air is presented in Table 4.4-11. This stream is representative of air based plants only. Vent streams from oxygen based plants are different in composition and flow rate. The vent gas stream from the absorber in one oxygen based plant is shown in Table 4.4-12. The composition of a purge gas from the CO_2 absorption system of the same plant is presented in Table 4.4-13.

TABLE 4.4-11. TYPICAL VENT GAS FROM RECTIFICATION TOWER IN AIR-BASED ETHYLENE OXIDE PLANT[a,b]25

Component	Composition (mol %)	Composition Average (mol %)	Average flow rate[c] (kg/hr)	Average flow rate[c] (lb/hr)
Nitrogen	13-25	18	181	398
Oxygen	1-26	2	23	51
Ethylene	2.5-8.0	4.5	46	101
Ethylene oxide	0-1.0	0.5	8	17
Carbon dioxide	62-80	75	1,131	2,491
Total		100.0	1,389	3,058

[a] dry basis

[b] 90 Gg/yr (200×10^6 lb/yr) ethylene oxide plant using air feed

[c] 475 scfm

TABLE 4.4-12. VENT GAS COMPOSITION FROM ABSORBER IN ETHYLENE OXIDE PLANT USING OXYGEN FEED[a,b,26]

Component	(mol %)	Flow rate (kg/hr)	Flow rate (lb/hr)
Nitrogen, argon	16.2	55	121
Oxygen	7.3	20	44
Methane	1.5	2	5
Ethane	14.2	37	81
Ethylene	13.5	33	72
Ethylene oxide	0.0005	0.02	0.04
Carbon dioxide	47.4	172	379
Total		319	702

[a] dry basis

[b] 90 Gg/yr (200×10^6 lb/yr)

TABLE 4-4.13. PURGE GAS FROM CO_2 ABSORPTION SYSTEM IN ETHYLENE OXIDE PLANT USING OXYGEN FEED[a,b,27]

Component	Concentration (mol %)	Flow rate (kg/hr)	Flow rate (lb/hr)
Oxygen	0.02	1	3
Ethane	0.12	8	18
Ethylene	0.16	10	22
Carbon dioxide	99.70	9,543	21,038
Total		9,562	21,081

[a] dry basis

[b] 90 Gg/yr (200×10^6 lb/yr)

4.4.4.2 Control Technology

The vent streams described in the previous section are uncontrolled at some locations. However, use of catalytic incineration to remove ethylene oxide from the fractionation tower vent gas is becoming prevalent. Efficiencies for ethylene oxide removal have been reported as high as 99.9+%.[28]

Catalytic converters are used in at least two plants and have been recommended as the best control system for emissions from the secondary absorber vent in air oxidation plants. They are designed to convert ethane and ethylene to CO_2 and water. The exhaust gas may be used to drive a turbine. Other combustion devices also may be used to reduce emissions. Combustion in a steam boiler is practiced in at least one ethylene oxide plant. Thermal incineration would also eliminate volatile organic emissions from the absorber vent, but applicability may be limited by the low organic content of the stream. The vent from the fractionation column in air oxidation plants can be incinerated, however. It has been suggested that combination and incineration of the absorber and fractionation vent streams may be feasible.[29] Flaring could be used, probably with the addition of fuel. A 90% combustion efficiency is usually assumed for this type of control method.[30]

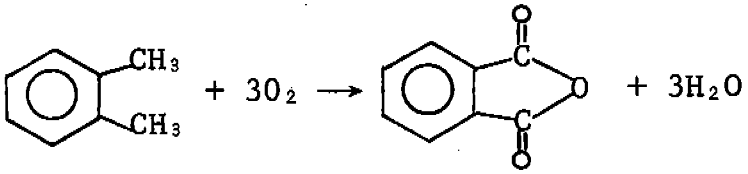
4.4.4.3 Cost, Energy, and Environmental Impact of Controls

Generalized costs, energy requirements, and environmental impacts of incineration devices and flares are included in Section 3 of this report. In addition there are some specific cost and energy data included in Tables 4.4-14 and 4.4-15 for controlling emissions from ethylene oxide plants in 1973.

The possibility of NO_x and CO formation and emission from combustion equipment exists under certain operating conditions. If supplemental fuel contains sulfur, SO_2 emissions will also result.

4.4.5 Phthalic Anhydride

The production of phthalic anhydride by oxidation of o-xylene is shown in the following chemical equation.



In addition to this reaction there are side reactions which produce CO_2 and maleic anhydride.

TABLE 4.4-14. ENERGY AND COST DATA FOR CONTROLLING VOLATILE ORGANIC EMISSIONS FROM ETHYLENE OXIDE PRODUCTION (AIR OXIDATION)[a,b,31]

Waste Stream	Control Technique	Energy Requirements Fuel	 Electricity	Annualized[c] Cost (1973)
Main process vent 15.3 m^3/s (32,402 scfm)	Catalytic incinerator	1.32 TJ/yr (1250×10^6 Btu/yr)	72 GJ/yr (20,000 kWh/yr)	\$3,400/yr[d]
CO_2 rich purge gas 0.226 m^3/s (480 scfm)	Catalytic incinerator	1.32 TJ/yr (1250×10^6 Btu/yr)	72 GJ/yr (20,000 kWh/yr)	\$4,000/yr[d]

[a] 90 Mg/yr (100,000 Tons/yr) production rate.

[b] 1973 dollars.

[c] Costs are based on several assumptions. See original reference. Costs are based on 1973 dollars and conditions. Current costs may be significantly higher.

[d] Includes heat recovery credit.

TABLE 4.4-15. ENERGY AND COST DATA FOR CONTROLLING VOLATILE ORGANIC EMISSIONS FROM ETHYLENE OXIDE PRODUCTION (OXYGEN PROCESS)[a] 32

Waste Stream	Flow Rate	Control Technique	Energy Requirements		Annualized Cost (1973)[b]
			Fuel	Electricity	
Main Process Vent	$0.330 m^3/s$ (699 scfm)	Steam boiler	3.96 TJ/yr (3750×10^6 Btu/yr)	72 GJ/yr (20,000 kWh/yr)	\$5,900/yr[c]
	$0.331 m^3/s$ (702 scfm)	Thermal incinerator	3.96 TJ/yr (3750×10^6 Btu/yr)	36 GJ/yr (10,000 kWh/yr)	\$9,600/yr

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[a] Production rate 90 Mg/yr (100,000 tons/yr).

[b] Costs are based on 1973 dollars and conditions. Current costs may be significantly higher.

[c] Includes heat recovery credit.

In the phthalic anhydride process, liquid o-xylene is vaporized and mixed with compressed, preheated air. A small amount of SO_2 is added to maintain catalyst activity. The mixture is fed to fixed-bed tubular reactors containing vanadium pentoxide catalyst. Temperature is controlled with a circulating molten salt bath. The effluent gases are cooled in switch condensers where the phthalic anhydride condenses as a solid. Condensers are heated to melt the crude phthalic anhydride which is stored in a storage tank. Vent gases from the condensers are directed through a cyclone for removal of entrained solids. The collected solids are melted and added to the storage tank. The remaining gas is usually scrubbed and may be incinerated to remove residual organics before it is vented. The crude phthalic anhydride is pretreated to remove water and some low boiling products. The pretreated, crude phthalic anhydride is purified by vacuum distillation before it is stored in molten or solid form. If solid product is required, a flaking and bagging operation is necessary. Figure 4.4-5 is a simplified flow sheet of the process.

4.4.5.1 Emission Characteristics

Average volatile organics emissions from phthalic anhydride production are estimated as 0.0001 kg/kg (0.0001 lb/lb) product. An estimate of total organic emissions from phthalic anhydride production is 45 Mg/yr (0.1×10^6 lbs/yr).[33] Emissions may occur at the switch condenser vents in the pretreatment section, at the fractionation columns, and at storage tank vents. The vent from the switch condensers is usually controlled by scrubbing and often by incineration. A typical composition of this vent stream before it is treated is given in Table 4.4-16. Pretreatment and product fractionation are performed under vacuum. Noncondensibles and light ends are emitted in the exhaust stream from the vacuum jet ejector.

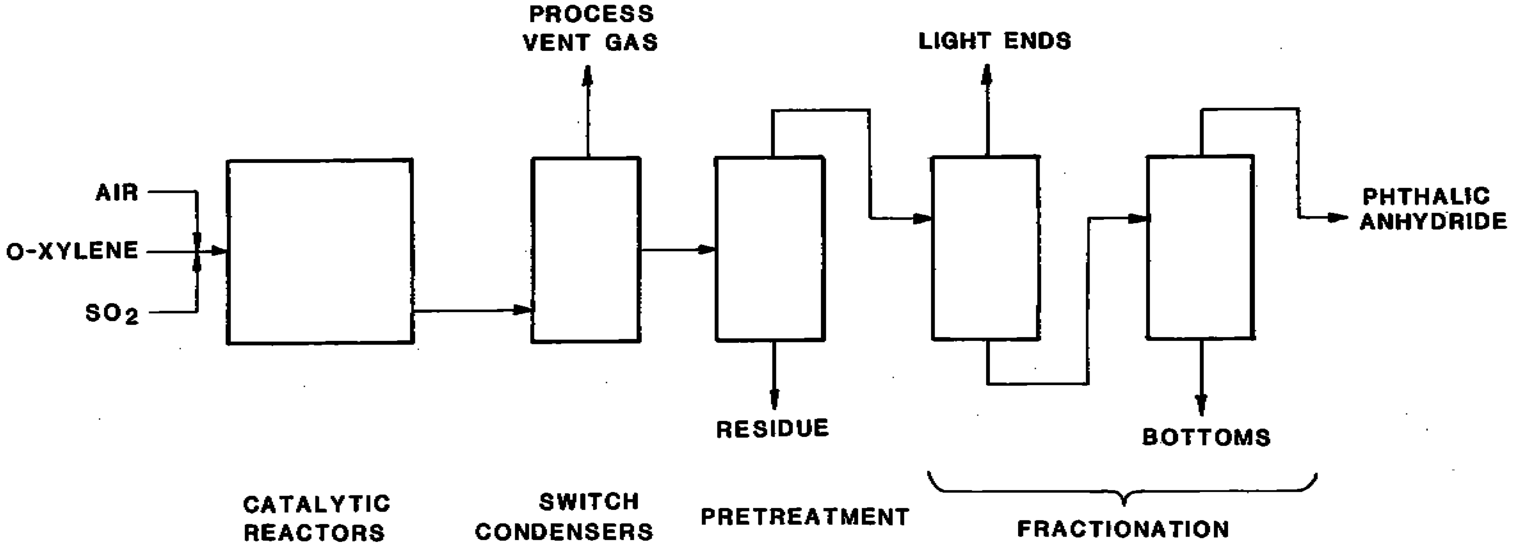


Figure 4.4-5. Flow diagram for production of phthalic anhydride from o-xylene.

TABLE 4-4-16. TYPICAL VENT GAS FROM SWITCH CONDENSERS BEFORE TREATMENT[a,34]

Component	Range in Average Composition (mol%)	Average Flow Rate (kg/hr)	Average Flow Rate (lb/hr)
Sulfur dioxide	0.006-0.012	34	75[b]
Carbon monoxide	0.4-0.5	1,094	2,411
Carbon dioxide	0.6-1.8	3,777	8,326
Nitrogen	76-79	184,957	407,760
Oxygen	16.5-16.9	46,239	101,940
Phthalic anhydride	0.050-0.065	167	368
Maleic anhydride		315	694
Benzoic acid		20	45
Misc. hydrocarbons	4.0-5.5		
Water		6,955	15,333
TOTAL		243,558	536,952

[a] Upstream of pollution control equipment

[b] New catalyst value. Value varies with age of catalyst.

Xylene feed is stored in fixed roof storage tanks with atmospheric vents. Resulting emissions are estimated at 0.0001 kg/kg (0.001 lb/lb) product.[35] Molten phthalic anhydride is stored at 150°C (300°F) and near stmospheric pressure with a continuous nitrogen purge. The purge produces a continuous gas stream which is vented to the air.

A small quantity of emissions is produced in the flaking and bagging exhaust (0.001 kg/kg, 0.001 lb/lb product) and in the heat transfer system at the switch condensers (0.0002 kg/kg, 0.0002 lb/lb product).[36]

See Sections 4.6, 4.1, and 4.15 for transportation emissions, fugitive emissions, and waste disposal emissions.

4.4.5.2 Control Technology

The current practice in the industry is to control the vent gas from the switch condenser using a variety of equipment. One method of control is water scrubbing followed by incineration of the wastewater. The system has an estimated volatile organic removal efficiency of about 96%. A problem encountered is that the scrubbing solution is very corrosive due to the presence of maleic acid from absorbed maleic anhydride.[37] Other methods for controlling the vent gas are a) water scrubbing followed by biological oxidation of the wastewater and b) direct thermal incineration.

Thermal incineration is employed by at least one plant to control emissions from the condenser vent. Combustion of 90-95% of the organics is estimated.[38,39] Thermal incinerators combined with waste heat boilers are also used. 97% destruction of organics was measured in a test of this equipment combination.[40]

Catalytic incineration is practiced in some phthalic anhydride plants which use naphthalene feed instead of o-xylene. Catalyst life is shortened by fouling and poisoning, and reported catalytic combustion efficiencies are only 40-60 percent.[41]

Combustion in a steam boiler has not been applied as a control method, although it could be effective if the vent stream is small compared to the total boiler requirement. Flaring might also be used for a control method on the condenser vent. However, efficiencies for removing contaminants are lower than for other combustion methods.

The effluent from the steam ejectors in the pretreatment and fractionation areas may be controlled by the condenser vent control equipment or it may be sent off-site for disposal (see Section 4.15). At least one installation has a separate incineration for ejector exhaust and by-product hydrocarbons from fractionation. Ninety-nine percent of the combustibles are reportedly burned.[42]

Storage tanks in phthalic anhydride plants are vented directly to the atmosphere. Some producers send portions of the vented gas to incinerators. At least one plant is equipped with condensers from which phthalic anhydride is removed manually. Recovery of phthalic anhydride in this manner amounts to about 0.0002 kg/kg of product (0.0002 lb/lb).[43]

4.4.5.3 Cost, Energy, and Environmental Impact of Controls

General discussions of energy requirements, costs, and environmental impacts of water scrubbing, incineration, and condensation are located in Section 3. Some more specific cost and energy data for control techniques for phthalic anhydride production in 1973 are included in Table 4.4-17.

Combustion devices have the potential for emissions of NO_x and CO. If supplemental fuel contains sulfur, SO_2 emissions will also result. If water scrubbing is used as a control method, a wastewater stream results which will require treatment before its disposal.

TABLE 4.4-17. ENERGY AND COST DATA FOR CONTROLLING VOLATILE ORGANIC EMISSIONS FROM PHTHALIC ANHYDRIDE PRODUCTION[a,45]

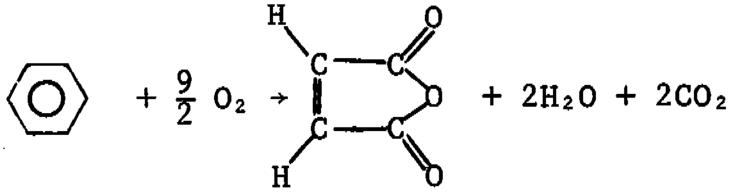
Waste Stream	Control Technique	Energy Requirements		Annualized[b] Cost (1973)
		Fuel	Electricity	
Vent gas from switch condensers $56.3\ m^3/s$ (119,300 scfm)	Water scrubbing and incineration	146.5 TJ/yr ($138{,}750\text{x}10^6$ Btu/yr)	10.8 TJ/yr ($3\text{x}10^6$ kWh/yr)	$420,100/yr
	Direct incineration	523.4 TJ/yr ($495{,}750\text{x}10^6$ Btu/yr)	7.13 TJ/yr (1,980,000 kWh/yr)	$395,100/yr
	Incineration and waste heat boiler	1.48 PJ/yr ($1{,}405{,}750\text{x}10^6$ Btu/yr)		$401,500/yr
Waste products 2.63 Mg/hr (5,792 lb/hr)	Direct incineration	33.8 TJ/yr ($32{,}000\text{x}10^6$ Btu/yr)	0.36 TJ/yr (100,000 kWh/yr)	$48,300/yr

[a] 60 Gg/yr (130 MM lb/yr) production rate.

[b] Costs are based on several assumptions. See original reference. Costs are based on 1973 dollars and conditions. Current costs may be significantly higher.

4.4.6 Maleic Anhydride

Maleic anhydride is produced by the catalytic oxidation of benzene. The reaction is shown in the following chemical equation.



Processing variations exist within the industry; however, the following process description is considered typical.[46] A mixture of benzene and air is introduced into a reactor containing vanadium pentoxide and molybdenum catalyst. Temperature control is achieved through circulating heat transfer fluid or molten salt. The reactor effluent is cooled before it passes through a partial condenser and separator. The overhead material is passed through an absorber for recovery of the anhydride as maleic acid. Maleic acid is generally dehydrated by azeotropic distillation with xylene. Some producers use thermal dehydration. The resulting anhydride is combined with maleic anhydride from the condenser. Purification is accomplished by vacuum distillation. The solid product is tableted or flaked before packaging or storage. The product may also be shipped in bulk liquid form. Figure 4.4-6 is a simplified flow sheet of the maleic anhydride process.

There are alternative processes using butane and butene feed. They are used by at least one U.S. producer and are used in several other countries. They might become more significant in the U.S., depending on the relative costs of the raw materials. With the exception of raw material storage and some reactor modifications, the C_4 system is about the same as the benzene process.

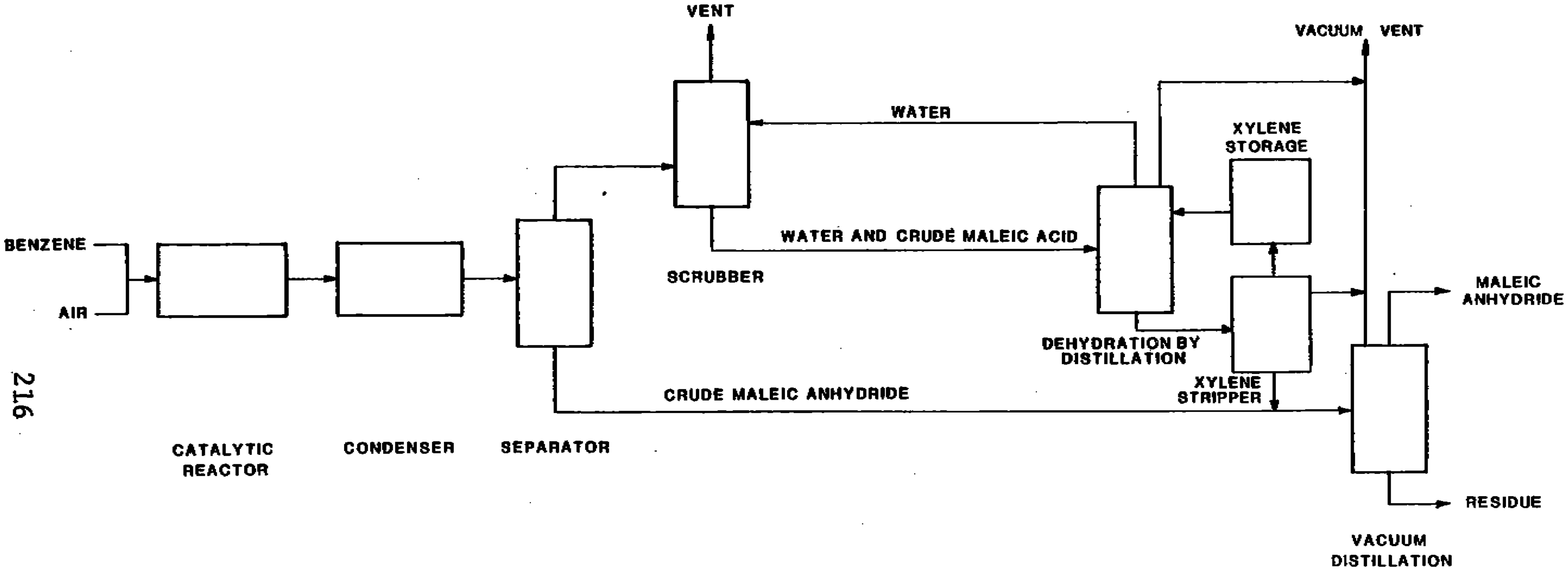


Figure 4.4-6. Flow diagram for production of maleic anhydride from benzene.

4.4.6.1 Emission Characteristics

Estimated volatile organic emissions from maleic anhydride production are 0.088 kg/kg product (0.088 lb/lb product), including vented process emissions, fugitive emissions, and emissions from the storage and handling of raw materials and product.[47] The estimates are based on uncontrolled emission sources. Two major sources are vents from the product recovery scrubber and the vacuum system in the fractionation section. Estimated average emissions from the product recovery scrubber vent are 0.086 kg/kg of product (0.086 lb/lb).[48] Benzene emissions from this vent average 0.067 kg/kg of product (0.067 lb/lb).[49] During short term process upsets emissions may be 3 to 5 times greater.[50] Other organic substances in the vent gas stream include maleic anhydride, maleic acid, formaldehyde, formic acid and xylene.[51]

Maleic anhydride emissions are produced in product handling operations such as flaking, pelleting, packaging, and storage. Estimates from one plant are emissions of 0.0002 kg maleic anhydride/kg product (0.0002 lb/lb). Another plant reported losses of 0.3 kg/hr (0.6 lb/hr) of maleic anhydride from the product storage area.[52]

4.4.6.2 Control Technology

Scrubbers are used on the gas stream from the separator to recover product. Some plants also treat vent gases from dehydration, fractionation, and storage tanks by scrubbing. Maleic acid removal efficiencies are quite high for scrubbing devices, but total hydrocarbon removal efficiencies are low.[53] Carbon adsorption and incineration are methods of control employed in several existing facilities to remove the remaining organics from the vent gas stream. Process modifications which increase feedstock utilization efficiencies may also be used to reduce emissions. Possible modifications include substitution of oxygen for air, use of fluidization, use of more selective catalysts, and use of recycle air.[54]

4.4.6.3 Cost, Energy, and Environmental Impact of Controls

Costs, energy requirements, and environmental impacts for absorption, adsorption, and incineration are included in Section 3. The information is of a general nature. More specific information for maleic anhydride production was unavailable in the sources consulted for this study.

Some general comments about potential environmental impacts of control methods may be made. Incineration has the potential for emitting NO_x and CO to the atmosphere. However, in the case of maleic anhydride, application of incineration may reduce potential CO emissions because there is a high concentration of CO in the stream to be incinerated. One company reports greater than 95% reduction in CO by the use of an incinerator.[55]

4.4.7 Vinyl Chloride Monomer by Balanced Process

The balanced process for making vinyl chloride monomer (VCM) includes the manufacture of ethylene dichloride (EDC) as well as vinyl chloride. Production of vinyl chloride by cracking ethylene dichloride results in a hydrogen chloride stream which is recycled to oxychlorination reactors for making more ethylene dichloride. Additional ethylene dichloride is made by direct chlorination of ethylene. The production of ethylene dichloride is balanced so that there is no net production or consumption of HCl.

Figure 4.4-7 is a simplified process flow sheet showing all three processes: ethylene dichloride by direct chlorination, ethylene dichloride by oxychlorination, and vinyl chloride production by cracking of ethylene dichloride. Variations exist in the industry, and Figure 4.4-7 represents a typical operation.

The overall reaction involved in producing ethylene dichloride by direct chlorination of ethylene is shown in the following chemical equation.

$$2CH_2{=}CH_2 + 2Cl_2 \rightarrow 2CH_2ClCH_2Cl$$

Ethylene and chlorine are fed to a constant temperature reactor. Temperature is controlled by using jacketed vessels, cooling coils, or external heat exchange. The reactor effluent usually consists of a vapor stream in addition to a liquid stream. The vapor stream passes through a condenser and an absorber using water or dilute caustic as a sorbent before it is vented.

A parallel oxychlorination process produces ethylene dichloride using by-product HCl from the vinyl chloride plant. The chemical reaction is shown in the following equation.

$$2CH_2{=}CH_2 + O_2 + 4HCl \rightarrow 2CH_2ClCH_2Cl + 2H_2O$$

Ethylene, hydrogen chloride, and air or oxygen are fed to a reactor at 0.24-0.62 MPa (20-75 psig) and 222-333°C (430-630°F). The highly exothermic reaction requires efficient heat removal from the reactor. The reactor effluent is cooled by indirect heat exchange or by direct contact with water and is then treated in a phase separator. Noncondensible gases are contacted with water and/or aromatic solvent before they are vented to the atmosphere. These operations reduce HCl and hydrocarbon

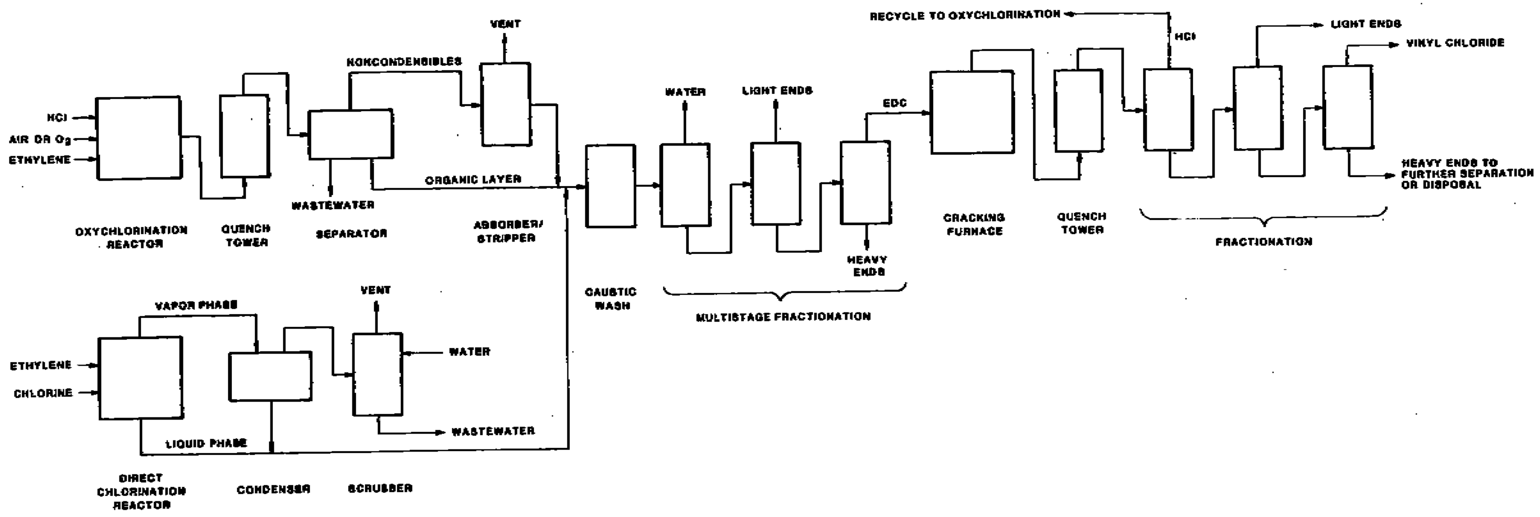


Figure 4.4-7. Flow diagram for production of ethylene dichloride and vinyl chloride monomer.

emissions. Some producers employ a direct chlorination step to reduce the amount of ethylene lost in the vent gas.

The organic liquid from the phase separator in the oxychlorination process is combined with the organic liquid from the direct chlorination process. The combined streams may be washed with caustic soda, or they may be sent directly to a distillation unit for removal of water and chlorinated hydrocarbon impurities. Chlorinated hydrocarbon impurities are sent off-site to disposal. Some plants employ another distillation step to further purify the ethylene dichloride. Other plants have no product fractionation facilities in the ethylene dichloride sections, however. In these cases the impurities may be rejected in downstream VCM facilities.[56] The aqueous phase collected in the phase separator is discharged as waste. It may be treated in stripping columns for hydrocarbon removal before it is sent to treatment or disposal.[57]

Ethylene dichloride is cracked in the cracking furnace at 480-510°C (900-950°F) and 0.45 MPa (50 psig). The hot effluent gases are quenched and partially condensed by direct contact with ethylene dichloride. Purification of vinyl chloride monomer is accomplished in several fractionation towers. HCl is recycled to oxychlorination, recovered ethylene dichloride is recycled to the process, and the remainder of the light and heavy ends are either further processed or disposed of. Vinyl chloride product is usually caustic washed and sent to product storage.[58]

4.4.7.1 Emission Characteristics

Oxychlorination Process

The estimated hydrocarbon emissions from the entire oxychlorination process are 0.028 kg/kg (0.028 lb/lb) EDC or 8.5 Gg/yr (18.8x10^6 lbs/yr).[59] These emissions are produced at the main process vent from the phase separator (usually scrubbed before venting), at product fractionation column vents, and at storage tank vents. Catalyst conditioning may contribute additional hydrocarbon emissions.

The vent gas from the oxychlorination process is usually exhausted to the air from a scrubber or absorber. This vent gas is the primary hydrocarbon emission source in the oxychlorination portion of the plant. The average vinyl chloride emissions were estimated to be 0.00036 kg/kg (0.00036 lb/lb) of ethylene dichloride produced. This number represents an average of emission numbers submitted by the industry.[60] However, since promulgation of the emission standards for vinyl chloride (41 FR 46560) in 1976, this emission factor has dropped.

Small gas streams containing hydrocarbons result from the fractionation column vents. All of the fractionation vent gases may be combined. The uncontrolled vent stream contains about 0.010 kg volatile organics/kg EDC produced (0.010 lb/lb).[61] VCM is about five percent of the volatile organics.[62]

Because the vapor pressure of ethylene dichloride is low, 21 kPa (3 psi) at 38°C (100°F), product storage tanks are normally vented to the atmosphere.[63] Vapor recovery is practiced to reduce emissions in some transfer operations for filling transportation equipment. Normal storage capacity is 1.5 to 2 day production.[64] Estimated EDC losses from storage tanks are 0.0006kg/kg EDC produced (0.0006 lb/lb).[65]

Direct Chlorination Process

The direct chlorination process vent is the major source of gaseous emissions from this area of the plant. The stream consists of inerts (0.018 kg/kg, 0.018lb/lb VCM), ethylene (0.0025 kg/kg, 0.0025 lb/lb VCM), ethylene dichloride (0.0016 kg/kg, 0.0016 lb/lb VCM), and small amounts of vinyl chloride.[66] The fractionation emissions are included in the oxychlorination section above.

Vinyl Chloride Process

The fractionation area of the vinyl chloride production process is the largest source of organic emissions from this area of the plant.[67] Estimates of organic emissions from an uncontrolled fractionation vent include 0.0021 kg hydrocarbons plus 0.0024 kg VCM per kg VCM product (0.0021 lb and 0.0024 lb, respectively, per lb product).[68] Hydrocarbon emissions from the quench tower are estimated at 0.00005 kg/kg (0.00005 lb/lb) product. Storage and fugitive losses are estimated to be 0.0001 kg hydrocarbons/kg VCM by one information source (0.0001 lb/lb).[69] Another source indicates that fugitive losses of VCM amount to 0.0012 kg/kg (0.0012 lb/lb) VCM product.[70] These emission factor estimates were made before promulgation of the emission standards for vinyl chloride; therefore, current emission factors will be significantly lower.

4.4.7.2 Control Technology

Oxychlorination Process

There are several methods currently used in oxychlorination facilities for control of emissions from the main process vent. Absorption is used on at least one installation to recover

EDC. The amount of EDC recovered using this method is 0.02 kg EDC/kg EDC product (0.02 lb/lb).[71] Condensation by refrigeration of the vent gas stream to -6 C^{o}(21^{o}F) is practiced in another facility.[72] Organic emissions after the refrigeration step are 0.015 kg/kg EDC (0.015 lb/lb).[73] Some producers using aromatic solvent absorber-stripper systems for product recovery use mist eliminators to prevent liquid carryover. Estimated solvent recovery for these systems is 0.010 kg solvent/kg EDC produced (0.010 lb/lb).[74] Some losses of the aromatic solvent occur (0.0009 kg/kg VCM)(0.0009 lb/lb), but total volatile organic emissions are lowered to 0.012 kg/kg (VCM (0.012 lb/lb).[75] Another method currently used for reducing ethylene emissions in the vent gas is direct chlorination. Data indicate that hydrocarbon emissions in the vent stream are reduced by about 50 percent when direct chlorination is employed.

Combustion devices reduce or eliminate volatile organic emissions from the process vent. Combustion of chlorinated hydrocarbons results in formation of HCl, Cl_2, and toxic gases, which cannot be vented to the atmosphere. However, these substances may be removed by scrubbing. Scrubbing equipment in contact with solutions of these substances may suffer severe corrosion. Combustion devices (boilers and thermal incinerators) would have to employ scrubbers for removal of HCl and Cl_2 from the effluent gases. For this reason flaring could not be used. Indications are that several companies are now using incinerators.

The product fractionation vents in EDC plants are currently controlled in some plants by refrigeration. Refrigeration removes about 85% of the hydrocarbons contained in the gas.[76] Gas cooling techniques are also applicable to the vent streams from absorber lean oil stripping, wastewater stripping, and EDC caustic scrubbing, but they are not widely used. One facility has a refrigeration control device on a vent stream from wastewater stripping. It removes about 70% of the hydrocarbons contained in the gas.[77] Hydrocarbon emissions from wastewater stripping without refrigeration are about 0.002 Kg/kg EDC produced (0.002 lb/lb).[78] Combustion devices could be used for elimination of hydrocarbon emissions from sources controlled by refrigeration, but the resulting HCl would be emitted to the atmosphere. Using a combustion device downstream from a gas cooling operation would result in a lower HCl concentration in the gas, but it would probably not be low enough to exhaust the gas to the atmosphere.

Control devices available for the fixed roof storage tanks containing purified EDC product include floating roof tanks and vent condenser. Vent condensers are currently used in some locations. Emissions from crude EDC storage are controlled by the layer of water blanketing the organic material.[79]

Direct Chlorination Process

Vent gas from the direct chlorination plant is usually condensed and scrubbed before it is vented. It could be sent to the control device provided for the oxychlorination plant.

Vinyl Chloride Process

The vents from fractionation in the VCM plant may be controlled in several ways. One VCM producer uses EDC to absorb VCM vapors before the gas is vented. Stripping removes VCM, and the EDC is recycled to the pyrolysis units. VCM recovery is estimated at 99%.[80] Another company uses a waste heat boiler to burn hydrocarbons and chlorocarbons, including VCM. It is operated with two parallel caustic scrubbers upstream and a water scrubber downstream to collect chlorine and HCl. VCM levels were reduced by 98-99% in a test run. Another possible control method is compression and refrigeration to condense VCM before venting the inerts. It is estimated that this operation would recover 87% of the VCM in the gas stream. Another possibility is carbon adsorption. It is estimated that under optimum conditions 99.9% recovery of VCM and EDC could be achieved using a carbon adsorption system.[81]

Refrigeration is used by some producers to recover losses of VCM from storage and loading operation vents. One producer reports using -23°C (-10°F) temperatures to recover 0.0001 kg/kg VCM (0.0001 lb/lb) in this manner. Another refrigeration process operated at 4°C (40°F) recovers about 85% of the VCM in the stream before venting the gas.[82] See Sections 4.5, 4.6, and 4.1 for storage, loading, and fugitive emissions controls.

4.4.7.3 Cost, Energy, and Environmental Impact of Controls

Costs, energy requirements, and environmental impacts of absorption, condensation, and incineration are discussed generally in Section 3.0. Fugitive emissions and storage tank losses are treated in Sections 4.5 and 4.1. Some costs and energy requirements for control methods in a balanced vinyl chloride plant are also included here in Table 4.4-18.

In combustion of vent gas streams in a vinyl chloride plant provision must be made to remove the HCl, Cl_2 and other chlorine compounds formed. The combustion process also has the potential for forming NO_x and CO. Carbon adsorption systems have an associated solid waste problem if the beds are not regenerated. If the beds are regenerated at high temperatures, atmospheric emissions may result.

TABLE 4.4-18. ENERGY AND COST DATA FOR CONTROL OF VOLATILE ORGANIC EMISSIONS FROM PRODUCTION OF VINYL CHLORIDE MONOMER BY THE BALANCED PROCESS,[a, 83]

		Energy Requirements		Annualized
Waste Stream	Control Technique	Fuel	Power	Cost[b,c]
Oxychlorination vent	Incinerator and waste heat boiler with caustic scrubbers	14GJ - 30GJ/hr (14-28x10^6 Btu/hr)[d]	0.36 GJ/hr (100 kWh/hr)	$1,140,000
EDC fractionation	Waste heat boiler with caustic scrubbers	2 GJ/hr (2x10^6 Btu/hr)	0.16 GJ/hr (45 kWh/hr)	$300,000
VCM fractionation	Refrigeration		0.14 GJ/hr (40 kWh/hr)	$200,000
	Waste heat boiler with caustic scrubbers	2 GJ/hr (2x10^6 Btu/hr)	0.16 GJ/hr (45 kWh/hr)	$300,000
Storage and loading	Compression and refrigeration		0.14 GJ/hr (40 kWh/hr)	$200,000
Fugitive losses	Continuous loop sampler	Utility requirements insignificant		$ 50,000
	Canned pumps			$200,000
	Monitoring of VCM leaks			$200,000

[a] 700 x 10^6 lb/yr production rate.
[b] January, 1975 dollars, capital costs.
[c] Costs are based on several assumptions. See original reference.
[d] 33,800 lb steam generated/hr (245 psig).

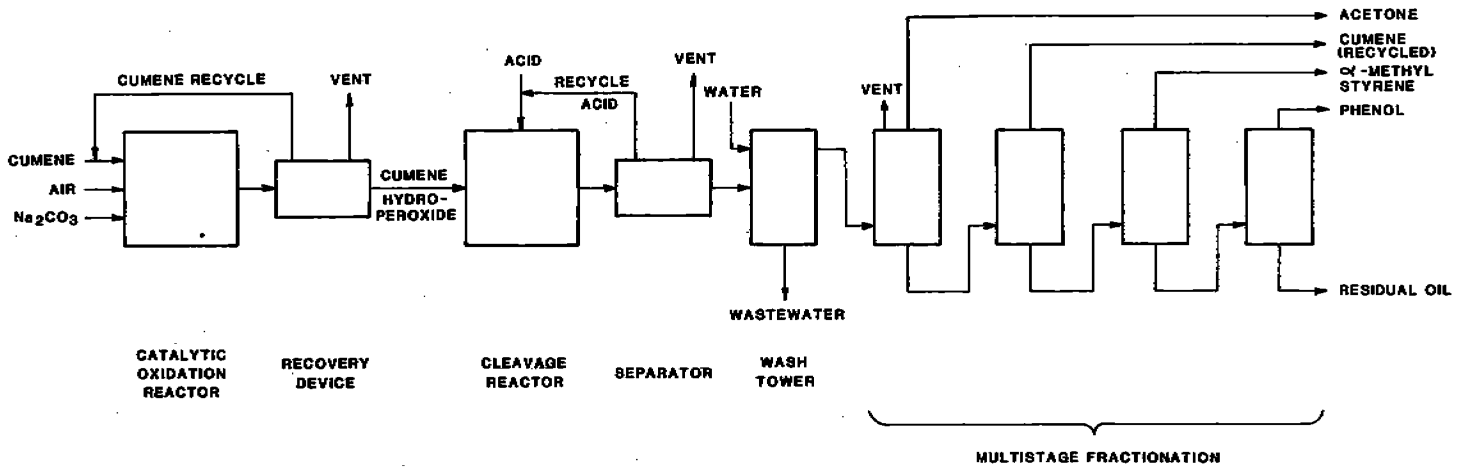


Figure 4.4-8. Flow diagram for the production of acetone and phenol from cumene.

4.4.8 Acetone and Phenol from Cumene

There are two steps involved in producing acetone and phenol from cumene. The first step is production of cumene hydroperoxide by oxidation. The second step is cleavage of cumene hydroperoxide to form acetone and phenol. The chemical reactions are shown in the following equations. α-methyl styrene and acetophenone are formed as by-products.

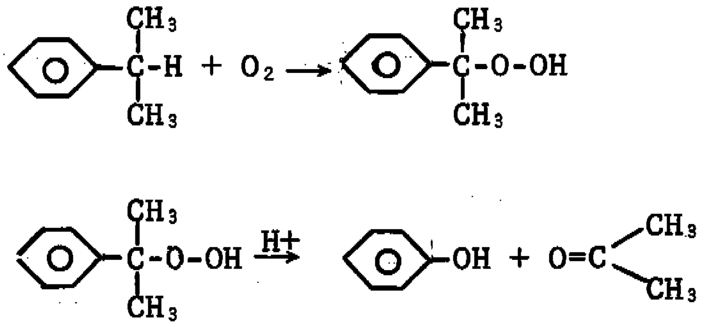


Figure 4.4-8 is a simplified process flow sheet of the process.

Air, sodium carbonate, and cumene are agitated in the reactor to produce cumene hydroperoxide. Catalysts and emulsifiers may also be used. Reactor gases are vented through refrigeration systems and other equipment for recovery of cumene.

Cumene hydroperoxide formed in the oxidation step is contacted with sulfuric acid in the cleavage step to produce acetone and phenol. The organic layer is washed with water before it is fractionated in a series of distillation towers. Cumene is recovered and recycled; α-methyl styrene is hydrogenated and recycled or may be recovered as product; and phenol and acetone are stored. The by-product, acetophenone, may be purified, or it may be left with the residual oil.

4.4.8.1 Emission Characteristics

The largest single source of emissions in the production of phenol and acetone from cumene is the vent from the oxidation reactor. Emissions are significant even though recovery devices are an integral part of the equipment. Volatile organic emissions reported from this source vary from trace amounts to 0.0067 kg/kg phenol produced (0.0067 lb/lb).[84] Equipment failures have reportedly caused 1-4 hr emission rates of 0.049 kg/kg phenol (49 lb/1000 lb).[85] A summary estimate of average emissions from acetone and phenol plants is 0.0038 kg hydrocarbons/kg phenol product from this vent gas (0.0038 lb/lb).[86]

Some producers have concentrators on the vent gas stream. The concentrator vents have low emission levels of 0.0003 Kg/kg phenol (0.0003 lb/lb) or less. The cleavage reactor vent also contributes "low to moderate" light organics emissions.[87] The emissions in the concentration and cleavage reactor section are estimated to be 0.0021 kg/kg phenol product (0.0021 lb/lb).[88]

Volatile organics are also emitted in the fractionation section at the distillation columns. The major organic emission is acetone. Formaldehyde may also be emitted as may trace amounts of cumene, mesityl oxide, α-methyl styrene, and phenol. An average estimate of hydrocarbon emissions from this section of the plant is 0.0038 Kg/kg phenol (0.0038 lb/lb).[89] One producer estimates 0.0043 kg acetone and 0.003 kg formaldehyde/kg phenol product (0.0043 and 0.003 lb, respectively, per lb product). Another estimates 0.0012 kg acetone and 0.0009 kg formaldehyde/kg phenol (0.0012 lb and 0.0009 lb, respectively, per lb product).[90] It is emphasized that the above emissions estimates are several years old. Current emissions are thought to be lower for most plants.

Storage tanks for raw materials and products also are emission sources. Other volatile organic emissions have been reported during equipment failure, start ups, and plant emergencies. Sources of fugitive emissions are valve packings, flanges, pump seals, compressor seals, relief valves, and agitator seals.

4.4.8.2 Control Technology

Carbon adsorption is used in several plants to recover cumene from the oxidation reactor vent with reported specific efficiencies of 82-91%.[91] Recently, one company indicated an efficiency ranging from 95-99% for their carbon adsorption system.[92] Refrigerated condensation also is used in several facilities to recover cumene from the oxidizer off-gas.[93] Although the specific purpose of the adsorption and refrigeration systems is product recovery, use of the systems reduces emissions. An incinerator is used in at least one installation to eliminate emissions from the oxidizer vent gas. Another facility sends light waste to plant boilers for use as fuel.[94] Emissions are reportedly controlled from the cleavage reactor and the fractionation area of one plant by cold water condensers and knock out drums.[95] Many producers have floating roof tanks, N_2 blankets, or other conservation devices on storage tanks. Floating roof and vapor seal devices have virtually eliminated emissions from storage in one plant.[96] See Sections 4.1 and 4.5 for fugitive and storage emissions and control.

4.4.8.3 Cost, Energy, and Environmental Impact of Controls

Costs, energy requirements, and environmental impacts for adsorption, condensation, and incineration are covered in a generalized manner in Section 3.0. Specific data for controlling volatile organic emissions from phenol and acetone production were not available in the sources consulted for this study.

Some general comments can be made about environmental impact of control methods. Incineration has the potential for emitting NO_x and CO to the atmosphere. Carbon adsorption has the potential for creating a solid waste problem if the beds are not regenerated. Atmospheric emissions may result if the beds are regenerated at high temperatures.

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4.5 Storage Tanks

The petroleum and chemical process industries include many operations. Petroleum production, refining, chemical manufacturing, transportation, marketing, and consumption all require some type of storage for volatile organic liquids. Storage tanks for volatile organic liquids can be sources of evaporative emissions. This section discusses the types of storage tanks, the sources and quantities of emissions from each type, costs of various types of tanks, and the major control techniques available.

Two recent studies on storage tank emissions indicate that emission factors in this section may be high by 50% or more. However, the studies are not comprehensive enough to generate revised emission factors. API is conducting a more comprehensive study of emission losses in floating roof and fixed roof tanks. Completion of test programs and publication of revised emission factors are expected in early 1979.

A new source performance standard has been promulgated in 40 CFR Part 60 Subpart K, Standards of Performance for Storage Vessels for Petroleum Liquids. These standards generally apply only to refineries and refinery-type products and are not generally applicable to chemical plants. Three categories of volatility are low, intermediate, and high. Table 4.5-1 defines volatility in terms of vapor pressure and lists the types of storage tanks acceptable for liquids in each range of volatility. Five types of storage tanks are listed in Table 4.5-1.

The following sections describe each type of storage tank, emissions from the tanks, and control techniques. Fixed roof storage tanks for low volatility liquids are described in Section 4.5.1. Several tanks for storage of intermediate

TABLE 4.5-1. STORAGE TANKS WHICH PROVIDE ACCEPTABLE LEVELS OF ORGANIC VAPOR EMISSION CONTROL DEPENDING ON VOLATILITY OF LIQUID STORED

Volatility of Stored Liquid	Vapor Pressure Range		Type of Storage Tank Required for Acceptable Levels of Control[a]
	kPa Metric	psia	
low	<10	<1.5	fixed cone roof tank
intermediate	10-79	1.5-11.2	floating roof tank covered floating roof tank variable vapor space tank (lifter roof and flexible diaphragm) with vapor controls for loading losses
high	>77	>11.2	pressure tanks sealed or vented to recovery systems a. low pressure 2.5-15 psig b. intermediate pressure 15-30 psig c. high pressure >30 psig

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[a] Minimum acceptable standard under NSPS

volatility liquids are described in Section 4.5.2. Pressure tanks for high volatility liquids are discussed in Section 4.5.3. Table 4.5-2 gives emission factors for evaporation from storage tanks for low and intermediate volatility liquids. Table 4.5-3 is an inventory of storage tanks and their emissions. Section 4.5.4 contains a discussion of cost, energy, and environmental considerations of controlling emissions from storage tanks.

4.5.1 Fixed Roof Storage Tanks for Low Volatility Liquids

Use of fixed cone roof tanks is the minimum accepted standar for storage of low volatility liquids. Construction costs for fixed cone roof tanks are lower than costs for other storage tanks. As shown in Figure 4.5-1, fixed roof tanks consist of a cylindrical steel shell topped by a coned roof having a minimum slope of 3/4 inches in 12 inches. The tanks are generally equipped with a pressure/vacuum vent designed to contain minor vapor volume changes. The recommended maximum operating pressure/vacuum for large fixed cone roof tanks is +207 Pa/-207 Pa (+0.8 in H_2O/-0.8 in H_2O).[3]

4.5.1.1 Emissions

As shown in Table 4.5-3, fixed roof tanks are responsible for 80% of the total volatile organic emissions from storage tanks. The two major sources of emissions from fixed cone roof tanks are breathing losses and working losses. Breathing losses occur during changes in temperature or barometric pressure. Working losses occur as a result of filling or emptying operations. Filling loss is the result of vapor displacement by the input of liquid. Emptying loss is the expulsion of vapors after product withdrawal and is attributable to

TABLE 4.5-2. EVAPORATIVE EMISSION FACTORS FOR FIXED ROOF, FLOATING ROOF AND VARIABLE VAPOR SPACE STORAGE TANKS[1]

	Fuel Oils		Jet Fuels		Crude Oil	Motor Gasoline		
	No. 6	NO$_2$	Kerosene	Naphtha		RVP 7	RVP 10	RVP 13
Vapor Pressure @ 16°C(Pa) 60°F(psia)	0.3 $4.3\text{x}10^{-5}$	51 $7.4\text{x}10^{-3}$	59 $8.6\text{x}10^{-3}$	9,000 1.3	19,000 2.75	24,000 3.5	36,000 5.2	48,000 7.0
FIXED ROOF TANKS								
Breathing Loss								
New Tank Conditions								
lb/day - 10^3 gal	.00014	.0034	.0037	0.074	0.055	0.14	0.20	0.26
Kg/day - 10^3 liters	.000017	.00041	.00045	0.0087	0.0066	0.017	0.024	0.031
Old Tank Conditions								
lb/day - 10^3 gal	.00016	.0038	.0042	0.085	0.063	0.16	0.23	0.30
Kg/day - 10^3 liters	.000020	.00046	.00051	0.0098	0.0075	0.019	0.027	0.036
Working Loss								
lb/10^3 gal throughput	.00018	.023	.027	2.5	2.8	5.7	8.2	10
Kg/10^3 liter throughput	.000022	.0028	.0032	0.3	0.34	0.68	0.99	1.2
FLOATING ROOF TANKS								
Standing Storage Loss								
New Tank Conditions								
lb/day - 10^3 gal	.000014	.00039	.00043	0.0094	0.0099	0.018	0.026	0.035
Kg/day - 10^3 liters	.0000017	.000046	.000051	0.0011	0.0012	0.0022	0.0032	0.0041
Old Tank Conditions								
lb/day - 10^3 gal	.000034	.00089	.0010	0.022	0.023	0.043	0.061	0.079
Kg/day - 10^3 liters	.0000041	.000111	.00012	0.0027	0.0028	0.0052	0.0074	0.0094
Withdrawal Losses								
lb/10^3 gal throughput	NA	NA	NA	NA	NA	0.018	0.018	0.018
Kg/10^3 liter throughput	NA	NA	NA	NA	NA	0.0022	0.0022	0.0022
VARIABLE VAPOR SPACE TANKS								
Filling Loss								
lb/10^3 gal throughput	.00017	0.022	0.025	2.3	2.3	5.4	7.7	9.6
Kg/10^3 liter throughput	.00002	0.0026	0.0030	0.28	0.28	0.65	0.93	1.2

TABLE 4.5-3. PETROLEUM STORAGE TANK INVENTORY AND EMISSIONS[a,b,2]

Vapor Pressure Range kiloPascals (psia)	Fixed Roof		Floating & Internal Floating Roof		TOTAL	
	Tanks	Emissions Gg/yr (1000 tons/yr)	Tanks	Emissions Gg/yr (1000 tons/yr)	Tanks	Emissions Gg/yr (1000 tons/yr)
10.5 to 35.5	5,840	406	7,093	64	12,933	470
(1.52 to 5.14)		(447)		(70)		(517)
35.5 to 62.7	1,396	135	3,357	61	4,753	196
(5.14 to 9.08)		(149)		(67)		(216)
62.7 to 76.5	49	16	218	9	267	25
(9.08 to 11.1)		(18)		(9.9)		(28)
TOTAL	7,285	557	10,668	134	17,953	691
		(613)		(147)		(870)

[a] Includes only tanks with greater than 150,000 liter capacity.
[b] Calculated from AP-42, Supplement 7, April, 1977.

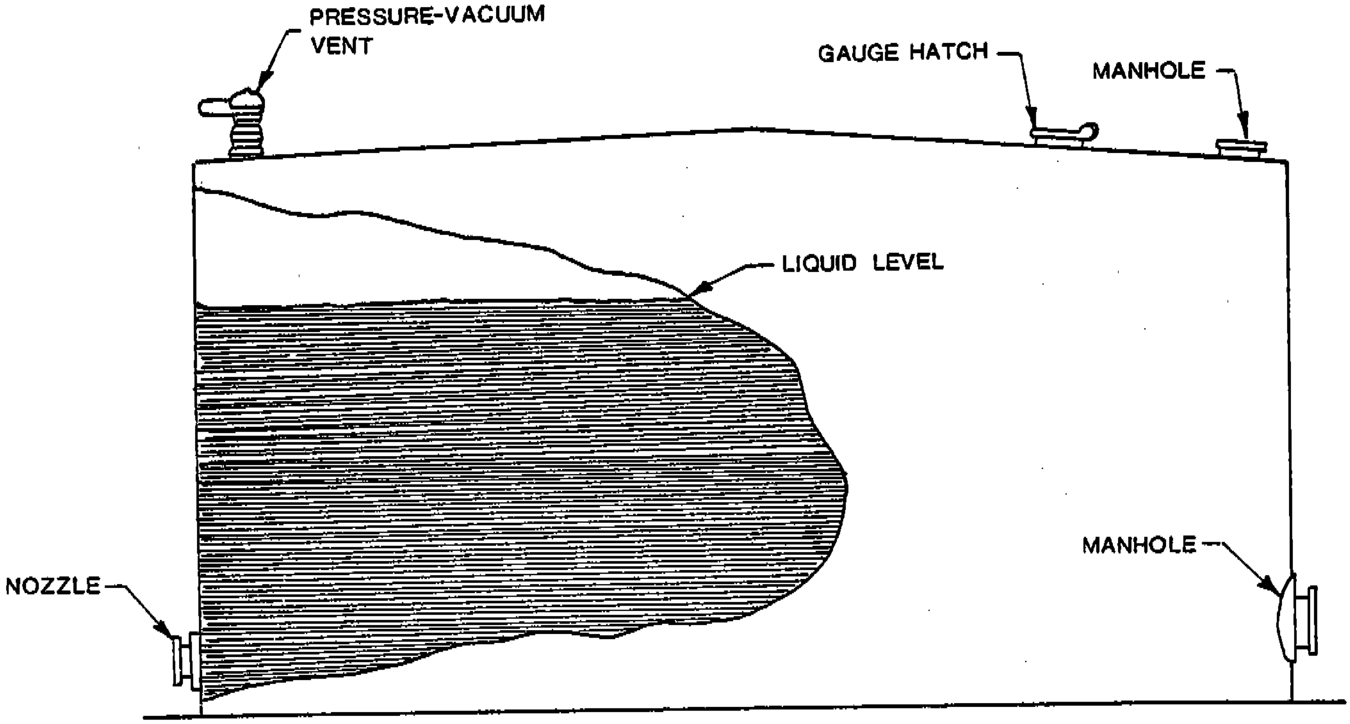

Figure 4.5-1. Fixed roof storage tank.

"vapor growth".[4] After product withdrawal, air enters the tank to fill the volume previously occupied by product. The stored liquid not withdrawn evaporates to the point of saturation in air. This process is called "vapor growth".

Factors affecting the rate of volatile organic loss from fixed roof storage tanks include:

1. True vapor pressure of the liquid stored
2. Temperature changes in the tank (primarily induced by diurnal ambient temperature changes)
3. Height of the vapor space (tank outage)
4. Tank diameter
5. Schedule of tank filling and emptying
6. Mechanical condition of tank and p/v valve seals
7. Tank design and type of exterior paint.

The American Petroleum Institute has developed emperical formulas, based on field testing, that correlate fixed cone roof tank evaporative losses with the above factors and other specific storage parameters. These equations and their application are presented in Supplement No. 7 of EPA document AP-42, Compilation of Air Pollution Emission Factors. The factors in AP-42 and the API bulletins are being revised. The equations are best suited for estimating average emissions for a group of tanks, and should be used with discretion for any specific tank. Emission rates calculated from these equations for some "typical" storage tank conditions are presented Table 4.5-2.

4.5.1.2 Control Technology

There are several ways to control emissions from storage of low volatility liquids. The first approach, applicable primarily to new construction, is to install storage tanks with lower loss rates than fixed cone roof tanks. Tanks with lower loss rates include floating roof tanks, internal floating covers, and variable vapor space tanks equipped with vapor recovery systems. These lower loss tanks are generally used for intermediate volatility liquids and are discussed in Section 4.5.2. The control efficiency of lower loss storage tanks is approximately 90 to 95 percent.[5]

A second approach to controlling evaporation losses from fixed roof storage tanks includes retrofit control technology such as internal floating roofs and vapor recovery systems. Internal floating roofs are large pans or decks which float freely on the surface of the stored liquid (Figure 4.5-2). The roof rises and falls according to the depth of the stored liquid. To insure that the liquid surface is completely covered, the roof is equipped with a sliding seal around its periphery which fits against the tank wall. Seals have also been developed for use where support columns must pass through the floating roof or cover. Internal floating roofs can generally be installed inside existing fixed roof tanks if they are of welded construction. However, if they are of bolted construction, they cannot be retrofitted.

Vapor recovery systems can also be installed on existing fixed cone roof tanks. Figure 4.5-3 is a flow diagram for a simplified vapor recovery system. Vapor recovery systems for tank farms, terminals, etc. are more complex than the example shown here. Vapors generated in the fixed roof tank are displaced through a piping system to a storage tank called a vapor saver. The vapor saver evens out surge flows and saves a reserve of vapors to return to the storage tank during inbreathing modes. Inbreathing saturated vapors instead of air prevents the evaporation of additional volatile organics. Several storage tanks can be manifolded into a single vapor saver and vapor recovery system. Vapor recovery systems are not usually as cost effective as internal floating roofs, particularly for tanks with high filling rates. They have not been widely used on large tanks and tank farms. The control efficiency of vapor recovery systems for fixed cone roofed tanks is approximately 90 to 98 percent.[6]

A third control technology, the use of conservation vents, is adequate only for low volatility product storage (less than 10.5 kPa, 1.52 psia). A conservation vent is a pressure and vacuum relief valve which vents only when a set pressure differential is exceeded.

4.5.2 Storage Tanks for Intermediate Volatility Liquids

Intermediate volatility liquids are generally stored in floating roof tanks, internal floating roof tanks, variable vapor space tanks with vapor recovery systems, and/or fixed roof tanks with vapor recovery systems. Although simple fixed roof tanks have been used for intermediate volatility liquid storage in the past, new source performance standards do not allow this practice.

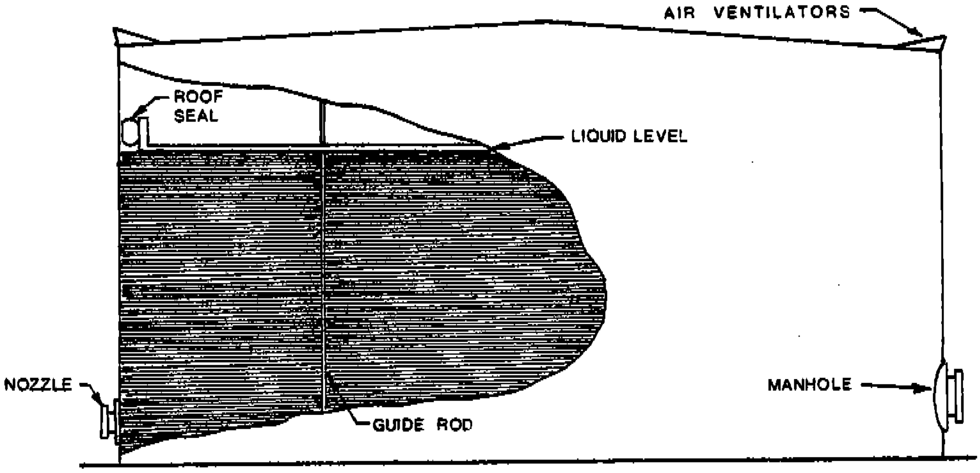

Figure 4.5-2. Covered floating roof storage tank.

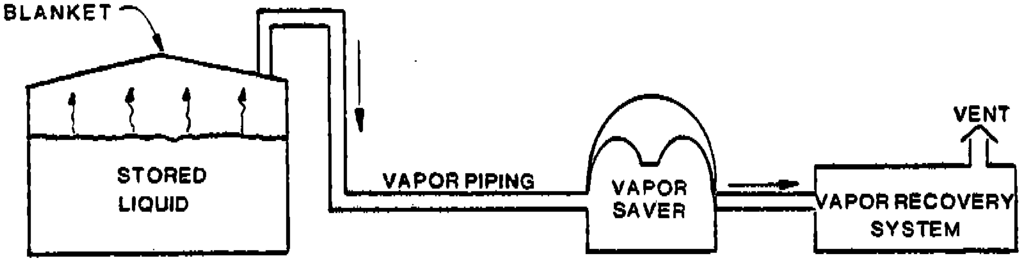

Figure 4.5-3. Example of simplified tankage vapor recovery system.

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Floating Roof Tanks

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 rises and falls according to the depth of stored liquid. To insure 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.

The most commonly used floating roof tank is the conventional open tank. The open tank roof deck is exposed to the weather, and provisions must be made for rain water drainage, snow removal, and sliding seal dirt protection. Floating roof decks are of three general types: pontoon, pan, and double deck.

The pontoon roof, shown in Figure 4.5-4, 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.

The pan roof shown in Figure 4.5-5 is a flat metal plate with a vertical rim and stiffening braces to maintain rigidity. 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.

As shown in Figure 4.5-6, the double deck roof has a hollow double deck covering the entire surface of the roof.

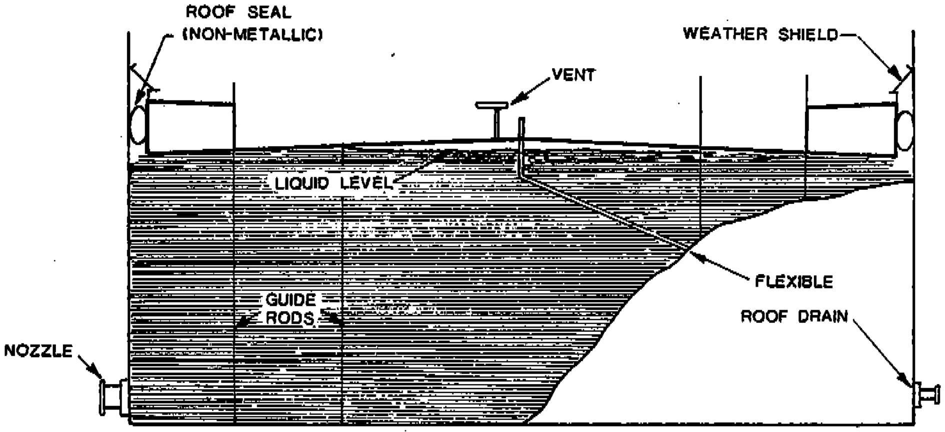

Figure 4.5-4. Single deck pontoon floating roof storage tank with non-metallic seals.

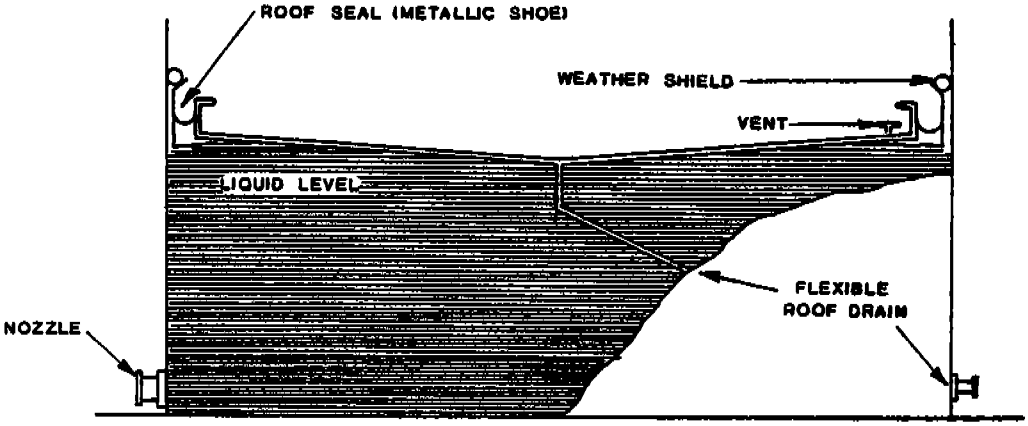

Figure 4.5-5. Pan-type floating roof storage tank with metallic seals.

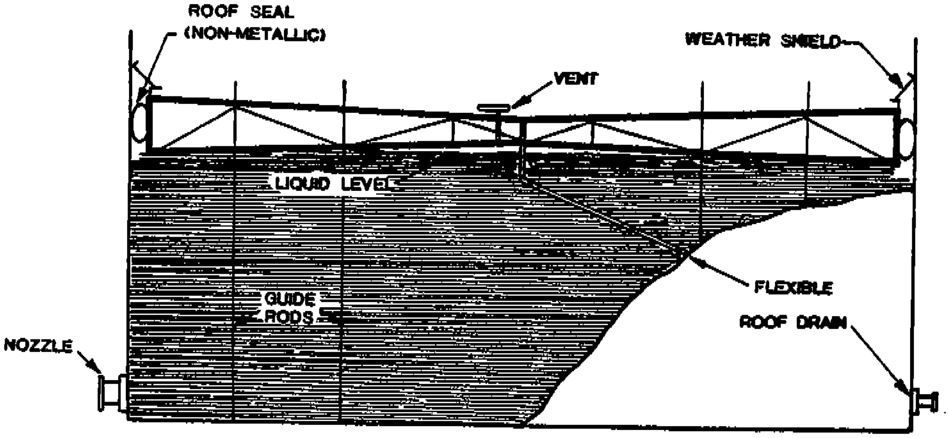

Figure 4.5-6. Double deck floating roof storage tank with non-metallic seals.

The double deck adds rigidity, and the dead air space between the upper and lower deck provides significant insulation from solar heating.[7]

Covered Floating Roof Tanks

The covered-type floating roof tank is essentially a fixed roof tank with a floating roof deck inside the tank (Figure 4.5-2). 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 seal 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 formation of a flammable mixture.

Variable Vapor Space Tanks

New variable vapor space tanks have not been built for several years. However, tank manufacturers have reported that new orders for variable vapor space tanks have been received.

Variable vapor space tanks are equipped with expandable vapor reservoirs to accommodate vapor volume fluctuations attributable to temperature and barometric pressure changes. A variable vapor space device is normally connected to the vapor spaces of one or more fixed roof tanks. The two most common types of variable vapor space tanks are lifted 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 4.5-7).[8]

Flexible diaphragm tanks utilize flexible membranes to provide the expandable volume. They may be separate gas-holder type units, or integral units mounted atop fixed roof tanks (Figure 4.5-8).[9]

4.5.2.1 Emissions

There are four major sources of emissions associated with the storage of intermediate volatility liquids: floating roof standing storage losses, floating roof withdrawal losses, vapor recovery system vents and variable vapor space filling losses.

Floating roof standing storage losses result from causes other than breathing or change 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. Some vapor may escape through the gaps created by these improper seal fits.

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.[10]

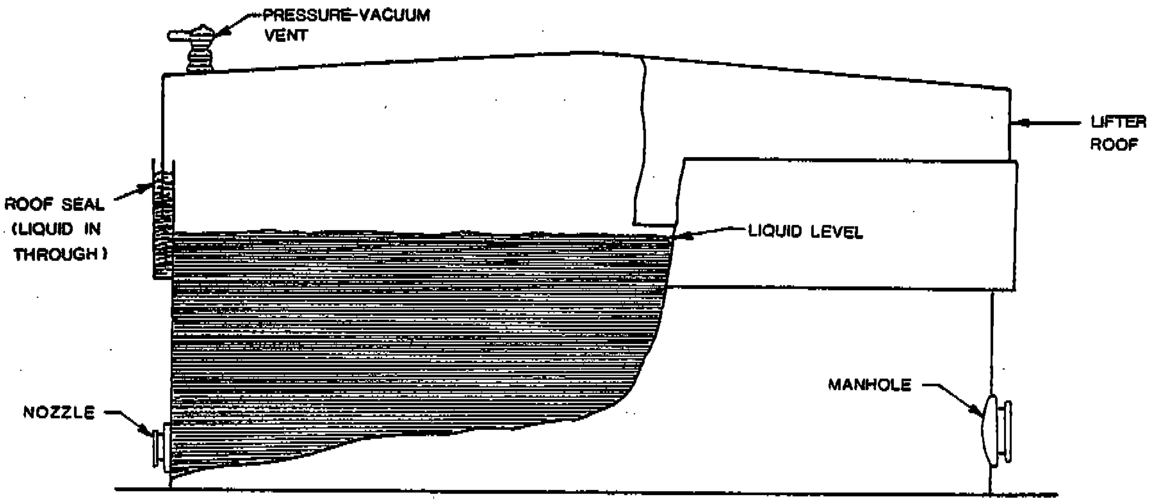

Figure 4.5-7. Lifter roof storage tank with wet seal.

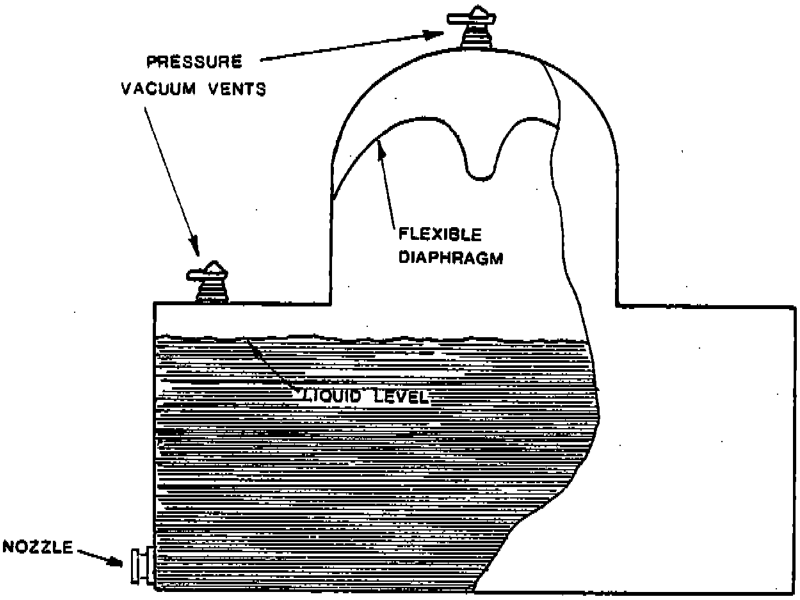

Figure 4.5-8. Flexible diaphragm tank (integral unit).

When intermediate volatility liquids are stored in fixed roof tanks with vapor recovery systems, there is an emission from the vapor recovery unit vent. Vapor recovery systems recover the organic portion of tankage vapors and vent the air portion back to the atmosphere. Because of inefficiencies in the vapor recovery systems, small quantities of volatile organics are also vented with the air to the atmosphere.[11] In many, if not most, vapor recovery systems where storage tank vapors are collected, the collected vapor stream, after heavy ends are collected, is burned directly in a furnace. In that case the system is not venting organic vapors to the atmosphere.

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.

The total amount of evaporation loss from storage tanks for intermediate volatility liquids depends on the factors listed in Section 4.5.1.1. The American Petroleum Institute has developed empirical formulas, based on field testing, that correlate evaporative losses for intermediate volatility liquids. These equations and their application are presented in Supplement No. 7 of EPA Document AP-42, Compilation of Air Pollutant Emission Factors.[12] Emission rates calculated from these equations for some "typical" storage tank conditions are presented in Table 4.5-2. The factors in AP-42 and the API bulletins on which they are based are presently being revised.

4.5.2.2 Control Technology

Although not generally applied, there are several approaches available for controlling emissions from the storage of intermediate vapor pressure liquids. For new construction tankage, emissions can be controlled by converting to another form of intermediate vapor pressure tankage with lower emission losses. It is also possible to control emissions by employing low pressure tankage. Low pressure tanks operating between 119 and 203 kPa (17-29 psia) have been used for the storage of motor gasolines, pentanes, and natural gasolines having vapor pressures up to 203 kPa (29 psia). With proper design, these low-pressure tanks can prevent breathing losses from intermediate volatility liquids. Working losses occur during filling when the pressure of the vapor space exceeds the pressure vent setting and vapors are expelled. These working losses depend on the pump-in rate, the rate of heat dissipation, and the pump-out rate. Working losses may be reduced by increasing the pressure of the vent setting; the increased cost of the high pressure tank may prohibit this option. Vapor recovery systems may be required to control working losses.[13]

4.5.3 Pressure Storage Tanks for High Volatility Liquids

High volatility liquids are generally stored in sealed pressure tanks. Pressure tanks are designed to withstand relatively large pressure variations without incurring a loss. They are constructed in many sizes and shapes, depending on the operating pressure range. Noded spheroid tanks have been accepted for operating pressures up to 203 kPa (29 psia). Spheroids have been operated at pressures up to 308 kPa (45 psia). High-pressure tanks, either cylindrical, spherical, or blimp-shaped, have been operated at pressures up to 1.8 MPa (265 psia).[14]

4.5.3.1 Emissions

Pressure tanks are generally sealed, no loss systems. However, pressure tank losses due to relief vent opening occur when the pressure inside the tank exceeds the design pressure. This happens only when the tank is filled improperly, or when abnormal vapor expansion occurs. Losses can also occur during the filling of low pressure tanks which are not equipped with means for disposing excess displaced vapors. These are not regularly occurring events, and pressure tanks storing volatile liquids are not a significant source of loss under normal operating conditions.[15]

4.5.3.2 Control Technology

High pressure tanks represent the highest level of emission control for volatile liquid storage. There should be no need for controls on high pressure tankage. If losses occur from high pressure tankage, they indicate that the tankage is misapplied or in improper working order. Good housekeeping and routine maintenance are the primary emission control technologies available for these losses.

4.5.4 Energy, Cost, and Environmental Impact of Controls

Controlling emissions of volatile organic compounds from storage tanks accomplishes two things: improvement of ambient air quality and conservation of a substance which is convertible to energy by combustion. Energy requirements for storage tank control measures are negative; that is, energy is saved by reducing losses of organic compounds to the atmosphere. An example of energy savings may be seen in Table 4.5-4 which presents a comparison of losses from fixed roof and floating roof

TABLE 4.5-4. ENERGY SAVINGS REALIZED BY USING FLOATING ROOF TANKS IN A TYPICAL 16,000m^3 (100,000 BBL/DAY) REFINERY[16]

Substance Stored	Storage Capacity[a]	Throughput	Fixed Roof Losses	Floating Roof Losses	Energy Savings[b]
Crude Oil (2.0 lb RVP)	185,551 m^3 (1,167,080 bbl)	8,000 m^3/day (50,000 bbl/day)	753 m^3/yr (4,738 bbl/yr)	43 m^3/yr (270 bbl/yr)	26 TJ/yr (2.5x10^{10} Btu/yr)
Crude Oil (6.0 lb RVP)	185,551 m^3 (1,167,080 bbl)	8,000 m^3/day (50,000 bbl/day)	3,604 m^3/yr (22,669 bbl/yr)	146 m^3/yr (921 bbl/yr)	129 TJ/yr (12.2x10^{10} Btu/yr)
Gasoline (regular)	75,970 m^3 (477,840 bbl)	7,000 m^3/day (45,000 bbl/day)	5,685 m^3/yr (35,758 bbl/yr)	192.7 m^3/yr (1,212 bbl/yr)	183 TJ/yr (17.3x10^{10} Btu/yr)
Gasoline (premium)	37,985 m^3 (238,020 bbl)	3,600 m^3/day (22,500 bbl/day)	2,845 m^3/yr (17,897 bbl/yr)	96.3 m^3/yr (606 bbl/yr)	91 TJ/yr (8.65x10^{10} Btu/yr)
				TOTAL	430 TJ/yr (40.65x10^{10} Btu/yr)

---

[a] A typical mix of tank sizes is assumed.

[b] Assumed heating values - 372 GJ/m^3 (5.6x10^6 Btu/bbl) for crude; 3.2 GJ/m^3 (5.0x10^6 Btu/bbl) for gasoline.

tanks storing crude and gasoline in a typical 16,000 m^3/day (100,000 barrel/day) refinery. The data are API estimates based on a typical mix of tank sizes.[17] Crude and gasoline storage represent the largest volume of products stored in a refinery, but the total energy potentially saved will be even larger if other refinery products are also stored in tanks using control measures.

Conserving the organic compounds represents a cost savings as well as an energy savings to the producer. In many cases the value of the recovered product exceeds the cost of the control method. Table 4.5-5 illustrates the cost involved in substituting floating roof tanks for fixed roof tanks. Costs for two tank capacities and three products are presented.

The cost effectiveness of retrofitting fixed roof tanks with floating roofs varies with the size of the tank, the true vapor pressure, and the number of turnovers. The cost (or credit) per megagram (ton) of controlled substance is presented in Table 4.5-6. Separate values are given for gasoline and crude oil because of the different economic values and emission rates of the two liquids. To illustrate the fact that larger tanks are more cost effective than smaller ones, the numbers are presented graphically in Figures 4.5-9 and 4.5-10. The parameters are explained more fully in "Control of Volatile Organic Emissions from Storage of Petroleum Liquids in Fixed-Roof Tanks," EPA, December 1977.

Estimates of installed costs for fixed roof tanks are $161,000 for 8000 m^3 (50,000 bbl) capacity, $257,000 for 16,000 m^3 (100,000 bbl) capacity, and $379,000 for 24,000 m^3 (150,000 bbl) capacity. Annual operating cost estimates are $29,900 for 8000 m^3 (50,000 bbl) capacity, $48,600 for 16,000 m^3 (100,000 bbl) capacity, and $72,200 for 24,000 m^3 (150,000 bbl) capacity.[22]

Figure 4.5-9. Cost Effectiveness of Controlling Emissions From Existing Fixed Roof Gasline Tanks

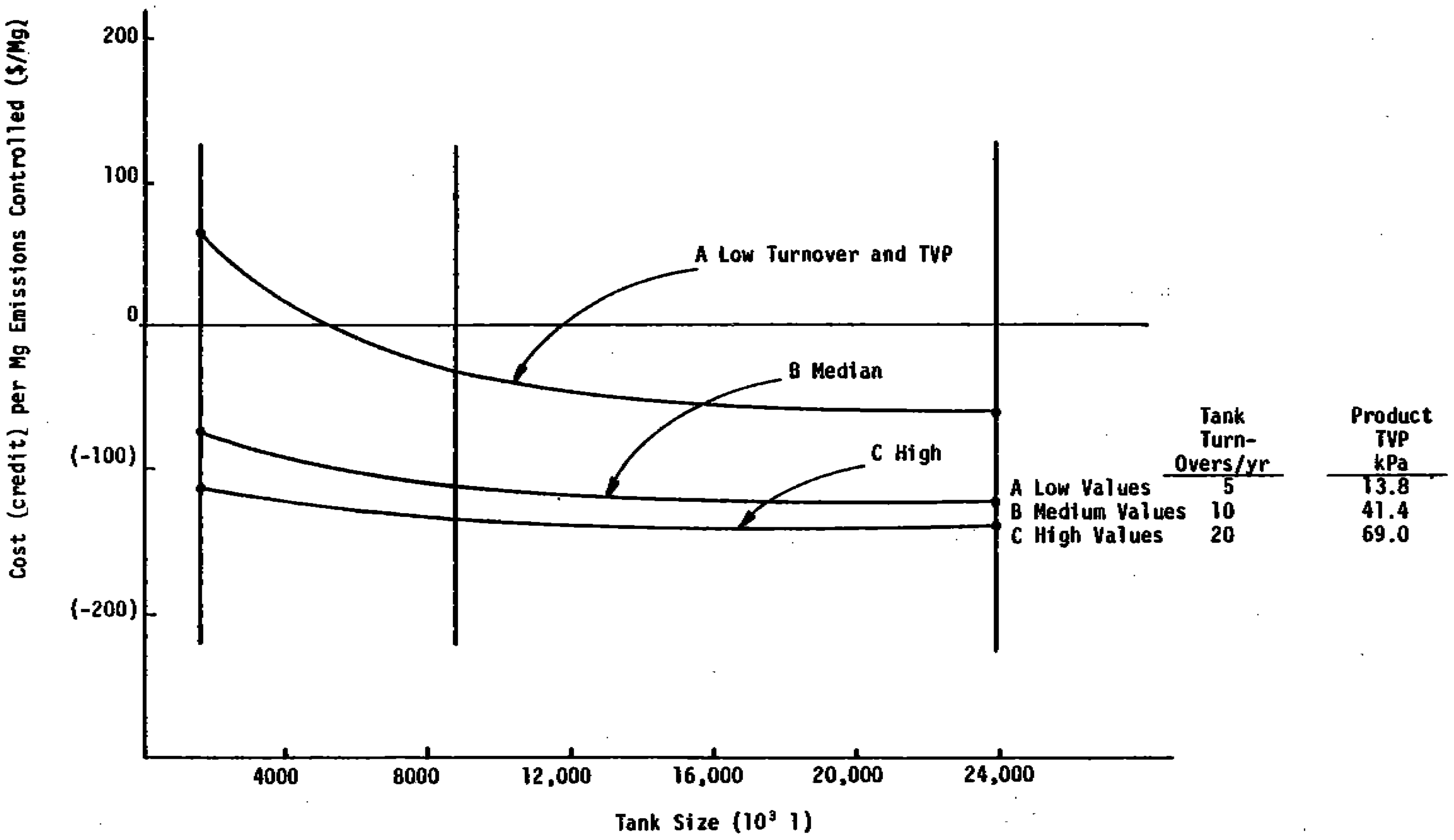

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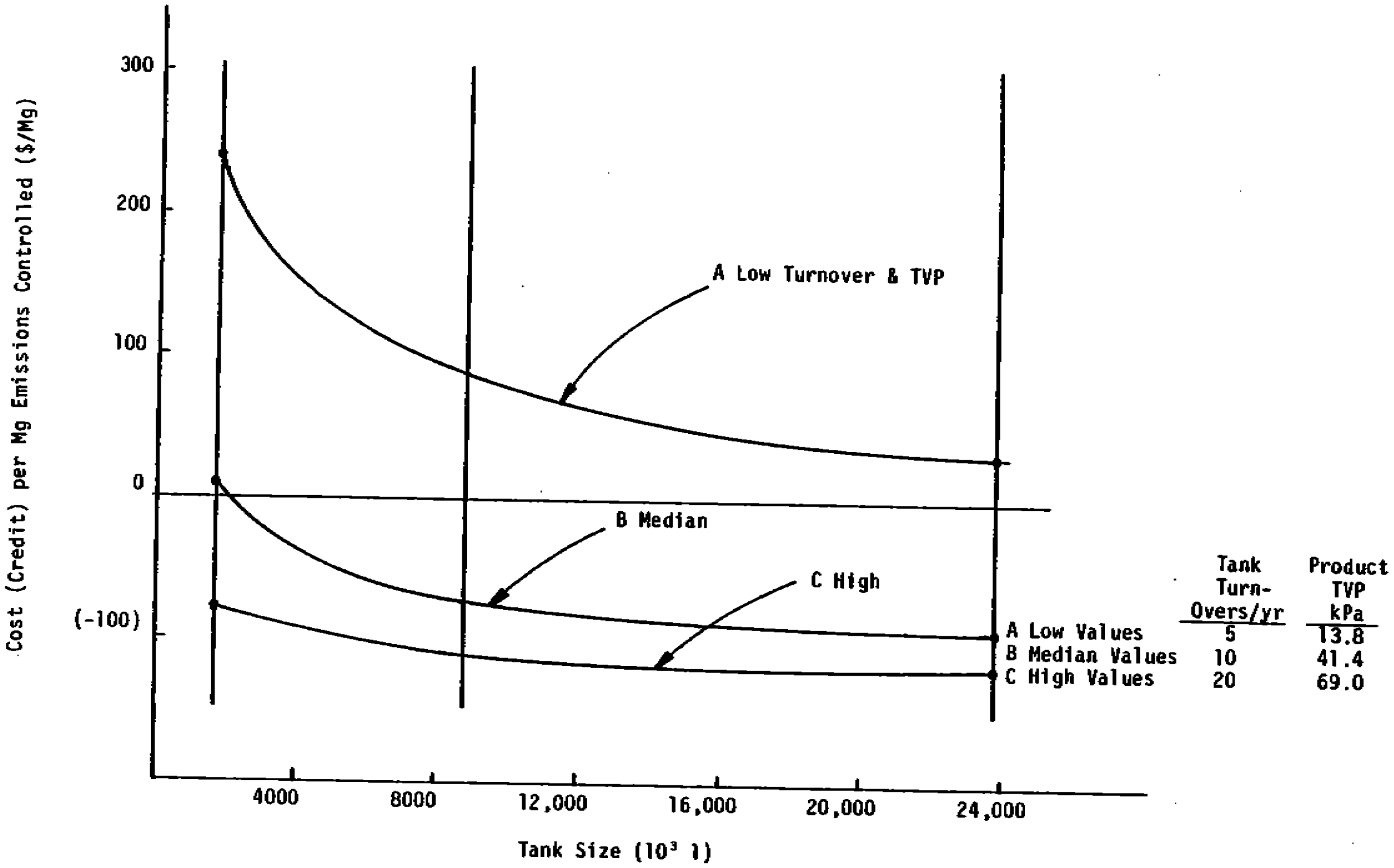
Figure 4.5-10. Cost Effectiveness of Controlling Emissions From Existing Fixed Roof Crude Oil Tanks



	Tank Turn-Overs/yr	Product TVP kPa
A Low Values	5	13.8
B Median Values	10	41.4
C High Values	20	69.0

TABLE 4.5-5. COSTS FOR SUBSTITUTING FLOATING ROOF TANKS FOR FIXED ROOF TANKS[a], [18]

Storage Capacity	Material Stored	New Tank Costs	Retrofit Costs[b]
13,000 m^3 (80,400 bbl)	Crude Oil	- 13,630	-6,950
10,000 m^3 (60,800 bbl)	Gasoline	- 16,690	-10,290
10,000 m^3 (60,800 bbl)	Naphtha Jet Fuel	-	17,520

[a] Costs are based on several assumptions. See original reference for bases for estimates.

[b] Negative signs indicate that savings from the recovered product exceed the annual cost.

TABLE 4.5-6. COST EFFECTIVENESS OF INSTALLING FLOATING ROOFS ON FIXED ROOF PETROLEUM LIQUID STORAGE TANKS, \$ PER Mg (\$ PER TON)[19]

	Low	Medium	High
True Vapor Pressure (kPa)	13.8	41.4	69.0
(psia)	(2.0)	(6.0)	(10.0)
No. Turnovers/Year	5	10	20
Tank Size			
1590 m^3 (10,000 bbl)			
gas	65	-75	-115
	(59)	(-68)	(-100)
crude oil	240	5	-80
	(220)	(4)	(-73)
8750 m^3 (55,000 bbl)			
gas	-35	-115	-135
	(-32)	(-100)	(-123)
crude oil	80	-75	-115
	(73)	(-68)	(-100)
23,850 m^3 (150,000 bbl)			
gas	-60	-125	-140
	(-55)	(-114)	(-130)
crude oil	30	-90	-120
	(28)	(-82)	(-110)

Costs for retrofitting existing fixed roof tanks with an internal floating cover and preliminary seal are presented in Table 4.5-7. These costs are for the model situations described above for Tables 4.5-6. Cost parameters are also given in the reference.

Annual operating costs for internal floating covers in fixed roof tanks are $28,600 for 8,000 m^3 (50,000 bbl) capacity, $45,600 for 16,000 m^3 (100,000 bbl) capacity and $66,000 for 24,000 m^3 (150,000 bbl) capacity.[24]

Estimated installed costs for pontoon floating roof tanks are $176,000 for 8000 m^3 (50,000 bbl) capacity, $279,000 for 16,000 m^3 (100,000 bbl) capacity, and $403,000 for 24,000 m^3 (150,000 bbl) capacity. Annual operating costs are estimated at $25,000 for 8,000 m^3 (50,000 bbl) capacity, $39,500 for 16,000 m^3 (100,000 bbl) capacity, and $57,100 for 24,000 m^3 (150,000 bbl) capacity.[25] Purchase prices for double deck tanks are estimated at $56,000 and $70,000 for 5,000 and 6,000 m^3 (30,000 and 40,000 bbl) capacity tanks.[26] Installed costs would be somewhat higher.

Table 4.5-7. CONTROL COST ESTIMATES FOR MODEL EXISTING FIXED ROOF TANKS

Control Device	Internal Floating Roof and Closure Seal		
Facility Size	15.2 m diameter 9.2 m height 1590 x 10 1 capacity	30.5 m diameter 12.2 m height 8750 x 10 1 capacity	45.7 m diameter 14.6 m height 23,850 x 10 1 capacity
Installed Capital Cost ($000):[a]	15.0	31.0	57.0
Annual Operating and Maintenance Cost ($000):[b]	0.9	1.8	3.4
Annualized Capital Charges ($000):[c]	2.1	4.5	8.3
Total Annual Control System Cost (not including petroleum credits) ($000):[d]	3.0	6.3	11.7

[a] Median installed costs of retrofitting internal floating roofs and closure seals on existing fixed roof tanks per references 5,6,7, and 8; does not include the costs of cleaning and degassing tanks, correction of tank defects and loss of use of tanks during retrofit.

[b] Per EPA estimate.

[c] Capital recovery costs (using capital recovery factor with 10% annual interest rate and 40 year internal floating roof life) plus 4% of installed capital cost for property taxes, insurance, and administration.

[d] Sum of annual operating and maintenance cost plus annualized capital charges; but, does not include petroleum credits (savings).

There are no secondary pollutant problems associated with utilizing the control techniques presented in this section. Preventing volatile organic emissions to the atmosphere is considered a positive environmental impact.

4.5.5 References

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3-4. American Petroleum Inst., Evaporation Loss Committee. Evaporation Loss from Fixed-Roof Tanks. Washington, D.C. Bull. 2818. 1962.

5. Reference 2.

6. Burklin, C.E., et al. Control of Hydrocarbon Emissions from Petroleum Liquids. Radian Corporation Contract No. 68-02-1319, Task 12. EPA 600/2-75-042. PB 256 650/ST. Sept. 1975.

7-8. American Petroleum Inst., Evaporation Loss Committee. Evaporation Loss from Floating-roof Tanks, Washington, D.C. Bull. 2517. 1962.

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10. Reference 7.

11. Reference 6.

12. Reference 1.

13. American Petroluem Inst., Evaporation Loss Committee. Evaporation Loss from Low-Pressure Tanks, Washington, D.C. Bull. 2516. 1962.

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16-17. American Petroleum Institute, Hydrocarbon Emissions from Refineries. Washington, D.C., Publication No. 928, July 1973.

18. Hark D., S. Sobotka, and W. Johnson, Economic Impact of EPA's Regulations on the Petroleum Refining Industry, Volume 2: Industry Description and Technical Analysis. EPA Contract No. 68-01-2830. Stamford Conn., Sobotka and Co. April 1976.

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22. MSA Research Corp., Hydrocarbon Pollutant Systems Study, Vol. 1, Stationary Sources, Effects, and Control, APTD-1499, PB 219073, Evans City, PA., MSA Research Corp, 1972.

23. Reference 2.

24-25. Reference 22.

26. Nichols, Richard A. Control of Evaporation Losses in Gasoline Marketing Operations, Irvin, Ca., Parker-Hannifir, 1973.

4.6 Petroleum Transportation and Marketing Systems

Figure 4.6-1 shows the operations involved in the transportation and marketing of petroleum liquids. Each operation represents a potential source of evaporative organic emissions. Crude oil is transported from production operations to the refinery via tankers, barges, tank cars, tank trucks, and pipelines. Refined petroleum products are conveyed to fuel marketing terminals and petrochemical industries in the same manner. 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 normally a motor vehicle gasoline tank. A similar distribution path may also be developed for fuel oils and other petroleum products.

This section presents the emissions and available control technology for the four major transportation and marketing systems: pipelines, ship and barge terminals, tank truck and rail car terminals, and gasoline service stations. Only the loading and unloading sources associated with these emissions are discussed in this section. The storage emissions associated with each of these systems are dicusssed in Section 4.5 on Storage Tanks.

4.6.1 Pipelines

The two primary sources of organic emissions from transportation by pipeline are compressor station engines and fugitive pipeline emissions. Sources of fugitive emissions and their control have been discussed in Section 4.1.

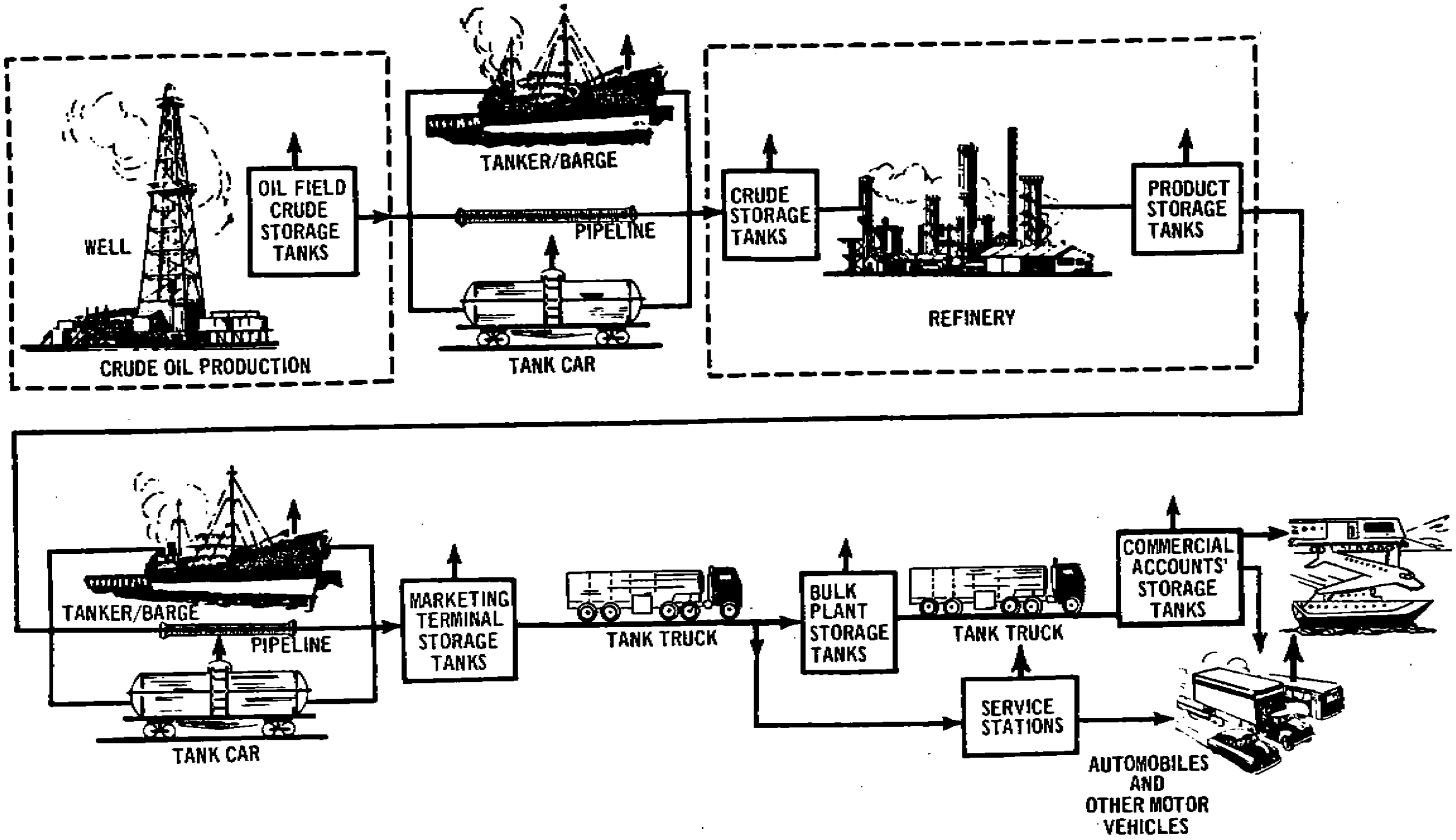


Figure 4.6-1. Flowsheet of petroleum production, refining, and distribution systems. (Sources of organic evaporative emissions are indicated by vertical arrows.

Compressor stations are employed to maintain the flow of petroleum fluids through long distance pipelines. Often the large pumps and compressors used in these compressor stations are driven by natural gas internal combustion engines. The natural gas used by these engines may be tapped from the pipeline or supplied by external sources.

The exhaust gases from internal combustion engines contain significant quantities of unburned hydrocarbons and organic products of incomplete combustion. Average measured hydrocarbon emissions from natural gas-fired internal combustion engines are 22 g/m^3 (1.4 $lb/10^3$ ft^3) fuel burned. Average aldehyde emissions are 1.6 g/m^3 (0.1 $lb/10^3$ ft^3) of fuel burned. A large portion of the hydrocarbon emissions from natural gas-fired internal combustion engines consists of methane, a hydrocarbon of low photochemical reactivity.[1,2,3]

Hydrocarbon and organic emissions from internal combustion engines can be controlled using technology developed for automobile exhaust emissions. The least expensive control technique is carburetion adjustment to achieve more efficient fuel combustion. Improved combustion efficiency results in the conversion of more fuel to CO_2 and H_2O thereby reducing the level of unburned fuel in the exhaust. Internal combustion engine exhaust can also be routed through catalytic converters which oxidize hydrocarbon and organic components to CO_2 and H_2O. Catalytic converters are considered very expensive for this application and have not been applied to pipeline compressors. Emission characteristics, control technology costs, energy requirements, and environmental impacts are further discussed in Section 4.13.2, Stationary Internal Combustion Sources.

The current trend is towards decreased use of internal combustion engines. Low reliabilities and increasing problems with the cost and availability of natural gas have decreased the use of internal combustion engines in recent years, and made the use of electric motors more favorable.[4]

4.6.2 Ship and Barge Terminals

Marine terminals are generally located at the end of pipelines or adjacent to refineries and chemical plants. Equipment located at marine terminals includes storage tanks, pumps, valves, and loading arms and hoses. The four major sources of hydrocarbon and organic emissions from marine terminals are storage tanks, leaks, loading operations, and ballasting operations. Emissions from storage tanks are discussed in Section 4.5, and emissions from leaks are discussed in Section 4.1.

4.6.2.1 Emissions from Loading Operations

Ship and barge loading is the largest source of emissions from marine terminal operations. Loading losses occur as hydrocarbon and organic vapors in empty cargo tanks are displaced to the atmosphere by the liquid loaded into the cargo tank. The vapors displaced from the cargo tanks are a composite of 1) vapors formed in the empty tank by evaporation of residual product from the previous haul, 2) vapors generated in the tank as new product is loaded, and 3) vapors in the ullage prior to discharging cargo. The quantity of hydrocarbon and organic losses from marine loading operations is, therefore, a function of the following parameters:[5]

1. physical and chemical characteristics of the previous cargo

2. method of unloading the previous cargo
3. operations during the transport of the empty vessel to the loading terminal (i.e., purging, cleaning, inerting, etc.)
4. method of loading the new cargo
5. physical and chemical characteristics of the new cargo.

The standard method of loading ships and barges is bottom loading (Figure 4.6-2). In the bottom loading method, the fill pipe enters the vessel tank from the bottom. During the major portion of the loading operation the fill pipe is below the liquid level, thereby reducing liquid turbulence and vapor-liquid contacting. Vapor emissions are significantly lower than those produced by splash loading.

The cruise history of a cargo carrier is another important factor in loading losses. Emissions are generally lowest when the 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 oil in the previous haul, or from cleaning or ventilating the empty cargo tank prior to loading operations.

Another cruise history factor affecting tanker emissions is the ballasting of cargo tanks. Ballasting is discussed in the following section. 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.

When the cargo tanks are filled, the pressure/vacuum valve (P/V) is opened. Organic vapors are vented through the open P/V valve at mast head level and/or through the ullage

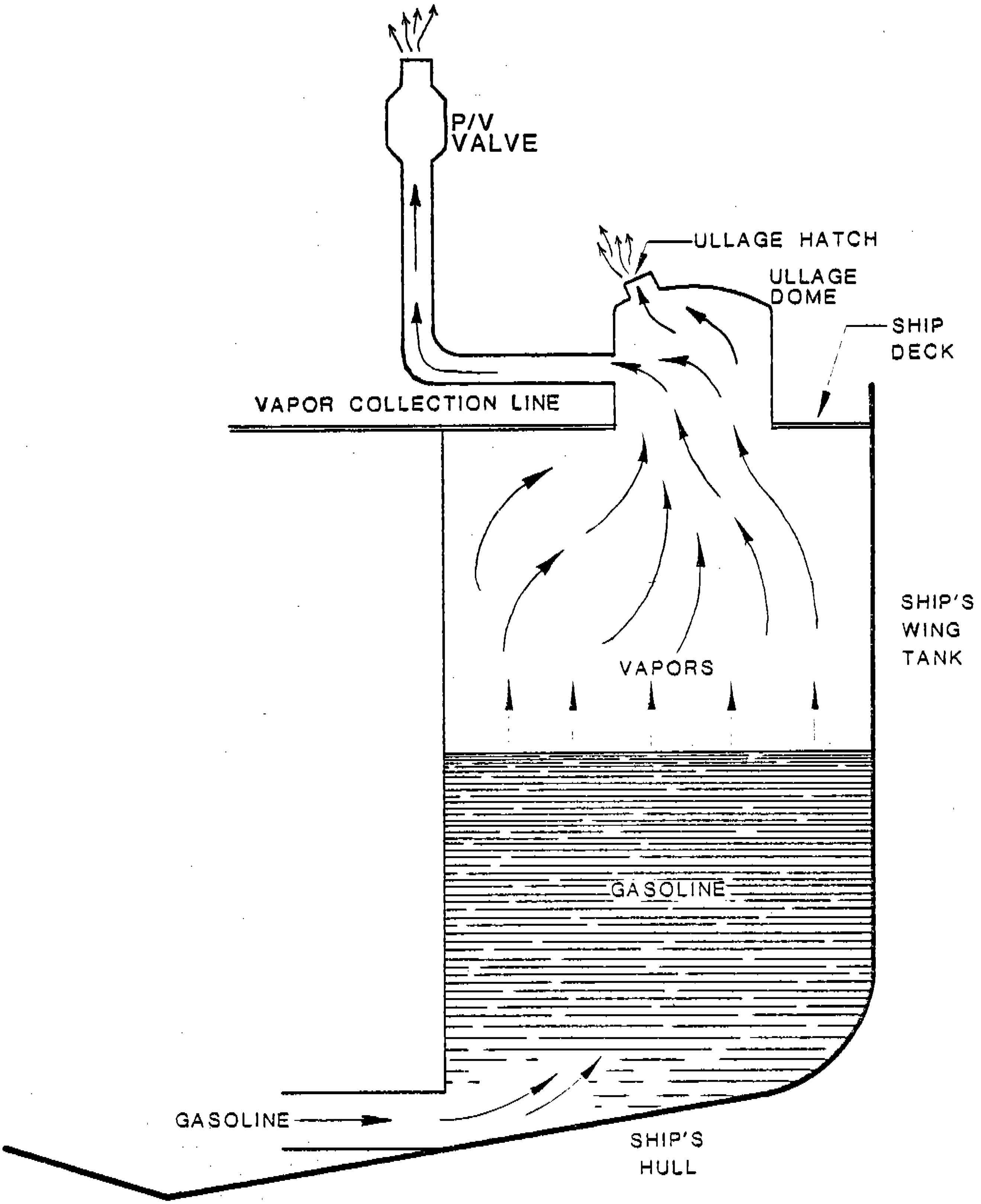


Figure 4.6-2. Emissions from uncontrolled vessel loading.

hatch at deck level. This practice varies depending on corporate safety policies.

Emissions from loading volatile liquids onto marine vessels can be estimated within 30 percent using the following expression:

$$L_L = K \frac{SPM}{T}$$

where:

L_L = loading loss, kg/m^3 of liquid loaded (lb/10^3 gal)
K = constant, 12.04 x 10^{-5} kg-mole °K/Pa m^3 (12.46 lb-mole °R/psia 10^3 gal)
M = molecular weight of vapors, kg/kg-mole (lb/lb-mole)
P = true vapor pressure of liquid loaded, Pa (psia).
T = bulk temperature of liquid loaded, °K (°R)
S = a saturation factor

The saturation factor (S) represents the expelled vapor's fractional approach to saturation and accounts for the variations observed in emission rates for different loading methods. The suggested saturation factor for loading ships is 0.2 and for loading barges is 0.5.[6]

Recent studies conducted by EPA, State Air Control Agencies, WOGA, API, and individual oil companies 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 4.6-1 and should be used instead of the above equation for gasoline loading operations at marine terminals. Data on losses from crude marine

TABLE 4.6-1. EMISSION FACTORS FOR GASOLINE LOADING ON SHIPS AND BARGES[7]

Vessel Tank Condition	Hydrocarbon Emission Factors[a]					
	Ships		Ocean Barges		Barges	
	Range	Average	Range	Average	Range	Average
Cleaned[b] and Vapor Free						
lb/10^3 gal transferred	0 to 2.3	1.0	0 to 3	1.3	c	1.2
kg/10^3 liter transferred	0 to 0.28	0.12	0 to 0.36	0.16		0.14
Ballasted						
lb/10^3 gal transferred	0.4 to 3	1.6	0.5 to 3	2.1	d	d
kg/10^3 liter transferred	0.05 to 0.36	0.19	0.06 to 0.36	0.25		
Uncleaned - dedicated service						
lb/10^3 gal transferred	0.4 to 4	2.4	0.5 to 5	3.3	1.4 to 9	4.0
kg/10^3 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/10^3 gal transferred	c	1.4	c	c	c	4.0
kg/10^3 liter transferred		0.17				0.48

a. Emission factors are rated B: good

b. Or prior low vapor pressure cargo

c. These values are not available

d. Barges are not normally ballasted

loading is available from Western Oil and Gas Association.

4.6.2.2 Emissions from Ballasting Operations

Non-segregated ballasting operations are the second largest source of organic emissions from marine terminals. Cargo tanks on large tankers are often filled with water after cargo is unloaded. The ballast water improves the stability of the empty tanker on rough seas. Ballasting emissions occur as organics-laden air in the empty cargo tank is displaced to the atmosphere by ballast water. However when separate segregated ballast tanks are employed to store ballast water, there are no ballasting emissions.

The quantity of hydrocarbon and organic losses from tanker ballasting operations is, therefore, a function of the physical and chemical characteristics of the unloaded cargo, the unloading method used, ambient conditions, and the quantity of ballast taken onboard. Although ballasting practices vary, individual cargo tanks are ballasted 80 to 100% and the total vessel is ballasted between 20% and 40% of capacity. Ballasting emissions from gasoline and crude oil tankers are approximately 0.09 kg/10^3 liter (0.8 lb/10^3 gal) total capacity and 0.07 kg/10^3 liter (0.6 lb/10^3 gal) total capacity, respectively. These estimates are for motor gasolines and medium volatility crudes with Reid vapor pressures of about 35 kPa (5 psia).[8] A measurement program being conducted by eight oil companies and known as The 8-31 Marine Emissions Study will soon provide data that may supercede these estimates.

4.6.2.3 Marine Terminal Control Technology[9]

Control measures for reducing marine terminal emissions include alternate loading and unloading procedures and vapor recovery equipment. Data on these control techniques is limited and much of it has not been verified.

Procedural changes which reduce the emissions from loading and ballasting operations are not well documented. Initial investigations indicate that vapor freeing ballasted and empty cargo tanks at sea can potentially reduce tanker loading losses from 50 percent to 60 percent. Cleaning is not considered an available control measure for barges.[10]

Limited additional emission reductions may be achieved by employing slow initial loading, fast bulk loading and slow final loading. Slow initial loading reduces the turbulence caused during the flow of liquids into the bottom of empty cargo tanks. The evaporation of volatile liquids is reduced under conditions of low turbulence. After the opening of the inlet pipe is covered with product, the cargo tank should be filled rapidly to reduce the tank filling time and consequently reduce the time available for additional vapor formation. The final filling rate should again be slow to reduce vapor turbulence in the vicinity of the ullage hatch as the liquid level approaches the top. It is estimated that changes in loading procedures would reduce loading losses from 60 to 80 percent.[11] These reductions have not been verified with actual operating data.

Procedural changes for reducing ballasting emissions include quick unloading of cargo, careful stripping of residual product from the empty tank bottom, and prompt partial ballasting. Although partial ballasting allows sloshing and provides insufficient stability in rough seas, additional ballast can be taken on out of port where ballasting emissions are of less concern. Estimates of the control efficiency of procedural changes in ballasting operations are unavailable.[12]

Theoretically, one of the most effective control measures for reducing loading and ballasting emissions would be the application of a vapor recovery system as shown in Figures 4.6-3 and 4.6-4. However, no controls are currently being applied on gasoline or crude oil marine terminals. A marine terminal vapor recovery system would include piping which collects vapors from each cargo tank and conveys them to an onshore vapor control unit. Theoretically, the vapor control unit would either incinerate the vapors or recover them by refrigeration, compression, adsorption, or absorption. The projected efficiency of vapor control units is 90+ percent.[13]

4.6.2.4 Energy, Cost, and Environmental Impact of Controls

The procedural changes mentioned above are very new ideas. For this reason and because of the very nature of the control technology, costs and energy considerations are difficult to define. Capital costs involved would be minimal; however, there would be an associated increase in operating costs.

Projected installed capital cost estimates for shoreside vapor recovery units in a marine terminal range from \$100,000 to \$2,000,000 per 1600 m^3 (10,000 bbl)/hr loading capacity. The average projected capital cost is \$1,000,000 per 1600 m^3 (10,000 bbl)/hr loading capacity. The average projected cost for ship modification is \$0.35 million per ship, and the average projected cost for barge modification is \$67,000 per barge. Average annual projected operating costs for shoreside vapor recovery systems are \$15 per 159 m^3 (1000 barrels) transferred.[14]

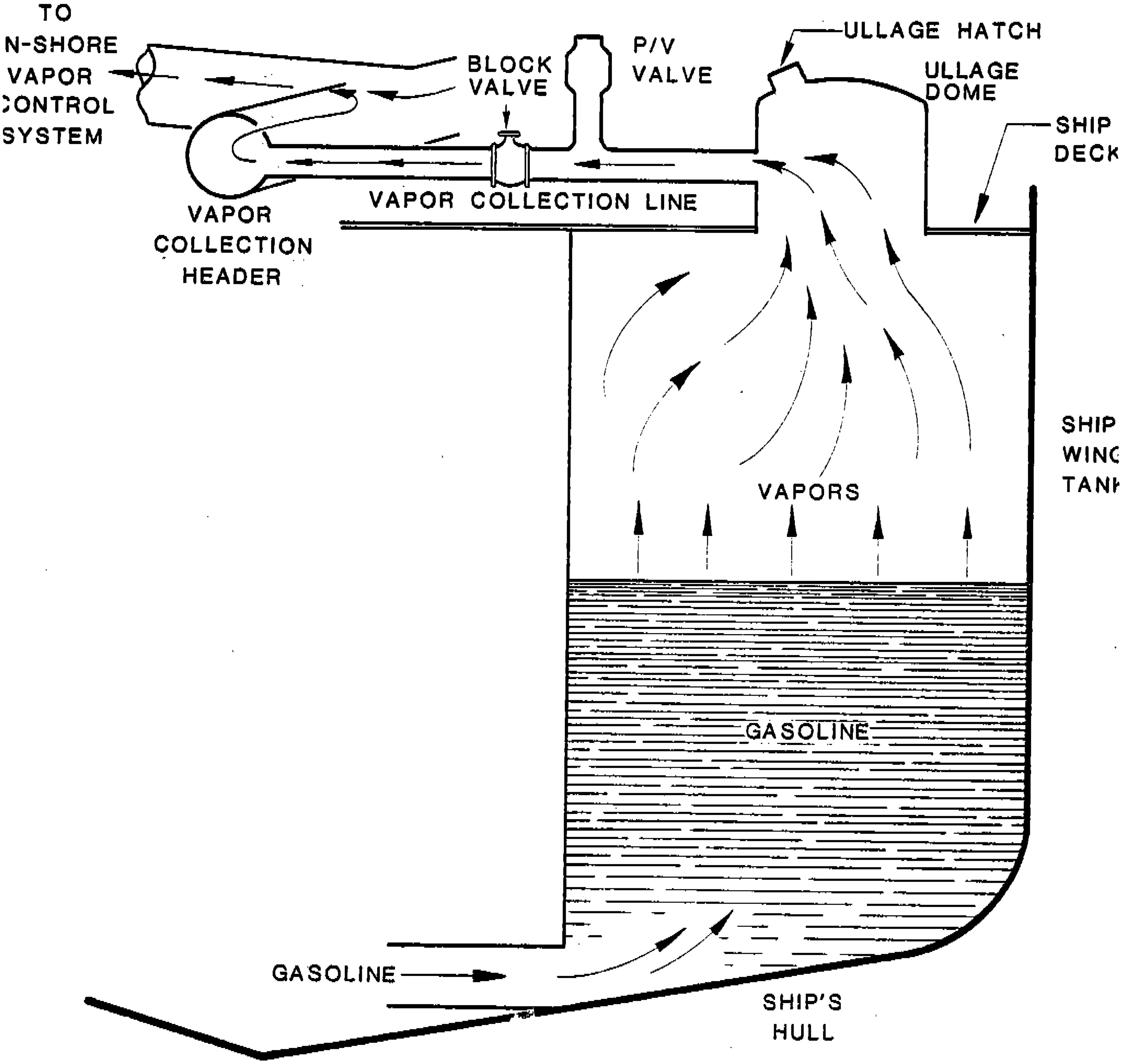


Figure 4.6-3. Ship-side vapor collection system.

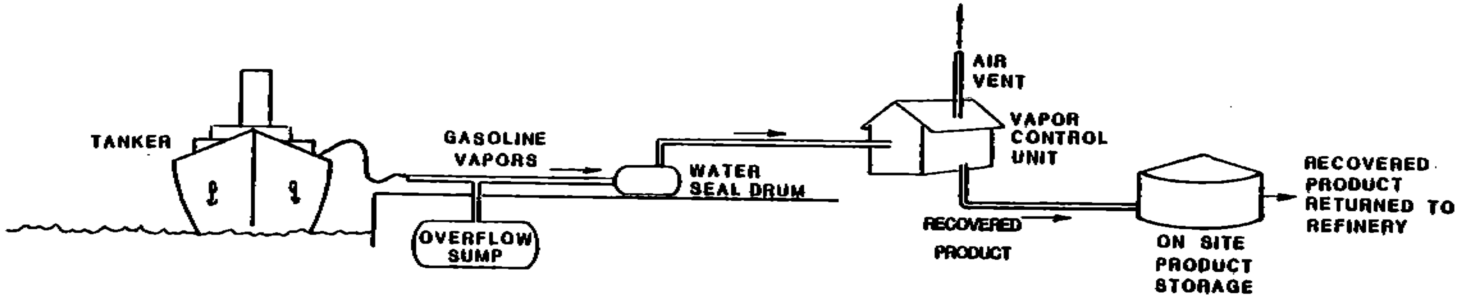


Figure 4.6-4. Typical Application of Vapor Collection System For Reduction of Marine Terminal Loading Emissions.

Condensing type vapor recovery units generate a minor purge stream of water which is condensed with the hydrocarbon vapors. This oily water is a small volume waste stream which can be piped to the refinery's waste water treatment plant.

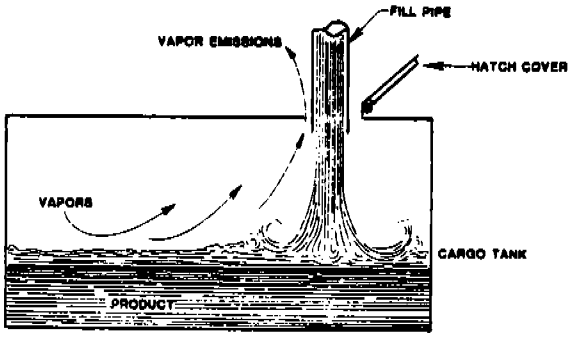
4.6.3 Tank Truck and Rail Car Terminals and Bulk Plants[15]

Tank truck and rail car terminals for the loading and unloading of crude oil, petroleum products, and organic chemicals are located at the end of pipelines or near refineries, marine terminals, and chemical plants. Bulk plants are secondary distribution facilities receiving product by tank truck and distributing it by smaller tank trucks. Equipment located at tank truck and rail car terminals and bulk plants include storage tanks, pumps, valves, and loading arms and hoses. The two major sources of hydrocarbon and organic chemical emissions from tank truck terminals, rail car terminals, and bulk plants are storage tanks and loading operations. Emissions from storage tanks are discussed in Section 4.5.

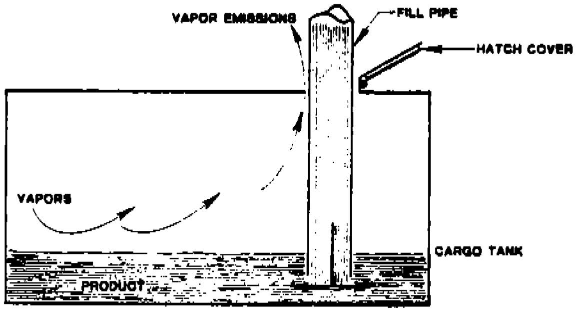
4.6.3.1 Emissions from Loading Operations

Loading operations are a very significant source of emissions from tank truck and rail car terminals and bulk plants. The mechanisms of vapor generation and the factors affecting loss rate are the same as those described for marine terminal loading operations.

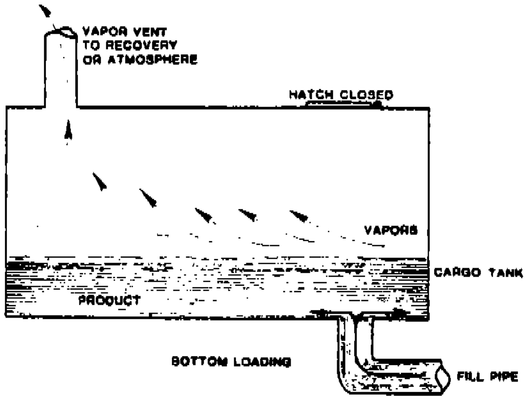
Methods of loading cargo carriers are shown in Figure 4.6-5. In the splash loading method, the fill pipe dispensing the cargo is only partially lowered into the cargo tank. Significant turbulence and air-liquid contacting occurs during splash loading, resulting in high levels of vapor generation and loss. If the turbulence is high enough, liquid droplets will be entrained in the vented vapors.



SPLASH LOADING



SUBMERGED FILL PIPE



BOTTOM LOADING

Figure 4.6-5. Three Methods of Loading Cargo Carriers.

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 submerged loading methods, the fill pipe opening is below the liquid level. The submerged loading method significantly reduces liquid turbulence and air-liquid contact. Submerged loading produces lower vapor losses than splash loading.

A cargo carrier in "dedicated gasoline service" transports only gasoline. Tanks are not cleaned or vented between trips. An empty cargo tank in dedicated gasoline service retains a significant concentration of vapors generated by evaporation of residual gasoline product. These residual vapors are expelled along with newly generated vapors during the subsequent loading operation.

Another type of cargo carrier is one in "dedicated gasoline balance service". Cargo carriers in dedicated gasoline balance service pick up vapors displaced during unloading operations and transport these vapors in the cargo tanks back to the loading terminal. Figure 4.6-6 shows a tank truck in dedicated gasoline balance service unloading gasoline to an underground service station tank. The tank truck is simultaneously being filled with displaced gasoline vapors to be returned to the truck loading terminal. The vapors in a cargo carrier in dedicated gasoline balance service approach saturation with hydrocarbons or organic compounds.

Emissions from loading tank trucks and rail cars can be estimated within 30 percent using the equation presented in Section 4.6.2.1. Table 4.6-2 lists suggested saturation factors for tank truck and rail car loading. The emission factor for

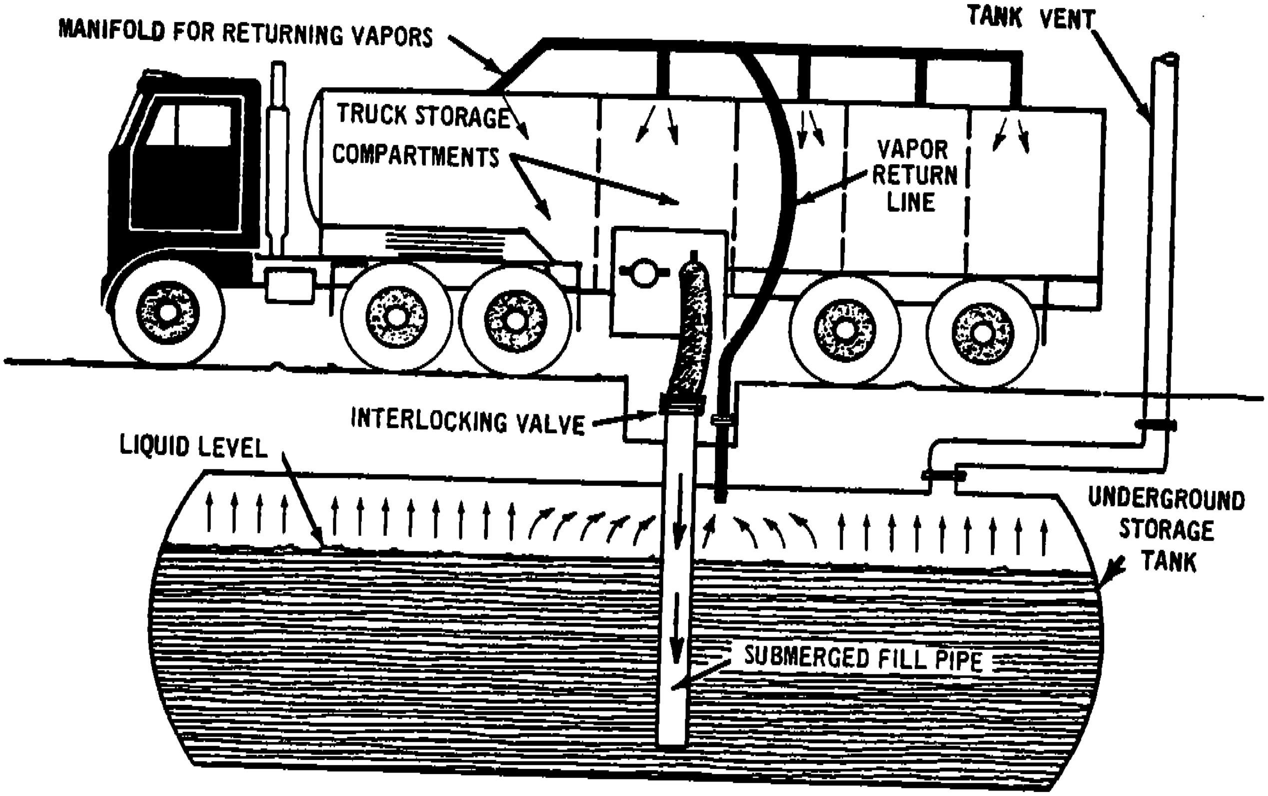


FIGURE 4.6-6 TANKTRUCK UNLOADING INTO AN UNDERGROUND SERVICE STATION STORAGE TANK. TANKTRUCK IS PRACTICING " VAPOR BALANCE " FORM OF VAPOR CONTROL.

TABLE 4.6-2. S FACTORS FOR CALCULATING TANK TRUCK AND RAIL CAR LOADING LOSSES[16,a]

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 gasoline service	0.60
	Splash loading: normal dedicated gasoline service	1.45
	Submerged loading: dedicated gasoline balance service	1.00
	Splash loading: dedicated gasoline balance service	1.00

[a] Emission factors are rated A: excellent

hydrocarbon emissions generated during submerged fill (top or bottom) gasoline loading operations is 600 mg hydrocarbons emitted per liter of gasoline loaded (5 lb/10^3 gal). This figure represents 40-50% hydrocarbon saturation of the air in the tank trucks.[1]

4.6.3.2 Control Technology

Emission control technology for tank truck and rail car loading includes the use of modified loading techniques, vapor recovery units, and the balance system. A 40 to 60 percent reduction in emissions can be achieved by the conversion of loading procedures from splash loading to bottom loading.[18] This conversion requires moderate piping modifications to both the cargo carrier and the loading rack.

If bottom loading is practiced in conjunction with the application of a vapor recovery system, the emissions from tank truck and rail car loading operations can be reduced 90 to 98 percent. A tank truck terminal vapor recovery system is presented in Figure 4.6-7. In a properly operating vapor recovery system, vapors displaced from the cargo tanks during product loading are collected in a vapor header on the cargo carrier and conveyed to a vapor recovery unit. Through processes such as refrigeration, condensation, compression, or absorption, the vapors are recovered as liquid product. Occasionally incineration and catalytic combustion systems are used to dispose of loading vapors.

The vapor balance system is an additional vapor control technique applicable only to facilities such as bulk plants which also receive their products by tank or rail car. In the vapor balance system, vapors displaced from the cargo tanks during product loading are collected in a vapor header on the

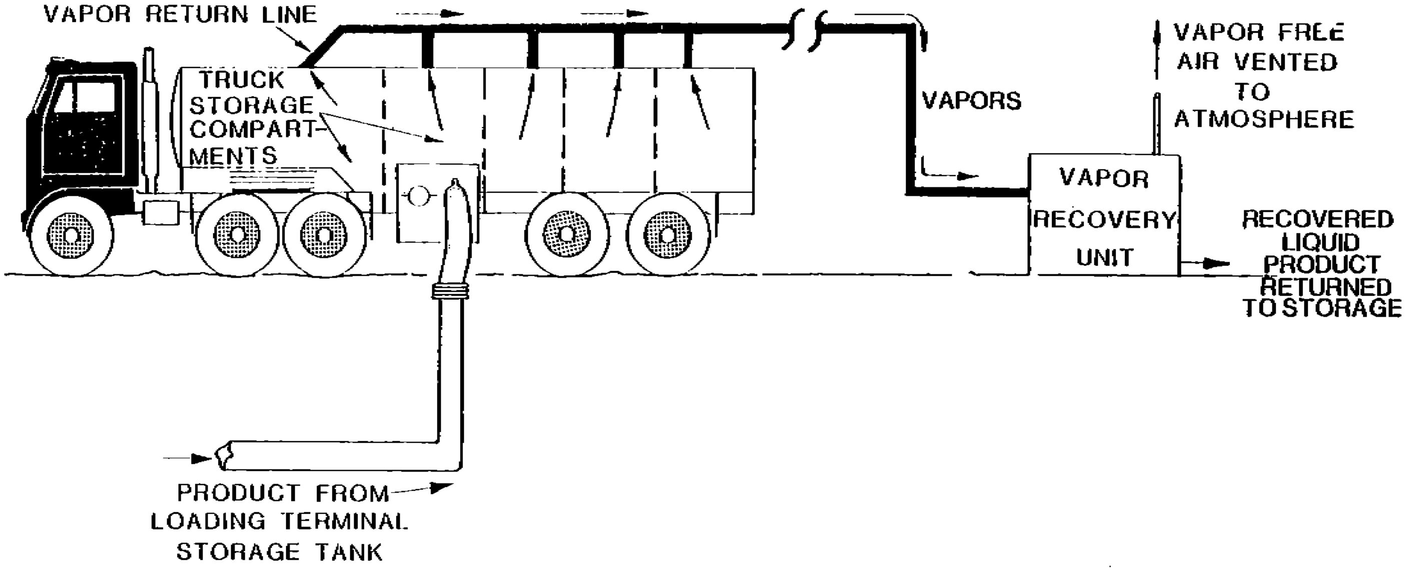


Figure 4.6-7. Tank Truck Loading With Vapor Recovery.

cargo carrier and conveyed to a vapor recovery unit. The recovered liquid product is returned to storage. This "balanced " exchange occurs because the volume of displaced vapors is approximately equal to the volume of liquid cargo transferred. When a cargo carrier arrives to refill the terminal storage tanks, it in turn applies the balance system, and exchanges vapors from the storage tank for unloaded cargo. The control efficiency of the balance system has been demonstrated to range from 90 to 100 percent.[19]

4.6.3.3 Energy, Cost, and Environmental Impact of Controls

The estimated costs associated with the control methods discussed in the previous section are listed in Table 4.6-3. A comparison of vapor recovery systems to thermal oxidizers shows lower capital cost for the thermal oxidizers. The combustion devices have higher operating costs, however, because there are no product recovery credits. As fuel costs increase, disposal methods will continue to become even less attractive than recovery methods for bulk plants with a high throughput. For plants with a low throughput, however, incineration may still be the most attractive alternative.

Energy requirements for loading modifications are minimal. The energy required to operate a vapor recovery unit is estimated to be 2 MJ/m^3 (2 $kWh/10^3$ gal).[20] This requirement is more than offset by the energy content of the recovered product.

Secondary pollutants resulting from the application of these controls are virtually non-existent. If the vapor recovery system is a condensation unit, a very small waste water stream is generated by condensation of water vapor along with

TABLE 4.6-3. ESTIMATED COSTS FOR VOLATILE ORGANIC CONTROL TECHNIQUES AT TANK TRUCK AND RAIL CAR TERMINALS AND BULK PLANTS[21,22,a]

	Facility Size and Type	Installed Capital Cost	Direct Operating Cost	Capital Cost	Net Annualized Cost (Including Gasoline Credit)
Vapor Recovery System	950 m^3/day ($2.1x10^5$ gal/day) tank truck or rail car terminal	\$185,000	\$10,500	\$31,500	\$20,600
Vapor balance system	75.7 m^3/day $20x10^3$ gal/day) bulk plant	47,000	--	--	--
Thermal oxidizers	950 m^3/day ($2.1x10^5$ gal/day) tank truck or rail car terminal	140,000	6,000	23,800	29,800

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[a] Costs are based on several assumptions. See original reference for bases.

the hydrocarbon vapors. This liquid stream must be treated in a wastewater treatment plant.

4.6.4 Gasoline Service Stations

Emissions of volatile organics are produced at gasoline service stations from two operations, bulk gasoline drops and motor vehicle refueling. Quantities of emissions and control methods for each operation are discussed in the following sections. Table 4.6-4 summarizes emission factors for losses produced by operations at service stations.

4.6.4.1 Emission Characteristics

Bulk Gasoline Drops

A major source of organic vapor emissions is the filling of underground gasoline storage tanks at service stations. Gasoline is delivered to service stations in 4-60m^3 (1000-16000 gal) tank trucks. Emissions are generated when hydrocarbon vapors in the underground storage tank are displaced to the atmosphere by gasoline loaded into the tank. The quantity of emissions depends on several variables including the size and length of the fill pipe, the method of filling, the tank configuration, and gasoline properties such as temperature, vapor pressure, and composition. An average emission rate for submerged filling is 0.88 kg/10^3 liter (7.3 lb/10^3 gallons) of gasoline transferred. The emission rate for splash filling is 1.38 kg/10^3 liter (11.5 lb/10^3 gallons) of transferred gasoline.[24]

Emissions from underground tank filling operations at service stations can be reduced by the use of the vapor balance system illustrated in Figure 4.6-6 and described in Section 4.6.3.1.

TABLE 4.6-4. ORGANIC VAPOR EMISSIONS FROM GASOLINE SERVICE STATION OPERATIONS[23]

Emission Source	Emission Factors	
	kg/10^3 liter throughput	(lb/10^3 gal throughput)
Filling Underground Tank		
Submerged filling	0.88	(7.3)
Splash filling	1.38	(11.5)
Balanced submerged filling	0.04	(0.3)
Underground Tank Breathing	0.12	(1)
Vehicle Refueling Operations		
Displacement losses (uncontrolled)	1.08	(9)
Displacement losses (controlled)	0.11	(0.9)
Spillage	0.084	(0.7)

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 0.04 kg/10^3 liter (0.3 lb/10^3 gallons) of transferred gasoline.

A second source of hydrocarbon emissions from service stations is underground tank breathing. Breathing losses occur daily due to gasoline evaporation from changes in temperature and barometric pressure. (The type of service station operation also has a large impact on breathing losses.) An average breathing emission rate is 0.12 kg/10^3 liter (1 lb/10^3 gallons) throughput. Currently, no controls are being installed on underground storage tanks for the control of tank breathing losses.[25]

Motor Vehicle Refueling

An additional source of organic vapor emissions at service stations is vehicle refueling operations. Vehicle refueling emissions occur from spills and when vapors are displaced from the automobile tank by dispensed gasoline. The quantity of displaced vapors is dependent on gasoline temperature, auto tank temperature, true vapor pressure of the gasoline, 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 emissions due to vapors displaced during vehicle refueling average 1.08 kg/10^3 liter (9 lb/10^3 gallons) of dispensed gasoline. The quantity of spillage loss is a function of the type of service station, vehicle tank configuration, operator technique, and operation discomfort indices. An average spillage loss is 0.08 kg/10^3 liter (0.7 lb/10^3 gallons) of dispensed gasoline.[26]

4.6.4.2 Control Technology

Control methods for the emissions produced by filling of underground storage tanks, referred to as Stage I control, are similar to control technology for tank truck and tank car unloadings at bulk stations. Section 4.6.3.2 contains information on such systems. Stage II controls or control methods for vehicle refueling are based on conveying the vapors displaced from the vehicle fuel tank to the underground storage tank. Figure 4.6-8 shows the hose, nozzle, and piping configuration employed. The three types of Stage II controls are "balance" vapor control system, "vacuum assist" vapor control system, and a hybrid of these two. In the "balance" system, vapors are conveyed by natural pressure differentials established during refueling. A vacuum pump assists the flow of vapors in the "vacuum assist" system. In this sytem an additional process (refrigeration or adsorption) may be utilized to increase efficiencies. The vapors in a hybrid system are assisted by a means to create a vacuum, usually an aspirator. The overall efficiency of vapor control systems for vehicle refueling emissions is estimated to be 88 to 92 percent.[27]

4.6.4.3 Energy, Cost, and Environmental Impact of Controls

Average installed costs for retrofitting an existing service station with a vapor balance system are estimated to be \$6000 for a 120 m^3 per month (32,000 gal per mo.) station. Vacuum assist units cost an additional estimated \$7,500. These costs are in 1975 dollars.[28] A study done for API in 1973 estimated a cost of \$2,565 for equipping a typical new station pumping 95 m^3/mo (25,000 gal/mo) with vapor balance systems.[29] However, more current estimates are probably near \$3,000. The differences between retrofit and new facility costs are largely due to concrete and blacktop which must be raised and repoured.[30] Operating costs and energy requirements are minimal,[31] and there are no secondary environmental pollutants involved.

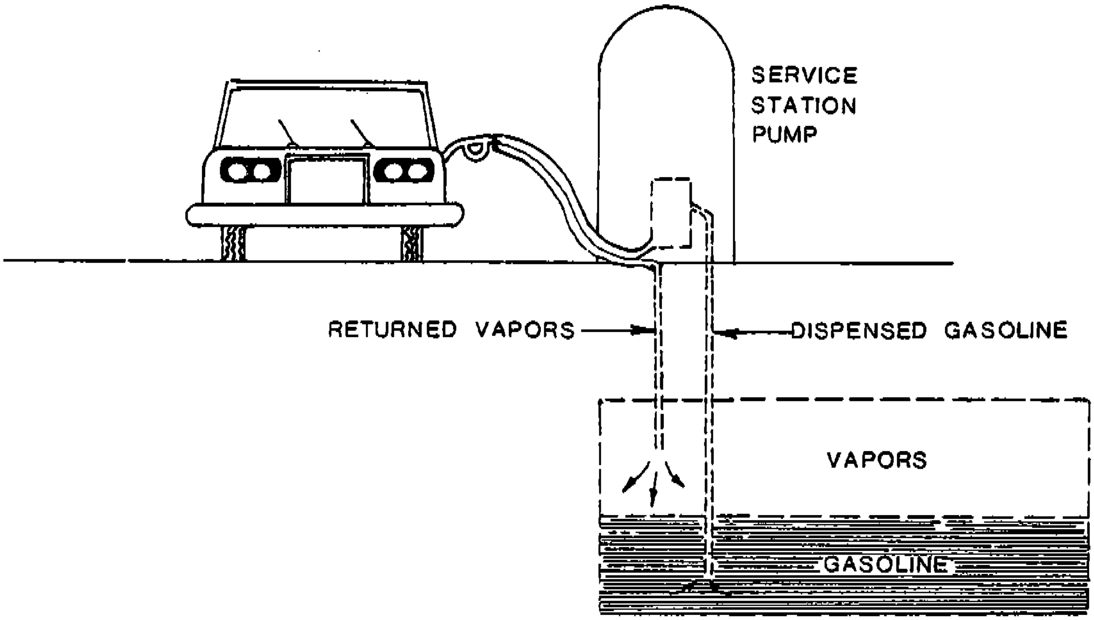

Figure 4.6-8. Automobile refueling vapor-recovery system.

4.6.5 References

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4.7 Polymers

Approximately 22 Tg (48 x 10^9 lbs) of polymers are produced annually for use in plastics, adhesives, foams, and other products. Total organic emissions from the U.S. polymer industry in 1976 amounted to over 235 Gg (517 x 10^6 lbs). Recent legislation should reduce emissions to approximately 154 Gg (338 x 10^6 lbs) per year.[1] Organic emissions include monomer, processing chemicals, and additives. Many of these compounds, such as vinyl chloride and phosgene, pose severe health hazards, while others are photochemically reactive.

As indicated in Table 4.7-1, the three largest volume polymers are polyvinyl chloride, polyethylene, and polystyrene. The discussion in this section is limited to the production and fabrication of the three largest volume products. Additional process and emission information is available for the polymer industry.[2]

4.7.1 Manufacturing Processes

4.7.1.1 Suspension Polymerization

Suspension polymerization is used to manufacture both polyvinyl chloride (PVC) and polystyrene. Figure 4.7-1 is a simplified flowsheet for this process.

In suspension polymerization the monomer (vinyl chloride or styrene), comonomer, initiators, catalyst, water, and suspending agents are mixed in a batch reactor. The reactor volume averages 11,000 to 23,000 liters (3,000-6,000 gallons).[4] The reactor is lined with glass or stainless steel and jacketed to provide steam heat or water cooling. The operating temperature is 50°C (120°F) for PVC and 90-130°C (195-265°F) for

TABLE 4.7-1. LARGE VOLUME PRODUCTS OF THE PLASTICS AND RESINS INDUSTRY[3]

	1975 Tg (billion lbs)	1974 Tg (billion lbs)
THERMOPLASTIC RESINS		
polyethylene, low density	2.15 (4.74)	2.69 (5.93)
styrene and copolymers	1.82 (4.01)	2.15 (4.74)
poly(vinyl chloride) and copolymers	1.65 (3.64)	2.20 (4.85)
polyethylene, high density	1.11 (2.45)	1.29 (2.84)
polypropylene and copolymers	0.86 (1.90)	1.02 (2.25)
THERMOSETTING RESINS		
phenolic and other tar acids	0.48 (1.05)	0.608 (1.34)
polyesters (unsaturated)	0.38 (0.83)	0.41 (0.91)
urea resins	0.31 (0.69)	0.38 (0.84)
epoxies (unmodified)	0.09 (0.20)	0.11 (0.25)
melamine resins	0.055 (0.12)	0.073 (0.16)

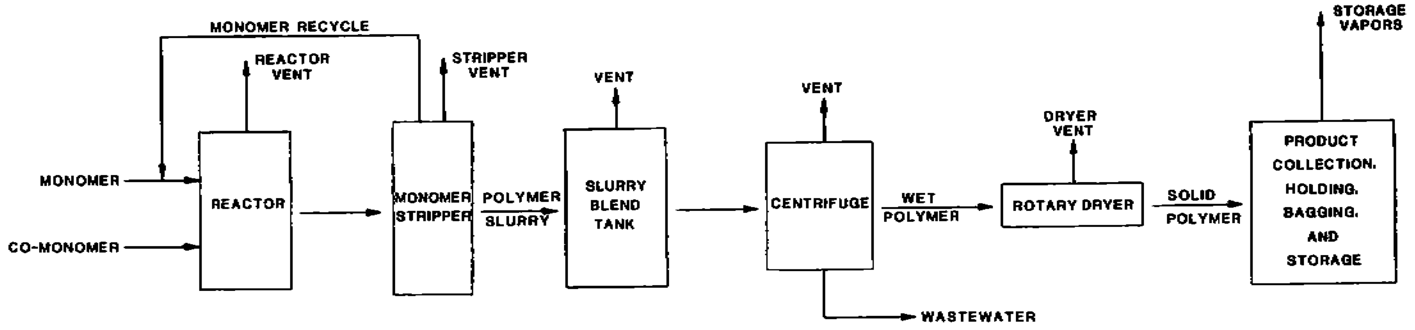

Figure 4.7-1. Simplified flow diagram for the suspension polymerization process.

styrene. Polymerization is carried out under continuous agitation at high pressure (1 MPa or 150 psi for PVC). Batch processing times of approximately 6 hours are required to achieve 85-90% completion.[5] The resultant slurry is transferred to a stripper where the residual monomer is separated from the polymer by heat and/or vacuum. After condensation the recovered monomer is returned to the storage tank. After stripping, the polymer is transferred to a blend tank where slurries from several different reactors are mixed to insure a uniform product. This mixture is then centrifuged, and the wet polymer is dried in a hot-air rotary dryer.[6] The dried polymer particles are finally collected, bagged, and sent to product storage.

4.7.1.2 Emulsion Polymerization

The emulsion polymerization process is very similar to the suspension polymerization process and is also used to produce PVC and polystyrene. Figure 4.7-2 is a simplified flowsheet for the process. The major difference is that the emulsion process produces both liquid latex and dried resin products. Resin particles from emulsion polymerization are smaller, but the polymer is of higher molecular weight. For dried resin, a spray dryer is used instead of a rotary dryer to insure a uniformly small particle size.

4.7.1.3 Mass Addition Polymerization

Mass addition polymerization is used to produce polystyrene and PVC. Both multistage batch operations and continuous processes are employed. A simplified flowsheet is shown in Figure 4.7-3 for a two-step process. Batch operations produce seed polymer in a pre-polymerization reactor (pre-po) from liquid monomer and very active initiators. No water is added. The reaction is carried out at 40-70°C (104-158°F)

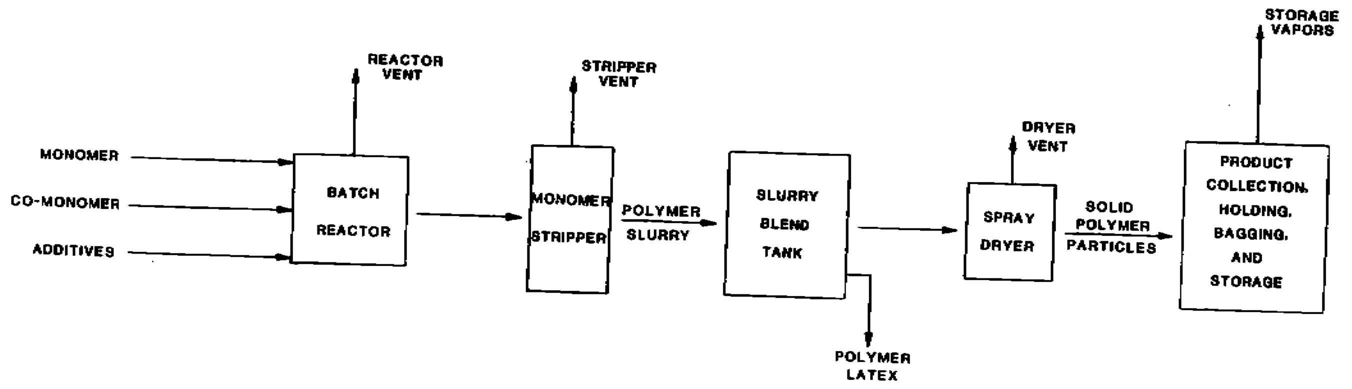

Figure 4.7-2. Simplified flow diagram for emulsion polymerization process.

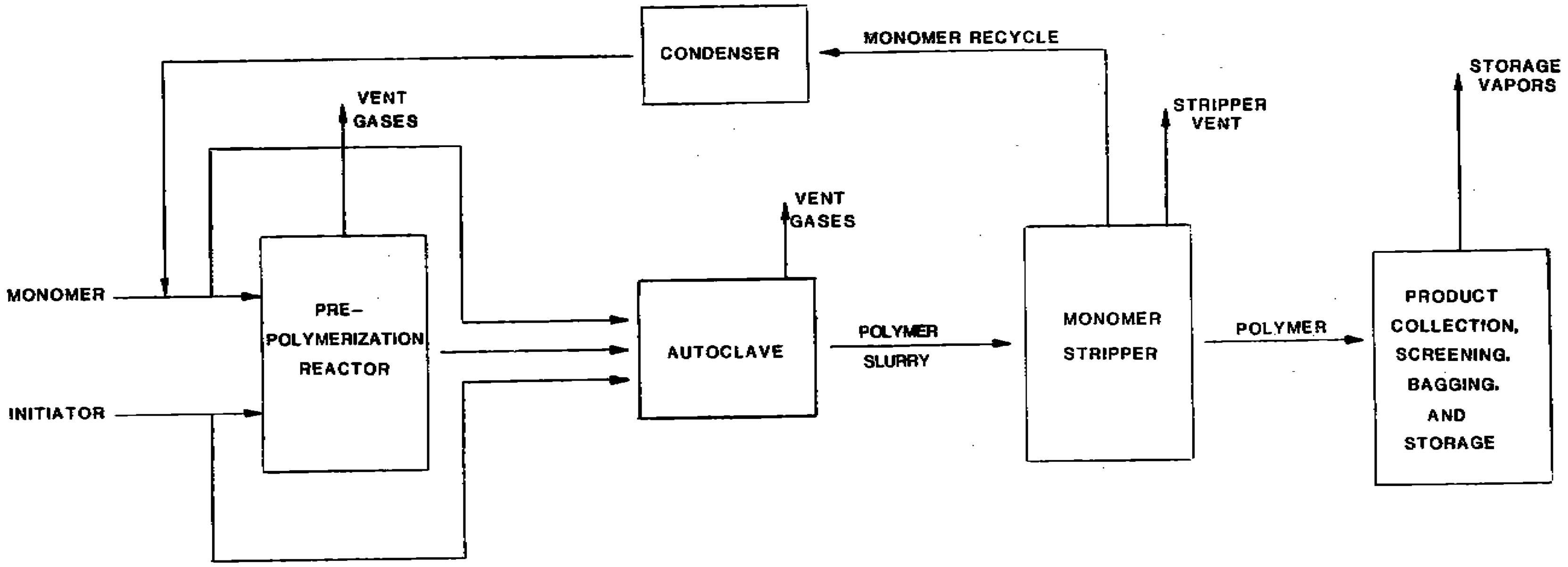

Figure 4.7-3. Simplified flow diagram for mass addition polymerization.

and 0.48-1.2 MPa (70-170 psi)[7] for PVC and 90-200°C (195-390°F) for polystyrene.[8] Monomer conversion is only 7-12%. In the second step the slurry is transferred to a larger horizontal reactor (autoclave) where monomer and initiator are added. The reaction temperature and pressure are similar to those in the prepolymerization reactor, but agitation is much stronger. After the polymerization reaction is 85 to 90 percent complete, the slurry is stripped of remaining monomer, screened, and bagged. No drying step is necessary, since water is not used in the process. The mass addition autoclave must be cleaned after every batch, but the pre-po does not require frequent cleaning.

4.7.1.4 High Pressure Mass Addition

High pressure mass addition is used exclusively to produce low density polyethylene. A very simplified flowsheet of the process is found in Figure 4.7-4. Ethylene, initiator, and other additives are combined in a kettle or tubular-type high pressure reactor. Reaction temperatures may reach 350°C (598°F). The reactions are carried out at very high pressures, 0.1-0.3 GPa (15,000-45,000 psi).[9]

After polymerization, the ethylene-polyethylene mixture is treated in a flash tank where solid resin is separated from the raw material. Ethylene vapors are purified and recycled as reactor feed. Tars, waxes, and oils are also separated and sent to disposal. The solid polyethylene is then extruded and devolatilized. Finally, it is pelletized and packaged for marketing.

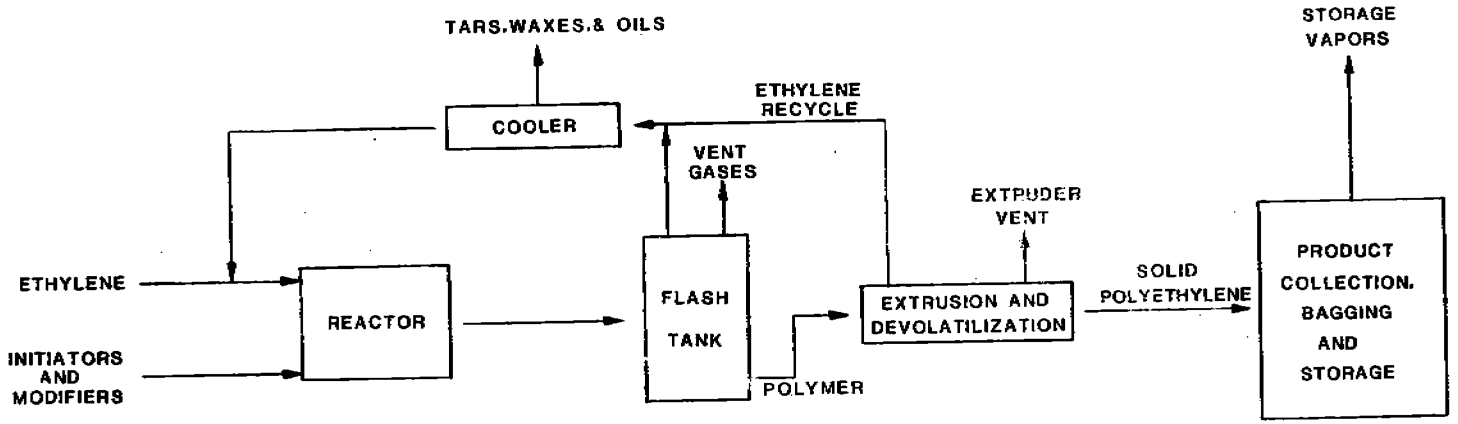

Figure 4.7-4. Simplified flow diagram of high pressure mass addition process for polyethylene polymerization.

4.7.1.5 Solution Polymerization

This manufacturing process is used to produce polystyrene, polyethylene, and small amounts of PVC and its co-polyme polyvinyl acetate. Figure 4.7-5 is a simplified flow sheet of th process. The reactor is charged with the co-monomer and a solvent, usually n-butane for PVC and ethylbenzene or toluene for polystyrene. After heating to 40°C (104°F), polymerization begins and the resin precipitates.[10] Slurry is drawn off and filtered, and the resin is dried by flash evaporation. The resin is very pure because emulsifiers and additives are not required. Solvent is recovered from the evaporator and the drying and devolatizing steps. Recovered solvent is recycled.

4.7.1.6 Particle Form Polymerization

The particle form process (Phillips Particle Form Polymerization Process) is used mainly to produce high density polyethylene in a continuous process. Figure 4.7-6 is a flow diagram for the process. The reaction is carried out in stirred or loop-type reactors. The monomer and co-monomer are pretreated to remove catalyst poisons such as CO, O_2, and H_2O. Raw material are dissolved in pentane or cyclohexane before addition to the reactor. An activated catalyst is also added. The polymerization reaction occurs at around 140°C (220°F) and 3 MPa (450 psi)

Slurry from the reactor is treated in a flash drum where solvent, ethylene, waxes, and light gases are removed. Both solvent and ethylene are recycled after purification. The catalyst remains in the resin. The purified polymer is dried, extruded, pelletized, and packaged.

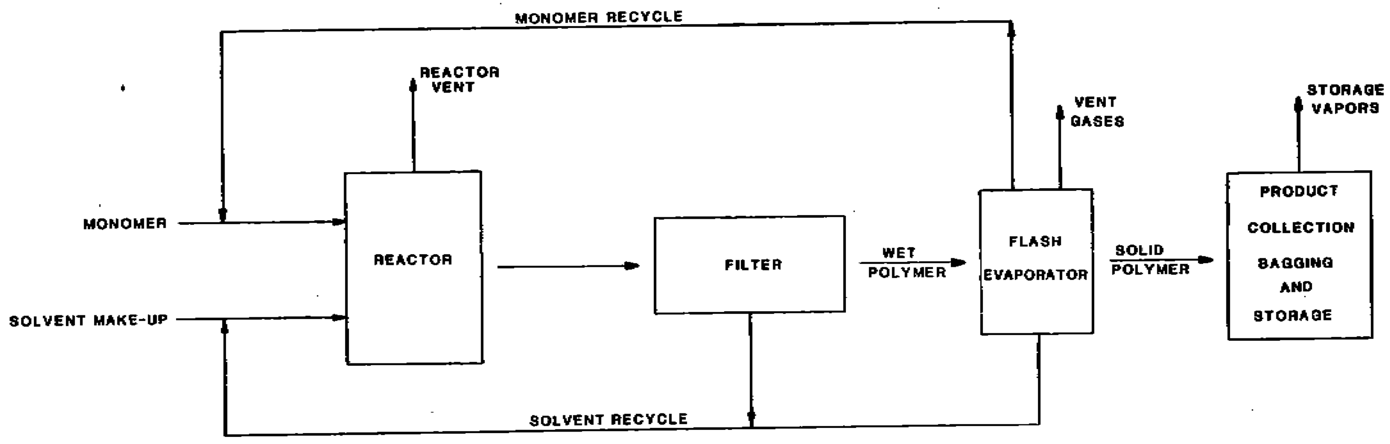

Figure 4.7-5. Simplified flow diagram for the solution polymerization process.

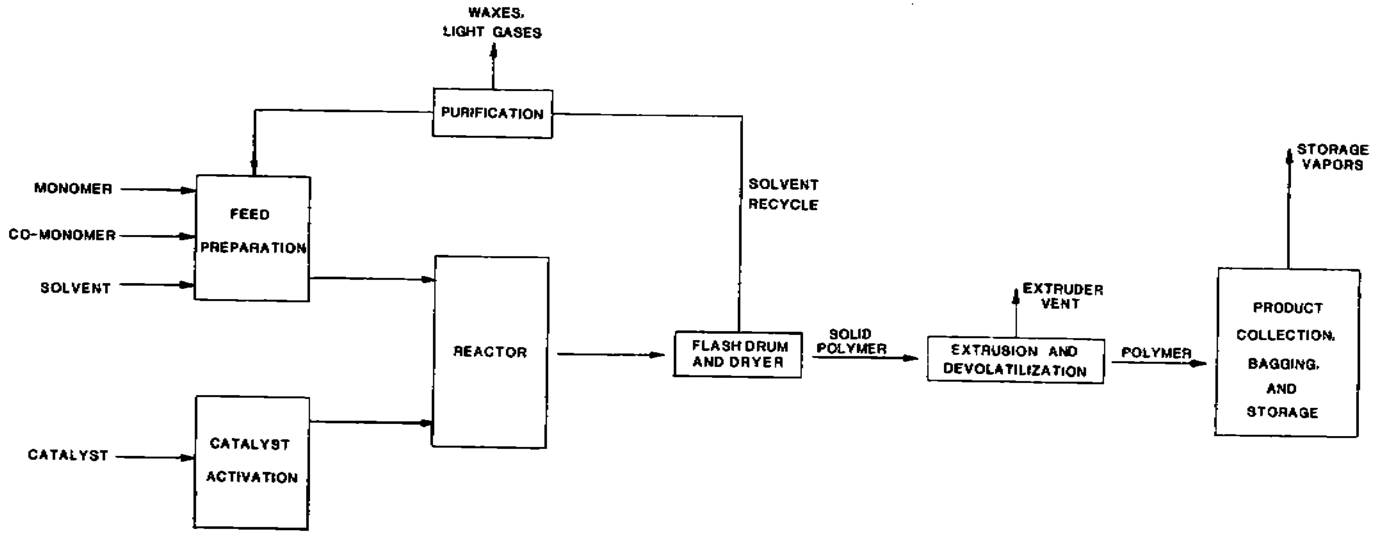

Figure 4.7-6. Simplified flow diagram for particle form polymerization.

4.7.2 Process Emissions

4.7.2.1 Polyvinyl Chloride

The three main processes for commerical polymerization of PVC are: 1) suspension process (78%), 2) emulsion process (13%) and 3) mass addition process (6%). A small amount of PVC is produced by the solution process (3%).[12]

Vinyl chloride monomer (VCM) emissions from all the polymerization processes are listed in Table 4.7-2. Because the suspension and emulsion processes are similar, emission sources are virtually the same. Emission rates are comparable except that the residual VCM in the emulsion process spray drying causes higher VCM emissions than the suspension process spray drying. The spray dryer may emit up to 85% of the total emissions from emulsion polymerization.[13]

One source estimates that 12 to 46 percent of total VCM suspension process emissions come from fugitive sources, 35% from process vents (dryer, air conveyor, storage bin, and centrifuge), and 11% from blend tanks.[14] The data for fugitive emissions include losses incurred from the following operations: 1) loading, unloading, sampling and storage of VCM, 2) leaks from pumps, compressors, valves, and agitators, 3) pipe and equipment flanges and manhole cover seals, 4) opening equipment for inspection and maintenance, 5) sampling for laboratory analysis, 6) VCM dissolved in process water exposed to the atmosphere, and 7) manual venting of equipment.[17]

VCM emissions occur each time the reactor is opened for cleaning. Scale on the walls of the reactor must be manually removed every 1-3 days for suspension or emulsion processes and

TABLE 4.7-2. VINYL CHLORIDE MONOMER EMISSION FROM PVC PRODUCTION (kg/100 kg PVC, lb/100 lb PVC,)[a,b,15,16]

Source	Emulsion Polymerization	Suspension Polymerization	Mass Addition Polymerization	Solution Polymerization
Fugitive Emissions - Total	1.13	1.50	0.48	0.03
Polymerization reaction	--	0.09[a]	--	--
Polymer isolation	--	1.12[a]	--	--
Other	--	0.29	--	--
Reactor Opening Loss	0.15	0.14	0.08	0.50
Reactor Safety Valve Vents	0.22	0.20	0.10	0.06
Venting Losses:				
Stripper	1.23	0.32	--	0.05
Monomer Recovery	0.50	0.48	1.50	0.31
Blend Tanks	0.34	0.42	--	--
Centrifuge	--	0.13	--	--
Collector Losses:				
Dryer exhaust	2.41	0.70	0.23	0.83
Silo storage				
Bagging				
Bulk Loading				
Process Water	0.025	0.025	0.011	0.002
TOTAL	6.01	3.92	2.40	1.78

[a] Emission data from reference 16, all other data are from reference 15.

[b] Emission factors were derived by EPA by averaging emission factors given by individual PVC producers in response to a May 30, 1974, request for information made by OAQPS under authority of Section 114 of the Clean Air Act.

after every batch in mass addition processes. Most VCM is removed by vacuum evacuation but residual gases are released to the atmosphere during purging with steam or air when the reactor is opened.[18]

The reactor safety valve vents produce intermittant emissions of 5 to 15 minutes duration. Safety vent gases can have very high concentrations of VCM. These losses occur when the polymerization reaction "runs away" due to equipment failure, power failure, or operator error. The reactor must be vented to prevent damage from over-pressuring. Emissions from this source can vary from 0.04-0.4 kg VCM/100 kg PVC (0.04-0.4 lb VCM/100 lb PVC).[19]

Organics are also released at vents on the stripper, blend tank, centrifuge, and dryer. Emissions from the product collection and holding bins and bagging operations are in the form of VCM and particulate PVC. VCM evaporates from centrifuge and cleaning waters when they are exposed to the atmosphere.

When a gasholder and scrubbing system is used to control reactor emissions, the composition of the vented organic vapors is changed.[20] Table 4.7-3 lists typical composition of the residue gas after absorption scrubbing.

TABLE 4.7-3. STACK GAS COMPOSITION AFTER ABSORPTION OF ORGANIC EMISSIONS[21]

	kg Moles/Day	lb Moles/Day
Acetylene	0.000089	0.00004
Butadiene	0.0014	0.00063
Methyl Chloride	0.0014	0.00063
Vinyl Chloride	10.0	4.5

4.7.2.2 Polyethylene

Polyethylene is produced in two forms, high density polyethylene (HDPE) and low density polyethylene (LDPE). About one-third of total polyethylene production is HDPE. It is manufactured by solution, particle form, and vapor-phase processes. However, the particle form process produces more resin than the other two methods combined.[22] LDPE is manufactured by high pressure mass addition.

Emissions from the particle form and high pressure mass addition processes are summarized in Table 4.7-4. Fugitive emissions account for the majority of total process emissions. An industry-wide survey[23] reported fugitive losses of solvent and monomer to be 3 Gg/year (7 x 10^6 lbs/year) for HDPE. Losses from solvent recovery, monomer recovery, and polymer stripping consist of the light and heavy ends from the purification process. Materials handling losses arise from the pneumatic conveying of finished and semi-finished polyethylene. Emissions from all sources are primarily ethylene, although in the particle form process, some solvent losses (pentane, cyclohexane) may occur.

TABLE 4.7-4. VOLATILE ORGANIC EMISSIONS FROM THE MANUFACTURE OF TWO FORMS OF POLYETHYLENE[24]

	High Density Polyethylene g/kg (lb/1000 lb) Product	Low Density Polyethylene g/kg (lb/1000 lb) Product
Fugitive	20	10
Materials Handling	3	5
Solvent and Monomer Recovery	2	1
Polymer Stripping	9	
	34	16

4.7.2.3 Polystyrene

Most polystyrene (PS) is produced by solution polymerization and suspension polymerization. Smaller amounts are produced by emulsion and mass addition polymerization. The first process produces a purer resin although the second process provides a more uniform product. Polystyrene is produced as the homopolymer and various copolymers such as ABS, SAN, and high impact PS. Figure 4.7-7 shows how these compounds are related.

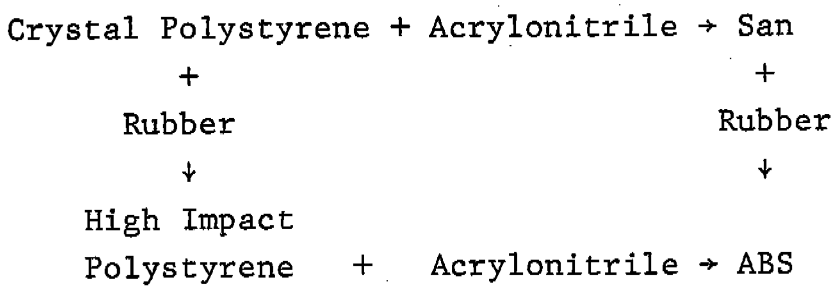

Figure 4.7-7. Relationships Between Polystyrene and its Co-Polymers[25]

Styrene is the main component of gaseous emissions from polystyrene production. Monomer loss occurs during feed preparation, from reactor venting, and from the solvent recovery system (see Table 4.7-5). Fugitive emissions are reportedly negligible, probably because the processes are carried out at low pressure.[27] Other emissions reported include small amounts of pentane and ethyl benzene.

TABLE 4.7-5. STYRENE EMISSIONS FROM POLYSTYRENE PRODUCTION[26]

	Solution Process g/kg (lb/1000 lb) Styrene	Suspension Process g/kg (lb/1000 lb) Styrene
Feed Preparation	.65	----
Reactor Vent	3.34	3.34
Solvent Recovery	1.84	----
Fugitive	----	----
Conveying Operations	.1	.1
	5.93	3.44

4.7.2.4 Fabrication and Adhesives Production

Extrusion and Molding

Emissions from plastics extrusion and molding processes are usually composed of gaseous monomer, additives, and solvent. The amount of material emitted depends on the plastic, temperature, previous processing history, and length of storage. If extrusion is carried out at the polymer production plant, emission rates will be comparable to those rates given earlier. Secondary extrusion and molding rates will vary from one process and material to another.

Adhesives

Polystyrene and polyvinyl chloride resins are widely used in adhesive manufacture. Synthetic adhesives may be of two types, thermoplastic and thermosetting, although PVC and PS are used only in the former. Emissions consist of the solvent used to dissolve the resin. Organic solvents commonly used in adhesives are methylethyl ketone, toluene, benzene, and naptha.[28] Table 4.7-6 lists estimated organic solvent usage for various adhesive applications.

TABLE 4.7-6. ESTIMATED ORGANIC SOLVENT USAGE IN ADHESIVES APPLICATIONS[2,9]

Application	Organic Solvent (metric tons/year)	Year
Flooring, tile, wall covering	11,000	1973
Other construction	14,000	1966
Aircraft assembly	900	1973
Automobile assembly	20,000	1973
Plywood and veneer	2,000*	1973
Particle board	1,300*	1973
Furniture assembly	7,300	1973
Other wood products	11,800	1973
Textile products	2,000	1973
Footwear	7,300	1973
Pressure sensitive tapes and labels	263,000	1974
Gummed tapes and labels	5,700	1973
Packaging laminates	5,800	1973
Other paper products	14,000	1973
Glass insulation	13,000	1973
Abrasive products	5,900	1973
Printing and publishing	6,300	1973
Rubber products	21,500	1973
Tires	1,000	1973
Other	67,600	1973
Total	481,400	

*EPA Estimate

4.7.3 Control Technology

A summary of control devices and emission levels for polyvinyl chloride is given in Table 4.7-7. Applicable control techniques include carbon adsorption, resin adsorption, incineration, absorption, refrigeration/condensation, vacuum stripping, and good housekeeping. The control of fugitive emissions is described in Section 4.1. A detailed description can be found in the Standard Support and Environmental Impact Statement for Vinyl Chloride , October 1975.[31]

Safety relief valve discharges can be controlled or prevented by venting the reaction mixture to a gasholder large enough to hold an entire batch of VCM, by injecting an inhibitor ("shortstop") to prevent polymerization, flaring, a cooling water jacket, or a power back-up system. Losses of monomer from reactor cleaning can be reduced by recipe reformulation, redesigning reactors, or applying a coating to the interior of the reactor to reduce scale formation. In new plants the frequency of reactor openings can be reduced to once every 80-90 batches.[32] VCM emissions from process and cleaning waters can be prevented by stripping these waste waters prior to release into plant treatment ponds.

Control devices currently used in polyethylene production are flares and incinerators. Many of the control devices used in PVC production could also be applied to polyethylene production.

Emissions from polystyrene production are controlled by flaring and through refrigeration/condensation vapor recovery. Also, it is possible to scrub styrene storage tanks using No. 2 fuel oil.[33] Control techniques described for PVC production are applicable to polystyrene production when the same manufacturing methods are used.

TABLE 4.7-7. CONTROL TECHNIQUES FOR VCM EMISSIONS FROM PVC PRODUCTION[30]

Emission Source	Control Technique	Uncontrolled Emission Rate $\frac{\text{kg VCM}}{\text{100 kg PVC}}$ $\left(\frac{\text{lb VCM}}{\text{100 lb PVC}}\right)$	Achievable Emission Rate $\frac{\text{kg VCM}}{\text{100 kg PVC}}$ $\left(\frac{\text{lb VCM}}{\text{100 lb PVC}}\right)$
Fugitive Total		1.53	0.16
1. Transfer Operations: loading & unloading	Purge to control device[a]		
2. Safety relief valve leaks & discharges	Rupture disks flare		
3. Pumps, compressors, & agitation seals	Double mechanical seals		
4. Laboratory sampling	Purge sample flasks back to process		
5. Equipment opening	Displace gas to control device		
6. In process wastewater	Strip VCM & vent to control device		
7. Leaks at flanges, seals	Multipoint fixed & portable monitoring devices		
Safety relief valve	Short stop, gasholder	0.2	0
Reactor opening losses	Displace gas to gasholder	0.46	0.001
Monomer recovery system	Reduce inerts Solvent absorber Carbon adsorber	0.48	0.001 0.001 0.001
Slurry blend tanks	Improved stripping Carbon adsorption Solvent absorption Incineration	0.42	0.013 0 0 0
Centrifuge	Improved stripping Carbon adsorption Solvent absorption Incineration	0.13	0.004 0 0 0
Dryers	Improved stripping Carbon adsorption Incineration	0.63	0.02 0.02 0.02
Storage silos	Improved stripping Carbon adsorption Incineration Silo stripping	0.07	0.002 0.002 0.002 0.002

[a] Control Devices include solvent absorbers, carbon adsorption, or incineration. Each can control emissions to 10 ppm.

4.7.4 Energy, Cost, and Environmental Impact of Controls

Energy, cost, and environmental impact of existing controls for polymer production are discussed in Sections 4.1 and 3.0.

4.7.5 References

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4.8 Paint, Varnish, and Ink Manufacture

Organic emissions from paint, varnish, and printing ink manufacturing and methods of control are described in Sections 4.8.1 through 4.8.3.

4.8.1 Paint Manufacture

Paint is defined as a pigmented liquid that is converted to a relatively opaque solid film after application as a thin layer.[1] Enamels are paints which form an especially smooth and glossy film

Paint manufacturing consists of the following operations:

1. Mixing pigment with sufficient vehicle to make a paste of proper grinding consistency
2. Grinding the paste on a mill until aggregates are broken down
3. Letting down (diluting) the ground paste with the remaining materials
4. Tinting to required color
5. Testing
6. Straining, filling, and packaging.

In some cases the mixing and grinding operations are done in one step. Paint manufacturing is still largely a batch process because of the large number of raw materials and finished products required. Many of the products must be custom formulated and processed.[2]

4.8.1.1 Emission Characteristics

Volatile organic emissions from uncontrolled manufacturing equipment average 15 g/kg (30 lb/ton) paint product.[3] From the study "Air Pollution Control Engineering and Cost Study of the Paint and Varnish Industry, " Publication No. EPA-450/3-74-031, June 1974, an average emission factor of 6 kg/m^3 (0.05 lb/gal) of solvent-based paint was used to calculate a volatile organic emission average of 4 g/kg (8 lb/ton) of paint product. The two sources of volatile organic emissions in paint manufacturing are grinding and thinning. During grinding, heat is produced which causes vaporization of certain ingredients. In the thinning operation, vaporization of solvent occurs. Thinning of premixed paint pastes to the required consistency for application involves dilution with aliphatic or aromatic hydrocarbons, alcohols, ketones, esters, and other highly volatile materials.[4] Because of the volatility of most thinners, mixing must be done in totally enclosed tanks to prevent solvent loss. A small amount of pigment fines is emitted from the mixing operation.

4.18.1.2 Control Technology

The use of afterburners, condensers and/or absorbers can eliminate 99% of the emissions from a source not using these controls. One to two percent of the solvent is lost even under well controlled conditions.[5]

4.8.1.3 Cost, Energy, and Environmental Impact of Controls

The above control methods are discussed in Section 3.0.

4.8.2 Varnish Manufacture

Varnish is an unpigmented surface coating composed of resins, oils, thinners, and driers. Varnishes dry by evaporation of the solvents and oxidation and polymerization of the remaining constituents. Table 4.8-1 lists common raw materials used in varnish manufacture.

TABLE 4.8-1. RAW MATERIALS USED IN VARNISH MANUFACTURE[6,7]

Oils	Resins	Solvents & Thinners	Dryers
Linseed Oil	Phenolics	Turpentine	CO, Mn, Pb, & Zn
Soybean Oil	Alkyd Acrylates	Xylol	Naphthenates
Tall Oil	Silicones	Toluol	Resinates
Tung Oil	Epoxies	Alcohols	Tallates
Castor Oil	Polyurethanes	Aromatic & Aliphatic	Lineoleates
Fish Oil	Rosin	Naphthas	
Coconut Oil	Copal	Dipentine	
Oiticia Oil	Dammar		
Other Oils	Manila & East India		

Oleoresinous varnishes are the most common and several types are produced. They are all solutions of natural or synthetic resins in a drying oil and a volatile solvent. Oleoresinous varnishes dry by oxidation; oxidation and condensation; or oxidation, condensation, and polymerization.[8] The other major type of varnish is spirit varnish, which consists of alcohol solvents plus natural or synthetic resins. Little or no oil is added to spirit varnish. Shellac is the most common spirit varnish. Spirit varnishes dry either by evaporation or by evaporation and polymerization.

Other important types of varnishes have been developed recently. Alkyd resin varnish is a solution of alkyd resin (a synthetic polyester co-reacted with a vegetable oil) in a volatile solvent with added drier. Asphalt varnish is a solution of asphalt in a volatile solvent. Lithograph varnish is used as a vehicle in pigmented lithographing printing ink.

The steps in varnish manufacturing include cooking, thinning, mixing, filtering, storing and aging, testing, and packaging. The most important step in this process is cooking. The cooking step performs many functions; some of the most important ones are:

1. Bodying of natural and synthetic oils

2. Melting materials to accelerate solubility and reaction

3. Esterification of rosin, phthalic anhydride, maleic anhydride, or tall oil with a polyhydric alcohol such as glycerol or pentaerythritol

4. Isomerization to eliminate extreme reactivity in some oils during oxidation

5. Preparation of alkyd resins

6. Distillation and evaporation to remove undesirable constituents such as volatiles in resins.

Cooking temperatures in varnish kettles range from 93 to 340°C (200 to 650°F) and are usually maintained for 4 to 16 hours.[9] The average batch starts to produce vapors at about 175°C (350°F); the rate of vaporization increases with temperature and reaches its maximum shortly after the maximum processing temperature is reached.[10,11] Vapor emission continues as long as heating is continued. The vaporization rate decreases after the maximum is reached.

Both open and closed kettles are used for cooking varnish, although the trend is toward closed kettles. The open kettle is heated over an open flame. The newer totally enclosed kettle is set over or within a totally enclosed source of heat. The open kettle allows vaporized material to be emitted to the atmosphere unless hoods and ventilation systems are provided to conduct the vapors to a control device.

4.8.2.1 Emissions Characteristics

Organic emissions from varnish manufacture are produced from two operations, cooking and thinning. Table 4.8-2 describes emissions from these two operations. In addition to the air contaminants listed in Table 4.8-2, sulfur compounds such as hydrogen sulfide, butyl mercaptan, thiophene, and allyl sulfide are emitted when tall oil is esterified with glycerine and pentaerythritol.[16] Tall oil is the third largest volume oil used in paint and varnish production (19.5 Gg or 43 x 10 lbs in 1973).[17]

TABLE 4.8-2. EMISSIONS SUMMARY FROM VARNISH MANUFACTURE

Source	Dependent on[12]	Type of Emission[13]	Compounds Emitted[14,15]
Cooking of Varnish	Raw Materials Rate of temperature application Maximum temperature reached	Low melting temperature constituents of natural gums, synthetic acids and rosins.	Fatty acids Aldehydes Water vapor Acrolein Glycerol Acetic acid Formic acid
	Amount of stirring Extent of air blowing Length of cooking	Thermal decomposition and oxidation products	
Thinning	Temperature of varnish Solvent used in thinning Method of addition of solvent and dryers	Volatile thinners	Turpentine Xylol Toluol Alcohols Aromatic and aliphatic naphthas Dipentine

The cooking operation is the greatest source of emissions. From 1 to 6 percent of the raw material is emitted during the cooking operation.[18] The type of varnish being produced influences not only the quality but also quantity of organic emissions from both cooking and thinning.

Many processes require the addition of solvents and thinners during the cooking process. Because the temperature of the cooker is near the boiling point, solvent loss to the atmosphere may be considerable, especially if open kettles are used. More solvent is vaporized if a small amount of cold solvent is added to a large volume of hot varnish than if a small amount of hot varnish is added to a large volume of cold solvent. Because of the high volatility of most solvents, most thinning operations must be done in totally enclosed tanks to prevent large losses.

Losses of solvents during thinning could range from 5 to 50% of the total solvent added if open thinning tanks are used. Solvent emissions depend on the method of addition and the length of time the thinned mixture is exposed to the air.[19] Most manufacturers use totally enclosed thinning tanks; therefore, the solvent losses generally amount to no more than 1 to 2% of the solvent used.[20]

Table 4.8-3 gives some emissions factors for volatile organic emissions from one manufacturer of four varnishes.

TABLE 4.8-3. VOLATILE ORGANIC EMISSIONS FROM VARNISH MANUFACTURE[a,21-26]

Varnish Product	Emission Factor	
	g/kg Product	lb/Ton Product
Bodying Oil	20	40
Oleo Resinous	75	150
Alkyd	80	160
Acrylic	10	20

[a] Data is considered of average quality, as explained in Introduction of Reference 12.

4.8.2.2 Control Technology

Integral condensers provide a considerable degree of control for existing processes. Other methods of controlling emissions include scrubbers, absorbers, carbon adsorbers, afterburners, reformulation of solvents, and sublimation.

4.8.2.3 Cost, Energy, and Environmental Impact of Controls

The above controls are discussed in Section 3.0.

4.8.3 Printing Ink Manufacture

There are two major categories of printing ink. Oil and paste inks are used for letterpress and lithography. Solvent inks are used in flexography and rotogravure processes. Solvent inks are similar to oil and paste inks, but they have a very low viscosity and dry by evaporation of highly volatile solvents.[27]

Three general processes are used in the manufacture of inks: 1) cooking and dyeing the vehicle (or "varnish"), 2) grinding a pigment into the vehicle and 3) replacing water in the wet pigment pulp with an ink vehicle (flushing). The cooking process for ink vehicles is the same as for regular varnish cooking. The vehicle is usually cooked in large kettles at 93 to 315°C (200 to 600°F) for an average of 8 to 12 hours. Pigment grinding is accomplished by three-roller or five-roller vertical or horizontal mills. Mixing of the pigment and vehicle is done in dough mixers or large agitated tanks.[28]

4.8.3.1 Emission Characteristics

Vehicle cooking is the largest source of ink manufacturing emissions. At about 175°C (350°F) the products begin to decompose, resulting in the emission of decomposition products from the cooking vessel. Emissions continue throughout the cooking process with the maximum rate of emissions occurring just after the maximum temperature has been reached. Cooling the varnish components - resins, drying oils, petroleum oils, and solvents produces odorous emissions.[29]

Emissions from the cooking of oleoresinous varnish (resin plus varnish) include water vapor, fatty acids, glycerine, acrolein, phenols, aldehydes, ketones, terpene oils, terpenes, and carbon dioxide.[30]

The quantity, composition, and rate of volatile organic emissions from ink manufacturing depend upon the cooking temperature and time, the ingredients, the method of introducing additives, the rate of stirring, and the extent of air or inert gas blowing. An estimate of organic emissions, based on limited information, is given in Table 4.8-4.

TABLE 4.8-4. VOLATILE ORGANIC EMISSIONS FROM VARNISH COOKING IN PRINTING INK MANUFACTURE[a, 31]

Varnish Cooking	Emission Factors	
	g/kg Product	lbs/Ton Product
General	60	120
Oils	20	40
Oleoresinous	75	150
Alkyds	80	160

[a] Data is considered of poor quality, as explained in Introduction of Reference 12.

4.8.3.2 Control Technology

Emissions from varnish cooking can be reduced 90% by the use of scrubbers or condensers followed by afterburners.[32,33] Emissions from solvent handling can be controlled with condensers and/or carbon adsorption systems.

4.8.3.3 Cost, Energy, and Environmental Impact of Controls

The above controls are discussed in Section 3.0.

4.8.4 References

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4.9 Surface Coating

According to the American Society for Testing and Materials, a surface coating is "a liquid, liquifiable, or mastic composition which is converted to a solid protective, decorative, or adherent film after application as a thin layer." The various types of surface coatings include paints, varnishes, lacquers, stains, shellacs, polymer films, waxes, and oils. These coatings are applied to metal, paper, fabric, wood, glass, stone, concrete, plastic, and other types of surfaces. The actual processes by which a surface coating is applied may vary considerably from one industry to the next. The application of coatings to metal, paper, fabric, and wood surfaces and the applications of adhesives are described in the following paragraphs.

Metal Coating

There are several industries involved in metal coating operations. The major industrial sources of organic emissions in metal coating are auto and light truck coating, can coating, coil coating, large appliance coating, metal furniture coating, and magnet wire coating. Other metal coating operations which also contribute significant quantities of organic emissions include small appliance finishing, fabricated metal products finishing, and industrial, farm, and commercial machinery finishing.

In auto and light truck coating the body is initially treated in a phosphate wash cycle to improve paint adhesion and corrosion resistance.[1,2] The first coat, a primer, is applied by dip and/or spray methods and then the unit is baked. The topcoat is then applied in one to three steps, usually with a bake step after each. Assembly is completed in the trim shop. If the coating is damaged during the trim step, repainting is done in a repair spray booth.

Two types of coatings are commonly used: enamels and lacquers. Enamels are coatings thinned with solvents; enamels form a coating by polymerization. Lacquers are resin-pigment combinations dissolved in solvents that form a coat by evaporation of the solvent and deposition of the resin and pigment.[3] Primers are usually enamels and top coats may be either enamels or lacquers.

Cans are manufactured in one of two ways depending on whether the can is two-piece or three-piece. A two-piece can is wall-ironed (extruded) from a shallow cup of aluminum or steel. The exterior body of the can is sometimes reverse-roll coated, usually with a white base coat. After baking, a rotary printer roll coats any design or lettering on the can. This can be followed by a direct roll coat of protective varnish before the final baking. In addition the can is spray-coated with a lacquer on the interior and baked.

In the manufacture of three-piece cans, large metal sheets are initially roll coated with an interior lining. This is sometimes followed by roll coating an exterior base coat or size coat before baking. After the exterior base coat, an ink design and over-varnish may be applied and baked. The sheets are then split into can body size blanks, formed into a cyclinder, and welded, cemented or soldered. The interior and exterior of the seam are usually sprayed with an air-dry lacquer to protect the exposed metal. Can ends are stamped from coated sheets of metal in a reciprocating press. The perimeter is coated with a synthetic rubber compound that functions as a gasket when the end is assembled on the can.[4]

Coil coating involves the coating of any flat metal sheet or strip that comes in rolls or coils. Prime coats can be applied on one or both sides usually by reverse or direct roll coating. Electrodeposition is also used for applying a prime coat on aluminum coils or a single coat on steel coils. After baking, the second coat or topcoat is applied by reverse or direct roll coating. The topcoat is baked on and the metal is ready for any printing or embossing before being shaped into a finished product. If an adhesive is applied, it is activated in the oven and then vinyl, fabric, metal, or other materials can be laminated onto the metal coil.[5]

In large appliance coating, prime coats are applied to interior parts by flow or dip coating techniques and often to exterior parts by flow or spray coating techniques. After baking, interior parts are ready for assembly and exterior parts receive a topcoat by automatic electrostatic spraying. Exterior parts for some appliances, such as refrigerators and freezers, are topcoated directly with no prime coat. Manual air spraying is used for touchup and shading. After final baking, the parts are assembled.

Metal furniture parts may be coated while they are unassembled, partially assembled, or completely assembled. A prime coat may be applied but is usually not necessary. The prime coat is usually baked before a top coat is applied. Prime and top coats are applied by spraying, dipping, or flowcoating. Spraying methods are preferred when frequent color changes are necessary. The coated furniture is usually baked in an oven, but may be air dried.[6]

Magnet wire coating is the application of insulation varnish or enamel onto an electrical wire. The wire is unwound from a spool, passed through a bath of coating, and then drawn through an orifice or die. Excess coating is scraped off, leaving a layer of uniform, predetermined thickness. During baking, the solvent is driven off and the coating is cured.

Paper, Film, and Foil Coating

Paper, film, and foil are coated for a variety of decorative and functional purposes. Waterborne, organic solvent-borne, or solventless extrusion type materials are used. A typical coating line consists of an unwind roll, a coating applicator, an oven, various tension and chill rolls, and a rewind roll. Coatings may be applied to paper by several different devices such as knives, reverse rollers, or rotogravure rolls. After coating, the paper is sent to an oven or dryer which may contain two to five temperature curing zones.[7]

Fabric Coating

Fabric coating involves the coating of a textile substrate with a knife or reverse roll coater. Fabric coating imparts properties that are not initially present, such as strength, stability, water or acid repellancy, and appearance.[8] Substrates can be either natural or man-made. Coatings may be either aqueous or organic borne and include latexes, acrylics, polyvinyl chloride, polyurethanes, and natural and synthetic rubbers.

A typical fabric coating line consists of four operations: milling, mixing, coating application, and drying and curing. Milling and mixing are coating preparation steps and vary with pigments, curing agents, fillers, and solvents. The fabric coating is normally applied by a knife or reverse roll coater, although rotogravure printing has recently been widely used in vinyl coating of fabrics. After coating, oven curing is used to increase the rate of solvent evaporation. For some coatings, oven curing produces chemical changes within the coating solids to give desired properties to the product.[9]

Application of Adhesives

Adhesives are used for joining surfaces in assembly and construction of a large variety of products such as pressure sensitive tapes and labels, rubber products, and auto assembly. Adhesives may be water-borne, organic solvent-borne, hot melt or high solids. Virtually all of the organic solvent used for the application of adhesives is emitted to the atmosphere when the adhesive dries.

Coating of Flat Wood Products

Flat wood products such as plywood, particle board, hardboard, cedar siding, and softwood molding are often coated with a variety of fillers, sealers, or topcoats. Application is usually by direct or reverse roll coating. Wood-grain patterns can also be printed. Following the application, the coating is dried in an infrared or steam-heated oven.

Wood Furniture Coating

Although the procedure for wood furniture coating may vary from one company to the next, the process typically consists of several coating applications. Various liquid mixtures are used to bleach, stain, fill, color, wash, highlight, or seal the wood surface. Application is most commonly done by dip or spray methods. Drying can be open air or oven bake at temperatures not exceeding 60°C (140°F).[10] Standing between coatings is optional. Almost all furniture manufacturing operations employ conveyors to transport articles from the woodworking department through finishing for storage or shipping.[11] Finish coatings are usually of very low solids content with attendant high emissions of volatile organics.

4.9.1 Emission Characteristics

According to one source, the total volatile organic emissions for industrial surface coating operations are 1.36 Tg/year (1.5 x 10^6 tons/year).[12] Quantities and sources of organic emissions from the industrial surface coating operations described in Section 4.9 are given in Table 4.9-1.

The quantity of emissions from each operation depends on several factors such as type of material to be coated, coating thickness, desired finish, coating process, percent overspray, and paint formulation (% water and % solvent). Materials on which coatings are to be applied can be as smooth as glass or as irregular as concrete. A lustrous finish may be required for visual appearance or a weather resistant finish may be required for endurance.

Coating processes vary significantly within the surface coating industry. For example, the auto industry may use either a dip or spray method of coating while paper and fabric coating rely almost exclusively on application by knife or reverse roll method. In most coating operations, 10 to 90 percent of the solvent is evaporated at the application and/or during subsequent air drying. The remaining 10 to 90 percent is evaporated in the oven. Table 4.9-2 provides a general range of emissions resulting from typical surface coating operations.

Spray coating produces high emission rates, and spray booths are usually open on one side. The amount of sprayed material that misses the surface to be coated (overspray) is a

TABLE 4.9-1. SOURCES AND ESTIMATED QUANTITIES OF ORGANIC EMISSIONS FROM INDUSTRIAL SURFACE COATING OPERATIONS[13]

Industry Process	Percent of Total Emissions	Annual Emissions	
		Gg/yr	(10^6 lb/yr)
METAL COATING			
<u>Automobile and Light Truck Assembly</u>		138	304
1) Spray booth and flash-off area	85-90		
2) Oven	10-15		
<u>Can Coating</u>		128	282
<u>Metal Furniture Coating</u>		92	202
1) Spray applications			
a) Spray booth and flash-off area	65-80		
b) Oven	20-35		
2) Dip or flowcoat applications			
a) Coating and flash-off area	50-60		
b) Oven	40-50		
<u>Coil Coating</u>		30	66
1) Coater area	8		
2) Oven	90		
3) Quench area	2		
<u>Large Appliances</u>		42	92
<u>Magnet Wire Coating</u>		8	18
PAPER COATING		392	862
1) Coating line	70		
2) Other sources	30		
FABRIC COATING		96	211
1) Coating line	40-70		
2) Fugitive emissions and cleanup	30-60		
ADHESIVES		212	466
FLATWOOD PRODUCTS		84	185
WOOD FURNITURE COATING		232	(510)
1) Spray booth	85		
2) Oven	15		

[a]Figures are for a typical can coating line

major factor in solvent emissions. Table 4.9-3 describes the percentage of overspray as a function of spraying method and sprayed surface. Solvent emissions from spray booth stacks can vary from less than 0.45 kg/day (1.0 lb/day) to more than 1,360 kg/day (3,000 lb/day), depending on the extent of the operation.[16] If a water curtain is used for the control of particulate emissions, a 10% reduction in the organic vapors discharged can be anticipated.[17] Solvent is recovered from contaminated water by a suitable separation technique.

TABLE 4.9-2. PERCENT OF TOTAL EMISSIONS FROM VARIOUS COATING PROCESSES[14]

	Coating Process		
Coating Method	Application	Pre/Air Dry	Bake
Spray Coat	30-60	10-40	10-40
Flow Coat	30-50	20-40	10-30
Dip Coat	5-10	10-30	50-70
Roller Coat	0-10	10-20	60-90

TABLE 4.9-3. PERCENTAGE OF OVERSPRAY AS A FUNCTION OF SPRAYING METHOD AND SPRAYED SURFACE[15]

Method of Spraying	Flat Surfaces	Table Leg Surface	Bird Cage Surface
Air atomization	50	84	90
Airless	20 to 25	90	90
Electrostatic			
Disc	5	5 to 10	5 to 10
Airless	20	30	30
Air atomized	25	35	35

The quantity of solvent emissions is highly dependent on the paint formulation. For example, emissions from application of a high solids coating (80% solids) are less than 0.24 kg of organic solvent per liter of solids applied (2.0 lb/gal). Application of lacquer produces more than 5.4 kg of organic solvent per liter of solids applied (45 lb/gal). This definite difference in emission rates due to paint formulation is well illustrated in Figure 4.9-1.

All of the previously discussed factors contribute significantly to the emission characteristics of a particular surface coating operation, but there are additional points to be considered. For instance, the extent of air drying which occurs prior to baking may mean that the solvent mixture remaining in the coating at the beginning of the baking operation is much richer in the high boiling solvents. This may result in chemical changes upon high temperature baking.

A suggested equation for estimating the potential solvent vapor emissions from surface coating operations is given below:

$$W = \frac{1000\ A\ n\ (1 - 0.01\ P)}{P\ f}\ \rho$$

W = weight of solvent vapors in kg

A = area coated (sq. m.)

n = thickness of dry coating (cm)

P = percent solids by volume

f = efficiency factor (dimensionless) empirically determined ($f \leq 1$)

ρ = solvent density (kg/liter)

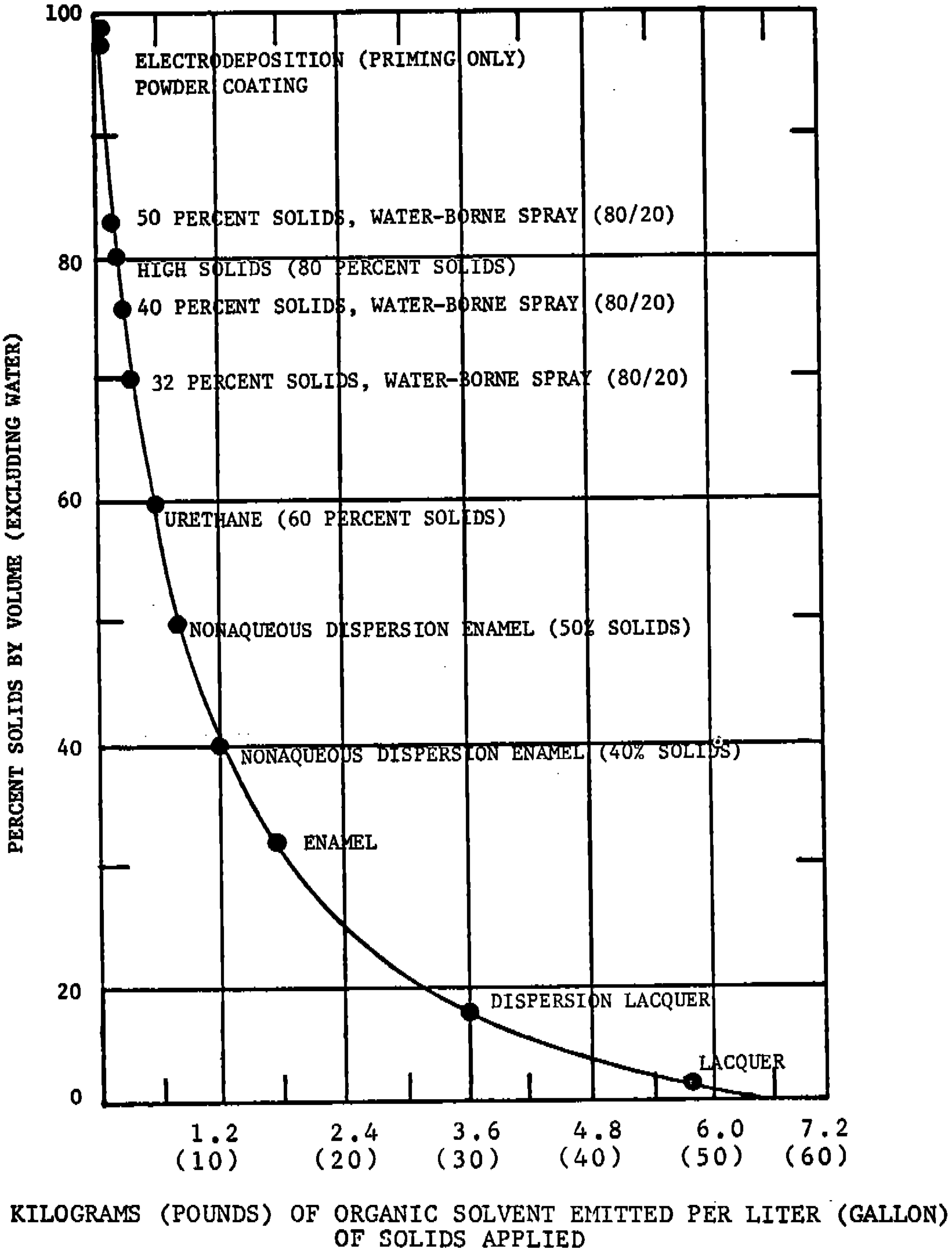

Figure 4.9-1. Percent of Solids Versus Kilograms (pounds) of Organic Solvent Emitted Per Liter (gallon) of Solids Applied. (Assumption: Solvent Density = 0.79 kg/l = 6.6 lb/gal).[18]

or

$$W = \frac{0.0623\ A\ n\ (1 - 0.01\ P)}{P\ f}\ \rho$$

W = weight of solvent vapors in lb.
A = area coated (sq. ft.)
n = thickness of dry coating (mils)
P = percent solids by volume
f = efficiency factor (dimensionless) empirically determined ($f \leq 1$)
ρ = solvent density (lb/gal)

This equation incorporates parameters for area to be coated, thickness of the coat, percent of solvent in the coating, and efficiency of coating application.[19]

4.9.2 Control Technology

Volatile organic emissions from surface coating operations can be reduced by add-on control devices and by process and material changes. Add-on devices include carbon adsorption units, incinerators, condensers, and scrubbers. Process and material changes include electrostatic spray coating, electrodeposition, electron beam curing, ultraviolet curing, and coating modification (waterborne coatings, high solids coating, powder coatings, and hot melt formulations). Since the surface coating industries vary in raw materials handled and products manufactured, each industry is faced with unique emission problems and alternate solutions. Tables 4.9-4 and 4.9-5 summarize the utility and efficiency of the many emission control schemes available to the major surface coating industries. The control efficiency is stated in terms of the percent reduction in organic emissions from application of the control method. Applicable control techniques are described for each industry in the following paragraphs.

TABLE 4.9-4. TYPICAL EFFICIENCIES FOR ADD-ON CONTROL EQUIPMENT[20-26]

Industry	Control Efficiency (Percent) Carbon Adsorption[a]	 Incineration Thermal/Catalytic[a]
Metal Coating		
Auto & Light Truck Assembly	85+[b]	95/95
Can Coating	85-90[b]	90-98/90
Coil Coating	b	90-98/90
Large Appliance Coating	b	90-95
Metal Furniture Coating	90	90
Magnet Wire Coating	b	90-95/90-95
Fabric Coating	90-95	90-95/90-95
Paper, Film, and Foil Coating	90+	95/95[b]
Adhesives Coating	b	b
Flat Wood Products Coating	b	90
Wood Furniture Coating	b	b

[a] Numbers represent percent reduction across the control device and do not include the capture efficiency into control device.

[b] Not widely used in this industry.

4.9.2.1 Metal Coating

Automobile and Light Truck Assembly

Emissions from automobile and light truck assembly are produced during priming and topcoating operations. While several control methods are applicable, the most effective way to minimize organic emissions from prime coating operations is electrophoretic priming with waterborne surfacer. For the prime coat, the use of waterborne spray coatings also merits consideration, although the reduction in emissions is somewhat less than for electrodeposition. Incineration of oven exhaust can be efficiently accomplished, but

TABLE 4.9-5. TYPICAL EFFICIENCIES FOR PROCESS AND MATERIAL CHANGES[27-30]

	Control Efficiency (Percent)						
	Waterborne Coatings	High-Solids Coatings	Powder Coatings	Hot Melt Formulations	Ultraviolet Curing	Plastisols	Extrusion Coatings
Metal Coating							
Auto & Light Truck Assembly	80-93[a] 40-92[b]	0-86	--	--	--	--	—
Can Coating	60-90	60-90	95-99	--	100	--	—
Metal Furniture Coating	90-95	50-80	95-99	--	--	--	--
Coil Coating	60-90	60-90	--	--	--	—	--
Large Appliance Coating	80 90[a]	60-80	95-99	--	--	—	—
Magnet Wire Coating	—	--	--	--	--	--	—
Fabric Coating	80-100	80-100	—	99^+	--	--	—
Paper, Film, and Foil Coating	80-99	--	—	99^+	--	95-99	99^+
Adhesives Coating	80-99	--	--	80-99	80-99	—	--
Flat Wood Products Coating	80	--	--	--	99^+	—	--
Wood Furniture Coating	c	c	--	--	c	--	--

[a] Electrodeposition of primer.

[b] Topcoat

[c] Statistics unavailable.

the reduction in emissions is minimal since less than 15% of the solvent evaporates there. The use of add-on equipment for prime spray booths is technologically feasible but will probably not occur due to the advantages of a transition to an electrophoretic coating.

The best means of controlling emissions from topcoating lines is by increasing the solids content in coating formulations or by using waterborne coatings. The reduction in solvent emissions is particularly significant for those plants using lacquers. Add-on devices for spray booths are technically feasible, but difficulties have been encountered in application. For example, excessive particulate matter can reduce carbon life in an adsorption system. There are also substantial energy requirements associated with the incineration of spray booth exhaust. As before, incineration of oven exhaust is effective but has little impact on the overall reduction of emissions.

Can Coating

In oven dried spray operations, about 50-75% of volatile organic emissions are fugitive. In air dried spray and end sealing operations of the can coating industry, about 100 percent of the organic solvent vapors emitted are fugitive emissions within the plant.[31] For this reason conversion to waterborne or high solids coatings is the best control option, as well as one of the most economical. In roll coating operations, conversion to water-borne, high solids, or ultraviolet curable coatings is the best option. The major problem with such solvent reformulation is that many coatings are still in the developmental stages or are undergoing tests by both the Food and Drug Administration and the packing customer. Incineration is a proven retrofit control system which can be economically designed to eliminate any incremental energy requirements through the use of primary and secondary heat recovery systems. Carbon adsorption can also be considered an economic alternative if recovered solvent mixtures are used as fuel to generate steam for carbon regeneration. The use of an incineration or carbon adsorption system will require that the coater either be covered with a hood which ducted to the oven exhaust stream or be enclosed up to the oven entrance so that the coater emissions are drawn directly into the oven.

Coil Coating

In the coil coating industry as in other industries, no single best control system is apparent.[32] Due to the typically high curing temperatures and the various mixtures of organic solvents found in the coatings, incineration is the best add-on control technique. Conversion to waterborne or "medium- to high-solids" coatings has been successfully applied, within limits, to several existing coil coating lines with favorable results. If incineration is chosen and no heat recovery techniques are incorporated, fuel requirements can be substantial. For coil coaters, significant advances have been made in the use of incinerators with heat recovery. In catalytic incineration care must be taken that solvents do not poison the catalyst or cause temperature limits to be exceeded.

Large Appliance Coating

Like many other surface coating industries, there are several emission control routes available for large appliance coating. Although the use of powder coatings and electrodeposition provide the greatest emission reduction, they usually require the most extensive equipment changes. On the other hand, waterborne and high-solids coatings can be applied with existing equipment but do not achieve the same degree of emissions reduction. The utility of retrofit devices such as adsorbers and incinerators may be limited by the cost, fuel requirement, and available space.

Metal Furniture Coating[33]

Emissions from metal furniture coating may be reduced by substitution of low solvent coatings or by add-on equipment. Powder coating and electrodeposition of a water-borne coating provide the greatest emissions reduction. The use of water-borne coatings requires no major equipment alterations and makes color changes a simple matter. The use of high solids coating is usually less efficient than the other methods. Carbon adsorption for application and flashoff areas is considered technically feasible but has not yet been applied. It would require a significant additional floorspace. Incineration has been successfully used for ovens.

Magnet Wire Coating

The most common emission control technique used in magnet wire coating is incineration (catalytic and thermal). Modern wire coating ovens are equipped with an internal catalytic incinerator which recovers heat by burning solvents inside the oven and eliminates malodors and the buildup of flammable resins in the stack. Only limited success has been achieved in developing powder coatings and waterborne coatings.

4.9.2.2 Paper, Film, and Foil Coatings

Both incinerators and carbon absorbers have been successfully retrofitted onto a number of paper coating lines. Several low solvent paper coatings (waterborne, plastisols, organisols, and hot melts) have recently been developed and show promise for the future. At present several technical problems still need to be solved. For instance, waterborne coatings are not as effective as organic solvent coatings in providing weather, scuff, and chemical resistance for some uses. In addition the use of waterborne coatings has resulted in wrinkling of the paper and other application problems. Hot melt application cannot be used for coating materials that char or burn.

4.9.2.3 Fabric Coating

As with other surface coating industries, the primary control systems for fabric coating are incineration and carbon adsorption. For an operation which uses a single solvent or solvent mixture, adsorption is the most economical option. Some companies have implemented this method and found it to be very efficient.[34] If, on the other hand, several solvents or solvent mixtures are required, then incineration (thermal or catalytic) with primary and secondary heat recovery is most applicable. The use of low solvent coatings has been encouraging but limited. Both high-solids and waterborne coatings have been used and often the coating equipment and procedures need not be changed to accomplish conversion. The major disadvantage is that every coating line is somewhat unique and many coated fabrics have different applications. This often means high research and development costs.

4.9.2.4 Adhesives Coating

Replacement of organic solvent-borne adhesives with waterborne, hot melt, solventless two component, or radiation cured adhesives is the best method for reducing emissions from adhesives coating operations where it is applicable. More than half of the total adhesives applications employ waterborne natural adhesives such as animal glue, starches, dextrin, and proteins. Water-borne synthetic adhesives have been developed recently which are comparable to waterborne natural adhesives. However, water-borne adhesives are not compatible with plastic substrates. In addition, the cost of retrofitting existing equipment to use hot melts or high-solid materials can be prohibitive.

4.9.2.5 Flat Wood Products Coating

Basically three emission control techniques are used in flat wood products coating: low-solvent ultraviolet (UV) curable coatings, waterborne coatings, and incineration. UV curable coatings rapidly polymerize to form a film when exposed to UV radiation. UV filters are frequently employed and occasionally UV curable topcoats are used. Opaque base coats are not yet available in a UV curable formula. It has been suggested that UV curable inks from the paper coating industry could be used for grain printing as well. A major problem with UV curable coatings in general is the difficulty in curing irregular shapes, although this is not a problem with flat wood products.

Waterborne coatings are available for filling and base coating but waterborne topcoats or graining inks are essentially unavailable. Some problems have been encountered with poor adhesion or staining and "blocking" (the sticking of the paper sheets used to separate the boards).

The use of afterburners on baking ovens has been successfully applied. There are no reports of the use of carbon adsorption units, although the application is technically feasible.

4.9.2.6 Wood Furniture Coating

In general, significant reductions in the organic solvent emissions from wood furniture coating can be realized by switching to waterborne coatings.[35,36] Small reductions can be realized by practicing proper spraying techniques or using electrostatic spraying.

Coating reformulation is currently one of the most promising means of reducing organic solvent vapor emissions in wood furniture coatings. Of particular interest is the advent of waterborne coatings, some of which contain 5 to 15 percent organic solvent by volume.[37] The composition of a typical nitrocellulose solvent-borne furniture coating is 12% solids and 88% organic solvent by volume. A typical waterborne furniture coating is 40% solids, 48% water, and 12% organic solvent by volume.[38]

Unfortunately, some problems have been encountered with the experimental use of waterborne coating. Longer drying times for waterborne coatings result in slower furniture production rates. Additional problems include appearance, repairability, compatibility between various coating layers, mar resistance, and resistance to water and alcohol stains.

4.9.3 Cost, Energy, and Environmental Impact of Controls

This section includes cost data, energy requirements, and environmental impact developed specifically for control methods for most surface coating operations discussed in the previous section. Specific data is unavailable in the consulted literature for large appliance coating, magnet wire coating, adhesives coating, and flat wood products coating. Section 3 of this document includes in-depth treatments of the major methods used for controlling volatile organic emissions in industry. The data given in this section are not as fully developed as those included in Section 3. For specific details, assumptions, and bases the reader is referred to the original source.

4.9.3.1 Metal Coating

Automobile and Light Truck Assembly

Substitution of electrophoretic dip priming for more traditional coating methods involves a high capital cost. The total installed capital cost is about $8 million for a typical plant. Increased operating costs are estimated to range from $108,000 to $948,000/yr. Electrical requirements are increased by about 1400 kW (4.8×10^6 Btu/hr) by switching to electrophoretic coating representing a 12 percent increase. The coatings contain amines which are driven off during the drying step, thus generating a secondary pollutant. Incineration has been used as a control method for this problem.[39] Capital costs for converting from lacquer to enamel are estimated by EPA to be about $1 million for a typical automobile and light truck assembly plant. A very rough estimate of annualized operating expenses is $120,000. The actual costs are difficult to assess, however, as they are very site-dependent. The overall energy requirements should be lower, but specific estimates were unavailable in the sources consulted.[40]

Capital costs for carbon adsorption control devices for spray booths are largely dependent on flow rate. Estimated costs for a 1300 m^3/min (50,000 ft^3/min) unit are $3-20 million capital costs and $1-7 million annualized costs. (The lower numbers represent the case for 50 percent solids, the higher ones represent the case for 12 percent solids.) Electrical and steam requirements are large: steam requirements are 3.42 Mg/hr (7.55×10^3 lb/hr). A potential water pollution problem exists because of steam regeneration in which organic substances are contacted directly with steam. The organic compounds would have to be separated from the condensed steam before disposal.[41] An alternate approach is incineration for the steam and solvent or hot air and solvent stream.[42-45]

Cost and energy data for incineration of top coat spray booth exhaust are presented in Table 4.9-6. The low flow rates and low organic vapor concentrations require the addition of larger amounts of fuel. Furthermore, the capacity for use of recovered heat is limited to primary heat recovery.[48] Incineration has a secondary pollutant potential. Combustion products, such as NO_x, SO_2, CO, and acids may all result, depending on the composition of the substance being combusted.

Incineration may also be used to control volatile organic emissions from primer and topcoat ovens. Costs and energy requirements are summarized in Tables 4.9-7 and 4.9-8 for incinerators operating at 10 and 15 percent of the lower explosive limit. Three cases are shown: no heat recovery, primary heat recovery only, and primary and secondary heat recovery. A comparison of the two tables illustrates the beneficial economics of minimizing dilution. Combustion devices have the potential for causing NO_x and CO emissions. If sulphur compounds are present, SO_2 emissions will also result, and combustion of halogenated compounds results in acid formation.

Converting a fairly new auto and light truck assembly facility for use of water-borne topcoats is estimated to cost about $20 million.[51] If the entire coating line must be replaced, the costs will be about twice that.[52] Increased operating costs are about $5 million per year for a typical plant. Electrical requirements are increased by 5000 kW (17.2×10^6 Btu/hr); this

TABLE 4.9-6. COSTS AND ENERGY REQUIREMENTS FOR INCINERATING EXHAUST GASES FROM AUTO AND LIGHT TRUCK ASSEMBLY TOPCOAT SPRAY BOOTHS[a,46,47]

	No Heat Recovery		Primary Heat Recovery (38 percent efficient)		Primary Heat Recovery (85 percent efficient)
	Catalytic	Noncatalytic	Catalytic	Noncatalytic	Noncatalytic
Captial Cost	\$1.6-12 million	\$1.3-9.4 million	\$2.0-14 million	\$1.5-11 million	\$2.1-16 million
Operating Cost	\$2.1-15 million	\$4.1-30 million	\$1.8-13 million	\$2.9-21 million	\$0.4-2.6 million
Fuel Requirements	53-390W (182-1330Btu/hr)	143-1050W (494-3610Btu/hr)	34-250W[b] (118-862Btu/hr)	91-670W[b] (314-2300Btu/hr)	15.4-110W (53-384Btu/hr)
Electrical Requirements	447-3260kW (1500-11000 MBtu/hr)	349-2550kW (1200-8800 MBtu/hr)	723-5280kW (2500-18000 MBtu/hr)	719-5250kW (2500-18000 MBtu/hr)	645-4720kW (2200-16000 MBtu/hr)

[a] The smaller numbers are for the 50 percent solids case, 7000 Nm^3/min (248,000 scfm). The larger numbers are for the 12 percent solids case, 48,000 Nm^3/min (1,815,000 scfm).

[b] Includes credit for recovered energy.

TABLE 4.9-7. ESTIMATES OF COSTS AND ENERGY REQUIREMENTS FOR INCINERATION OF EXHAUST FROM PRIMER AND TOPCOAT OVENS IN AN AUTO AND LIGHT TRUCK ASSEMBLY PLANT[49] (10% Lower Explosive Limit)

	No Heat Recovery				Primary Heat Recovery				Primary and Secondary Heat Recovery			
	Catalytic		Noncatalytic		Catalytic		Noncatalytic		Catalytic		Noncatalytic	
	a	b	a	b	a	b	a	b	a	b	a	b
Capital Cost for both ovens	$136,000	$298,000	$132,000	$238,000	$204,000	$396,000	$157,000	$298,000	$182,000	$422,000	$185,000	$349,000
Total Annual Operating Cost	$ 60,700	$237,000	$ 99,200	$424,000	$ 73,000	$212,000	$ 83,700	$311,000	$ 61,000	$182,000	$ 71,000	$209,000
Net Energy Requirement kW (10^6Btu/hr)	430 (1.5)	2500 (8.8)	1900 (6.6)	1100 (39.0)	230 (0.8)	1300 (4.6)	1100 (3.9)	6800 (23.5)	negligible negligible	negligible negligible	negligible negligible	3000 (10.8)
Electrical Requirement kW (MBtu/hr)	13 (45)	110 (380)	12 (41)	83 (290)	21 (72)	14 (48)	18 (62)	127 (440)	24 (83)	166 (570)	24 (83)	166 (570)

[a] Lower flot rate (50% solids enamel) 43 Nm^3/min (1600 scfm) for primer oven and 91 Nm^3/min (3400 scfm) for topcoat oven.

[b] Higher flow rate (32% solids primer and 12% lacquer topcoat) 120 Nm^3/min (4500 scfm) for primer oven and 670 Nm^3/min (25,000 scfm) for topcoat oven.

TABLE 4.9-8. ESTIMATES OF COSTS AND ENERGY REQUIREMENTS FOR INCINERATION OF EXHAUST FROM PRIMER AND TOPCOAT OVENS IN AN AUTO AND LIGHT TRUCK ASSEMBLY PLANT[50] (15% Lower Explosive Limit)

	No Heat Recovery				Primary Heat Recovery				Primary and Secondary Heat Recovery			
	Catalytic		Noncatalytic		Catalytic		Noncatalytic		Catalytic		Noncatalytic	
	a	b	a	b	a	b	a	b	a	b	a	b
Capital Cost Both Ovens	$106,000	$281,000	$107,000	$239,000	$123,500	$340,000	$123,000	$281,000	$143,000	$400,000	$144,000	$343,000
Total Annual Operating Cost	$ 48,600	$197,000	$ 58,800	$254,000	$ 42,500	$147,000	$ 48,500	$163,000	$ 42,500	$105,000	$ 44,000	$102,000
Net Energy Requirement kW (x 10^6 Btu/hr)	35 (1.2)	260 (9)	81 (2.8)	620 (21.5)	5.8 (0.2)	260 (9.0)	33 (1.3)	620 (21.5)	-19[c] (-.67)	-150[c] (05.0)	-3.8[c] (-.13)	-29 (-1.0)
Electrical Requirement kW (x 10^6 Btu/hr)	10.6 (.37)	80 (2.7)	8.2 (.28)	62 (2.1)	13.3 (.46)	100 (3.4)	12.2 (.42)	92 (3.2)	16.0 (.55)	120 (4.2)	16.2 (.55)	122 (4.2)

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[a] Lower flow rate: (50% solids enamel) 30Nm^3/min (1,100 scfm) for primer oven and 59Nm^3/min (2,200 scfm) for topcoat oven.

[b] Higher flow rate: (32% solids primer and 12% solids topcoat) 223Nm^3/min (8,333 scfm) for primer oven and 445Nm^3/min (16,666 scfm) for topcoat oven.

[c] Negative sign indicates energy recovery exceeding energy input.

represents a 42 percent increase.[53] An assessment of the environmental impact of changing to water-borne pigments must include consideration of the fact that the liquid effluent from water-borne pigment systems will require treatment prior to disposal. In addition, a solid waste problem is created because water-borne coatings do not dewater well in the overspray collection water.[54]

Can Coating

Conversion to high-solids, water-borne pigments, or powder coatings in can coating plants may require some expensive equipment changes, depending on the existing equipment. The costs are largely undefined at this time. The coatings themselve are often more expensive, as well. To be added to the total expense are research and development costs for testing of the product.[55] Some cost data developed for using carbon adsorption in the can coating industry are presented in Table 4.9-9 for an "ideal" facility. An environmental effect may be caused by the requirement for a filter before the carbon beds. The particulate matter collected in the filter forms a solid waste stream which must be disposed of. Waste water effluents must be considered if steam is used for regeneration (due to water miscible solvents the condensate stream must be treated in a manner which circumvents a water pollution problem.[57]

Ultraviolet curable coatings are about twice as expensive as conventional coatings. Energy requirements are reduced by about 60 percent, however.[58] Some cost data for an "ideal" can coating plant using incineration as a control method are presented in Table 4.9-10.

TABLE 4.9-9. COSTS OF CARBON ADSORPTION IN THE CAN COATING INDUSTRY[56]

(15% Lower Explosive Limit)

Costs	No Solvent Recovery		Solvent Recovery Cited at Fuel Value		Solvent Recovery Credit at Chemical Market Value	
	$130 Nm^3/min$ (5000 scfm)	$400 Nm^3/min$ (15000 scfm)	$130 Nm^3/min$ (5000 scfm)	$400 Nm^3/min$ (15000 scfm)	$130 Nm^3/min$ (5000 scfm)	$400 Nm^3/min$ (15000 scfm)
Installed Capital Cost	$162,000	$302,000	$162,000	$302,000	$162,000	$302,000
Annualized Operating Costs	$60,000	$142,000	$42,000	$90,000	$15,000	$1000

[a] Costs are based on several assumptions. See original reference for basis.

Metal Furniture Coating[59]

Water-borne and high solids coatings are generally more cost effective than are incineration and carbon adsorption for controlling the emissions from metal furniture coating. Powder coating is not as cost effective as are water-borne and high solids coatings because of high material costs.

Energy consumption may be reduced by the use of high solids coatings and as much as 70% by the use of powder coatings.[60] Energy consumption increases with the use of other control methods. There are liquid and solid waste disposal problems with water-borne coatings and carbon adsorption. A potential health hazard is associated with the use of isocyanates in some high solids coatings. Powder coatings are also subject to explosions.[61] SO_x and NO_x emissions may result from incineration.

Coil Coating

Some costs and energy requirements developed specifically for use of incineration in coil coating facilities are presented in Table 4.9-11. Secondary pollutants (CO, NO_x, SO_2, acids) may be emitted by combustion devices depending on the composition of the combustion mixture.

The costs involved in converting to water-borne and high-solids coatings are largely undefined. It has been estimated, however, that energy consumption may be reduced by 50 percent.[64]

4.9.3.2 Paper, Film, and Foil Coatings

Some specific cost data for incineration in a typical paper coating operation are presented in Table 4.9-12. Specific costs for carbon adsorption control devices used in paper coating operations are presented in Table 4.9-13. Unless a solvent mixture can be recovered in a useable form, it is considered more economical to incinerate and recover heat than to install a carbon adsorber.[67] Costs of equipment necessary for changing to low solvent coatings can be very expensive. Initial development of the coatings can also be very expensive.[68] A cost comparison of various types of silicone application systems is shown in Table 4.9-14.

TABLE 4.9-14. COST COMPARISON OF APPLICATION METHODS FOR SILICONE COATINGS[69]

Application System	cost $/lb Silicone Solids on Paper
Organic Solvent (with recovery)	8.20
Organic Solvent (with incineration)	7.38
Solventless (heat set)	7.11
Organic Solvent (no recovery)	6.69
Water Emulsion System	5.28

4.9.3.3 Fabric Coating

There are some costs developed specifically for incineration and adsorption as control method in fabric coating plants. These data are included in Tables 4.9-15 and 4.9-16. Energy consumption for the incinerators can be very large, but heat recovery can help reduce this requirement. Secondary pollutants to be considered are combustion gases from incineration which may contain pollutants such as NO_x, SO_2, CO, and acids.

TABLE 4.9-15. INCINERATION COSTS FOR A FABRIC COATING PLANT[a,b,70]

	No Heat Recovery		Primary Heat Recovery		Primary and Secondary Heat Recovery	
	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
Installed Cost	$125,000	$155,000	$150,000	$180,000	$183,000	$220,000
Annualized Cost	$105,000	$100,000	$66,000	$75,000	$26,000	$54,000

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[a] Costs are based on several assumptions. See original reference for bases.

[b] 25% Lower Explosive Limit. 400 Nm^3/min (15,000 scfm)

TABLE 4.9-16. CARBON ADSORPTION COSTS FOR A TYPICAL FABRIC COATING OPERATION[a,b, 71]

	No Solvent Recovery	Solvent Recovery Credit at Fuel Value	Solvent Recovery Credit at Chemical Market Value
Installed Cost	$320,000	$320,000	$320,000
Annual Operating Cost	$127,000	$ 60,000	-$100,000

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[a] Costs are based on several assumptions. See original reference for bases.

[b] 25% Lower Explosive Limit. 400 Nm^3/min (15,000 scfm)

35. Reference 11.

36. Reference 29.

37. Johnson, William. Environmental Protection Agency. Research Triangle Park, N.C. Report of meeting with Guardsman Chemicals, Inc. on Sept. 21, 1976.

38. Johnson, William. Environmental Protection Agency. Research Triangle Park, N.C. Report of meeting with Reliance Universal, Inc. on September 21, 1976.

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42. Sussman, Victor H., Ford Motor Company, Dearborn, Michigan, Letter to James McCarthy dated August 6, 1976 as cited in Reference 7.

43. Radian Corporation. Evaluation of a Carbon Adsorption Incineration Control System for Auto Assembly Plants. EPA Contract No. 68-02-1319, Task 46. Austin, Texas. January 1976. As cited in Reference 7.

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4.10 Rubber and Rubber Products

Rubber is an elastomer which can be processed (vulcanized) into a material that can be stretched to at least twice its original length and will return with force to approximately its original length when the stress is removed. Synthetic rubber is produced by polymerization or copolymerization of monomers. Raw materials used in the production of synthetic elastomers include polymers of butadiene, styrene, ethylene, propylene, isoprene, isobutylene, acrylonitrile, and chloroprene. Products are marketed in both solid (crumb, or slab) and liquid (latex) forms. Natural rubber production is not covered in this chapter.

The total production of synthetic rubber for the years 1974, 1975, and 1976 was 2.5 Tg (5.5×10^9 lb), 1.94 Tg (4.3×10^9 lb), and 2.3 Tg (5.1×10^9 lb), respectively.[1] These figures reflect the economic recession of 1975 and the rubber industry strike in 1976. Tire production in 1972 accounted for about 66% of that total.[2] Organic emissions and control technology for synthetic rubber, rubber products, and reclaimed rubber production are discussed in Sections 4.10.1 and 4.10.3.

4.10.1 Synthetic Rubber[3,4]

Two processing technologies, emulsion polymerization and solution polymerization, are used in the manufacture of synthetic rubber. Emulsion polymerization is the more widely used process. The production of crumb styrene-butadiene (SBR) by emulsion polymerization as described below is essentially typical of all emulsion crumb processes.

Styrene and butadiene (monomers) are piped or shipped to the plant and stored in a tank farm. Inhibitors which prevent premature polymerization are removed in a caustic scrubber using a 20% NaOH solution. Soap solution, catalyst, activator, and modifier are then added to the monomer mixture. The continuous polymerization process occurs in a series of reactors which may produce "cold" (4-7°C, 105-210 kPa) (40-45°F, 0-15 psig) or "hot" (50°C, 385-525 kPa) (122°F, 40-60 psig) rubber. For "cold" polymerization the emulsion is cooled prior to reaction. An inhibitor (shortstop) is added to the mixture leaving the reactor to stop the polymerization. Two common shortstops are sodium dimethyl dithiocarbamate and hydroquinone.

Unreacted monomers are recovered from the solution, purified, and recycled. Antioxidants are added to the reactor product and various recipes are mixed. A dilute $NaCl-H_2SO_4$ solution is used to precipitate the rubber. Carbon black and oil extenders may be added during the coagulation step. The rubber is then separated on a shaker screen, rinsed with water, dried, and pressed into bales.

Latex production includes the same processing steps as emulsion crumb production except for the coagulation, rinsing, drying, and baling.

4.10.1.1 Emission Characteristics

Fugitive volatile organic emissions from the emulsion crumb process and other industry processes are possible because of leaking valves and seals. Other gaseous emissions arise from monomer and solvent recovery processes, from product drying, and from storage areas and tanks. On the basis of limited information, it is estimated volatile organic emissions average 41 g/kg product (82 lb/ton).[5] A breakdown of this total is given in Table 4.10-1.

4.10.1.2 Control Technology

Odor control is accomplished by chemical, thermal, and catalytic oxidation; condensation; absorption with water scrubbers and adsorption with activated charcoal. Hydrocarbons recovered by adsorption are sometimes recycled.[7]

4.10.1.3 Cost, Energy, and Environmental Impact of Controls

Cost, environmental impact, and energy requirements for the above controls are discussed in Section 3.0. Organics recovered by adsorption provide a cost credit and an indirect energy credit.

Oxidation controls have the potential to produce NO_x and CO emissions. Organic emissions may also be produced if incineration is not carried out properly. Water scrubbers produce a contaminated wastewater stream. Without extra wastewater treatment, the potential exists for pollution of the plant's water effluent stream.

4.10.2 Rubber Products[8,9]

A wide variety of synthetic rubbers is used for the manufacture of tires and other specialty products. Most passenger car tires are made from SBR and 25% to 35% polybutadiene.[10] Fillers, extenders and reinforcers, of which carbon black and oil are the most common, are used to dilute the raw rubber in order to produce a greater weight or volume and to increase the strength, hardness, and abrasion resistance of the final product.

TABLE 4.10-1. EMISSIONS SUMMARY OF SYNTHETIC ELASTOMERS PRODUCTION[6]

Source	Emission factor, g/kg (lb/ton) of rubber produced		Percent total emissions
Emulsion (90% of total production)			
Styrene storage (breathing)	0.02	(0.04)	0.4
Solvent storage (fugitive)	0.07	(0.14)	1.5
Reactor section (fugitive)	0.4	(0.8)	8.9
Recovery area (fugitive)	0.1	(0.2)	2.3
Butadiene recovery	0.6	(1.2)	13.3
Coagulation, dewatering, drying	0.6	(1.2)	13.3
Solution (10% of total production)			
Styrene storage (breathing)	0.02	(0.04)	0.05
Hexane storage (breathing)	0.5	(1.0)	1.2
Storage (fugitive)	0.07	(0.14)	0.25
Purification area (fugitive)	0.2	(0.4)	0.6
Reactor area (fugitive)	0.61	(1.2)	1.6
Desolventization (vent)	2.7	(5.4)	6.6
Desolventization (fugitive)	0.2	(0.4)	0.6
Dewatering, drying	20.2	(40.4)	49.4

Specialty rubber products include rubber footwear, hose and belting; gaskets, packing and sealing devices; insulated wire; and various other fabricated rubber products. The manufacture of rubber products involves compounding, calendering, building of the product, and vulcanization. The steps are similar to those in tire manufacture but they are practiced on a smaller scale and with varying proportions of other materials.

Tires, Inner Tubes and Retreading

Tire production employs a Banbury mixer to compound the rubber, carbon black, oil and other ingredients such as antioxidants, curing agents, and catalysts. Textiles, cord, and wire are dipped into a rubber cement or latex dip and dried in an oven. They are then calendered (coated) with rubber. The rubber and coated materials are then cut and molded into the basic tire components. The tire tread is often coated with rubber cement or solvents to "tackify" it before it is built into a tire. After the components have been assembled, the green tire is sprayed with a release agent such as silicone oil. The tires are molded and cured (vulcanized) in an automatic press at 38 to 149°C (100 to 300°F) for periods of from a few seconds to several minutes.

Inner tube manufacture proceeds similarly except that the compounded rubber is extruded onto a continuous cylinder. The tube is cut to length and the ends are spliced. Inner tubes are cured in the same manner as tires.

Tire retread shops usually buy the tread from tire manufacturers and only cementing, curing, and buffing are done on-site. New tread stock may also be extruded directly onto the carcass.

Rubber Footwear

The rubber footwear industry includes the manufacture of canvas footwear and waterproof footwear. Canvas footwear is the major product. Canvas footwear production is on a much smaller scale than is tire production, as is the production of all specialty rubber products.

In the mixer, white pigments are used in lieu of carbon black and care must be taken to avoid discoloration. The stock may be extruded as a strip or in a thin sheet. Soles and innersoles may be cut from sheets or formed by injection, compression or transfer molding techniques. The boxing between sole and upper is extruded as a long strip.

Canvas uppers are cut and sewn from several layers of fabric which have been glued with latex and passed over a heated drum. The upper is cemented at its edges, then the shoe is built on a last with a latex adhesive. The shoe may be partially or entirely dipped in latex, then air or oven dried. The shoe is cured at 30 to 40 psi (207 to 276 kPa) for about one hour with anhydrous ammonia.

Hose and Belting

Rubber hose consists of three parts: the lining, the reinforcement (rubberized fabric) and the cover. Rubber belting consists of a rubberized fabric carcass sandwiched between layers of rubber sheeting. Production steps include compounding, calendering, reinforcement, extrusion, vulcanizing, and finishing.

After compounding, the rubber stock is sheeted for belting or extruded to form a tube for hose. Fabric is calendered and cut on a bias. The hose or belt is then built; the hose is mounted on a mandrel (metal rod) for support. Cement may be used for adhesion of the components. Curing is carried out in a steam autoclave.

Gaskets, Packing and Sealing Devices

Gaskets and packing and sealing devices are made by three molding techniques: compression, injection and transfer. All three techniques may be used in one plant. Larger facilities, or those with special needs, compound their own stock.

In compression molding the stock is placed in the mold and the two halves of the mold are held together by hydraulic oil pressure during curing. In transfer molding the stock is placed in a transfer cavity fitted with a ram. The applied force of the ram plus heat from the mold causes the rubber to soften and enter the mold cavity, curing simultaneously. In injection molding the stock is injected into the mold cavity, then cured.

After molding, rubber overflow is removed (deflashing) by grinding, press-operated dies, or tumbling in dry ice.

Insulated Wire

Insulation is applied to wire by extrusion. The wire is passed perpendicular to the extruder so that the rubber compound completely surrounds the wire. The wire goes directly into the curing device for continuous vulcanization. Another covering of textile or metallic braid, lead, or another rubber may be applied.

Other Fabricated Rubber Products

Other fabricated rubber products include others which are molded or extruded and those made of latex or rubber cement. Latex is an emulsion of rubber in water; cement is a solution of rubber in an organic solvent. Latex and cement products are usually formed by dipping a form into a bath, curing, then stripping the item off of the form.

4.10.2.1 Emission Characteristics[11,12]

The rubber products industry is based on mechanical and dry manufacturing processes, therefore, organic emissions are relatively low. Potentially hazardous organic solid wastes are not incinerated. Volatile organic emissions are most likely from the processes in which temperatures are high (above 72°C), particularly compounding, extrusion and vulcanization. Rubber adhesives, solvent, cement, excess spray and spray residue, etc., and other additives may be volatilized during vulcanization. There may also be leaks in materials storage areas.

A summary of available volatile organic emission data for tire, inner tube, and specialty rubber products manufacture is given in Table 4.10-2.

4.10.2.2 Control Technology

The principal techniques used to control organic emissions from rubber processing are reformulation, condensation, adsorption, absorption, and incineration. Direct-flame incineration has proven to be very successful in controlling both hydrocarbons and odors from rubber processes such as cord drying. Carbon adsorption and incineration have been used to

TABLE 4.10-2. VOLATILE ORGANIC EMISSIONS FROM RUBBER PRODUCTS MANUFACTURE[13]
g/kg (lb/1000 lb) product

Process	Tire and Inner Tube	Rubber Footwear	Hose and Belting	Fabricated Rubber Goods	Rubber Gaskets, Seals & Packing	Nonferrous Wiredrawing and Insulation	Tire Retreading
Green Tire Spraying	19.7						
Fabric Cementing	5[b]		12.5[b]				
Tire Building	3.6						
Undertread Cementing	1.25[b]						
Tread End Cementing	0.25[d]						
Rubber Cementing		95	6.0				
Bonding				2.0			
Molding		0.11[b]		0.11[b]	0.22		
Adhesive Spraying				1.8	3.6		
Curing	0.22	0.08[b]	0.16	0.08[b]		0.6	0.09
Latex Dipping and Drying		0.1[d]		0.13[c]			
Compounding	0.1	0.1	0.01	0.1	0.1		
Milling	0.05	0.05	0.05	0.05	0.05		
Calendering	0.04[a]	0.05	0.05	0.025[b]	0.05		
Extrusion	0.01[d]		0.02[b]	0.015[b]		0.04	
Painting and Trimming							3.2
Cement Spraying							2.75
Solvent Storage	0.01						
TOTAL	30.23	95.49	18.83	4.31	4.02	0.64	6.04

[a] Assumed to be utilized in 80% of the final product weight.
[b] Assumed to be utilized in 50% of the final product weight.
[c] Assumed to be utilized in 25% of the final product weight.
[d] Assumed to be utilized in 20% of the final product weight.

a very limited degree. Control efficiencies as high as 97 percent have been achieved in one plant. Adsorption is used for the emissions from tread cementing. Based on this information, the potential reduction of volatile emissions in rubber processing plants is estimated to be over 90 percent. Water-based release agents have also been used successfully as a substitute for the silicone oil.[14]

4.10.2.3 Cost, Energy, and Environmental Impact of Controls

Cost and energy requirements are discussed in Section 3.0. Recovered organics produce a cost credit and an indirect energy credit.

Incineration may produce NO_x and CO emissions if not properly operated. Incineration of materials containing sulfur may produce SO_x emissions.

4.10.3 Reclaimed Rubber[15,16,17]

The reclaiming of old tires involves two steps: mechanical preparation and separation of the rubber, and physicochemical modification, usually called devulcanization.

Devulcanizers are of two types: the reclaimator and the dynamic devulcanizer. A reclaimator is a screw device which generates high temperature and pressure. Reclaiming oils are added to the rubber in the reclaimator. The dynamic devulcanizer operates at steam pressures of 3.5 to 7 MPa (500-1000 psia).

The product from the reclaimator is in the form of thin flakes which can be processed into sheet or crumb form.

The material from the dynamic devulcanizer is further compounded on a mixing strainer, then passed through mills which produce a crumb form similar to synthetic rubber.

4.10.3.1 Emission Characteristics

In the reclaimator, lighter fractions of the reclaiming oil are driven off. When the hot oil is mixed with the water used to cool it, the mist formed is 2 percent organics. Similar quantities of organics are emitted in the vent stream from the dynamic devulcanizer. Solvent may also be lost during addition to the dynamic devulcanizer. Based on data obtained from state permit applications for an assumed representative rubber reclaiming plant, the emission factor is calculated to be 30 g/kg (30 lb/1000 lb) product. The emission factor will vary with each type of process.[18]

4.10.3.2 Control Technology

Emissions from the reclaimator are controlled by condensation and scrubbing. In at least one establishment the recovered oil is recycled to the process.[19] Steam pressure from the dynamic devulcanizer can be relieved through control equipment consisting of a venturi scrubber discharging to a barometric condenser. Direct-flame incineration is also a possible control technique, but it is generally considered too costly.[20]

4.10.3.3 Cost, Energy, and Environmental Impact of Controls

Costs and energy requirements are discussed in Section 3.0. Recovered oil provides a cost credit and an indirect energy credit.

Incineration may produce NO_x and CO emissions. If there is any sulfur in the reclaiming oil, incineration may also produce SO_x emissions.

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4.11 Pharmaceuticals

The pharmaceutical industry produces drugs, enzymes, hormones, vaccines, and blood fractions. The main processes used in the industry are fermentation, organic and inorganic synthesis, biological extraction and fractionation, and botanical extraction.

Organic emissions consist mainly of solvent used in manufacturing processes. Solvents commonly used are acetone, acetonitrile, amylacetate, benzene, butyl acetate, chloroform, ethanol, ethylene dichloride, isopropyl alcohol, methanol, methyl isobutyl ketone, toluene, xylene, ethylene glycol, monomethyl ether, heptane, methylene chloride, and naphtha.[1]

Emissions and control technology for fermentation, drug synthesis, and biological and botanical extraction operations are described in Sections 4.11.1 through 4.11.3.

4.11.1 Fermentation

Biological fermentation is used in the pharmaceutical industry to produce antibiotics. In 1974 estimated domestic sales of antibiotics was $760 million.[2] Figure 4.11-1 illustrates the processing steps in antibiotic production. Living microorganisms such as fungi or bacteria are cultured in a nutrient rich broth. The crude antibiotic is recovered by extraction, precipitation, or adsorption. The product is then purified by several recrystallization steps, filtered and dried. Product modification may be required prior to the drying step. An example of product modification is the conversion of penicillin to procaine penicillin.

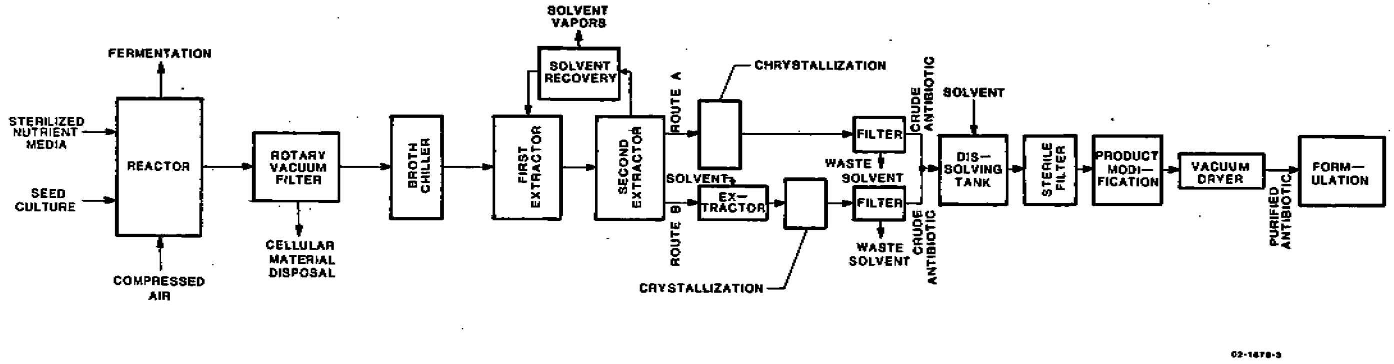

Figure 4.11-1. Simplified flow diagram for antibiotic production.[3]

4.11.1.1 Emission Characteristics

Significant volatile organic emissions arise during extracting procedures and fermentation. The fermentation process produces gaseous by-products which are vented. The vent gases have a very strong odor but contain low concentrations of volatile organics.[4]

Solvent emissions result from evaporation of solvent during processing and drying. Another potential emission source is evaporation of waste solvent. The volume amount of solvent emissions depends on the control methods used. Waste solvent is usually disposed of by incineration. Table 4.11-1 lists typical waste solvent values for the production of procaine penicillin G. In 1973, 12 Gg (26 x 10^6 lb) of waste solvent concentrate was produced by fermentation operations.[5] Of this total, 5 Gg (11 x 10^6 lbs) were incinerated on site. The balance was sent to outside contractors for disposal. Some organic vapors may be emitted from the on-site incineration.

TABLE 4.11-1. SOLVENT WASTES FROM PRODUCTION OF PROCAINE PENICILLIN G[6]

Solvent Waste Concentrate	m^3/Mg Product	gal/1000 lb Product
Solvent (butyl acetate)	0.6	72
Other Dissolved Organics	0.6	72
Total	1.2	144

Solvent losses from sources other than waste solvent disposal depend on the equipment, type of solvent, and control devices in use.

4.11.1.2 Control Technology

Wet scrubbing carbon adsorption, and ozonation are potential control methods for fermentation vent odors, although their use has been limited. Incineration, though, has been demonstrated as very effective. Fermentation vent gas has been successfully used as combustion air in plant boilers.[7]

4.11.1.3 Cost, Energy, and Environmental Impact of Controls

Incineration is discussed in Section 3.1.

4.11.2 Synthesized Drugs

Synthesis of organic medicinals may involve the complete synthesis of a complex chemical such as aspirin or a one-step modification of an antibiotic or botanical or biological extract. Production of specific organic medicinals can be large or small. Only 0.9-1.8 Mg (1-2 tons) of a specialty drug may be produced per year.[8] Large volume drugs, such as aspirin, are produced on a scale of 13.6 Gg/yr (30 x10^6 lbs/yr).[9] Batch processing methods are employed. Average yields and number of processing steps vary considerably. The aspirin production process employs 2 steps and an 80% yield is achieved. Vitamin A synthesis requires 13 steps and has an overall yield of 15 to 20 percent.

Synthesized inorganic medicinals include antacids and laxatives. Both are usually compounded from magnesium hydroxide or aluminum hydroxide, which are precipitated from solutions of soluble magnesium and aluminum salts. Since organic compounds are not used in their preparation, there are no organic hydrocarbon emissions. Further discussion of synthesized medicinals will apply only to organic compounds.

4.11.2.1 Emissions Characteristics

Total emissions depend on the solvents used, manufacturing processes, and the type of control technology employed. Organic emissions come from evaporation of waste solvents as well as from in-process losses. The average organic medicinal plant produces 100 kg (220 lbs) of waste halogenated solvent and 700 kg (1,500 lbs) nonhalogenated solvent per Mg (2,200 lbs) of product.[10] For 1973, solvent wastes from synthetic organic medicinal plants were estimated to be 3.4 Gg (7.5 x 10^6 lbs) and 23.8 Gg (52.4 x 10^6 lbs), respectively. Emissions occur when the waste solvents are incinerated on-site. The rest is sent to independent contractors for disposal.[11]

In-process solvent losses also occur. Because of the varied nature of the different drug syntheses, no definite sources can be given, although they might include such operations as distillation, drying, and filtration. Emissions are probably similar to process losses from the organic chemical industry.

4.11.2.2 Control Technology

It has been reported that all waste solvents are incinerated. An estimated 10.1 Gg/yr (22 x 10^6 lbs) are incinerated on site.[12] The rest is sent to off-site contractors.

Processing solvent losses can be controlled in a number of ways, depending upon the particular process parameters.

4.11.2.3 Cost, Energy, and Environmental Impact of Controls

Incineration is discussed in Section 3.1.

4.11.3 Biological Extractions and Fractionation

There are three major methods for producing medicinals from animal products: extraction, fractionation, and precipitation. Drugs produced include insulin, heparin, vaccines, various serums, toxoids, and blood fractions.

Extraction is used to obtain hormones or enzymes from animal tissues. Beef and hog pancreas are used for insulin; heparin is obtained from lung tissue. Figure 4.11-2 shows a simplified production scheme for obtaining insulin. The ground organs are first treated with acidic alcohol (ethanol or methanol). The extract is recovered by centrifugation or filtration, neutralized, then filtered again to remove precipitated protein. The extract is then acidified again, concentrated, treated to remove fats, and clarified. The crude insulin is finally precipitated with NaCl. Further purification may include isoelectric precipitation.

Precipitation and fractionation are generally used to produce vaccines, toxoids, serum, and blood fractions. Vaccine viruses such as influenza virus are cultured in fertile chicken eggs. The antigen is then extracted from the egg with a salt solution and precipitated with ammonium sulfate. Toxoids such as poliomyelitis toxoid are recovered from formaldehyde treatment of culture media previously innoculated with a virus.

Serum and blood fractions are all derived from whole blood. Serums, such as tetanus anti-serum, can be obtained from horse blood, but blood fractions are produced only from

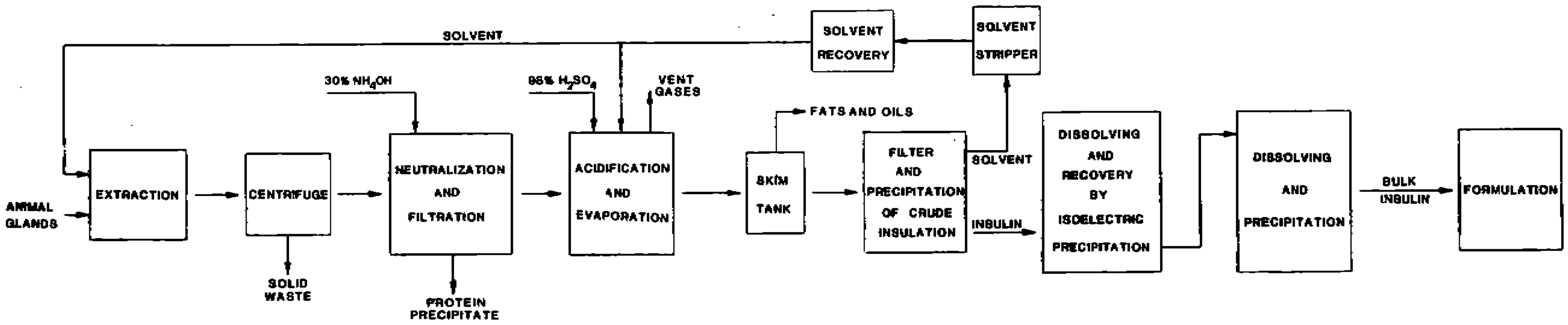

Figure 4.11-2. Simplified production scheme for insulin.[13]

human blood. Useful protein fractions include gamma-globulins, thrombin, albumin, and antihemophilic globulin. These fractions are obtained by first centrifuging whole blood to obtain the plasma. Protein fractions are then precipitated with ethanol of various concentrations and at varying conditions of pH.[14]

4.11.3.1 Emission Characteristics

Organic emissions result from the use of solvents. Waste organic solvents in 1973 for biological medicinals were estimated to total 1.05 Gg (2.31 x 10^6 lbs) (see Table 4.11-2). Waste solvent is generally incinerated, although a small amount from extraction processes is sent to wastewater treatment facilities.[15] (See Section 4.15, Waste Handling and Treatment.) Process emissions of solvent vapors also may occur.

TABLE 4.11-2. WASTE SOLVENTS FROM BIOLOGICAL MEDICINALS[16]

Source of Solvents	Mg of Waste (Dry Basis)	10^6 lbs
Medicinals from Animal Glands (may be up to 50% water)	800	1.76
Ethanol from Blood Fractionation	250	.55
TOTAL	1,050	2.31

4.11.3.2 Control Technology

As stated above, waste organic solvents are usually incinerated, with a small portion sent to biological wastewater treatment facilities. Control techniques for process vapor losses were not specified, and depend on the manufacturing equipment.

4.11.3.3 Cost, Energy, and Environmental Impact of Controls

Incineration is discussed in Section 3.1.

4.11.4 Botanical Extractions

Certain types of secondary organic compounds from plants can be extracted and used as pharmaceuticals. Alkaloids, steroids, and various other compounds can be extracted from bark, leaves, roots, and fruits.

The medicinal is usually extracted from the dried plant material with an acidified, water-miscible solvent such as an alcohol. This liquid is extracted with a water-immiscible solvent, such as ethylene dichloride. The crude product is then recovered by vacuum evaporation and purified by crystallization, precipitation, ion exchange, or chromatography.[17]

A different extraction technique is used for preparing steroids. The production of stigmasterol from soybeans is typical. Still bottoms from soybean oil refining are dissolved in a mixture of hot hexane (37%) and ethylene dichloride (63%). After a series of crystallizations, the solvent is removed in a vacuum oven. The stigmasterol crystals are about 97% pure.[18]

4.11.4.1 Emissions Characteristics

Organic emissions arise from waste solvent streams and process vapor losses. Table 4.11-3 lists typical solvent waste streams for alkaloid extractions. Waste solvents are usually incinerated to prevent organic emissions.

TABLE 4.11-3. SOLVENT WASTES FROM ALKALOID EXTRACTION[19]

Hazardous Waste	kg/kg (lb/lb) Product
Halogenated Solvent	9
Methanol-water Concentrate	120
Nonhalogenated Solvent	20

4.11.4.2 Control Technology

In 1973 an estimated 1.2 Gg (2.6 x 10^6 lbs) of waste solvent was generated from botanical extractions. Incineration was used to control emissions. 60% of waste solvent was sent to off-site contractors.[20] Control technology used to curtail solvent vapor losses depends on process parameters and the types of solvent used.

4.11.4.3 Cost, Energy, and Environmental Impact of Controls

Incineration is discussed in Section 3.1.

4.11.5 Formulations

The formulation of pharmaceuticals involves making the product into tablet, capsule, liquid, or ointment form and packaging for marketing. Organics are probably emitted from this operation, but no data are available at present.

4.11.6 References

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4.12 Graphic Arts

The graphic arts industry includes about 40,000 establishments, most of which are small operations. About half employ less than 100 people.[1] The industry includes the printing of newspapers, books and magazines, cans, sheet metal, floor and wall coverings, and fabrics. About half of the establishments are in-house printing services in non-printing industries.[2]

4.12.1 Process Descriptions

Direct printing is the transfer of an image directly from an image surface to the print surface; offset printing involves the use of an intermediate surface. Material to be printed may be web-fed to the press from a roll and remain continuous throughout the printing operation, as with some paper and fabrics; or it may be fed in individual items or sheets. Emission characteristics depend mainly upon the solvent content of the ink.

There are five types of printing processes which vary according to the nature of the image surface. Letterpress, flexography, lithography, gravure, and screen process printing are described in the following Sections.

4.12.1.1 Letterpress

Letterpress is the original printing process, in which ink is applied to a raised image surface and transferred to the print surface. Many small printers who still use the letterpress process work with sheet-fed equipment.

The newspaper industry uses the web letterpress. The ink is made of carbon black and oils which are absorbed by the porous paper and thus present no emission problems. Emissions of inert ink mist and paper dust are controlled by air conditioning.[3]

Conventional letterpress inks for nonporous paper contain 30 to 45 percent organic solvent. Drying occurs by solvent evaporation in a drying tunnel. The solvent in high-speed operations generally is a selected petroleum fraction akin to kerosene and fuel oil with a boiling point of 200-370°C (400-700°F).[4] Low-speed operations use a slow-drying alkyd or vegetable oil which dries by oxidation or polymerization.[5]

4.12.1.2 Flexography

When the plates used in the letterpress process are rubber, the process is known as flexography. It is widely used in multicolor printing on a variety of surfaces.[6]

Inks for flexography must be very fluid, typically about 60% solvent, and must not damage the rubber. They dry by solvent evaporation, usually at temperatures below 120°C (250°F). Typical solvents are alcohols, glycols, esters, ketones and ethers. Some flexography inks are more viscous than others.

4.12.1.3 Lithography

In lithography the printing and nonprinting surfaces are on the same plane. The image area is made of material that can only be wet by ink and the non-image area is made of material that can only be wet by water. The plates are first wet with water containing 0 to 30 percent isopropanol, then with ink.[7] Most lithographic operations are web-offset. The sheet-fed lithographic process is widely used for small and large applications. Most plants classified under commercial lithography operate with sheet-fed lithographic equipment.

Inks used for web-offset lithography must dry within one second to avoid smudging as the web moves rapidly through other operations. "Heat-set" inks developed for this application contain 35 to 45 percent petroleum hydrocarbons and are dried at 200-260°C (400-500°F).[8]

4.12.1.4 Gravure

The image area of a gravure press is recessed relative to the nonimage area. A very fluid ink fills the image area and is scraped off the nonimage area with a "doctor knife". The image is transferred directly to the printing surface. When the process is roll-fed, it is known as "rotogravure".[9] Sheet-fed gravure is not widely used.

Rotogravure inks contain 40 to 80 percent solvent which may be an alcohol, aliphatic naphtha, aromatic hydrocarbon, ester, glycol-ether, ketone, nitroparaffin or water. The inks are dried at 38-120°C (100-250°F).[10]

4.12.1.5 Screen Process Printing

In screen process printing a fine screen is used as the image area, and nonimage areas are masked off. Inks similar to the more viscous flexographic inks are forced through the pores of the image area onto the print surface.[11]

Screen process inks contain 20 to 50 percent solvent. Drying is done either at room temperature or in an oven. Solvents include aliphatic hydrocarbons, aromatic hydrocarbons, or oxygenated solvents. Oxygenated solvents such as esters, ethers, glycol ethers, and ketones are widely used.[12] Screen printing operations are generally small operations.

4.12.2 Emission Characteristics

The main source of organic emissions from printing establishments is the release of ink solvent during drying. Solvent may be released to the atmosphere during ink application in the flexographic and gravure processes.[13] These emissions are controlled at some plants. The most common odorants are alcohols and partially oxidized alcohols such as ketones.[14] There is a linear relationship between ink consumption and emission rates.

Low levels of organic emissions are derived from the paper stock during drying. The type of paper, coated or uncoated, has little effect on the quantity of emissions. The chemical composition of the emissions, however, will vary.[15]

Total annual emissions from the industry are estimated to be 360 Gg (400,000 tons). These emissions are assumed to be hydrocarbons or organic solvents. No methane is emitted. Of this total, lithography processes emit 25%, letterpress 20%, gravure 40%, and flexography 15%.[16]

4.12.3 Control Technology

Emission controls for the printing industry include removal of the solvent vapors from the effluent by incineration or adsorption and/or use of a low solvent ink. Specific control techniques are not applicable to all processes.

Incineration is used for web-offset lithography, letterpress and small rotogravure operations. The effective temperature for thermal incineration ranges from 590 to 830°C (1100-1500°F).[17] The optimum range is usually 650-760°C (1200-1400°F). NO_x emissions become a problem at higher temperatures. Efficiency of volatile organic removal is about 95%.[18] Besides initial equipment installation costs, the major expense is for fuel. Heat exchangers may be incorporated into the design, so that waste heat can be used to heat the drying ovens. With this design fuel costs for incineration may be reduced as much as 70%, but equipment costs will be higher.[19]

The application of catalytic incinerators also reduces the fuel costs associated with incineration. Temperatures range from 330-510°C (625-950°F).[20] The most common catalyst is a platinum and/or palladium-coated ceramic pellet, but other transition metals or their oxides are also used. The catalyst may be irreversibly poisoned by heavy metals, halogenated hydrocarbons, or organosilicon compounds, or it may be thermally aged by excess heat. The use of heat exchangers will further reduce fuel costs.[21] Efficiency of the heat exchangers is 90 to 95 percent.[22]

Carbon adsorption is an especially successful volatile organic control technique at large rotogravure plants where simple mixtures of water-immiscible solvents are used. A 90% recovery rate can be achieved.[23] The carbon bed is regenerated with steam. If the recovered solvent cannot be reused, it can be sold to other industries.[24]

Low-solvent inks have been developed which are set by thermal catalysis, ultraviolet light, or electron beam. Thermally catalyzed inks for heat-set letterpress and lithography contain up to 30% solvent and use the same dryers as conventional inks, but they cost 40 to 100 percent more. The ink is set by the polymerization of monomers and prepolymers with heat and a catalyst. The use of these inks requires a 15% increase in fuel costs.[25] The higher temperature required to cure these inks causes degradation of the paper. This factor coupled with instability of the inks on the press has led to the conclusion that heat catalyzed inks are not a viable printing method.[26]

Substitution of inks which polymerize upon exposure to ultraviolet light is a potential control method for sheet and web-fed offset lithography. Though UV setting inks cost 85 to 100 percent more than conventional inks and new equipment must be purchased, their use has several advantages. Emission control equipment is not required, drying equipment is simplified, energy costs are reduced and ink does not dry in equipment during shutdowns. However, workers must be protected from the UV radiation and from the inks, which are skin and eye irritants.[27,28] No commercial application of UV inks has been developed for flexography or gravure.[29]

Waterborne inks contain up to 20% water soluble solvent. They cannot be used in lithography, and their use in other areas is limited.[30] They are used in letterpress, flexography, and some gravure operations. Microwave drying may eliminate the problem of the high heat of vaporization and make these inks more feasible in the future.[31]

Another approach to the pollution problem is web-heatset printing in the use of a "press coating" which seals all the ink components onto the paper. The use of this method eliminates the need for oven drying. Press coating can also be used in letterpress or offset operations if the paper is smooth.[32]

4.12.4 Cost, Energy, and Environmental Impact of Controls

Information is provided above in Section 4.12.3. Additional information on incineration and adsorption can be found in Sections 3.1 and 3.2, respectively.

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4.13 Stationary Fuel Combustion

Stationary fuel combustion sources may utilize external or internal combustion. External combustion sources include boilers for steam generation, heaters for the heating of process streams, and driers and kilns for the curing of products. Internal combustion sources include gas turbines and reciprocating internal combustion engines.

4.13.1 Stationary External Combustion Sources

External combustion sources are categorized according to the type of fuel burned in the unit. Coal, fuel oil, and natural gas are the primary fuels used in stationary external combustion units. LPG, wood and other cellulose materials are also used to a lesser degree in external combustion sources. The largest market for liquified petroleum gas, LPG, is the domestic-commercial market, followed by the chemical industry and the internal combustion engine.

Bituminous coal is the most abundant fossil fuel in the United States. Capacities of coal-fired furnaces range from 4.5 kg (10 lb) to 360 Mg (400 tons) of coal per hour. Approximately 480 Tg (530×10^6 tons) were consumed in 1972 to supply thermal energy in the United States.[1]

Anthracite coal is used in some industrial and institutional boilers and is widely used in hand-fired furnaces. It has a low volatile content and a relatively high ignition temperature.

Lignite is a geologically young coal with properties that are intermediate to those of bituminous coal and peat.

Lignite has a high moisture content 35 to 40 percent by weight and the heating value of 1.5 - 1.8 J/kg (6000-7500 Btu/lb) is low on a wet basis. It is generally burned in the vicinity of where it is mined. Although a small amount is used in industrial and domestic applications, it is mainly used for steam production in electric power plants.

The two major types of fuel oil are residual and distillate. Distillate oil is primarily a domestic fuel, but it is used in commercial and industrial applications where high-quality oil is required. Residual oils are produced from the residue remaining after the lighter fractions (gasoline, kerosene and distillate oils) have been removed from the crude oil. More viscous and less volatile than distillate oil, residual oils must be heated for easier handling and for proper combustion. Residual oils also have higher ash and sulfur contents.

Natural gas is used mainly for industrial process steam and heat production and for space heating. It consists primarily of methane with varying amounts of ethane and smaller amounts of nitrogen, helium, and carbon dioxide. In 1974, 616 km^3 (22 trillion ft^3) of natural gas were marketed in the United States, the majority of which was used as fuel.[2]

Wood is no longer a major energy source for industrial heat or power generation. However, it is still used to some extent in industries which generate considerable quantities of wood/bark wastes. Wood is also used as a domestic heat source. Wood/bark waste may include large pieces such as slabs, logs, or bark strips as well as smaller pieces such as ends, shavings, or sawdust.

Liquified petroleum gas consists mainly of butane, propane, or a mixture of the two, and trace amounts of propylene and butylene. It is sold as a liquid in metal cylinders under pressure and also from tank truck and tank cars. The heating value ranges from 26.3 kJ/m^3 (97,400 Btu/gal) to 24.5 kJ/m^3 (90,500 Btu/gal).

4.13.1.1 Emission Characteristics

Volatile organic emissions from stationary external combustion sources are dependent on type and size of equipment, method of firing, maintenance practices, and on the grade and composition of the fuel. Considerable variation in organic emissions can occur, depending on the efficiency of operation of the individual unit. Incomplete combustion leads to more emissions. Estimates of the emission rates of organics from externally fired units in 1975 are presented in Table 4.13-1. Emission factors are given in Table 4.13-2. All ambient air contains some organics from natural and manmade sources. Therefore, net organics from fuel combustion should be derived by subtracting the organics that were present in the combustion air at the burner from the total emissions.

TABLE 4.13-1. ORGANIC EMISSIONS FROM STATIONARY EXTERNAL COMBUSTION SOURCES[3,4,5]

Source	1975 Emissions Gg/yr (10^3T/yr)			
	Coal	Fuel Oil	Natural Gas	Wood
Industrial	55.4 (61)	56.4 (63)	76.4[a] (85)	0.28[a] (3)
Commercial	8.9 (10)		1.8 (2)	
Residential	11.7 (13)	24.3 (27)	12.4 (14)	0.043 (0.048)
Utility	105.0 (117)	20.8 (23)	1.7 (1.9)	

[a] For the year 1972.

TABLE 4.13-2. EMISSION FACTORS FOR STATIONARY EXTERNAL COMBUSTION SOURCES[a], [6-22]

	Coal, g/kg (lb/ton)			Fuel Oil	Natural Gas	Wood
	Bituminous	Anthracite	Lignite	kg/m^3 (lb/10^3 gal)	kg/hm^3 (lb/10^6 ft^3)	g/kg (lb/ton)
EPA Accuracy Rating[c]	A	B	B	A	A	B
Unit Type						
Utility & Large Industrial	0.15 (0.3)		0.5 (1)	0.12 (1)	16 (1)	
Large Commercial & General Industrial	0.5 (1)	$\sim$0.1 (0.2)		0.12 (1)	48 (3)	1-35 (2-70)[b]
Commercial & Domestic	1.5 (3)			0.12 (1)	128 (8)	
Hand-fired	10 (20)	1.25 (2.5)				

[a] expressed as methane

[b] use lower numbers for well designed and operated units

[c] a rating of A indicates "excellent" accuracy; a rating of B indicates "good" accuracy developed from limited data

4.13.1.2 Control Techniques

Volatile organic emissions from stationary external combustion sources can be most effectively reduced by improved operating practice and equipment designs which improve combustion efficiency. Organic emissions are directly related to residence time, temperature, and turbulence in the combustion zone. A high degree of fuel and air turbulence greatly increases combustion efficiency. The trend toward better steam utilization in steam-electric generating plants results in improved efficiency in the conversion of thermal energy from fossil fuels into electrical energy. Continued research in the areas of magnetohydrodynamics, electrogas dynamics, fuel cells, and solar energy may result in improved fuel usage and consequently reduced organic emissions.

Guidelines for good combustion practice are published by the fuel industry, equipment manufacturers, engineering associations, and government agencies. Stationary combustion units should be operated within their design limits, according to the recommendations of the manufacturer, and in good repair at all times. Sources of information on good operating practice include:

1. American Boiler Manufacturers Association
2. American Gas Association
3. American Petroleum Institute
4. American Society of Heating, Refrigerating, and Air-Conditioning Engineers
5. American Society of Mechanical Engineers
6. The Institute of Boiler and Radiator Manufacturers

7. Mechanical Contractors Association of America
8. National Academy of Sciences - National Research Council
9. National Coal Association
10. National Fire Protection Association
11. National Oil Fuel Institute
12. National Warm Air Heating and Air-Conditioning Association
13. U.S. Bureau of Mines

There is no information available on the reduction in organic emissions resulting from the use of these controls. The percent reduction is probably small for the small commercial and residential units. Small units have less efficient air-fuel mixing than large units and operate at somewhat lower temperatures; therefore, they have lower average combustion efficiencies. The potential for reduction of the emissions from wood-fired furnaces may be moderate since most are not regularly maintained.

Flue gas monitoring systems such as oxygen and smoke recorders are helpful in indicating the efficiency of furnace operation. The substitution of gas or oil for coal in any type of furnace reduces emissions when good combustion techniques are used. This reduction is largely effected by the better mixing and firing characteristics of a liquid or gaseous fuel compared to those of a solid.

4.13.1.3 Cost, Energy, and Environmental Impact of Controls

Improved combustion efficiency produces cost and energy credits by reducing fuel consumption. Justification of the capital costs to replace or modify a combustion unit is site specific.

CO emissions are reduced by improved combustion efficiency, while NO_x emissions are increased.

4.13.2 Stationary Internal Combustion Sources

Internal combustion engines include gas turbines or large heavy-duty, general utility reciprocating engines. Most stationary internal combustion engines are used to generate electric power, to pump gas or other liquids, or to compress air for pneumatic machinery.

Stationary gas turbines are used primarily in electrical generation for continuous, peaking or stand-by power. The primary fuels are natural gas and No. 2 (distillate) fuel oil, although residual oil is sometimes used.[23] Emissions from gas turbines are considerably lower than emissions from reciprocating engines; however, reciprocating engines are generally more efficient. The rated power of reciprocating engines ranges from less than 15 kW to 10,044 kW (20 to 13,500 hp).[24] There are substantial variations in both annual usage and engine duty cycles.

4.13.2.1 Emission Characteristics

The organic emissions from stationary internal combustion sources result from incomplete combustion of the fuel. The emissions contain unburned fuel components as well as organics formed from the partial combustion and thermal cracking of the fuel. Combustion and cracking products include aldehydes and low molecular weight saturated and unsaturated hydrocarbons. Emissions from compression engines, particularly recip-rocating engines, are significantly greater than those from external combustion boilers. Table 4.13-3 presents estimates of the annual organic emissions from fuel oil and gas-fired stationary internal combustion sources.

TABLE 4.13-3. ORGANIC EMISSIONS FROM STATIONARY INTERNAL COMBUSTION SOURCES[25]

Source	Emissions (Gg/yr)	Emissions (10^3 Tons/yr)
Industrial - Gas	237.0	261.2
Utility - Oil	68.2	75.2
Utility - Gas	11.8	13.0

Emission factors have been calculated on both a time basis and a fuel basis for 116 electric utility single turbine units operating in 1971.[26] For both gas-fired and oil-fired units, organic emissions were 0.36 kg/MWh (0.7 lbs/MWh). On a fuel basis, gas-fired units emitted 637 kg hydrocarbon per hm^3 gas (39.8 lbs/10^6 ft^3) and oil-fired units emitted 0.668 kg hydrocarbon per cubic meter of oil (0.0417 lbs/ft^3).

Emission factors for heavy-duty natural gas-fired pipeline compressor engines, and gasoline and diesel-powered industrial equipment are presented in Table 4.13-4. The engines used to determine the results in this table cover a wide range of uses and power. The listed values are not representative of emissions from large stationary diesel engines. Emission factors for natural gas-fired pipeline compressor engines, based on the amount of fuel burned, are reported in Section 4.6.1, Pipelines.

4.13.2.2 Control Technology

Emissions from internal combustion sources can be minimized by proper operating practices and good maintenance. Emissions could be reduced greatly with the application of catalytic converters, thermal reactors or exhaust manifold air injections to the engine exhaust.

TABLE 4.13-4. EMISSION FACTORS FOR HEAVY-DUTY INDUSTRIAL ENGINES[27-30]

	Engine Category			
	Natural Gas-fired Compressor		Industrial Equipment	
Pollutant	Reciprocating	Gas Turbine	Gasoline	Diesel
Emission Factor Accuracy	Excellent	Excellent	Fair	Fair
Hydrocarbons as C[a]				
μg/J	1.64	0.03		
(lb/10^3 hphr)	9.7	0.2		
kg/$\underline{N}$ hm^3 [b]	21,800	280		
(lb/10^6 scf)[b]	1,400	23		
Carbon Monoxide				
g/hr			5,700	197
(lb/hr)			12.6	0.434
μg/J			74	1.13
(g/hphr)			199	3.03
kg/m^3			472	12.2
(lb/10^3 gal)			3,940	102
Exhaust Hydrocarbons				
g/hr			191	72.8
(lb/hr)			0.421	0.160
μg/J			2.49	0.42
(g/hphr)			6.68	1.12
kg/m^3			15.8	4.49
lb/10^3 gal			132	37.5

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[a] Total Hydrocarbons, of which 5 to 10% are estimated to be nonmethane hydrocarbons

[b] Calculated from the above factors assuming a heating value of 39.3 MJ/$\underline{N}$ m^3 (1,050 Btu/scf) for natural gas and an average fuel consumption of 3,380 k cal/KW (10,000 Btu/scf) for gas turbines and 2,530 k cal/KW hr (7,500 Btu/hphr) for reciprocating engines.

These systems have not been tested on large bore units; it is assumed that such applications would require careful design to assure a homogeneous high temperature environment throughout the unit.

The catalytic converter has been proven effective on mobile gasoline engines. It contains a catalyst which causes the oxidation of HC and CO to water and CO_2 at reduced temperatures. Unleaded low-sulfur fuel should be used to protect the catalyst and prevent the formation of H_2SO_4.

A thermal reactor provides a site for oxidation at elevated temperatures maintained by the heat released from the oxidation of CO and HC. Air is added to the exhaust stream in a container specially designed to maximize both the residence time and turbulence of the charge.

Air injection into the exhaust system is similar to the thermal reactor. However, since the existing shape of the exhaust system is not changed and the volume is not optimized for maximum residence time, heat retention or mixing, air injection is not as effective as the thermal reactor.[31]

4.13.2.3 Cost, Energy, and Environmental Impact of Controls

Volatile organic emission controls for small and medium-bore engines are similar to devices used on mobile sources. A retrofit catalytic converter for an automobile, including an air pump, cost between $105 and $260 in 1974.[32] The cost of modified devices for stationary engines may be considerably higher.[33] The need to use unleaded, low-sulfur fuel increases operating costs for engines fitted with catalytic converters.

Energy is required to operate air pumps for thermal reactors, air injection systems, and catalytic converters that use extra air for combustion. Energy credits are provided for installations that use waste heat boilers for secondary heat recovery.

Catalytic converters produce SO_x emissions from any sulfur in fuel. By combusting at lower temperatures than thermal incinerators and air injection systems, however, they have a lower tendency to produce NO_x emissions. The solid waste impact from disposal of spent catalyst is minimal.

Volatile organic emissions from uncontrolled large-bore engines are generally low: in the range achievable by control of medium-bore engines on mobile sources. Control of large-bore engines is only necessary when volatile organic emissions are increased as the result of control techniques for other emissions, such as NO_x. Therefore, there are no direct costs or energy requirements for control of volatile organic emissions from large-bore engines.[34]

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4.14 Metallurgical Coke Plants

The majority of coke manufacturing in the United States is performed to supply the steel industry with blast furnace coke. There are generally two methods of coke manufacturing practiced today: by-product coking and beehive coking. Beehive coking does not include recovery of volatilized organics. This may result in much higher organic emission rates. By-product coking, however, is used for almost 99 percent of U.S. coke production.

In by-product coking coal is charged by gravity flow from large, hopper carrying cars (larry cars) on wide guage rails into narrow, rectangular ovens. The ovens are lined with silica brick and are typically 45 cm (18 in) wide, 12 m (39 ft) long, and 4.5 m (15 ft) high.[1] The ovens are arranged side by side in groups called batteries and are heated by burning gas in flues between the walls of adjacent ovens.

Instead of burning, the coal bakes at temperatures ranging from 870°C to 1260°C (1600°F to 2300°F)[2] for 16 to 25 hours. During baking air is excluded from the ovens and the intense heat releases volatiles contained in the coal. These vapors are transferred to a chemical plant for recovery of gas, tar, and ammonia liquor. About 45% of the coke-oven gas produced is used to heat the ovens. The remaining gas is used as fuel in other steel mill operations.

At the end of the coking period, a large ram is used to push the coke out of the oven and into a railway car. The car is taken to a quench tower where the coke is drenched with water to lower the temperature to a point below the ignition temperature. Afterward, the quench car moves to a coke wharf where the coke is transferred by conveyor belt to the coke handling area.

In the beehive process the coal is deposited and leveled on the floor of a refractory-lined enclosure with a dome-shaped roof (the beehive). By regulating openings to the beehive oven, the amount of air reaching the coal is controlled. Carbonization begins at the top of the coal pile and proceeds downward through it. All volatile matter escapes to the atmosphere through a opening in the roof. When coking is completed, the coke is watered out or quenched.[3]

4.14.1 Emission Characteristics

Since beehive coking is not widely practiced and emission characteristics are not well described, this section is limited to emissions from by-product coking.

Although coke itself is almost pure carbon, it is made from coal that contains an average of 20 to 32 percent of other elements. The other elements are released as gases during the coking process. Volatile organic emissions can occur during charging, coking, and discharging. Estimates of these emissions are given in Table 4.14-1. Emissions can also occur during quenching.

TABLE 4.14-1. TYPICAL EMISSION FACTORS FOR VOLATILE ORGANICS FROM COKE-OVEN OPERATION[4]

	Emission Factor[a]	
	g/kg coal charged	lb/ton coal charged
By-Product Coking:		
Charging	1.25	2.5
Coking Cycle	0.75	1.5
Discharging	0.1	0.2
Beehive Ovens	4	8

[a] Factors rated average (c) according to explanation in introduction to Reference 4. The numbers are rough estimates due to the lack of good emissions data.

4.14.1.1 Charging

Although coke-oven charging is an intermittent source of emissions, it is also one of the largest single contributors of volatile organic emissions in the coking operation. Since charging begins shortly after discharging of the previous batch, the oven interior is extremely hot and the coal begins to "bake" upon entering. When uncontrolled, steam, gas, and air blow out of the open oven ports carrying organics, ammonia, sulfur dioxide, and particulates.

4.14.1.2 Coking Cycle

Since the coking cycle can take as long as 16 to 25 hours, emissions during this step in the coking process can be considered continuous. Most of these emissions are the result of leaks in and around the coking oven. Significant points of oven leakage are charging lids, oven doors, standpipe lids, cracks in the oven offtakes, flange connections, and cracks in the refractory oven walls.

Due to the extremely high temperatures, charge lids and seats become distorted and difficult to seal. A luting material is used to create an effective seal. Luting involves pouring a wet mixture of clay and coke breeze into a channel between the lid and seat. Cleaning of the lids and seats is essential for a proper seal.

Luting is also used at a few plants to seal oven doors at the joint between the door and the jam. Newer oven door designs feature a self-sealing metal-to-metal contact. The design relies on a mechanical arrangement for exerting pressure between a machined surface and a knife edge. A stringent maintenance program must be followed since leaks will eventually occur.[5]

Another common leakage point in many plants is the standpipe lid. This is usually the result of poor lid positioning by an operator or heat distortion from months of use. The problem can often be eliminated by careful positioning after charging and by luting. New lid designs are being investigated.[6]

Cracks in coke-oven walls result in increased emissions. For years it has been standard practice to depend to a certain extent on the natural formation of carbon at relatively fast coking rates to seal many cracks and open joints. However, with slower operating rates and lower temperatures, and in the event of particularly large cracks, the current practice is to rely on regular oven patching crews.

Other possible leakage points are door sills, standpipe base seals, collecting mains, and gooseneck extension elbows. As with other coke-oven leaks, an adequate maintenance program, including prompt replacement of faulty equipment, will eliminate most emissions.

4.14.1.3 Discharging

The intermittent volatile organic emissions from coke-oven discharging (oven-pushing) are relatively small. Although the emissions depend on a number of factors, the heaviest organic emissions are almost always caused by pushing "green" coke. Green coke results from incomplete carbonization of coal during the coking cycle.

Green coke is produced by both old and new ovens, but for different reasons. Heating deficiencies in older ovens result from heavy oven-to-flue leakage, excess quantities of coal piled up against the end flue heating surfaces, poor combustion control, and poor regenerator efficiency. Related problems arise from oven wall cracking and brickwork movement at the oven ends. In new ovens the problems are poor oven wall maintenance, prevention of good heating by overfilling, overtaxing end flue heating capabilities by accumulating excess coal volumes at the oven ends, or poor coal blending. Green coke may also be produced by pushing early. Whatever the circumstances, an emission reduction can often be achieved through major oven repairs, reduced coal volumes, or slower coking rates.[7]

4.14.1.4 Quenching

Volatile organic emissions from quenching are intermittent or continuous, depending on the quenching technique. Levels of emissions depend on the purity of the quench water. Volatile organics in the water evaporate upon contacting the hot coke. Emissions have been caused by using quenching towers for the disposal of polluted by-product coke plant or metallurgical mill wastewaters. Some emissions may also originate from green coke.

4.14.2 Control Technology

Each coke manufacturing operation has unique emission problems depending on the size of the coke-oven battery, age of the equipment, ability to retrofit and/or modify existing processes, and many other details. These differences, the attempts of many vendors to get into the market, and the attempts of many steel companies to solve their own problems account for the wide variety of control techniques.

4.14.2.1 Charging

Due to the extremely high emissions of organics and other compounds associated with the charging of coke-ovens, many control methods have been proposed for this operation. The possible alternatives include aspiration by steam jet or liquor spray, larry-mounted wet scrubbers or disintegrators, fixed-duct secondary collectors, staged or sequential charging, and closed or sealed charging.

Aspiration systems use a steam jet or liquor spray to artificially increase the net draft on a coke oven while it is being charged. The increase in net draft depends on the aspiration rate and nozzle size and placement. The induced draft draws potential emissions up a standpipe and into a collector main. Some systems have two collector mains located at opposite ends of the oven to avoid loss of aspiration if coal happens to block off part of the open space at the top of the oven during charging. Steam aspiration alone does not provide complete emission control.[8]

Wet scrubbers or disintegrators mounted on larry cars were designed as an add-on device to control charge-hole emissions that occur in spite of aspiration. The larry cars are specially equipped with shrouds or hoods that surround the charge holes and drop sleeves. Gases drawn up through these shrouds are combusted and scrubbed, and then exhausted through fans and stacks on the larry car. Some difficulties encountered with these devices include severe maintenance problems, disposal of polluted wastewater, sensitivity of adjustment, and ignition failure.[9]

Fixed-duct secondary collectors are not an independent control method but are supplemental to aspiration systems and larry-mounted wet scrubbers. Instead of exhausting directly to the atmosphere, the effluent from the scrubber is channeled to a secondary scrubber system where particulates and smoke are removed. Although fixed-duct secondary collectors are in use, the expense is high and the efficiency is limited by the solubility of organics in the scrubbing liquor.

Unlike the previously discussed control methods, staged or sequential charging is a process change and not a retrofit device. The principle of staged charging is to assure the adequacy of aspiration alone as a primary control. Staged charging involves charging to one or, at most, two ports at a time. A normal coke oven has four charging ports, all of which are used simultaneously. In staged charging a definite sequence is followed: for example, first ports 1 and 4 are charged, followed by 2, and then 3. When a port is not being charged, the lid is closed and the induced draft created by the aspirator is more effective since the smallest possible opening to the atmosphere is maintained.

Actual charge times are estimated at 2.75 minutes on a 3.7 m (12 ft) battery and 3.5 minutes on a 4.3 m (14 ft) battery.[10] Some requirements for staged charging include individually operated charging port lids and coal hoppers, two-way drafting of the free space at the top of the oven, adequate aspiration, and crew coordination. Use of special equipment is minimized.

Closed or sealed charging involves radical changes in the present coke-oven charging process. One system transports preheated coal at 260°C (500°F) via pneumatic pipeline directly into the ovens. Estimates are that coke production is increased by 50% due to reduced coking time.[11] Other proposed systems employ conveyors with fixed charging chutes to the coke ovens or larry cars. All these systems were designed primarily to increase coke production per unit volume of coke oven. The methods allow the use of lower quality coals without reduction in coke quality.[12] The fact that both charging methods provide an effective means of emission control is an additional advantage. Capability to retrofit depends on the ability to make oven work changes and the availability of space for preheater and pipeline equipment.

4.14.2.2 Coking Cycle

Emissions during the coking cycle are predominantly the result of leaks caused by cracks in the coke-oven walls and improper seals at lids, doors, and standpipes. Several methods have been considered for eliminating leaks from coke-oven cracks. Several companies have achieved some success with a pressurized dusting process in which fine refractory material (silica) is fed into empty ovens to fill small cracks. Larger cracks are filled by remote control gunning of patching compound. Still other plants have attempted to reduce emissions by reducing oven back pressures. There is some danger, however, that the infiltrated air may cause the burning of gas at oven openings. Good control appears to require a conscientious maintenance program with good operating practices.

Emissions resulting from improper seals can be considerable. One report states that for a battery of eighty 6.4 m (21 ft) coke ovens, operating on a 16-hour coking cycle, the length of end door seals broken and remade every 24 hours amounts to almost 3.7 km (2.3 mi).[13] These seals must be closely fitted under extremely hot, dirty, corrosive conditions. Luting is rarely practiced on large, fast ovens, and most plants rely on self-sealing doors. The seals may either be mounted on a flexible plate (diaphragm-type seals) or on the door frame (strip-type seals). Emissions from door leaks may be collected in hoods. Good control of emissions requires proper maintenance of seals to prevent buildup of carbon and tar deposits.

4.14.2.3 Discharging

Even though the worst discharge emissions result from pushing green coke, no technique has been developed to anticipate green coke formation. Therefore, to ensure proper emission control, the plant must be prepared for the possibility of green coking at any time. The most common approach has been the containment of emissions by some type of hood or covering device.

There are many variations on this method. For instance, one plant uses a partially open entrapment structure which completely covers the discharge area including the quench car. A 150 kW (200 hp) motor is used for continuous evacuation at a rate of approximately 66 m^3/sec (140,000 ft^3/min).[14] Another plant employs a mobile hood which covers the coke guide and quenching car. Contaminated gases are conducted to scrubbers on the same platform. There are numerous other hooding systems and the choice of system depends partially on the retrofit capabilities for the plant under consideration.

Another recent development is related to rapid or continuous quenching of the discharged coal. The design calls for a completely enclosed hot car which accepts the discharged hot coke for transfer to either a mobile rotary kiln or a series of conveyor belts for quench. Gases from the enclosed hot car are easily collected and scrubbed. Prototype enclosed hot cars have performed very well.

4.14.2.4 Quenching

Emissions from quenching can be reduced by using clean water. Many control agencies already require that quenching water be purified to a quality that can be disposed in rivers and streams.

Dry quenching is an alternate quenching technique that controls volatile organic emissions by eliminating the use of water. Coke is cooled in a closed system by a circulating stream of inert gas. Sensible heat picked up from the coke is transferred to a waste heat boiler for the production of steam. Dry quenching produces a better quality of coke than wet quenching. Lower grades of coal, therefore, can be used to charge the coke ovens. The steady cooling of dry quenching also increases the usable coke output by 2-3% by decreasing the production of fine coke particles.

Dry quenching facilities, however, have some inherent problems. They require more ground area than comparable wet quenching facilities. Retrofit, therefore, may be difficult or impossible. They also require continuous monitoring and careful maintenance to prevent explosions caused by oxygen leaking into the closed system. Although successfully employed in several foreign countries, dry quenching is not currently used in the United States.[15]

4.14.2.5 New Technology

The advent of pelletized or formed coke could mean the end of coke-oven emissions by eliminating the need for coke ovens. A fluidized bed is used to accomplish the conversion of coal to coke while simultaneously removing the volatiles. In some cases pitch recovered from the gas stream is used as the binding material for the coke pellets. This process is completely enclosed and produces minimal emissions. Although formed coking is in the demonstration stages, commercial production is not likely for another seven to nine years.[16]

4.14.3 Cost, Energy, and Environmental Impact of Controls

Most control techniques for coke ovens are still undergoing testing and development. Ease of retrofit for each control is also site specific. As a result, costs, when available are estimates at best and may vary considerably for actual installations.

Most techniques have been developed to control particulate emissions. Capability to control volatile organic emissions is secondary. If any of these methods are already employed for particulate emission control, there will be no additional cost, energy, or environmental impact associated with volatile organic emission control.

4.14.3.1 Charging

Most coke ovens are already equipped with steam aspiration systems for particulate control.[17] Therefore, there will be no additional impact from this control technique.

Estimates of capital and annual costs for larry mounted scrubbers, staged charged, and pipeline charging are presented in Table 4.14-2. Data is provided for retrofit installations to a typical plant producing 1.13 Tg/yr (1.24×10^6 tons/yr).

TABLE 4.14-2. ESTIMATES OF CAPITAL AND ANNUAL COSTS FOR RETROFIT INSTALLATIONS OF VARIOUS CHARGING EMISSION CONTROLS IN A TYPICAL (1.13 Tg/yr (1.24×10^6 ton/yr) COKE PLANT[a], [18]

Control Technique	Variation	Larry Car	Capital[b]	Annual[c]
Larry mounted scrubbers	N.A.[d]	New	$2,730,000	$411,150
		Modified	1,980,000	324,750
Staged Charging	Single Collecting Main (AISI/EPA)	New	3,800,000	431,000
	Dual Collecting Main	New	5,650,000	781,000
		Modified	5,350,000	745,000
	Jumper Pipe	New	2,690,000	297,400
		Modified	2,890,000	403,650
Pipeline Charging	N.A.	N.A.	29,350,000	4,014,700

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[a] Early 1973 costs.

[b] Capital costs are installed equipment costs including environmental units for larry car operators to satisfy OSHA requirements.

[c] Annual costs include annualized capital costs, operating, maintenance, and repairing costs, taxes, and insurance.

[d] N.A. indicates not applicable.

Larry mounted scrubbers require energy to pump scrubbing liquor and consume fuel or electricity to support combustion. They also increase the plant's water use. Scrubbers involve an environmental impact due to production of a polluted wastewater stream that must be treated before disposal. Costs for wastewater treatment are included in the annual cost estimates in Table 4.14-2. Combustion of volatile organic emissions from coke production produces SO_x and has the potential to produce NO_x, CO, and particulates. Unless removed by upstream control devices, these pollutants will be emitted to the atmosphere. General discussions of scrubbers and incinerators are provided in Sections 3.1 and 3.3.

Effective staged charging requires an aspiration system capable of producing a strong draft. This can be accomplished by modifying the existing aspirating system to operate at higher steam pressures. The increased pressure requires no extra costs or energy, since steam is normally provided to a coke plant at an elevated pressure and is then reduced to a designated pressure before aspirating.[19] The corresponding increase in the volume of steam required, however, increases costs and energy requirements for the production of steam. It also increases the amount of water used and the resultant volume of polluted wastewater. Costs for extra steam are included in Table 4.14-2.

Costs to retrofit pipeline charging are too high to justify installation for emission control alone. Cost and energy credits provided by increased productivity and the ability to use lower grades of coal, however, may offset these costs. A new pipeline charging installation costs about 10% less than a new conventional uncontrolled oven of the same capacity.[20]

Fixed duct secondary collectors have been used in Japan, but are considered to have very little potential effectiveness relative to their cost.[21] Since they are wet scrubbers, they require energy for pumps and increase the plant's water requirements. Production of polluted wastewater from the scrubbers requires treatment facilities. Additional information on scrubbers can be found in Section 3.3.

4.14.3.2 Coking Cycle

Maintenance costs to control leaks are the costs of labor and materials. Costs and energy requirements depend on the age and condition of the ovens and the type of patching method chosen.

Automatic methods for cleaning the mating surfaces of self-sealing doors include mechanical scrapers and water-jets. Cost and energy information is unavailable in the consulted literature.

4.14.3.3 Discharging

Some form of hood can be adapted to almost any existing plant. Capital costs are high for sites with inadequate clearance or inadequate support in existing structures.[22] Totally enclosed sheds are generally less expensive to construct than partially open hoods but a poorly designed shed creates a dirty and potentially dangerous work place. Enclosed hot cars are a more expensive option.[23]

Energy requirements for hoods and sheds might be quite high. Since partially open hoods are open to the atmosphere, fans in the range of 373-1,492 kW (500-2000 hp) may be necessary to create an adequate draft for efficient emission control. Enclosed sheds require more energy for fans. They have more air to move in order to provide adequate ventilation, to eliminate the buildup of explosive or poisonous gases, and to dissipate heat. The secondary pollution from the production of the enormous amounts of power required to drive these fans could conceivably exceed benefits from the control device.[24]

All associated scrubbers require energy for pumps and increase the plant's water requirements. A polluted wastewater stream results from their use. General information on scrubbers is provided in Section 3.3.

4.14.3.4 Quenching

Costs and energy required to produce clean water are no higher than what would normally be required to treat wastewater for disposal.

Estimates of capital and annual costs for three types of Soviet dry-quenching facilities are presented in Table 4.14-3. The facilities are designed to process 2 Tg of coke per year (2×10^6 tons/yr). Cost credits are provided by the ability to use lower grades of coal, increased usable output, and the recovery of waste heat in the form of steam. For each facility, the credits exceed operating costs and are high enough to pay for the facility within four years.

Energy recovery is a distinct advantage of dry quenching over wet quenching. Of the 3.22 kJ/g (2.78×10^6 Btu/ton) used to coke coal, 52% (1.67 kJ/g or 1.44×10^6 Btu/ton) is retained as sensible heat. All of this energy is lost by wet quenching. Dry-quenching towers recover 1.37 kJ/g (1.18×10^6 Btu/ton) or 82% of the heat lost by wet quenching. Recovered heat can be used to produce steam or electricity, or it can be used to preheat coal for a closed charging operation.[26]

Dry quenching eliminates the plume of steam and particulates associated with wet quenching. However, coke produced by dry quenching is dustier. Extra particulate control measures may be necessary for handling dry-quenched coke.

TABLE 4.14-3. ESTIMATES OF CAPITAL AND ANNUAL COSTS FOR SOVIET DRY-QUENCHING FACILITIES CAPABLE OF PROCESSING 2 Tg OF COKE PER YEAR (2,000,000 TONS/YR)[25]

Type	Number of Towers	Capital Costs[a] 10^6\$	Annual Costs[b] 10^6\$	Pay-Out period After Taxes
A	5	10.2 to 11.32	-4.051[c]	3.9 yr
B	4	8.8 to 9.8	-3.394[c]	3.9 yr
C	2	7.1 to 7.8	-3.327[c]	3.4 yr

[a] Capital costs include materials and manpower.

[b] Annual costs include costs for electricity, labor, and maintenance and credits from ability to use lower grade coke, increased usable productivity, and recovery of heat for steam production. Annualized capital costs are not included.

[c] Negative sign indicates that credits exceed operating costs.

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4.15 Waste Handling and Treatment

The disposal of gaseous, liquid, and solid wastes generated by industrial, commercial, agricultural, municipal, and residential activities employs a diverse and complicated scheme of handling and treatment systems. Emissions resulting from waste disposal are often unique to a particular industry or process. This section includes separate discussions of waste treatment for the petroleum refining and organic chemical industries (Section 4.15.1), and solid waste incineration (Section 4.15.2). For a discussion of waste solvent disposal see Section 4.19, Degreasing.

4.15.1 Petroleum Refinery and Organic Chemical Waste Disposal

The petroleum refining and organic chemical manufacturing industries are highly complex operations which process many feedstocks into a multitude of final products. Consequently, the wastes from these industries come from many different sources and many different control methods are required. The wastes are gaseous, liquid, or solid.

Gaseous Waste

In the past, waste gases were either vented to the atmosphere or mixed with large amounts of liquid wastes and burned in open pits. These methods of disposal are no longer environmentally acceptable or economically practical. For the most part, the industry now relies on direct flaring and on blowdown systems followed by product recovery, combustion and heat recovery, or flaring (see Section 4.1, Emission Sources Common to the Petroleum and Chemical Process Industries).

Liquid Waste

The term "liquid waste" almost always signifies water which has become contaminated by oil, chemicals, metals, or suspended solids. A wastewater system handles water from a number of sources including cooling water, process water and steam condensates, storm runoff, blowdown water, sanitary wastes, and ship ballast waters. Wastewater treatment is usually accomplished in three stages (primary, secondary, and tertiary) by a series of physical, chemical, and/or biological treatment techniques. These various treatment methods are shown in Table 4.15-1.

Solid Waste

The most common methods of solid waste disposal are land disposal and incineration. Due to the low cost and convenience, land disposal has been the predominant means of handling solid waste. Incineration, on the other hand, can be used for wastes which are too heavily contaminated with toxic substances for land disposal. In most instances incineration is not a complete waste disposal method in itself since there is an ash or residue which remains after combustion. After incineration, however, the volume of solid waste is reduced considerably and can be handled easily by conventional land disposal methods. For further information on solid waste incineration see Section 4.15.2.

Salvage and reuse is another solid waste disposal method which has recently received more attention. Increasing costs of both waste disposal and raw materials make recycling economically attractive as well as environmentally beneficial. For an overview of the various solid waste disposal methods used in industry see Table 4.15-2.

TABLE 4.15-1. INDUSTRIAL WASTEWATER TREATMENT METHODS[1]

PHYSICAL TREATMENT

1) Gravity separation
    a) Oil separation
    b) Sedimentation
2) Stripping processes
3) Solvent extraction
4) Adsorption
5) Combustion
6) Filtration

BIOLOGICAL TREATMENT

1) Activated sludge
2) Trickling filter processes
3) Aerated lagoons
4) Waste stabilization ponds

OTHER METHODS

1) Dilution
2) Deep well disposal
3) Ocean disposal
4) Submerged combustion
5) Incineration
6) Discharge into municipal sewerage systems

CHEMICAL TREATMENT

1) Neutralization and pH adjustment
2) Coagulation and precipitation
3) Oxidation processes
4) Ion exchange

REDUCTION OF WASTE LOADS BY INTERNAL IMPROVEMENTS

1) Reduction of raw material losses
2) Recovery of usable reaction products
3) Process modifications
4) Water reuse
5) In-plant control
6) Waste stream segregation

TABLE 4.15-2. INDUSTRIAL SOLID WASTE DISPOSAL METHODS[2,3]

Disposal Method	Waste Type						
	Water Treatment Sludge	Ashes, Flyash & Incinerator Residue	Plastic	Catalysts	Organic Chemicals	Inorganic Chemicals	Sludges, Filter Cakes, Viscous Solids
Land Disposal							
a) Lagoon	X			X	X	X	X
b) Spread on land	X	X		X	X	X	X
c) Sanitary landfill	X	X	X	X			X
d) Dump	X	X	X	X		X	X
Incineration							
a) Open pit			X				
b) Rotary kiln			X		X	X	X
c) Stationary hearth	X		X				
d) Multiple hearth			X				X
e) Liquid burner					X	X	
f) Fluidized bed reactor	X				X	X	X
Ocean Disposal							
a) Bulk dumping					X	X	
b) Sealed container dumping					X	X	
Chemical Treatment					X	X	
Biological Treatment					X		
Salvage & Recycle		X	X	X		X	

4.15.1.1 Emission Characteristics

The amount of hydrocarbon and solvent vapor emissions resulting from industrial waste disposal practices is not well known. Emissions from gaseous wastes are relatively small if blowdown systems are controlled and flares operated properly. Emissions associated with liquid and solid wastes can be appreciable.

Uncovered drainage and wastewater systems allow evaporation of organics and hydrocarbons. A drainage system usually consists of collection systems and interceptor systems. The collection system is a series of small lines with trapped inlets and open ditches that carry wastewater from small installations such as pumps to junction (sewer) boxes. In refineries, there are also oily water sumps for the collection of polluted waters in remote areas. These sumps are simply large, open boxes with oil skimming devices.

The interceptor system is made up of large concrete or corrugated steel trunk drains which lead to the wastewater treatment plant through several liquid-sealed sewer boxes. The manholes for the sewer boxes are usually equipped with vented covers or elevated standpipes. Excess flows of wastewater are typically sent to open holding basins and final wastewater effluent is discharged to large lagoons.[4]

Any part of the drainage system that conveys contaminated water and is open to the atmosphere is a potential source of emissions (see Section 4.2.3, Oil-Water Effluent Systems). Factors which determine the amount of emissions are concentration, volatility, temperature, and agitation. For a refinery it has been estimated that uncontrolled organic emissions from process drains and wastewater separators average 0.30 g/ℓ (105 lb/10^3bbl) of refinery feed. Maximum emissions are 0.57 g/ℓ (200 lb/10^3bbl).[5]

As with liquid wastes, the major emissions resulting from solid waste disposal occur from processes or operations which are open to the environment. Possibly the most significant example is the open pit dumping of sludges, filter cakes, and organic chemicals. Waste units open to the atmosphere in petroleum refineries include gravity or mechanical thickeners, dissolved air flotation units, aerobic sludge digestors, drying beds and evaporation ponds. Evaporative losses occur from all of these units, but emissions have not been quantified.

4.15.1.2 Control Technology

Hydrocarbon and organic solvent emissions from waste handling and disposal can best be reduced by minimizing the amount of waste to be treated. The volume of waste can be minimized through modern process design, proper plant maintenance, and general good housekeeping.

Waste reduction often involves extensive process modifications and/or extreme capital expenditures. The next best alternative is to modify existing waste disposal systems to insure better emissions control. Enclosing wastewater systems produces a dramatic reduction in hydrocarbon emissions. Controls include covered ditches, catch basin liquid seals, and fixed or floating roofs on oil-water separators. There is also some potential for lowering the temperature of wastewater to reduce evaporation or for installing vapor recovery devices on certain equipment such as oil-water separators. According to studies on refineries in Los Angeles County, organic emissions from controlled wastewater systems can be as low as 30 mg/ℓ (0.01 lb/bbl) of refinery feed.[6] This represents a 90% reduction in emissions from the average refinery wastewater system. The same can be said for solid waste disposal systems. Enclosure of solid wastes containing volatile pollutants and proper incineration are excellent measures for reducing emissions.

4.15.1.3 Cost, Energy, and Environmental Impact of Controls

Wastewater drainage systems and oil-water separators are discussed in Section 4.1.10 and 4.2.3, respectively.

4.15.2 Solid Waste Incineration

According to the Solid Waste Disposal Act of 1965, the term "solid waste" is defined as garbage, refuse, and other discarded solid materials resulting from industrial, commercial, and agricultural operations, and community activities. Such wastes may or may not be combustible.[7] Incineration has long been an economical way of reducing the total volume of solid waste requiring disposal. According to one source, an incinerator fill site requires less than one sixth the volume necessary for sanitary disposal of compacted crude refuse.[8]

There are varied estimates of the actual amount of solid waste incinerated in the United States. One estimate states that the per capita generation rate of urban and industrial waste is approximately 4.5 kg/day (10 lb/day), half of which is burned.[9] This combustion is accomplished in several different types of incinerators. Very little open burning is allowed today.

Municipal incinerators have capacities greater than 45.3 Mg/day (50 tons/day) and are usually equipped with automatic charging mechanisms, temperature controls, and movable grate systems.[10]

Industrial and commercial incinerators have capacities ranging from 22.7 kg/hr to 1.8 Mg/hr (50 lbs/hr to 2 tons/hr) and may be either single or multiple-chamber in design. Some resemble municipal incinerators and most are often manually charged and intermittently operated. These units have well designed emission control systems such as gas-fired afterburners and scrubbers.[11]

A trench incinerator is simply a horseshoe shaped pit. Air nozzles located along the top edge of the pit and directed slightly downward provide both an air curtain across the top of the pit and air for combustion within the pit. The trench incinerator was originally designed for the combustion of wastes which have relatively high heat content and low ash content. Trench incinerators are used for other purposes due to the low construction and operating costs.

Domestic incinerators are designed for residential use and typically have single or multiple chambers with an auxiliary burner to aid combustion.

Flue-fed incinerators are commonly found in large apartment buildings where the tenants dispose of refuse through an incinerator flue into the combustion chamber. Some flue-fed incinerators are equipped with afterburners and draft controls.

Pathological incinerators are used for the disposal of animal remains and other high moisture organic material. Typical units have capacities ranging from 22.7 to 45.4 kg/hr (50 to 100 lb/hr) and are equipped with combustion controls and afterburners.[12]

Controlled air incinerators have a two chamber design. In the first chamber wastes are burned without a complete supply of oxygen to produce a highly combustible gas mixture. Combustion is completed in the second chamber with the addition of excess air. These units employ automatic charging devices and frequently exhibit high effluent temperatures.

Conical burners are truncated metal cones with a screened top vent. Charging to a raised grate is accomplished by either a bulldozer or conveyor belt. Additional combustion air is provided by underfire air blown below the grate and overfire air introduced through peripheral openings in the shell.[13]

Sewage sludge incinerators are usually either multiple hearth or fluidized bed units. In a multiple hearth furnace the sludge enters the top and is dried by contact with hot combustion gases rising from the lower hearths. The sludge is burned as it slowly moves down and the ash residue is removed at the bottom. Temperatures for multiple hearth furnaces approach 540°C to 650°C (1000°F to 1200°F) at the inlet, peak at about 760°C to 1100°C (1400°F to 2000°F) in the central hearths, and finally drop to 320°C (600°F) in the ash residue. In a fluidized bed reactor, combustion occurs in a hot, suspended bed of sand and much of the ash residue is discharged with the flue gas. Fluidized bed reactors have fairly uniform temperatures ranging from 680°C to 820°C (1250°F to 1500°F). Either furnace may require supplemental fuel for startup or incineration of high moisture sludge.[14,15,16]

Open burning is still practiced for the disposal of municipal waste, auto body components, landscape refuse, agricultural field refuse, wood refuse, and bulky industrial refuse. The burning can be done in open drums or baskets, fields, or large open pits.[17]

4.15.2.1 Emission Characteristics

Organic emissions from solid waste incineration depend on several factors including the operating conditions, refuse composition and moisture content, basic incinerator design, and level of maintenance. For instance, the relatively low temperatures associated with open burning are operating conditions which increase the emission of hydrocarbons. As another example, conical burners are often missing doors and have numerous holes in the shell due to poor maintenance. The result is excess air, low temperatures, and high emission rates of combustible organics.

Typical emission factors for organics from various types of solid waste incineration are given in Table 4.15-3. These factors should be used with caution as they represent intermediate values; higher or lower emissions could result depending on the factors previously mentioned.

4.15.2.2 Control Technology

The best means of controlling emissions from solid waste disposal is to incorporate an efficient incinerator design (multiple chamber), proper operating conditions, and conscientious maintenance. Underfire air which might disturb the combustion bed should be avoided. Auxiliary burners and temperature controls should be used to maintain proper combustion temperature. If necessary, gas-fired afterburners should be used to insure complete combustion. A rigorous inspection and repair program can eliminate uncontrolled sources of excess air.

TABLE 4.15-3. EMISSION FACTORS FOR VARIOUS TYPES OF SOLID WASTE INCINERATION[18-42]

Source	Emission Factor[a,b] g/kg	Emission Factor[a,b] lb/ton
Municipal Refuse Incinerator		
Multiple chamber, uncontrolled	0.75	1.5
With settling chamber & water spray system	0.75	1.5
Industrial/Commercial Incinerator		
Single chamber	7.5	15
Multiple chamber	1.5	3
Controlled air	Neg.	Neg.
Flue-fed Single Chamber Incinerator	7.5	15
Flue-fed Modified Incinerator (with afterburners and draft controls)	1.5	3
Domestic Single Chamber Incinerator		
Without primary burner	50	100
With primary burner	1	2
Pathological Incinerator	Neg.	Neg.
Conical Burners		
Municipal refuse	10	20
Wood refuse[c]	5.5	11
Sewage Sludge Incinerator[d]		
Uncontrolled	0.75	1.5
After scrubber	0.5	1
Open Burning		
Municipal refuse	15	30
Automobile components[e]	15	30
Unspecified field crops	12	23

a - total organics expressed as units of methane per unit of waste incinerated
b - average factors based on EPA procedures for incinerator stack testing
c - moisture content as fired is approximately 50 percent
d - unit weights in terms of dried sludge
e - upholstery, belts, hoses, and tires burned in common

Only minimal gaseous emission reductions result from retrofitted particulate control equipment. One source reported a 33% reduction in hydrocarbon emissions when a scrubber was installed on a sewage sludge incinerator.[43]

4.15.2.3 Cost, Energy, and Environmental Impact of Controls

Gas-fired afterburners are discussed under incineration in Section 3.1.

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4.16 Food Processing

Organic emissions are produced from varied sources in the food processing industry. Table 4.16-1 lists some important source categories and their yearly estimated emission rates. Eight food processing operations are discussed separately in Sections 4.16.1 through 4.16.8. These are not the only sources of emissions, but they are the only ones for which data were found. Animal food processing, meat slaughtering, and inedible fat and tallow rendering are not covered.

4.16.1 Coffee Roasting

Coffee processing begins with the imported green bean which is cleaned, blended, roasted, and packaged for sale. Only thirty percent of the raw material is processed into instant coffee, and 5 percent is decaffeinated with trichloroethylene prior to roasting.[1] Volatile organics are emitted during roasting and decaffeination. Table 4.16-2 lists estimated emissions of organic compounds for continuous and batch roasters. Emissions can be almost completely eliminated by a direct-fired afterburner operating in the range of 650-750°C (1200-1400°F).[2] Solvent loss (trichloroethylene) is the main emission from the decaffeination step. No solvent control techniques are used.[3] Afterburners are discussed under incineration in Section 3.1.

4.16.2 Alcoholic Beverage Production

Whiskey production is the main emphasis of this section. Wine and beer production involve virtually no volatile organic emissions.[4,5] The four main production stages in whiskey manufacturing are 1) brewhouse operations, 2) fermentation, 3) aging, and 4) packaging.

TABLE 4.16-1. ESTIMATED VOLATILE ORGANIC EMISSIONS FROM THE FOOD PROCESSING INDUSTRY

Emission Source	Year	Emissions Mg/yr (tons/yr)	Reference
Coffee Roasting	1974	1,400 (1,500)	6
Distilled Liquor	1973	10,600 (11,700)	7
Vegetable Oil	1976	10,300 (11,400)	8
Fruit and Vegetable Processing	1973	47,700 (52,500)	9
Deep Frying	1975	6,090 (6,700)	10
Fish and Seafood Processing	1973	745 (820)	11
Meat Smokehouses	1975	462 (510)	12

TABLE 4.16-2. COMPOSITION OF EMISSIONS FROM COFFEE ROASTING[13]

	Aldehydes ppm	Organic Acids ppm
Batch Roaster	42	175
Continuous Roaster	139	223

Of these, only aging results in significant organic emissions. A rough estimate for aging emissions is 24 kg/m^3 of whiskey stored (10 lb/bbl of whiskey stored).[14] Emission controls are not applied.[15]

4.16.3 Flavors and Essential Oils

Food flavorings can be defined as 1) spices and herbs, 2) fruit and fruit juices, 3) essential oils and extracts, and 4) aliphatic, aromatic, and terpene compounds. Volatile organic emissions arise only from producing the latter two categories.

Essential oils are produced in large-scale operations by steam distillation or by solvent extraction of botanical material. The solvent used may be benzene (with or without added acetone and petroleum ether), liquified butane gas, or alcohol. Solvent is recovered by distillation because it is expensive. The residual material (concrete) is then extracted with alcohol, filtered to remove wax, and redistilled.[16] No estimates of volatile organic emissions are available, but they are probably similar to those for botanical extractions in the pharmaceutical industry (Section 4.11).

Aliphatic, aromatic, terpene, and other organic compounds are used as artificial flavorings. These compounds may be synthesized or extracted from food material. Emissions from synthetic compounds would be similar to those described for the organic chemicals in Section 4.4. Available emission rates for some synthetic flavoring compounds are given in Table 4.16-3.

Compounds that are extracted from food materials are produced by distillation or extraction. Emissions vary widely due to processing differences. One example of emissions of this sort is 2-Propanol, used to extract lemon pulp in a California plant. Solvent concentrations in process exhaust were 8300 ppm.[17] This type of solvent loss can be eliminated with the use of a carbon adsorption system. Adsorption is discussed in Section 3.2.

TABLE 4.16-3. ORGANIC EMISSIONS FROM PRODUCTION OF ARTIFICIAL FOOD ADDITIVES[18]

	Organic Emissions Mg/yr (tons/yr)
Sorbitol	26.6 (29.3)
Saccharin	0.4 (0.44)
Saccharin - via toluene sulfonamide	0.7 (0.77)
Monosodium Glutamate	9.6 (10.6)

4.16.4 Fruit and Vegetable Processing

Fruits and vegetables from the field undergo several processing steps before sale either as a canned or frozen product or as a fresh commodity. The fruit or vegetable must first be washed and sorted. If the final product is canned or frozen, subsequent processing includes peeling, slicing, blanching, cooking, cooling, and preserving. Fresh products are sometimes exposed to heat, moisture, ethylene, and oil-soluble dyes to promote ripeness and improve color.

Organic emissions occur from processing operations. Probable significant sources are cooking operations and artificial ripening of the fruits and vegetables. One 1975 estimate for yearly emissions was 21 Gg (23,000 tons) from fruit and vegetable freezing, 26 Gg (29,000 tons) from canning operations, and 544 Mg (600 tons) from artificial ripening.[19] Applicable control techniques are incineration and adsorption. Incineration and adsorption are discussed in Section 3.1 and 3.2, respectively.

4.16.5 Fats and Oils

4.16.5.1 Animal Fats

Animal fats are of two major types, rendered and unrendered. Unrendered fats such as butter require no cooking. Production of unrendered fats does not produce organic emissions. Rendered fats are those obtained by cooking and pressing fatty animal tissues. United States consumption of these oils for 1971 totaled 942 Gg (1045 x 10^3 tons).[20]

Animal fats are rendered by dry, wet, or digestive processes. Dry rendering is the simplest and involves heating the very finely ground oil stock to 110°C (230°F). Heating melts the fats and dehydrates the residual connective tissue which is easily strained and pressed free of fat.[21] Wet rendering is carried out in the presence of large quantities of water. Melted fat rises to the surface of water and is skimmed off. Digestive rendering is carried out at low temperatures by chemicals or enzymes and is not widely used.

Organic emissions are produced by the rendering processes. Emission rates are low but the emissions are noticeable because of odor problems. The use of spray contact condensers is recommended as an effective control device.[22] Condensers are discussed in Section 3.2.

4.16.5.2 Vegetable Oils

The major vegetable oils processed in the United States are soybean, cottonseed, corn, peanut, linseed, and safflower oil. Table 4.16-4 lists consumption for the major vegetable oils in 1971.

TABLE 4.16-4. U.S. VEGETABLE OIL CONSUMPTION FOR 1971[23]

Oil	Gg	(10^6 lbs)
Soybean	2617	(5816)
Cotton seed	334	(717)
Corn	176	(391)
Peanut	83	(184)
Palm	71	(158)
Palm kernel	31	(69)
Olive	28	(62)
Safflower	15	(33)
Coconut	3	(7)
Other	159	(354)
TOTAL	3517	(7791)

The processes for oil production are 1) preliminary treatment, 2) oil extraction, and 3) oil refining. Mechanical crushing to release the oil is the method generally used on seeds of high oil content. Solvent extraction is used mainly to remove soybean oil although it may be applied to cotton, flax, or corn germs. Hexane is the usual solvent; trichloroethylene is used for small batches.

The vegetable oil industry is estimated to have emitted 10.3 Mg (11.4 x 10^3 tons) hydrocarbons in 1976.[24] Major emission points are the basket extractors, miscella (oil/solvent mixture), desolventizer toaster and stripper column, solvent pumps, miscella pumps, and the operation involving recovery of solvent from meal.[25]

Because of the high cost of solvent, recovery techniques are employed. Hexane may be recovered with condensers and oil absorption units, or, in older plants, in carbon adsorbing towers. In a few cases, recovered hexane has been burned in an afterburner.[26] These control methods are discussed in Section 3.0.

4.16.5.3 Refining and Bleaching

Refining by liquid-liquid extraction, deodorizing, and bleaching processes is used to improve color and flavor of both animal and vegetable oils. Liquid-liquid extraction is used to bleach and refine inedible tallows and greases, field damaged vegetable oils, or other very dark oils. Good solvent recovery techniques are employed.[27] Organic emissions are probably comparable to those from solvent extraction of soybean and castor bean oil. Caustic refining may produce emissions of low boiling fatty acids, but no information on emissions was found.

Adsorbent bleaching is used for both edible and inedible oils. Natural bleaching earth (Fuller's Earth), acid-activated clays, or activated carbon are used. Amounts varying from 0.25% (for lard) to 5% (for dark-colored inedible tallows and greases) of the amount of oil to be bleached are required. The spent earth retains a certain amount of oil (20-45% of their own weight). The earth is usually discarded without treatment because the recovered oil is of low purity. The oil can be recovered by prolonged boiling in a weakly alkaline solution. Boiling reduces the oil lost from 30-40% to only 6-8% of the input material.[28]

The deodorization process is used to remove undesirable flavors and odors from oils used in salad oils and margarines. The oils are steam stripped to remove ketones, terpenoid hydrocarbons, and unsaturated aldehydes. These compounds usually constitute less than 0.1% of the total weight of the oil.[29] No attempt is made to recover these compounds.

4.16.6 Meat Smokehouses

The smoking of meat, fish, or poultry is an ancient method of preserving food. Today, it is used mainly to impart flavor and color to specific food products. Smoke is produced by the burning of damp or dry sawdust. The smoke is usually recirculated at high temperatures.[30] Table 4.16-5 lists the components of a typical wood smoke used in a meat smokehouse. Even with smoke recirculation, emissions do occur (see Table 4.16-1.) The rate and composition of emissions are dependent on the type of wood, type of smoke generator, moisture content of the sawdust, air supply, and degree of recirculation. Emission factors are given in Table 4.16-6. Direct-fired afterburners can be used to reduce emissions significantly.[31] Afterburners are discussed under incineration in Section 3.1.

TABLE 4.16-5. ANALYSIS OF WOOD SMOKE USED IN MEAT SMOKEHOUSES[32]

Component	Concentration (ppm)
Formaldehyde	20-40
Higher aldehydes	140-180
Formic acid	90-125
Acetic and higher acids	460-500
Phenols	20-30
Ketones	190-200
Resins	1,000

4.16.7 Fish Processing

The fish processing industry includes two major segments, the canning, dehydration and smoking of fish for human consumption, and the manufacture of by-products such as fish meal and oil. A large fraction of the fish received in a cannery is processed into by-products.[35]

TABLE 4.16-6. EMISSION FACTORS FOR MEAT SMOKING[33,34]

Organic Compound	Emission Factor[a] Uncontrolled g/kg of meat	Uncontrolled (lb/ton of meat)	Controlled[b] g/kg of meat	Controlled[b] (lb/ton of meat)
Hydrocarbons	0.035	(0.07)	Neg	(Neg)
Aldehydes	0.04	(0.08)	0.025	(0.05)
Organic acids (Acetic)	0.10	(0.2)	0.05	(0.1)

[a] Factors considered "Below Average" according to definition in Introduction to Reference 4.

[b] Controls are either a wet collector and low voltage precipitator in series or a direct-fired afterburner.

The major sources of organic emissions in the cannery are the cooker, presser and grinders, and rotary dryers.[36] All fish products are cooked before further processing.

The principal component of organic emissions is trimethylamine, $(CH_3)_3N$. Table 4.16-7 lists emission rates for cookers processing fish for fish meal production. Rates may vary depending on the type of fish being cooked. Cooker off gases are usually passed through a contact condenser prior to venting to remove water vapors and oils.[37] Condensers are discussed in Section 3.4.

TABLE 4.16-7. TRIMETHYLAMINE EMISSION FACTORS FOR COOKERS USED IN FISH MEAL PRODUCTION[38]

Material Cooked	Trimethylamine Emissions[a] g/kg of fish	Trimethylamine Emissions[a] (lb/ton of fish)
Fresh Fish	0.15	(0.3)
Stale Fish	1.75	(3.5)

[a] Factors rated "Average" according to Introduction to Reference 4.

4.16.8 Food Cooking Operations

The cooking of food releases organic vapors. Restaurants, bakeries, and candy making operations produce the greatest volume of emissions.

Kitchen emissions from restaurants come from the grill and fryer, vegetable cookers, and steam tables. One source estimates a total emission rate for restaurants of 0.72 kg/day/1000 people (1.6 lb/day/1000 people) but does not differentiate between volatile organic, particulate, or aerosol emissions. The identity of the hydrocarbon varies with the food being cooked. Acrolein is present in emissions from frying operations.[39] Deep frying is a major source of emissions as shown in Table 4.16-1. Carbon adsorption is an accepted method for pollution control.[40] Adsorption is discussed in Section 3.2.

Baking and candy manufacturing operations emit low concentrations of organics. The main identified constituent of emissions from the baking industry is ethanol. The roasting of cocoa beans is the main source of emissions.[41] No quantitative data were found for this source.

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4.17 Dry Cleaning Industry

The dry cleaning industry is a significant source of volatile organic emissions. The annual emission rate is estimated to be 230 Gg/yr (254,000 tons/yr).[1] Dry cleaning produces 1.34% of the total annual volatile organic emissions from stationary sources in the U.S. A summary of emissions from dry cleaning operations is included in Table 4.17-1.

There are three types of dry cleaning establishments. According to 1976 projections there are 540 industrial, 26,200 commercial, and 31,500 coin operated units.[4] These operations differ not only in size and type of service, but also in the type of solvent used. These solvents are fluorocarbon, perchloroethylene, and petroleum solvents. Dry cleaning operations for each solvent system are discussed in the following sections, 4.17.1 through 4.17.3.

4.17.1 Petroleum Solvent-Based Systems

About 270 industrial plants and 6,200 commercial units use petroleum solvents and consume approximately 72 Gg solvent/year (80,000 tons/yr).[5] The two main types of solvent used are Stoddard and 140-F. Both are combustible, kerosene-like mixtures, with approximate chemical compositions of 46% paraffins, 42% naphthenes, and 12% aromatics. Los Angeles County Rule 66 (now SCAQMD Code #442) has led to reformulation of some solvents to less than 8% aromatics. Because the solvents are relatively inexpensive (45-60¢ gal), there is little economic incentive for controlling solvent losses.

Figure 4.17-1 is a simplified diagram of a petroleum solvent based dry cleaning plant. Steps in the operation include washing, extracting, and drying. Dryers are separate from the

TABLE 4.17-1. SUMMARY OF VOLATILE ORGANIC EMISSIONS FROM DRY CLEANING OPERATIONS[2]

Solvent System	Source	Emission Level kg/100kg (lb/100 lb) Materials Cleaned	Control Technique	Controlled Emission Level kg/100kg (lb/100 lb) Materials Cleaned
Petroleum Solvent	Dryer Evaporation	18	Carbon adsorption, incineration	2-3
	Filter Muck Retention	5-10	Vacuum distillation, centrifugal separation, cartridge filters, incineration	1 or less
	Miscellaneous Sources	4	Good housekeeping	1-2
Perchloroethylene	Dryer Evaporation After Condenser	3-6	Carbon adsorption	0.3[a]
	Filter Muck	1-14	Cartridge filters, longer cooking times	0.5-1.0[a]
	Miscellaneous	4	Good housekeeping, longer distillation	2[a]
Fluorocarbons	Dryer Evaporation	0	-	-
	Cartridge Filters	1[3]	Drying in unit	0.5[a]
	Miscellaneous	1-2	-	1-2[a]

[a] Data substantiated by EPA tests.

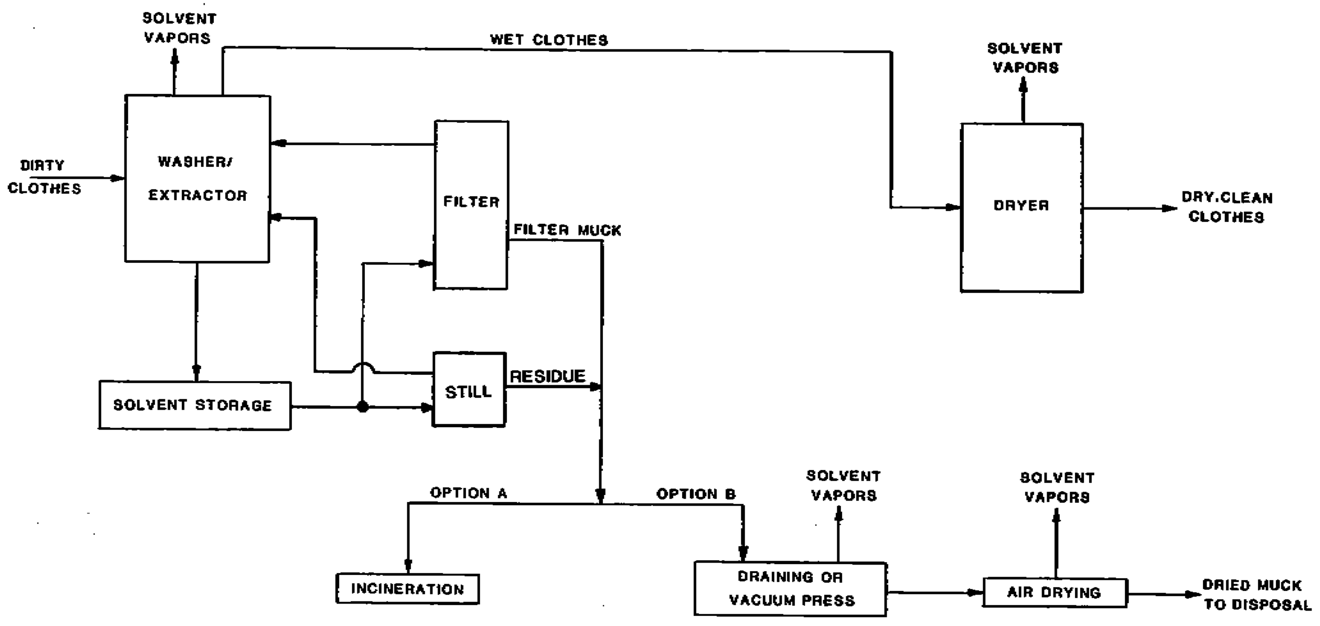

Figure 4.17-1. Petroleum-Solvent based dry cleaning plant.

washer and extractor. In all new plants washing and extracting are done in the same equipment. A few older plants have separate extractors. Clothes are washed in more than one bath of solvent. In some cases a solvent wash is followed by a water wash. In newer equipment, solvent is continuously filtered and returned to the washer during a wash cycle. Next, the clothes are spun to extract as much solvent as possible. Wet clothes are then transferred to the dryer where they are tumbled in hot air. Most dryers have a cool-down cycle to prevent wrinkling. All dryer exhaust is vented directly to the atmosphere.

Used solvent from the washer must be filtered before it can be reused. The resulting filter muck is composed of diatomaceous earth, carbon, lint, detergents, oils, and solvent. Some industrial plants incinerate this solid waste stream. In most plants it is drained by gravity or vacuum press, air dried, and discarded.[6]

4.17.1.1 Emission Characteristics

The primary source of emissions are evaporation in the dryer and filter muck treatment. Estimates of these emissions are given in Table 4.17-1. An industry survey has estimated total average emission rates to be 29 kg solvent/100 kg materials cleaned.[7]

4.17.1.2 Control Technology

At present, few controls are used in petroleum solvent plants to prevent solvent loss. Four methods are considered technologically feasible: 1) good housekeeping, 2) carbon adsorption, 3) incineration, and 4) waste solvent treatment. The use of condensation/refrigeration systems has been suggested. Problems with the application of condensation systems include the high stream volume from the dryer (4.7-7.1 m^3/sec or 10,000-15,000 cfm)[8] required to keep the solvent below 25% of the lower explosive limit, the risk of explosion from the condensate, and the low temperature required.

Good housekeeping is the simplest approach to controlling solvent losses and is the only method practiced by the industry today. Fugitive emissions occur at valves, flanges, seals, covers on storage tanks, and other sources. Good housekeeping requires no extra equipment and little additional maintenance effort. It has been shown that good housekeeping can reduce total emissions in a transfer machine-type operation from 23 to 15.5 kg solvent/100 kg materials cleaned (468 to 310 lbs solvent/ton materials cleaned).[9]

A carbon adsorption system has been developed for recovering petroleum solvent vapors from dryer streams. There are several inherent problems in applying carbon adsorption. First, the bed capacity of the activated carbon for the solvent is low (6%). The adsorber bed must be rather large because dryer streams are high volume and very dilute. In addition, the hot exhaust gases must be cooled from 78 to 38°C (172 to 100°F) before adsorption will take place.[10] Also, since petroleum solvents are highly combustible, carbon chambers are potential fire hazards.

Despite these drawbacks, carbon adsorption can be used to efficiently curb emissions. Carbon adsorption is employed at three petroleum solvent-based dry cleaning plants in Derby, England. The units were designed to reduce inlet concentrations by

95%.[11] A prototype model of an adsorber that was 95 percent efficient was introduced in the U.S. in 1973, but no market was found for the capital intensive units.[12] In May 1977, one vendor had installed an adsorber on a petroleum dryer in an industrial dry cleaning plant. While the unit did not perform at expected levels during tests conducted in June 1977, mass efficiency was as high as 75-80% on some closely monitored cycles.[13]

Incineration is the third method of reducing dryer emissions. The dryer stream is vented to a large incinerator where the petroleum vapors are burned. There are disadvantages to the system. The high volume of the dryer stream usually precludes the use of the plant boiler for incineration, so additional fuel is required. However, because there is a high steam demand in industrial plants, waste heat can be recovered in a steam boiler. Incineration is estimated to be 98% efficient as an emission control method and may reduce outlet concentrations to 20-30 ppm.[14]

Solvent retained in filter muck can be recovered by vacuum distillation or centrifugal separation. Both methods can reduce process solvent losses due to filter muck retention from 5 to 1 kg solvent/100 kg materials cleaned.[15] Instead of on-site recovery of waste solvent from the filter muck, solvent can be disposed of by incineration. Incineration is practiced at some industrial plants. Off-site solvent recovery by an independent contractor is sometimes practiced and cartridge filtration can be employed to reduce emissions.

With the use of this technology, emissions from petroleum solvent-based dry cleaning facilities can be greatly reduced. The addition of a carbon adsorption unit or incineration system and a waste solvent recovery scheme to a well maintained plant can potentially lower its emissions to a level of 4-6 kg solvent/100 kg materials cleaned.[16] The technology for application of these systems is currently available.

4.17.1.3 Cost, Energy, and Environmental Impact of Controls

Costs for good housekeeping are negligible.[17] Estimates of capital and annualized costs for other control techniques are presented in Table 4.17-2. Data are presented for four sizes of model plants. Costs for actual installations may vary considerably. Credits for solvent recovery are low because of the low cost of petroleum solvents. As the costs of petroleum solvents rise, however, recovery techniques will become more economically attractive.

Estimates of the energy impact from the use of carbon adsorbers and incinerators are presented in Table 4.17-3. Data are provided for typical commercial and industrial plants. Carbon adsorbers consume fuel to produce steam for desorption, while incinerators consume supplementary fuel to support conbustion.

Solvent recovered by carbon adsorbers is recycled. The volume of solvent recovered in an industrial plant is approximately three times the volume of fuel consumed.[23] Assuming that at least one kilogram (pound) of fuel is required to produce one kilogram (pound) of solvent, solvent recovery can be expressed as an indirect energy credit. As shown in Table 4.17-3, use of carbon adsorbers results in a net gain in energy for both commercial and industrial applications.

TABLE 4.17-2. ESTIMATES OF CAPITAL AND ANNUALIZED COSTS OF VOLATILE ORGANIC EMISSION CONTROLS FOR MODEL PETROLEUM SOLVENT DRY CLEANING PLANTS[a,b,c,18,19,20,21]

			Dryer Emission Controls						Filter Muck Emission Controls			
			Carbon Adsorption		Incineration with Heat Recovery		Incineration without Heat Recovery		Centrifugal Separator		Cartridge Filter[d]	
Type of Plant	Washer Capacity	Facility	Capital	Annual	Capital	Annual	Capital	Annual	Capital	Annual	Capital	Annual
Commercial	27kg (60 lb)/load	New	14.4	2.9	40.6	10.6	24.0	10.5	4.4	0.9	2.4	1.0
		Existing	16.8	3.5	50.8	12.7	30.0	11.7	5.0	1.0	2.5	1.0
	54kg (120 lb)/load	New	27.4	5.4	49.3	14.2	28.5	16.0	4.4	0.7	2.8	1.6
		Existing	31.9	6.7	61.6	16.8	35.6	17.5	5.0	0.8	2.9	1.6
Industrial	136kg (300 lb)/load	New	61.2	1.8	84.1	25.1	40.5	29.1	4.7	-3.2[e]		
		Existing	71.2	4.4	105.1	29.3	50.6	31.2	5.2	-3.1[e]		
	227kg (500 lb)/load	New	91.0	0.1	116.0	35.7	51.8	42.5	4.7	-6.2[e]		
		Existing	110.0	5.1	145.0	41.6	64.7	45.1	5.2	-6.1[e]		

[a] Fourth quarter 1976 costs expressed in thousands of dollars.
[b] Capital costs include design, purchase, and installation.
[c] Annualized costs include labor, maintenance, utilities, credits for solvent recovery, costs for waste disposal, and charges for depreciation, interest, overhead, property taxes, and insurance.
[d] Cartridge filters are not used in industrial plants because the amount of dirt collected would clog the filters.
[e] Negative sign indicates that credits from solvent recovery exceed operating costs and capital charges.

Incinerators, on the other hand, have adverse energy impacts. The data provided in Table 4.17-3 assumes no heat recovery. With primary heat recovery, fuel consumption and net energy use can be reduced by one-half.[24] In industrial plants that require steam, the energy impact can be further reduced by using a waste heat boiler for secondary heat recovery.

Energy information for filter muck emission controls is unavailable. Since the control techniques recover solvent, at least part of the energy requirements are compensated by the indirect credit from solvent recovery.

SO_x, NO_x, CO, and particulate emissions are produced by combustion associated with carbon adsorbers and incinerators. Assuming the use of No. 2 fuel oil containing 0.2 percent sulfur, the impact from the combustion of fuel to produce steam for carbon adsorbers is negligible.[25] Estimates of SO_x, NO_x and particulate emissions from incinerators are listed in Table 4.17-4. CO emissions are highly variable, depending on the type of petroleum solvents incinerated.

TABLE 4.17-4. ESTIMATES OF EMISSIONS FROM INCINERATION IN TYPICAL PETROLEUM SOLVENT DRY CLEANING PLANTS[a,26]

Type of Plant	SO_x Mg/yr (tons/yr)	NO_x Mg/yr (tons/yr)	Particulates Mg/yr (tons/yr)
Commercial	0.28 (0.31)	0.78 (0.86)	0.15 (0.16)
Industrial[b]	2.8 (3.1)	7.8 (8.6)	1.5 (1.6)

[a] Assumes that incineration is equivalent to steam boilers using No. 2 fuel oil.
[b] This application reduces volatile organic emissions by 100 Mg/yr (110 tons/yr).

TABLE 4.17-3. ENERGY IMPACT ESTIMATES FOR DRYER EMISSION CONTROLS IN TYPICAL PETROLEUM SOLVENT DRY CLEANING PLANTS[a,22]

Type of Plant	Control Technique	Energy Use GJ/yr (10^6 Btu/yr)	Energy Recovery GJ/yr (10^6 Btu/yr)	Net Use GJ/yr (10^6 Btu/yr)
Commercial	Carbon Adsorption[a]	28 (27)	316 (300)	-288 (-273)[b]
	Incineration[c]	16,000 to 32,000 (15,000 to 30,000)	0	16,000 to 32,000 (15,000 to 30,000)
Industrial	Carbon Adsorption[a]	280 (270)	3160 (3000)	-2880 (-2730)[b]
	Incineration[c]	16,000 to 32,000 (15,000 to 30,000)	0	16,000 to 32,000 (15,000 to 30,000)

[a] Based on data from a perchoroethylene plant (including energy for a muck cooker).
[b] Negative sign indicates that energy recovery exceeds energy use.
[c] No heat recovery.

Carbon adsorption systems add to the plant's water requirement because of the need for steam for desorption. The condensate, containing a portion of desorbed solvent, is added to the wastewater stream. Estimates of increased water requirements for carbon adsorption systems in typical petroleum solvent dry cleaning plants are listed in Table 4.17-5. Also presented are estimates of the quantities of solvent disposed of in the plant's wastewater.

TABLE 4.17-5. ESTIMATES OF INCREASED WATER USE AND SOLVENT DISPOSED OF IN WASTEWATER AS A RESULT OF APPLYING CARBON ADSORPTION IN TYPICAL PETROLEUM SOLVENT DRY CLEANING PLANTS[a, 27]

Type of Plant	Increased Water Use[b] kg/yr (lb/yr)	Solvent Disposed of in Wastewater[c] kg/yr (lb/yr)
Commercial	13,500 (29,700)	1.4 (3.0)
Industrial	135,000 (297,000)	13.5 (29.7)

[a] Based on measurements for perchloroethylene dry cleaning plants.
[b] Includes requirements for a muck cooker.
[c] Assumes that solvent content will be the same as for perchloroethylene plants ($\leq$100 ppm).

The solid waste impact produced by the disposal of spent carbon from carbon adsorption systems is negligible.[28]

4.17.2 Perchloroethylene-Based Systems

Perchloroethylene, or "perc" is the most widely used solvent in the industry today. 270 industrial plants, 20,000 commercial units, and 30,000 coin-operated units consume an estimated 15.6 Gg (173,000 tons) of the solvent yearly.[29] Perchloroethylene is the only chlorinated hydrocarbon in widespread use. It is superior to petroleum solvents because it is nonflammable. Its disadvantages are high cost, aggressiveness to clothing, and slight corrosiveness. In addition, perchloroethylene has been indicated as a potential carcinogen.[30] Perchloroethylene plants with good solvent recovery techniques are economically competitive with petroleum solvent based plants.

Figure 4.17-2 is a simplified flow diagram for a perchloroethylene dry cleaning operation. The basic cleaning steps are similar to those of a petroleum solvent plant. Dirty clothes are washed in a single solvent bath and solvent is extracted by spinning. The washing and extracting steps are accomplished in the same piece of equipment. The clothes are then dried in a reclaiming type dryer. The dryer may be separate (transfer-machine) or part of the washer extractor (dry-to-dry machine).

The reclaiming dryer used for perchloroethylene plants is different from the dryer used in petroleum solvent plants. Evaporated solvent is removed from the exhaust gas by condensation on a cooling coil. This exhaust is returned to the dryer until the solvent concentration is too low to condense. Fresh air is then used to finish the drying cycle and evaporate the remaining solvent. This air is vented to the atmosphere.

Most plants have a muck cooker by economic necessity. Most of the solvent is cooked from the filter muck, condensed, and recycled. The cooked muck and remaining solvent are stored for later disposal. Solvent that has been filtered must be distilled to remove soluble impurities (fats, oils, greases). Distillation bottoms are also stored for later disposal with the filter muck.[31]

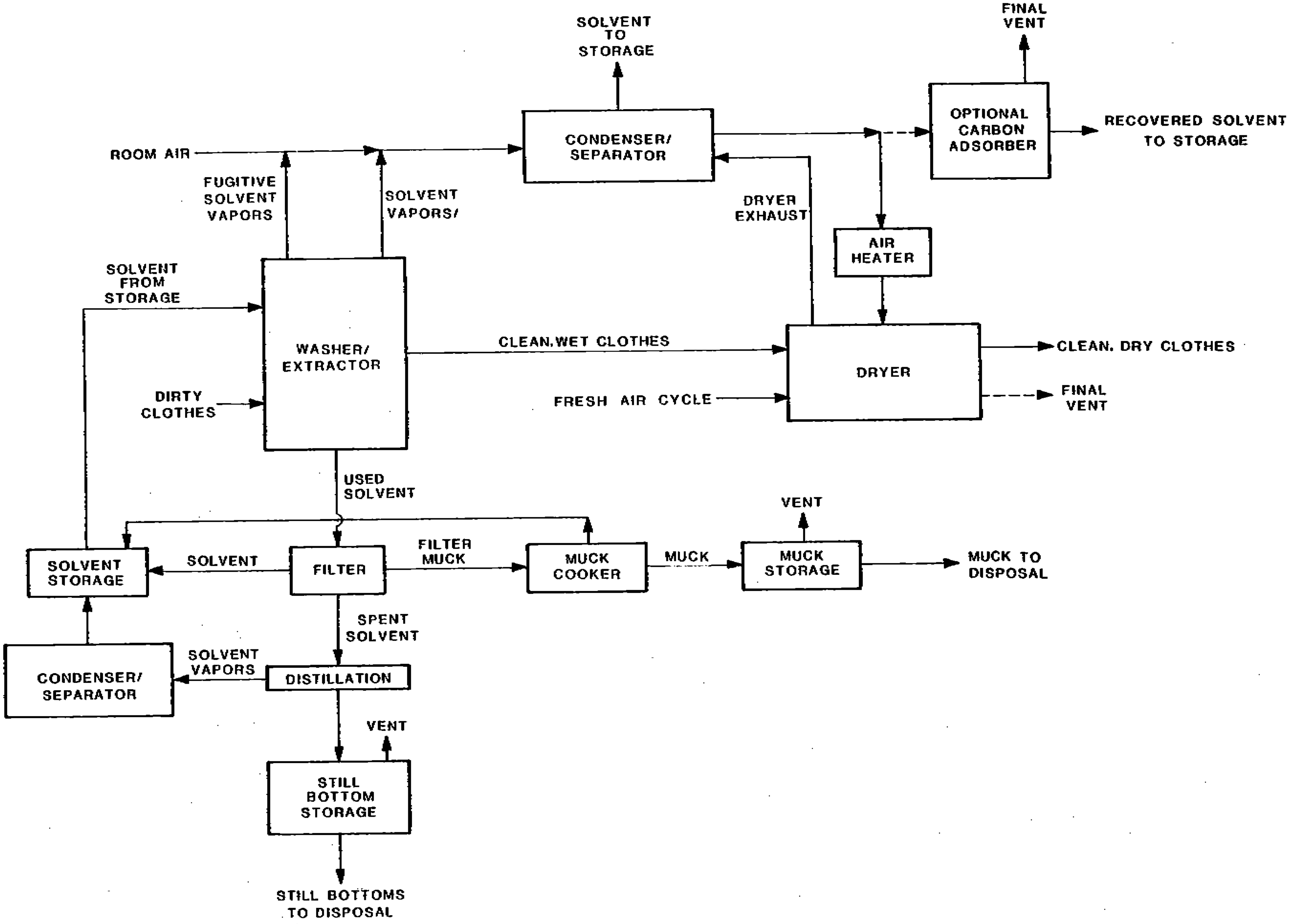

Figure 4.17-2. Flow diagram for a dry cleaning plant using perchloroethylene solvent.

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4.17.2.1 Emission Characteristics

Emissions of perchloroethylene vary greatly due to equipment differences and the type of solvent recovery method used. An uncontrolled commercial or industrial plant can lose more than 22 kg solvent/100 kg (22 lb/100 lb) materials cleaned. Potentially 14 kg/100 kg (14 lb/100 lb) of solvent could be lost in the filter muck and 3-6 kg/100 kg (3-6 lb/100 lb) in the dryer stream, assuming a condenser is used before venting.[32] Due to economic considerations, most plants possess a regenerative filter system and a muck cooker that can reduce losses in that area to only 1-1.5 kg/100 kg (1-1.5 lb/100 lb), for a plant total of 8.1 kg/100 kg (8.1 lb/100 lb). Plants that use a carbon adsorption system on dryer exhausts can reduce losses by another 40% to 4.0 kg/100 kg (4 lb/100 lb).[33,34] An industry survey[35] estimates the average emissions of both controlled and uncontrolled commercial and industrial plants to be 10-12 kg solvent/100 kg (10-12 lb/100 lb) materials cleaned. Coin-operated systems usually emit twice that amount.

4.17.2.2 Control Technology

Economic incentives have brought about the use of several different types of systems to curb solvent losses. As in petroleum based systems, the most important method of emission control is good housekeeping. The competence of the operator is another important factor. An IFI survey[36] has recorded differences in excess of 17.5 kg solvent/100 kg (17.5 lb/100 lb) materials cleaned for uncontrolled plants. In another study[37] emissions from plants employing carbon adsorption varied from 3.5 to 9.4 kg solvent/100 kg (3.5 to 9.4 lb/100 lb) materials cleaned. These differences were due to housekeeping standards and operator competency.

The best option for controlling solvent losses from the dryer stream is carbon adsorption. This method is used by at least 33.5% of the industry.[38] All perchloroethylene dryers are of the recovery type; the dryer stream passes over water-cooled condenser coils before venting. Condensers recover 75% of the solvent vapor, allowing 3-6 kg/100 kg (3-6 lb/100 lb) to escape. The addition of a carbon adsorption unit can reduce solvent losses to 0.3 kg solvent/100 kg (0.3 lb/100 lb) materials cleaned with an average outlet concentration of 25 ppm or less.[39,40]

Perchloroethylene retention in filter muck results in a large potential solvent loss. Economic incentives have brought about virtually industrywide use of regenerative filters and muck cookers. Solvent is "cooked" out of the used filter materials and is then steam distilled. This process reduces emissions to 1-1.5 kg/100 kg (1-1.5 lb/100 lb).[41] With the use of cartridge filters or longer distillation times, emissions can be reduced to 1.0 kg/100 kg (1 lb/100 lb).[42]

Incineration, a process suggested for petroleum exhaust streams, is not practical for perchloroethylene systems. Perchloroethylene is virtually nonflammable, and combustion forms undesirable by-products such as hydrochloric acid (HCl), chlorine (Cl_2), and phosgene ($COCl_2$). These by-products could be removed by water scrubbing, but that would create an additional water pollution control problem.

The emission controls best suited for perchloroethylene dry cleaning operations are good housekeeping, carbon adsorption filters on dryer exhaust streams, and the use of filter muck cookers. The combination of these three methods can reduce an uncontrolled plant emission rate of 22 kg/100 kg (22 lb/100 lb) to 4-6 kg/100 kg (4-6 lb/100 lb).[43] A summary of emission rates and sources can be found in Table 4.17-1.

4.17.2.3 Cost, Energy, and Environmental Impact of Controls

Costs for good housekeeping are negligible.[44] Estimates of capital and annualized costs for carbon adsorption systems are listed in Table 4.17-6. Data are presented for five sizes of model plants. Costs for actual installations may vary significantly. Specific costs for muck cookers and filters are unavailable.

Perchloroethylene is more valuable than petroleum solvents. As a result, there is a much greater economic incentive to employ recovery techniques in perchloroethylene plants. Table 4.17-6 shows that costs for carbon adsorption systems are exceeded by credits from solvent recovery in all but coin-operated facilities. As mentioned earlier, muck cookers and regenerative filters are already being used by most of the industry because of the economic incentive of solvent recovery.

Energy is required to produce steam for desorption of carbon adsorbers and to provide heat for muck cookers. Table 4.17-7 lists estimates of the energy impact from these controls in typical plants. Recovered solvent provides an indirect energy credit by reducing the energy requirements for the production of fresh solvent. (See Section 4.17.1.3 for a more detailed discussion.) For all installations, the indirect credit from solvent recovery exceeds energy consumption.

The air pollutants generated by the combustion of fuel to provide energy for the above control methods are considered negligible for all applications.[49] Estimates of water requirements for carbon adsorption systems in perchloroethylene plants are listed in Table 4.17-8. The water is required in the form of steam for desorption. A portion of the desorbed solvent remains with the condensate which becomes part of the plant's wastewater stream. Estimates of the amount of solvent disposed of with the wastewater are also shown in Table 4.17-8.

TABLE 4.17-6. ESTIMATES OF CAPITAL AND ANNUALIZED COSTS FOR CARBON ADSORBERS IN MODEL PERCHLOROETHYLENE DRY CLEANING PLANTS[a,b,c,45,46,47]

Type of Facility	Capacity	Installation	Capital Cost	Annualized Cost
Coin-op	2 units @ 36 kg/load	New	6.1	1.5
	@ (8 lb/load)	Existing	7.3	1.8
Commercial	11 kg/load (25 lb/load)	New	2.2	-0.1[d]
		Existing	2.9	0.1
	23 kg/load (50 lb/load)	New	3.3	-0.7[d]
		Existing	4.1	-0.6[d]
Industrial	91 kg/load (200 lb/load)	New	6.1	-9.8[d]
		Existing	7.5	-9.4[d]
	136 kg/load (300 lb/load)	New	7.0	-15.3[d]
		Existing	9.0	-14.8[d]

[a] Fourth quarter 1976 costs expressed in thousands of dollars.

[b] Capital costs include design, purchase, and installation.

[c] Annualized costs include labor, maintenance, utilities, credits for solvent recovery, costs for waste disposal, and charges for depreciation, interest, overhead, property taxes, and insurance.

[d] Negative sign indicates that credits from solvent recovery exceed operating costs and capital charges.

TABLE 4.17-7. ENERGY IMPACT ESTIMATES FOR CARBON ADSORBERS AND MUCK COOKERS IN TYPICAL PERCHLOROETHYLENE DRY CLEANING PLANTS [48]

Type of Plant	Energy Use GJ/yr (10^6 Btu/yr)	Energy Recovery GJ/yr (10^6 Btu/yr)	Net Use GJ/yr (10^6 Btu/yr)
Coin-op	7.0 (6.6)	26 (25)	-20 (-19)[a]
Commercial	28 (27)	45 (43)	-17 (-16)[a]
Industrial	280 (270)	450 (430)	-170 (-160)[a]

[a] Negative sign indicates that energy recovery exceeds energy use.

TABLE 4.17-8. ESTIMATES OF INCREASED WATER USE AND SOLVENT DISPOSED OF IN WASTEWATER AS A RESULT OF APPLYING CARBON ADSORPTION IN TYPICAL PERCHLOROETHYLENE DRY CLEANING PLANTS[50]

Type of Plant	Increased Water Use[a] kg/yr (lb/yr)	Solvent Disposed in Wastewater[b] kg/yr (lb/yr)
Coin-op	1,600 (3,500)	0.2 (0.4)
Commercial	13,500 (29,700)	1.4 (3.0)
Industrial	135,000 (297,000)	13.5 (29.7)

[a] Includes requirements for a muck cooker.
[b] Based on measurements of solvent concentrations $\leq$100 ppm in perchloroethylene plant wastewater streams.

Disposal of spent carbon from carbon adsorption systems creates a negligible solid waste impact.[51]

4.17.3 Fluorocarbon Based Systems

Fluorocarbon solvents are used by a small sector of the dry cleaning industry. Currently less than 1,500 coin-operated units consume about 900 Mg (1,000 tons) of fluorocarbon solvents per year.[52]

The solvent, 1,1,2-trichlorotrifluoroethane or Freon 113*, is sold as "Valclene*", a charged dry cleaning agent containing detergents. Some of its advantages are non-flammability, low toxicity, and non-aggressive solvent properties. This last property makes it suitable for cleaning fine and specialty items. The only drawbacks to widespread use are the high cost of the solvent and possible ozone depletion effects. Cost may preclude

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*Trademark of E.I. DuPont de Nemours & Co.

its use in some applications and make efficient solvent recovery a necessity.

The fluorocarbon based system utilizes only the dry-to-dry type of machine where washing and drying are performed in the same machine. All have built-in control devices. Solvent is filtered through cartridge filters and distilled before it is recycled. The filters can then be dried in the drum before disposal.

The machine is completely closed to the atmosphere during operation. This means there is no exhaust gas stream from the dryer. Figure 4.17-3 shows the air flow pattern for a typical fluorocarbon drying circuit. Expansion and contraction of the air stream is accounted for by an elastomeric "lung" not pictured.[53]

4.17.3.1 Emission Characteristics

Average solvent losses are unknown. In tests conducted by EPA and one solvent manufacturer, emissions were usually less than 5 kg/100 kg (5 lb/100 lb) materials cleaned.[54] Losses can be attributed to solvent retention in filter media, leaks from pumps, valves, and gaskets, and certain fixed losses. Solvent losses in the filter media amount to 1 kg solvent/100 kg (1 lb/100 lb) materials cleaned. Leaks from pumps, valves, and gaskets contribute 1-2 kg solvent/100 kg (1-2 lb/100 lb) materials cleaned. Fixed losses include solvent retained by clothes (minimal) and solvent vapor lost from the cleaning wheel when the door is opened between loads.[55]

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4.18 Fiber Production

This section describes organic emissions from the production of natural and synthetic fibers. Fiber production is one of the steps in textile manufacturing. Other textile processing steps such as texturizing, dyeing, and carpet manufacture may also emit organics, but are not covered in this section.

The three classes of fibers are synthetic fibers, cellulose derived (semi-synthetic) fibers, and natural fibers. Synthetic fibers such as nylon and polyester are spun from polymers synthesized from organic chemicals. Acetate, rayon, and other cellulose-derived fibers are manufactured by chemical recovery of cellulose from a natural source such as wood or cotton. Natural fibers such as wool and cotton are produced by mechanical processing steps rather than chemical synthesis.

Organic emissions and control technology for man-made synthetic and cellulose-derived fibers are discussed in Section 4.18.1. Section 4.18.2 discusses natural fibers.

4.18.1 Man-Made Fibers

Man-made fibers include synthetic fibers (Section 4.18.1.1) and semi-synthetic cellulose-derived fibers (Section 4.18.1.2).

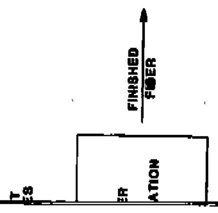
4.18.1.1 Synthetic Fibers

Some 22 Tg (48,400 x 10^6 lbs) of polymer are produced annually. Roughly 19% of polymer production is used to produce synthetic fibers.[1] Table 4.18.1 lists the most important synthetic fibers, their uses, constituents, and spinning processes.

Wet spinning is used to produce acrylic, modacrylic and spandex fibers. In the wet spinning process polymer chips are dissolved in a solvent. The solution is extruded through spinnerets into a coagulating bath where the fibers are formed. A washing step is required after spinning to remove traces of solvent and other impurities. Both batch and continuous washing steps are employed.[6] Table 4.18-2 lists typical solvents and coagulants used in wet spinning.

ERS: PRODUCTION, USES,
NNING PROCESSES^{2,3}

	Constituents	Spinning Process
cord,	Dimethyl terephthalate or terephthalic acid and ethylene glycol, catalyst	Melt
pet, s	Nylon 6: carpolactam. Nylon 66: adipic acid and hexamethlyene diamene	Melt
parel	Acrylonitrile; acrylate monomers (acrylic) or vinyl monomers (modacrylic); additives	Wet, Dry
ines,	Polyethylene or polypropylene, additives	Melt
	Spandex, vinyon, saran, fluorocarbons	Varied



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17. Reference 13.

Synthetic fibers are spun from melted or dissolved polymer chips. The three major spinning processes employed are melt, dry, and wet spinning. The process used for a particular polymer depends on its melting point, melt stability, and solubility in organic solvents.[4] Figure 4.18-1 is a flow diagram for the three spinning processes.

Melt Spinning

Melt spinning is generally used to produce polyester, nylon, polyolefin, and saran fibers. Resins used in this process must be stable at high temperatures to prevent decomposition. Polymer chips are melted in a heated screw extruder, processed in a nitrogen atmosphere, then filtered through a series of metal gauzes or a layer of graded sand. The molten polymer is extruded under pressure and at a constant rate through spinnerets. Extrusion is followed by air cooling. The fibers may be steam conditioned before merging into a "spun" yarn.[5]

Wet Spinning

Wet spinning is used to produce acrylic, modacrylic and spandex fibers. In the wet spinning process polymer chips are dissolved in a solvent. The solution is extruded through spinnerets into a coagulating bath where the fibers are formed. A washing step is required after spinning to remove traces of solvent and other impurities. Both batch and continuous washing steps are employed.[6] Table 4.18-2 lists typical solvents and coagulants used in wet spinning.

14. Reference 4.

15. Fluidized Recovery System Nabs Carbon Disulfide. Chem. Eng. 70(8): 92-94, April 15, 1963. As cited in Environmental Protection Agency, Compilation of Air Pollution Emission Factors. Second Edition with Supplements. Office of Air Quality Planning and Standards. Research Triangle Park, North Carolina. Publication Number AP-42. February 1976. 462 p.

16. Lund, H. F. Industrial Pollution Control Handbook. New York, McGraw Hill, 1971.

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4.19 Degreasing and Waste Solvent Disposal

Degreasing or solvent metal cleaning employs non-aqueous solvents to remove soils from the surface of metal articles which are to be electroplated, painted, repaired, inspected, assembled, or further machined. Metal workpieces are cleaned with organic solvents because water or detergent solutions exhibit a slow drying rate, electrical conductivity, high surface tension, a tendency to cause rusting, and a relatively low solubility for organic soils such as greases. A broad spectrum of organic solvents is available, such as petroleum distillates, chlorinated hydrocarbons, ketones, and alcohols. Although solvents may vary, there are basically three types of degreasers: cold cleaners, open top vapor degreasers, and conveyorized degreasers.

Descriptions for the three degreasing processes are given in Section 4.19.1. Emission characteristics are discussed in Section 4.19.2 and control technology is described in Section 4.19.3.

4.19.1 Process Descriptions

4.19.1.1 Cold Cleaners

Cold cleaners are the simplest, least expensive, and most common type of degreaser. They are used for the removal of oil base impurities from metal parts in a batch-load procedure that can include spraying, brushing, flushing, and immersion. The cleaning solvent is generally at room temperature. Although it may be heated slightly, the solvent never reaches its boiling point. When parts are soaked to facilitate cleaning, it is not uncommon for the solvent to be agitated by pumps, compressed air, mechanical motion, or sound.

There are several methods for materials handling in cold cleaning operations. Manual loading is used for simple, small-scale cleaning operations. Batch loaded conveyorized systems are more efficient for complex, large scale operations. Loading systems can be set to automatically lower, pause, and raise a work load. By dipping in a series of tanks, each with increasingly pure solvent or possibly a different solvent, a "cascade" cleaning system is established.

4.19.1.2 Open Top Vapor Degreasers

The open top vapor degreaser cleans by condensing vaporized solvent on the surface of the metal parts. The soiled parts are batch loaded into the solvent vapor zone of the unit. Solvent vapors condense on the cooler surface of the metal parts until the temperature of the metal approaches the boiling point of the solvent. The condensing solvent dissolves oil and grease, washing the parts as it drips down into the tank. Sometimes the cleaning process is modified with spraying or dipping.

To condense rising vapors and prevent solvent loss, the air layer or freeboard above the vapor zone is cooled by a series of condensing coils which ring the internal wall of the unit. Most vapor degreasers also have an external water jacket which cools the freeboard to prevent convection up hot degreaser walls. The freeboard protects the solvent vapor zone from disturbance caused by air movement around the equipment.

4.19.1.3 Conveyorized Degreasers

Conveyorized degreasers operate on the same principles as open top degreasers; the only difference is in materials handling. In conveyorized cleaners, parts may be dipped but manual handling is mostly eliminated. In addition, conveyorized degreasers are almost always hooded or covered.

There are many designs for conveyorized degreasers. These include monorail, cross-rod, vibra, ferris wheel, belt, and strip degreasers. Each conveying operation can be used with either cold or vaporized solvent. The first four designs listed above usually employ vaporized solvent. Conveyorized degreasers are used in a wide range of applications and are typically found in plants where there is enough production to provide a continuous stream of products to be degreased.

4.19.2 Emission Characteristics

Solvent consumption statistics indicate that total national degreasing emissions are about 680 Mg/yr. The actual breakdown of sources is shown in Table 4.19-1. Although a cold cleaner has the lowest emission rate, there are many units in operation. As a result, cold cleaners are the primary contributor of solvent emissions from metal cleaning operations. Emissions occur due to evaporation from the solvent bath, solvent carry-out, agitation, waste solvent evaporation, and exhaust.

Solvent emissions resulting from bath evaporation include diffusion and convection losses. These losses are increased through failure to close the cover whenever parts are not being handled. Open top vapor degreasers and conveyorized degreasers have a vapor/air interface at the top of the vapor zone. Here, evaporated solvent mixes with the air as a result of diffusion, drafts, and turbulence from parts being inserted and removed. Warm solvent-laden air is carried upward by convection, and the solvent vapors diffuse into the room. Estimates for

TABLE 4.19-1. TYPICAL EMISSIONS FROM ORGANIC SOLVENT METAL CLEANING OPERATIONS[1]

Type of Degreaser	Approximate No. of Units in use	Estimated National Emission		Average Emission Rate/Unit	
		$\frac{\text{Gg}}{\text{yr}}$	$\frac{\text{tons}}{\text{yr}}$	$\frac{\text{Mg}}{\text{yr}}$	$\frac{\text{tons}}{\text{yr}}$
Cold Cleaner	1,220,000	380*	(420,000)	0.3	(0.33)
Open Top Vapor Degreaser	21,000	200	(220,000)	10	(11.0)
Conveyorized Degreaser	3,700	100	(110,000)	27	(30)

*450
-(25) for wiping losses
-(25) for conveyorized cold cleaning
-(20) for non-evaporative waste solvent disposal
380

solvent diffusion emissions are 0.24 kg/hr-m^2 (0.05 lb/hr-ft^2), if no appreciable drafts cross the top of the tank.[2] Conveyorized degreasers are normally enclosed, so convection and diffusion losses are minimized.

Carry-out emissions result from entrainment of liquid and vaporous solvent as clean parts are removed from the degreaser. This problem can be complicated by the shape of the part. Crevices and cupped portions may hold solvent even after the part appears to be dry. Carry-out emissions are usually the major emission from conveyorized degreasers because of the inherently large work load.

Agitation of solvent in cold cleaners increases emissions. The extent of this increase depends on the use of a cover, the type of agitation, and adjustments to the agitation system. Emissions are normally insignificant if the cover is closed during agitation. However, if the cover is left open, emissions from all types of agitation are significant.

Solvent emissions due to spray evaporation are usually only a problem in cold cleaners. Increased emissions in open top vapor degreasers are not a problem if sprays are kept below the condensing coil level. The amount of emissions will depend on the pressure and drop size of the spray, the volatility of the solvent, and the tendency to splash and overspray. Common practice is to keep the spray at a pressure less than 68.9 kPa (10 psig) and in a solid, fluid stream.

Excessive exhaust emissions result when exhaust rates for open top vapor degreasers and conveyorized degreasers are set too high. Disruption of the vapor/air interface can occur, causing solvent vapors to be carried out by the exhaust system. The average exhaust rate is 15 m^3/min-m^2 (50 ft^3/min-ft^2) of degreaser opening.[3] However, this rate may be exceeded to comply with OSHA regulations on worker exposure levels. In any case, there should be a cover that closes beneath the exhaust intake vents to prevent withdrawal of solvent-laden vapor.

Waste solvent evaporation is a source of emissions from all degreasers, but the fraction of total emissions due to waste solvent varies for each type. Estimates are that approximately one third, 280 Gg/yr (309,000 tons/yr), of the total solvent emissions from degreasing operations can be attributed to waste solvent evaporation. Estimated percentages are 45-70 percent for cold cleaners, 20-25 percent for open top vapor degreasers, and 10-20 percent for conveyorized degreasers.[4] The amount of waste solvent evaporation is a function of the quantity of waste solvent handled and the method of disposal.

The breakdown in waste solvent disposal methods is given in Table 4.19-2. Not all of these methods are ideal; recommended methods include reclamation, direct incineration, and chemical landfills. Unacceptable disposal routes include flushing down sewers, spreading on dirt roads for dust control, and land-filling where evaporation or soil leaching can occur.

TABLE 4.19-2. CURRENT WASTE SOLVENT DISPOSAL METHODS[5,6,7]

Disposal Method	Percent of Waste Solvent Handled
1) Dumping, open storage containers, municipal or chemical landfills, and deep well injection	35
2) With waste crankcase oil	15
3) Properly controlled incineration	5
4) Reclamation	45

4.19.3 Control Technology

There are several methods for controlling organic solvent vapor emissions from degreasing operations. In all instances, emissions reduction can be accomplished through better equipment design and improved operating practices. For example, the emissions from spray evaporation can almost be eliminated by careful operation and a sensible, low pressure design. Furthering this example, designs can include internal spray chambers which completely eliminate emissions due to spraying. In many cases, additional emissions reduction can be achieved with add-on control equipment.

Solvent emissions resulting from diffusion and evaporation from the solvent bath can be reduced by using an improved cover, a higher freeboard, refrigerated chillers, carbon adsorption, incineration, or liquid absorption. For vapor degreasers the use of a cover, which operates in a horizontal motion so that the vapor/air interface is not disturbed, is the single most important control device. These covers can be a roll type plastic cover, canvas curtain, or guillotine cover. It has been shown that covers reduce total emissions by approximately 20 to 40 percent.[8]

For open top vapor degreasers a higher freeboard would provide greater protection of the vapor/air interface from outside disturbance. The freeboard ratio (defined as freeboard height divided by width of the air/solvent area, i.e., F/W) is usually 0.5-0.75. By increasing the freeboard ratio from 0.5 to 0.75 for an idle open top vapor degreaser, emission reductions of 25-30 percent are expected. By increasing the freeboard ratio from 0.5 to 1.0, the reductions may be as high as 50 percent.[9] However, for open top vapor degreasers with a normal workload, the emission reductions may be somewhat less. Increasing the freeboard height on cold cleaners is only effective when high volatility solvents are used.

Refrigerated chillers are a second set of condenser coils located slightly above the primary condenser coils of a degreaser. The purpose of refrigerated chillers is to create a cold blanket of air immediately above the vapor zone which reduces the mixing of air and solvent vapors. This can be done by circulating a below freezing coolant, -23°C to -30°C (-10°F to -20°F), or an above freezing coolant, 1°C to 5°C (34°F to 40°F). One variation on the refrigerated chiller eliminates the need for a second set of consenser coils. Refrigerant is circulated in the primary coils. The refrigerant cooling rate must be 100-120% of the heat input rate to the boiling sump.[10] Estimates are that refrigerated chillers will reduce emission rates by approximately 40%. Representative below freezing units have achieved reductions of 43 to 62%.[11]

Carbon adsorption is a well proven technology for the control of solvent emissions from degreasing operations, particularly for spray chambers where the area must be exhausted to protect the operator. Activated carbon has a very good capacity for commonly used solvents such as trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane.[12] Although carbon adsorption units can remove 95-100% of the organic input to the bed, reductions in the total solvent emission are only 40-65%. Some systems achieve less than 40% emission reduction because of poor inlet collection efficiency and an improperly maintained or adjusted carbon adsorber.[13]

Liquid absorption is also a well-known method of controlling organic emissions, but has design problems which make it an impractical alternative. For example, trichloroethylene vapors are easily absorbed by mineral oil. The absorption column is operated at 30°C (86°F) and the column effluent contains about 120 ppm mineral oil vapors. In essence, one emission problem is exchanged for another. Chilling the absorbing fluid would reduce the concentration of mineral oil in the exhaust gas, but would also lead to ice formation within the column and greatly increase the energy requirement. Liquid absorption is practical only for the recovery of high concentrations of solvent vapors, very valuable vapors, or toxic chemical vapors.

Carry-out emissions can be appreciable if proper materials handling procedures are not followed. Drainage facilities are used to control emissions from cold cleaners and drying tunnels and rotating baskets are used for conveyorized cleaners.

Drainage facilities for cold cleaners consist of a rack or basket which is mounted internally or externally. The liquid solvent drips from the parts into a drainage trough which channels it back into the solvent bath. The EPA recommends an average draining time of about 15 seconds.[14]

A drying tunnel is an extension of sheet metal from the end of a conveyorized degreaser which allows the cleaned parts more time to dry. Drying tunnels are more effective when used in conjunction with a carbon adsorber. Rotating baskets are perforated cylinders which rotate slowly as they carry the parts to be cleaned through the system. The slow rotation prevents liquid solvent from being trapped in the parts. Rotating baskets can be used on cross-rod degreasers and ferris wheel degreasers but are not normally retrofitted. Drying tunnels can be retrofitted if space allows. The effectiveness of these devices has not been quantified.

Recently two other systems have been developed for the control of solvent bath and carry-out emissions. The automated cover-conveyor system has a cover which opens only for the purpose of transferring parts into and out of the degreaser. During cleaning, draining, and drying the cover is closed. Since emissions can occur only during the brief time when parts are entering or exiting, the automated cover-conveyor system is expected to provide a high degree of emission control.

Refrigeration condensation involves the direct condensation of solvent vapors from exhaust air streams. Very low temperatures on the order of -25°C (-13°F) are required for effective condensation of low vapor concentrations. The result is rapid ice formation on heat exchange surfaces and increased energy requirements. One equipment manufacturer reported successful use of refrigeration condensation technology in a prototype system.[15]

Solvent reclamation is considered the best method for reducing emissions from evaporation of waste solvent. Reclamation can be done through a private contractor or in-house distillation. Private contractors usually collect waste solvent, distill it, and return the reclaimed portion. Users are charged about half the market value of the solvent. This method is economically attractive in industrial areas where users are not separated by large distances.

In-house distillation is common among users employing several degreasers. One report states that the annual operating costs of an in-house reclamation system are recovered from the first 1320 liters (350 gal) of chlorinated solvents distilled. For nonchlorinated solvents, the breakeven point would be six to twelve times this quantity.[16] In-house distillation involves some significant problems. These include disposal of distillate bottoms containing metals and other contaminants, decomposition of chlorinated solvents, flammability of nonchlorinated solvents, formation of azeotropes, and occurrence of adverse chemical reactions.

Direct incineration is not as desirable as reclamation since it does not result in a usable product. Furthermore, chlorinated solvents cannot sustain combustion without supplementary fuel. Petroleum distillate solvents, however, are more suitable for incineration and can even be used as supplementary fuel for the incineration of chlorinated solvents.

Most chemical landfills are presently inadequate as waste solvent disposal methods. Chemical landfills would be suitable if steps were taken to eliminate evaporation and permeation. One method being used involves sealing the waste solvent in lined drums and surrounding these drums with 1.2 to 6.1 m (4-20 ft) of packed clay. It has not been demonstrated that even this landfill method eliminates organic emissions.

4.19.4 Energy, Cost, and Environmental Considerations

Discussions of costs, energy requirements and environmental impacts are included in section 3 for the five major control methods: adsorption, absorption, condensation, flaring, and incineration. There are some specific data for degreasing facilities included in this section as well.

Tables 4.19-3, 4.19-4, and 4.19-5 contain cost estimates for cold cleaners, open top degreasers, and conveyorized degreasers Estimates are made for new and retrofit conditions.

There are several secondary environmental effects to be considered with application of controls to degreasers. Improper

TABLE 4.19-3. CONTROL COST ESTIMATES FOR TYPICAL COLD CLEANERS[a,b,17]

	New Facilities		Existing Facilities	
	Low Volatility[d] Solvent	High Volatility[e] Solvent	Low Volatility[d] Solvent	High Volatility[e] Solvent
Installed Capital Cost	\$25	\$45	\$25	\$65
Annualized Cost	\$0.50	-\$29.84[c]	\$0.50	-\$25.61[c]

[a] Costs are based on several assumptions. See original reference for bases.

[b] Vapor to air area $0.5 m^2$ ($5.5 ft^2$).

[c] Negative signs indicate that value of recovered solvent exceeds cost of control.

[d] Controls for low volatility solvent are drainage facilities.

[e] Controls for high volatility solvent are drainage facilities plus a mechanically assisted cover.

TABLE 4.19-4. CONTROL COST ESTIMATES FOR OPEN TOP VAPOR DEGREASER[a,18,19,20]

	New Facilities				Existing Facilities			
	Manual Cover	Carbon Adsorption	Refrig-erated Chiller	Extended Freeboard & Power Cover	Manual Cover	Carbon Adsorption	Refrig-erated Chiller	Extended Freeboard & Power Cover
TYPICAL SIZE[b]								
Installed capital cost	$250	$7400	$4900	$2500	$300	$10,300	$6500	$8000
Net annualized cost	-$807[d]	$ 300	-$ 191[d]	-$ 631[d]	-$799[d]	$ 797	$ 84	$ 311
SMALL SIZE[c]								
Installed capital cost	$230	$7400	$2700	$430	$270	$10,300	$4030	$ 570
Net annualized cost	-$381[d]	$ 962	-$ 24[d]	-$490[d]	-$375[d]	$ 1,459	$ 204	-$ 466[d]

[a] Costs are based on several assumptions. See original reference for bases.

[b] Vapor to air area $1.67 m^2$ ($18 ft^2$).

[c] Vapor to air area $0.8 m^2$ ($8.6 ft^2$).

[d] Negative signs indicate that value of recovered solvent exceeds cost of control.

TABLE 4.19-5. CONTROL COST ESTIMATES FOR CONVEYORIZED DEGREASERS[a,b,21,22]

	New Facilities				Existing Facilities			
	Monorail Degreaser		Cross-rod Degreaser		Monorail Degreaser		Cross-rod Degreaser	
	Carbon Adsorber	Refrig-erated Chiller	Carbon Adsorber	Refrig-erated Chiller	Carbon Adsorber	Refrig-erated Chiller	Carbon Adsorber	Refrig-erated Chiller
Installed capital costs	\$11,800	\$5,725	\$11,800	\$5000	\$17,600	\$8,550	\$17,600	\$7,460
Annualized costs	-\$ 2,639[c]	-\$4,221[c]	\$ 520	-\$1066[c]	-\$ 1,638[c]	-\$3,734[c]	\$ 1,516	-\$ 646[c]

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[a] Costs are based on several assumptions. See original reference for bases.

[b] Vapor to air area 3.8 m^2 (41 ft^2)

[c] Negative signs indicate that value of recovered solvent exceeds cost of control.

maintenance of carbon adsorption systems and refrigerated chillers could, in fact, result in increased volatile organic emissions. Carbon adsorption systems have other secondary effects as well. The steam required for regeneration causes a slight increase in boiler emissions, and the condensate from steam regeneration of the beds may cause a water pollution problem due to contamination with organic materials. Solvent associated with waste water may enter the sewer, thus eventually reaching water systems. Evaporative emissions may also result from the condensate. Solid waste is created when spent carbon is discarded.

Handling of waste solvent may cause some environmental problems. Incineration creates emissions of NO_x and CO, and combustion of chlorinated solvents requires gas cleaning to prevent emissions of toxic and corrosive substances. Distillation requires steam, thus increasing boiler emissions. Disposal of waste solvent by landfill is unacceptable because of the potential for leakage into the environment.

The large energy consumers in degreasing control methods are carbon adsorbers, refrigerated chillers, and distillation units. Carbon adsorbers consume the greatest amount of energy because of the steam regeneration step. Energy consumption of a typical degreaser may be increased 20 percent by a carbon adsorption system.[23] A typical refrigerated freeboard chiller may increase energy consumption of a typical degreaser by 5 percent.[24] Distillation requires about 0.1 to 0.2 kWh/kg (160 to 320 Btu/lb) recovered solvent, but the cost of the distillation energy is considered insignificant.[25] Power requirements for powered covers and power hoists are also considered insignificant. In all cases, the energy expended to conserve the solvent is far less than the sum of the energy required to manufacture replacement solvent and the heating value of the feedstock to this manufacturing process which otherwise could have been used as fuel.[26]

4.19.5 References

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21. Reference 8.

22. Reference 1, p. 4-19.

23. Reference 20.

24. Reference 1, p. 5-5.

25. Reference 8.

26. Reference 1, p. 5-6.

4.20 Cutback Asphalt

Cutback asphalt is a prepared form of asphalt cement used for paving. Asphalt cement is the semi-solid residue that remains after all other components of crude petroleum have been distilled off (either naturally or in refineries). It may be used directly for paving or it may be liquified. There are two types of liquified asphalt.

1) Cutback asphalt-prepared by diluting asphalt cement with volatile petroleum distillates, and

2) Emulsified asphalt-prepared by suspending asphalt cement in water with an emulsifying agent, such as soap.

Liquified asphalts are formulated in a wide variety of types and grades.

Uses of asphalt for pavements range from a thin spray to control dust on a dirt road to thick layers of asphalt mixed with aggregate (crushed rock, gravel or sand) placed on a well prepared bed. Heat requirements for application vary for the different forms of asphalt. Asphalt cement must be heated to be converted to a usable liquid. A small amount of heat is usually required to facilitate spraying of cutback asphalts. Most emulsified asphalts require no heat at all.[1]

The percentage of paving operations that use cutback asphalt varies widely from state to state. A total of 3.72 Tg (4.10×10^6 tons) of cutback asphalt were used nationally in 1975.[2]

4.20.1 Emission Characteristics

Cutback asphalts are a significant source of volatile organics emissions. Annual emissions from cutback asphalts in 1975 were estimated to be 673 Gg (742×10^3 tons). This is 2.3% of the 1975 national volatile organic emissions.[3]

Cutback asphalts are considered to be moderately to highly reactive in terms of oxidant formation. The environmental impact is compounded because road paving occurs primarily during the warmer months when the photochemical activity of volatile organics is more prevalent.

The petroleum distillate content of cutback asphalts averages 35%.[4] A proportion of these diluents is evaporated to the atmosphere as the asphalt cures. Cutback asphalts fall into three general categories, depending on the volatility of the diluent. A list of these categories along with estimates of the proportion of the diluent that will evaporate is presented in Table 4.20-1.

TABLE 4.20-1. CHARACTERISTICS OF CUTBACK ASPHALTS

Category	Diluent	Proportions of Diluent Evaporated[5]
Slow cure (road oil)	Heavy residual oil	20-30%
Medium cure	Kerosene	60-80%
Rapid cure	Heavy naptha or gasoline	70-90%

The kinetics of evaporation are not well understood. It is thought that most emissions occur early during paving operations. The diluents then continue to evaporate at ever decreasing rates over a long period of time.[6]

4.20.2 Control Techniques

Substitution of emulsified asphalts for cutback asphalts is an effective control technique. Most emulsified asphalts have virtually no volatile organic emissions.[7] Emissions, therefore, can essentially be reduced to zero. Some form of emulsified asphalt can be used for almost any application. There are a few applications, however, for which cutback asphalts may still be needed.

Emulsified asphalts are classified as nonionic, anionic, or cationic, depending on the type of emulsifying agent used. Nonionic and anionic emulsified asphalts cure (break) with the evaporation of water. Cationic emulsified asphalts cure by electrochemical interactions between the emulsion and a negatively charged aggregate.[8]

There are several limitations to the use of emulsified asphalts:[9]

1) Because they depend on the evaporation of water, nonionic and anionic emulsified asphalts cannot be used when rain is anticipated or when temperatures fall below 10°C (50°F).

2) Dust causes the emulsion to break prematurely. Emulsified asphalts, therefore, cannot be used to spray on dusty roads unless the roads are swept prior to spraying.

3) Emulsified asphalts cannot be stockpiled as long as cutbacks. This is a problem for remote locations; however, it can be solved by using portable mixing plants or by stockpiling an asphalt emulsion mix.

4) Emulsified asphalts have a longer curing time than cutback asphalts. Roads may have to be closed to traffic for two hours to two days, depending on the weather.

5) Additional training is necessary to learn how to select and effectively use the proper formulation of emulsified asphalt. One or two days training is sufficient.

4.20.3 Cost, Energy, and Environmental Impact of Controls

Emulsified asphalts are attractive in terms of energy conservation and cost. Their use has increased in many states for these reasons alone.[10] Energy is conserved by eliminating the use of petroleum distillates and by reducing heat requirements for application. Capital and operating costs for cutback asphalts and emulsified asphalt operation are currently equivalent. Both use the same construction equipment and have roughly the same material costs. As the costs of petroleum distillates rise, however, emulsified asphalts will become relatively less expensive.

In 1975, 1,600,000 m^3 (10,000,000 barrels) of petroleum distillates were used to formulate cutback asphalt.[11] All of these distillates were evaporated to the atmosphere or trapped in the asphalt. These same distillates could have been used for or converted to fuel. Including the energy equivalent of the diluent, the total energy associated with manufacturing, processing, and laying cutback asphalts is about 14.0 GJ/m^3 (50,200 Btu/gal). The associated energy requirement of emulsified asphalts is only about 0.789 GJ/m^3 (2,830 Btu/gal).[12]

According to available literature, there is virtually no environmental impact related to the use of emulsified asphalt.

4.20.4 References

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8-12. Reference 1.

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16. ABSTRACT

This document is a revised and updated version of a March 1970 EPA publication entitled Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources (AP-68). The document is intended primarily as a general reference for State and local air pollution control engineers. It provides:

1. basic information on sources of photochemical oxidant precursors and control of these sources,
2. estimates of control costs,
3. estimates of control technique energy requirements, and
4. estimates of emission reductions achievable through control application.

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