~ ʸS͗ʸ₆

United States	Office of Air Quality	EPA-450/4-91-031
Environmental Protection	Planning and Standards	August 1993
Agency	Research Triangle Park NC 27711	

Air

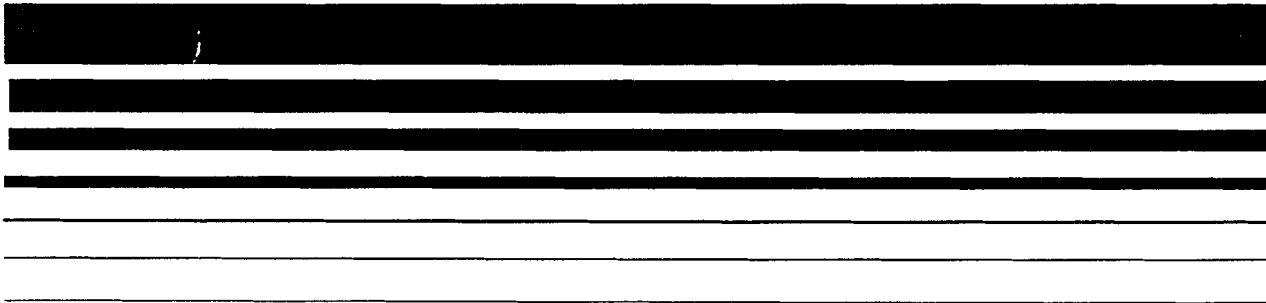# ♻EPA　Guideline Series

Control of Volatile Organic Compound Emissions from Reactor Processes and Distillation Operations Processes in the Synthetic Organic Chemical Manufacturing Industry

Guideline Series

Control of Volatile Organic Compound

Emissions from Reactor Processes and

Distillation Operations Processes in the

Synthetic Organic Chemical Manufacturing Industry

Emissions Standards Division

GUIDELINE SERIES

The guideline series of reports is issued by the Office of Air Quality Planning and Standards (OAQPS) to provide information to State and local air pollution control agencies; for example, to provide guidance on the acquisition and processing of air quality data and on the planning and analysis requisite for the maintenance of air quality. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Reports published in this series will be available - as supplies permit - from the Library Services Office (MD-35), U. S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, or for a nominal fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

The Clean Air Act (CAA) amendments of 1990 require that State implementation plans (SIP's) for certain ozone nonattainment areas be revised to require the implementation of reasonably available control technology (RACT) for control of volatile organic compound (VOC) emissions from sources for which the U. S. Environmental Protection Agency (EPA) has already published control techniques guidelines (CTG's) or for which the EPA will publish a CTG between the date of enactment of the amendments and the date an area achieves attainment status. Section 172(c)(1) requires nonattainment area SIP's to provide for, at a minimum, "such reductions in emissions from existing sources in the area as may be obtained through the adoption, at a minimum, of reasonably available control technology..." As a starting point for ensuring that these SIP's provide for the required emission reductions, the EPA defines RACT as: "The lowest emission limitation that a particular source is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility," as published in the Federal Register (44 FR 53761 [September 17, 1979]).

The CTG's are intended to provide State and local air pollution authorities with an information base for proceeding with their own analyses of RACT to meet statutory requirements. The CTG's review current knowledge and data concerning the technology and costs of various emissions control techniques. Each CTG contains a "presumptive norm" for RACT for a specific source category, based on the EPA's evaluation of the capabilities and problems general to that category. Where applicable, the EPA recommends that States adopt requirements consistent with the presumptive norm. However, the presumptive norm is only a recommendation. States may choose to develop their own RACT requirements on a case-by-case

1-1

basis, considering the economic and technical circumstances of an individual source. It should be noted that no laws or regulations preclude States from requiring more control than is recommended as the presumptive norm for RACT. A particular State, for example, may need a more stringent level of control in order to meet the ozone standard or to reduce emissions of a specific toxic air pollutant.

This CTG is 1 of at least 11 CTG's that the EPA is required to publish within 3 years of enactment of the CAA amendments. It addresses RACT for control of VOC emissions from two types of process vents occurring at plants in the Synthetic Organic Chemical Manufacturing Industry (SOCMI): reactors (other than those involving air oxidation processes) and distillation columns. The SOCMI chemicals applicable under this CTG are listed in Appendix A. Distillation columns that are part of a polymer manufacturing process are not subject to this CTG.

Reactor process and distillation emissions sources, as well as other emission sources at SOCMI plants, such as air oxidation vents, storage vessels, equipment leaks, and wastewater, are addressed by CTG documents, new source performance standards (NSPS) and national emission standards for hazardous air pollutants (NESHAP). A CTG for air oxidation processes was published in 1985, NSPS rules for the air oxidation and distillation process vents were promulgated in June 1990, and an NSPS for reactor processes was proposed in June 1990 and is nearing promulgation. Additionally, the proposed hazardous organic NESHAP (HON) will be applied to a portion of the process vents within SOCMI, namely, those process vents that emit hazardous air pollutants (HAP's).

As noted in the preceding paragraph, there are different regulations that can apply to the same SOCMI facility, process unit, or process vent. For example, a given SOCMI facility could potentially be subject to all three NSPS (air oxidation, distillation, reactor processes), to the HON (for process vents), and to regulations developed in accordance with this CTG. The required control efficiency for a combustion control device is the same in all these various regulations. Thus, any process vent that is controlled with a combustion device to meet the requirements of the HON, NSPS, or regulations in accordance with the air oxidation CTG would meet recommended RACT in this CTG, and it is unnecessary to test for

applicability for VOC regulation developed in accordance with this CTG. Section 7.3 presents the appropriate rules and regulations to which a SOCMI facility may be subject.

2.0   INDUSTRY CHARACTERISTICS AND EMISSIONS

The synthetic organic chemical manufacturing industry (SOCMI) is a large and diverse industry producing hundreds of major chemicals through a variety of chemical processes. A process is any operation or series of operations that causes a physical or chemical change in a substance or mixture of substances. A process unit is the apparatus within which one of the operations of a process is carried out. Materials entering a process unit are referred to as feedstocks or inputs, while materials leaving a process unit are called products or outputs.

The major processing steps employed in organic chemical manufacturing plants can be classified in two broad categories: conversion and separation. Conversion processes are chemical reactions that alter the molecular structure of the compounds involved. Conversion processes comprise the reactor processes segment of a SOCMI plant.

Separation processes typically follow conversion processes and divide chemical mixtures into distinct fractions. Examples of separation processes are distillation, filtration, crystallization, and extraction. Among these, the predominant separation technique used in large-scale organic chemical manufacturing plants is distillation. Distillation is a unit operation used to separate one or more inlet feed streams into two or more outlet product streams, each having constituent concentrations different from the concentrations found in the inlet feed stream.

This chapter describes the use of reactor processes and distillation operations in the SOCMI. Section 2.1 focuses on general industry information, while Sections 2.2 and 2.3 discuss basic concepts of reactor processes and distillation operations, respectively. In the final sections of this chapter, the characteristics of typical reactor process and distillation operation vent stream emissions are summarized.

2-1

Section 2.4 examines reactor emission characteristics, while Section 2.5 presents distillation emission characteristics.

2.1 GENERAL INDUSTRY INFORMATION

Most organic chemicals are manufactured in a multi-faceted system of chemical processes based on about 15 feedstocks that are processed through one or more process levels and result in hundreds of intermediate or finished chemicals. These feedstocks (presented in Table 2-1) originate from three basic raw materials: crude oil, natural gas, and coal. Figure 2-1 shows the highly integrated supply system for these feedstock chemicals from the three basic raw materials.

The chemical industry may be described in terms of an expanding system of production stages. Refineries, natural gas plants, and coal tar distillation plants represent the first stage of the production system. As illustrated in Figure 2-1, these industries supply the feedstock chemicals from which most other organic chemicals are made. The organic chemical industry represents the remaining stages of the system. Chemical manufacturers use the feedstocks produced in the first stage to produce intermediate chemicals and final products. Manufacturing plants producing chemicals at the end of the production system are usually smaller operations, since only a narrow spectrum of finished chemicals is being produced. The products from ethylene shown in Figure 2-2 are an example of a system of production stages from a feedstock chemical. The production of feedstock chemicals is an extremely dynamic industry that may quickly change its sources of basic raw materials depending upon availability and costs.

The estimated total domestic production for all synthetic organic chemicals in 1988 was 124×10^6 megagrams (Mg) [273×10^9 pounds (lb)]. This production total includes over 7,000 different chemicals.[1] A study conducted in the early 1980's indicated that a relatively small number of chemicals dominate industry output, as illustrated in Table 2-2. The table shows the number of chemicals with production output above various production levels (i.e., chemicals with total national production greater than the listed production level). The scope of this CTG includes approximately 719 chemicals. The applicable chemicals are listed in Appendix A.

TABLE 2-1. FEEDSTOCK CHEMICALS FOR CHEMICAL PRODUCTION PROCESSES

Benzene	Ethylene	Pentane
Butane	Isobutane	Propane
1-Butene	Isopentane	Propylene
2-Butene	Methane	Toluene
Ethane	Naphthalene	Xylenes
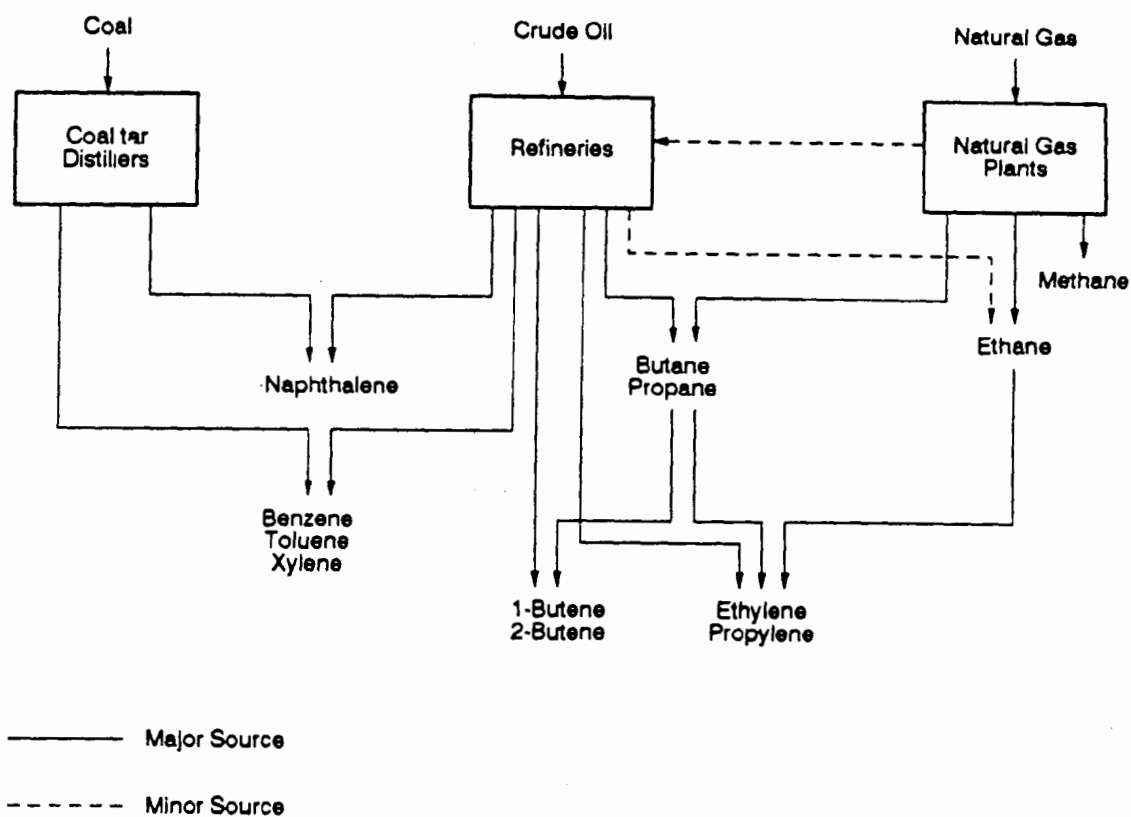
Figure 2-1. The interwoven nature of feedstocks for the organic chemicals manufacturing industry.

Ethylene Dichloride

Other Chemicals

Ethylene

Ethanol

Ethylbenzene

Other Chemicals ◄——— Ethylene Oxide ———► Ethanolamines

Ethylene Glycol

Ethylene Glycol Acetate

Latex Paints

Polyester Fiber
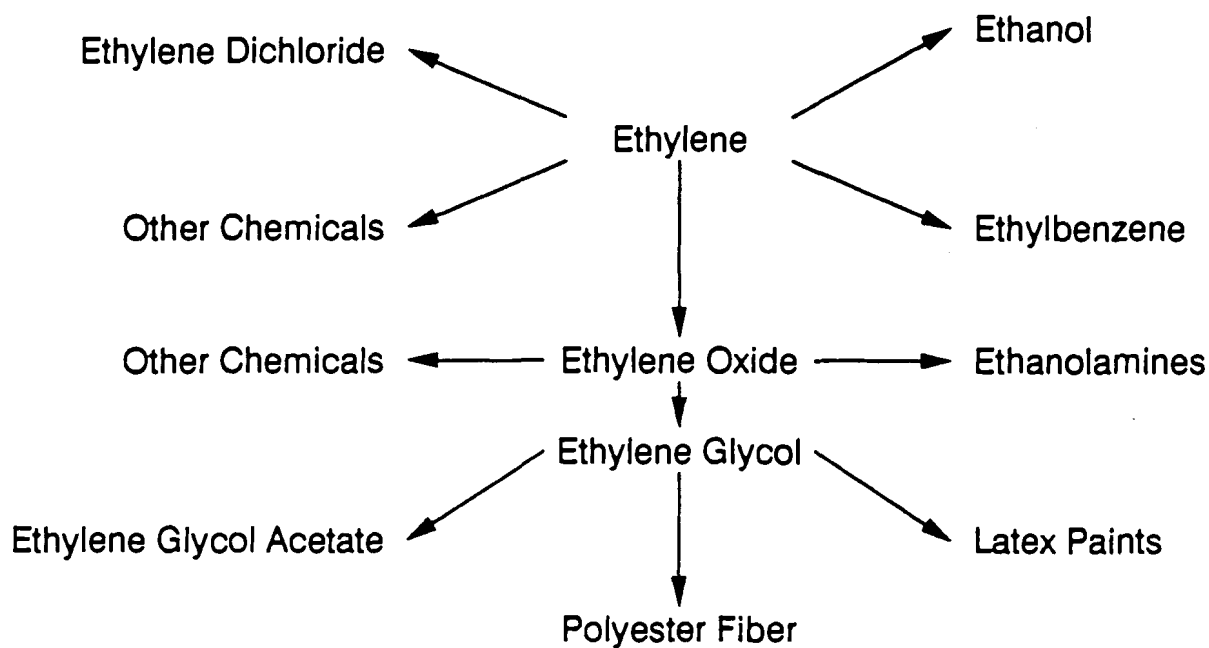
Figure 2-2. Chemical derivatives made from the feedstock ethylene.

TABLE 2-2. ESTIMATED PRODUCTION AND CHEMICAL COVERAGE
FOR VARIOUS PRODUCTION LEVELS

Production level-Mg/yr (million lb/yr)	Number of chemicals[a]	Percentage of national production covered
453,600 (1,000)	63	N/A
226,800 (500)	102	N/A
113,400 (250)	155	N/A
45,400 (100)	219	92
27,200 (60)	283	94
13,600 (30)	410	N/A
9,100 (20)	506	N/A
4,500 (10)	705	97

[a]This number signifies the number of chemicals with national production greater than the production level considered.

N/A = Not applicable.

2.2 REACTOR PROCESSES

2.2.1 Scope of Reactor Processes

The term "reactor processes" refers to means by which one or more substances, or reactants (other than air or oxygen-enriched air), are chemically altered such that one or more new organic chemicals are formed. A separate CTG document has already been developed for air oxidation processes; thus, chemicals produced by air oxidation are not included in the scope of this study.

2.2.2 Chemical Reaction Descriptions

Between 30 and 35 different types of chemical reactions are used to produce 176 high-volume chemicals.[2] Some of these chemical reactions are involved in the manufacture of only 1 or 2 of the 176 chemicals, while others (such as halogenation, alkylation, and hydrogenation) are used to make more than a dozen chemicals. Table 2-3 identifies most of the chemical reaction types and the number of chemicals produced by each type. In addition, some of the chemicals produced by reactions listed in Table 2-3 do not result in process vent streams. In this document, a process vent stream means a gas stream ducted to the atmosphere directly from a reactor, or indirectly, through the process product recovery system.

This section briefly describes the major SOCMI chemical reactions involving reactor processes. Only descriptions of the larger volume chemicals are included in this discussion. Each chemical reaction description contains a discussion of the process chemistry that characterizes the reaction and the major products resulting from the reaction. In addition, process vent stream characteristics are presented for chemicals where industry data are available.[3] The emission data profile (EDP) for reactor processes is included in Appendix B. Descriptions of the major large-volume chemical reactions are presented in alphabetical order in the remainder of this section.[4]

2.2.2.1 Alkylation. Alkylation is the introduction of an alkyl radical into an organic compound by substitution or addition. There are

TABLE 2-3.   RANKING OF CHEMICAL REACTION TYPES

Rank[a]	Chemical reaction type	Number of chemicals produced
1	Pyrolysis	7
2	Alkylation	13
3	Hydrogenation	13
4	Dehydration	5
5	Carboxylation/hydroformylation	6
6	Halogenation	23
7	Hydrolysis/hydration	8
8	Dehydrogenation	4
9	Esterification	12
10	Dehydrohalogenation	1
11	Ammonolysis	7
12	Reforming	4
13	Oxyhalogenation	1
14	Condensation	12
15	Cleavage	2
16	Oxidation	4
17	Hydrodealkylation	2
18	Isomerization	3
19	Oxyacetylation	1
20	Oligomerization	7
21	Nitration	3
22	Hydrohalogenation	2
23	Reduction	1
24	Sulfonation	4
25	Hydrocyanation	2
26	Neutralization	2
27	Hydrodimerization	1
28	Miscellaneous	6
29	Nonreactor processes[b]	26

[a]Ranking by amount of production for each chemical reaction type.

[b]Chemicals produced solely by air oxidation, distillation, or other nonreactor processes.

six general types of alkylation, depending on the substitution or addition that occurs:

- Substitution for hydrogen bound to carbon;

- Substitution for hydrogen attached to nitrogen;

- Addition of metal to form a carbon-to-metal bond;

- Substitution for hydrogen in a hydroxyl group of an alcohol or phenol;

- Addition of alkyl halide, alkyl sulfate, or alkyl sulfonate to a tertiary amine to form a quaternary ammonium compound; and

- Miscellaneous processes such as addition of a alkyl group to sulfur or silicon.

The major chemical products of alkylation reactions are ethylbenzene and cumene. The single largest category of alkylation products is refinery alkylates used in gasoline production. Other chemical products of alkylation processes include linear alkylbenzene, tetramethyl lead, and tetraethyl lead.

In general, based on data for production of ethylbenzene, cumene, and linear alkylbenzene, reactor volatile organic compound (VOC) emissions from alkylation processes appear to be small compared to other unit processes. The commercial synthesis of ethylbenzene from ethylene and benzene is an example of the first type of alkylation reaction described above. The reaction can be carried out in two ways. One production process involves a high pressure, liquid-phase reaction method using an aluminum chloride catalyst, while the other operates in the vapor phase at low pressure with various solid catalysts. Data from one plant that produces ethylbenzene by liquid-phase alkylation indicate that reactor VOC emissions are relatively small. (Although no emissions data are available for the vapor-phase alkylation process, the associated VOC emissions are expected to be small due to the high operating pressure.) Reactor offgas from the liquid-phase alkylator is vented to a VOC scrubber where unreacted benzene is removed from the gas stream and recycled to the reactor. According to data contained in the EDP, the scrubber vent stream contains inerts and a small amount of VOC's and is vented to the atmosphere at a rate of approximately 0.5 standard cubic meter per minute

2-9

(scm/m) [17 standard cubic foot per minute (scfm)]. The estimated heat
content of the vent stream is 6.7 megajoules per standard cubic meter
(MJ/scm) [180 British thermal units per standard cubic foot (Btu/scf)].
The VOC emissions to the atmosphere from the gas scrubber are estimated to
be 2.7 kilograms per hour (kg/hr) (16 lb/hr).

Cumene is produced by the vapor-phase catalytic alkylation of
benzene with propylene. The reaction takes place at 690 kilopascals (kPa)
[100 pounds per square inch absolute (psia)] in the presence of a
phosphoric acid catalyst. No reactor streams are vented, and thus, no
reactor VOC emissions to the atmosphere are associated with this process
at the five cumene plants included in the EDP. Excess benzene required
for the alkylation reaction is recovered by distillation in the cumene
product purification process and recycled to the reactor.

Dodecylbenzenes, also referred to as linear alkylbenzenes (LAB), are
produced by alkylation of mono-olefins or chlorinated n-paraffins with
benzene. Emissions of VOC's from both processes are small or nonexistent.
In the case of the mono-olefin production route, only high purity raw
materials can be used, thus eliminating the introduction of dissolved
volatiles. Furthermore, the hydrogen fluoride (HF) catalyst used in the
process is a hazardous chemical and a potential source of acidic emissions
that must be minimized. As a result, operators of one mono-olefin
production route for LAB indicate that process vent streams have little or
no flow associated with them. The alkylation reaction producing LAB from
chlorinated n-paraffins generates hydrogen chloride (HCl) gas and some VOC
by-products. Benzene and HCl are removed from the process vent stream
before discharging to the atmosphere. Data from a plant producing LAB
from chlorinated n-paraffins indicate that the processes vent stream
following the scrubber is intermittent and emits no VOC's to the
atmosphere.

2.2.2.2 Ammonolysis. Ammonolysis is the process of forming amines
by using ammonia or primary and secondary amines as aminating agents.
Another type of ammonolytic reaction is hydroammonolysis, in which amines
are formed directly from carbonyl compounds using an ammonia-hydrogen

mixture and a hydrogenation catalyst. Ammonolytic reactions may be divided into four groups:

- Double decomposition--NH_3 is split into $-NH_2$ and $-H$; the $-NH_2$ becomes part of the amine while the $-H$ reacts with a radical such as Cl that is being substituted;

- Dehydration--NH_3 serves as a hydrant, and water and amines result;

- Simple addition--both fragments of the NH_3 molecule ($-NH$ and $-H$) become part of the newly formed amine; and

- Multiple activity--NH_3 reacts with the produced amines resulting in formation of secondary and tertiary amines.

The major chemical products of ammonolysis reactions are acrylonitrile and carbamic acid. Reactor emissions from acrylonitrile production involve air oxidation processes, so they are not discussed here. Two other categories of ammonolysis products are ethanolamines and methylamines.

Based on information on ethanolamine production, ammonolytic processes appear to be a negligible source of reactor VOC emissions. Ethanolamines, including mono-, di-, and triethanolamines, are produced by a simple addition reaction between ethylene oxide and aqueous ammonia. According to information on two process units producing ethanolamines, no reactor VOC are emitted to the atmosphere from this process. The reactor product stream is scrubbed to recover the excess ammonia required for the reaction before proceeding to the product finishing unit.

The manufacture of methylamines involves a vapor-phase dehydration reaction between methanol and ammonia. In addition to methylamines, di- and trimethylamines are also formed by the reaction. Although no process unit data for this process are included in the EDP, available information suggests that reactor VOC emissions from the process are small or negligible. Staged distillation immediately follows the reactor to separate the coproducts. As a result, all potential VOC emissions to the atmosphere are associated with distillation operations and are not reactor related.

2.2.2.3 Carboxylation/Hydroformylation.
Carboxylation/hydroformylation reactions are used to make aldehydes and/or

2-11

alcohols containing one additional carbon atom. Carboxylation is the combination of an organic compound with carbon monoxide. Hydroformylation, often referred to as the oxo process, is a variation of carboxylation in which olefins are reacted with a mixture of carbon monoxide and hydrogen in the presence of a catalyst. Major chemical products of carboxylation/hydroformylation reactions are acetic acid, n-butyraldehyde, and methanol.

Carboxylation/hydroformylation processes typically generate relatively large process vent streams with high heat contents, compared to other unit processes. Thus, process vent streams from these reactions are normally combusted.

One carboxylation process for acetic acid manufacture reacts liquid methanol with gaseous carbon monoxide at 20 to 70 megaPascals (MPa) (2,900 to 10,200 psia) in the presence of a catalyst. At one plant that produces acetic acid by this high pressure process, the reactor products are passed through two gas liquid separators. The vent from the first separator, consisting primarily of carbon dioxide and carbon monoxide, is scrubbed and sent to carbon monoxide recovery. The vent from the second separator is scrubbed to recover excess reactant and then combined with other waste gas streams and flared. No data are available on the VOC content of the two vent streams. However, the only point where reactor VOC's are potentially emitted to the atmosphere is the vent from the second separator, which is ultimately discharged to a flare.

In the oxo process for producing n-butyraldehyde, propylene is reacted with synthesis gas (carbon monoxide and hydrogen) in the liquid phase at 20 to 30 MPa (2,900 to 4,400 psia). An aromatic liquid such as toluene is used as the reaction solvent. A relatively large amount of VOC's is contained in the process vent stream for this reaction. Industry information suggests that this process has generally been replaced by an unnamed, low VOC-emitting process. No data, however, are available for this process. Information from one plant producing n-butyraldehyde by the oxo process indicates that the reactor vent stream consists of hydrogen, carbon monoxide, and VOC and is used as fuel in an industrial boiler. Prior to combustion, the estimated vent stream flow rate at this plant is 21 scm/min (741 scfm) and the heating value is 46 MJ/scm (1,200 Btu/scf).

The VOC flow rate prior to combustion is approximately 1,100 kg/hr (2,425 lb/hr).

2.2.2.4 <u>Cleavage</u>. Acid cleavage is the process by which an organic chemical is split into two or more compounds with the aid of an acid catalyst. This chemical reaction is associated with production of two major chemicals, phenol, and acetone.

Production of phenol and acetone begins with oxidation of cumene to cumene hydroperoxide. The cumene hydroperoxide is usually vacuum distilled to remove impurities, and is then agitated in 5 to 25 percent sulfuric acid until it cleaves to phenol and acetone. The mixture is neutralized to remove excess sulfuric acid, phase separated, and distilled. One process unit producing phenol and acetone from cumene hydroperoxide reports little or no flow in the process vent stream at the cleavage reactor. High purity of the cumene hydroperoxide intermediate is the major reason for this "no flow" vent.

2.2.2.5 <u>Condensation</u>. Condensation is a chemical reaction in which two or more molecules combine, usually with the formation of water or some other low-molecular weight compound. Each of the reactants contributes a part of the separated compound. Chemical products made by condensation include acetic anhydride, bisphenol A, and ethoxylate nonylphenol.

Reactor emissions to the atmosphere from condensation processes are expected to be small. Available data indicate that emissions from acetic anhydride production are minimized by combustion of the process vent stream. There are no reactor VOC emissions from bisphenol or ethoxylated nonylphenol production. (Bisphenol A has emissions from distillation operations only.)

Acetic anhydride is produced by the condensation of acetic acid and ketene. Ketene for the reaction is made by pyrolysis of acetic acid. After water removal, the gaseous ketene is contacted with glacial acetic acid liquid in absorption columns operated under reduced pressure. The process vent stream from the absorber contains acetic acid, acetic anhydride, traces of ketene, and any reaction by-product gases generated. The VOC content of the vent stream is particularly dependent on impurities that may be contained in the acetic acid feed, such as formic or propionic acid, that cause side reactions to occur. Scrubbers are normally used to

2-13

remove acetic acid and acetic anhydride from the vent stream. At two process units producing acetic anhydride, the vent streams are burned as supplemental fuel in pyrolysis furnaces. No data on the vent stream characteristics or VOC content were provided for one of these process units; however, data from the other source on acetic anhydride production identify the major components of the process vent stream after scrubbing to be carbon monoxide, carbon dioxide, and VOC. The typical VOC flow rate of the vent stream after scrubbing was estimated to 138 kg/hr (304 lb/hr), based on assumptions about the purity of the reactants.

Bisphenol A is produced by reacting phenol with acetone in the presence of HCl as the catalyst. The reaction produces numerous by-products that must be eliminated in order to generate high purity bisphenol A. Removal of these by-products requires distillation and extraction procedures, and thus no reactor vents to the atmosphere are associated with this process.

2.2.2.6 Dehydration. Dehydration reactions[a] are a type of decomposition reaction in which a new compound and water are formed from a single molecule. The major chemical product of dehydration is urea.

Commercial production of urea is based on the reaction of ammonia and carbon dioxide to form ammonium carbamate, which, in turn, is dehydrated to urea and water. The unreacted ammonium carbamate in the product stream is decomposed to ammonia and carbon dioxide gas. A portion of the ammonia is urea and water. The unreacted ammonium carbamate in the product stream is removed from the process vent stream, leaving primarily carbon dioxide to be vented to the atmosphere. No data are included in the EDP for VOC emissions from urea production, but one study indicates that VOC emissions from urea synthesis are negligible.[5] Urea is the only chemical of those that use dehydration to be included in the EDP.

2.2.2.7 Dehydrogenation. Dehydrogenation is the process by which a new chemical is formed by the removal of hydrogen from the reactant. Aldehydes and ketones are prepared by the dehydrogenation of alcohols.

---

[a] This process refers to chemical dehydration and does not include physical dehydration in which a compound is dried by heat. Stucco produced by heating gypsum to remove water is an example of physical dehydration.

Chemicals produced by dehydrogenation processes include acetone, bivinyl, cyclohexanone, methyl ethyl ketone (MEK), and styrene.

In general, dehydrogenation processes produce relatively large, hydrogen-rich process vent streams that are either used as a fuel in process heaters or industrial boilers, or as a hydrogen feed for other processes. The two process units for which data are available have high heat content process vent streams. These occur as a result of the hydrogen generated in the dehydrogenation reaction. Although these process vent streams can be quite large, there is generally little VOC contained in them.

Acetone and MEK are produced by similar processes involving the catalytic dehydrogenation of alcohols. The emissions profile contains four process units in the EDP that produce MEK via the dehydrogenation of sec-butanol. In all cases a hydrogen-rich process vent stream is produced. One process unit uses a VOC scrubber to remove MEK and sec-butanol from the process vent stream prior to flaring. In all four process units, reactor VOC emissions are well controlled or nonexistent. One acetone production process unit has an additional reactor process vent stream on a degasser directly following the reactor. This degasser reduces the pressure on the product stream to allow storage of the product at atmospheric pressure. The pressure reduction step causes dissolved hydrogen and low boiling point VOC's to escape from the liquid-phase product. This purge stream, which is relatively small, is routed to a water scrubber to remove some VOC's before it is released to the atmosphere. This is the only acetone production process unit in the EDP that stores the acetone as an intermediate product, and as a result, it is the only plant with a degasser process vent stream.

Two process units in the EDP manufacture styrene via the hydrogenation of ethylbenzene. One plant produces a hydrogen-rich (90 percent by volume) process vent stream that is normally combusted to recover the heat content. The other plant produces a process vent stream that is first condensed and then combusted in a flare system. The vent stream flow rate is relatively large (16 scm/min [565 scfm]); the stream contains 23 percent VOC's including toluene, benzene, ethylbenzene, and

2-15

styrene. The heat content is estimated to be 11 MJ/scm (300 Btu/scf), which would support combustion without the addition of supplemental fuel.

2.2.2.8 <u>Dehydrohalogenation</u>. In the dehydrohalogenation process, a hydrogen atom and a halogen atom, usually chlorine, are removed from one or more reactants to obtain a new chemical. This chemical reaction is used to produce vinyl chloride, vinylidene chloride, and cyclohexene.

Vinylidene chloride is made by dehydrochlorinating 1,1,2-trichloroethane with lime or aqueous sodium hydroxide. The reactor product is separated and purified by distillation. The process vent stream at one vinylidene chloride process unit is incinerated and then scrubbed with caustic before discharging to the atmosphere. Before incinerating, the vent stream flow rate is estimated to be 0.28 scm/min (10 scfm) and the heat content is 22 MJ/scm (591 Btu/scf). The VOC emission rate of the vent stream is approximately 19 kg/hr (42 lb/hr). At a second plant producing vinylidene chloride, no reactor vent streams are used. The process vent streams are associated with distillation operations.

2.2.2.9 <u>Esterification</u>. Esterification is the process by which an ester is derived from an organic acid and an alcohol by the exchange of the ionizable hydrogen atom of the acid and an organic radical. The major chemical product of esterification is dimethyl terephthalate. Other esterification products include ethyl acrylate and ethyl acetate.

The VOC emissions associated with esterification processes are small, based on information on the production of methyl methacrylate, ethyl acrylate, and ethyl acetate.

Ethyl acrylate is produced by the catalytic reaction of acrylic acid and ethanol. The vent stream flow rate from reactor equipment producing ethyl acrylate in one process unit is reported to be 2.1 scm/min (74 scfm). The heat content for this stream is estimated to be 3.8 MJ/scm (102 Btu/scf). The VOC emission rate of the vent stream is 2.8 kg/hr (6.1 lb/hr).

Methyl methacrylate is produced by esterifying acetone and hydrogen cyanide with methanol. Limited information is available on reactor VOC emissions from this process. The EDP includes one plant producing methyl methacrylate; the process vent stream at this plant is combusted in an

incinerator. Although the incinerator is used primarily to destroy VOC's in offgases from another plant process, combustion of the methyl methacrylate process vent stream in the incinerator allows the plant to use less supplemental fuel by recovering the heat content of the vent stream. No vent stream flow rate or heat content data are available for this plant; however, the VOC emission rate is estimated to be very low (0.05 kg/hr [0.1 lb/hr]).

Ethyl acetate production involves an esterification reaction between acetic acid and ethanol. Two process units producing ethyl acetate are included in the EDP. Following condensation of the process vent stream to recover product, both process units discharge the vent stream to the atmosphere. Vent stream data reported by one of the process units indicate the VOC content of the vent stream to be low, i.e., (0.2 kg/hr [0.4 lb/hr]).

2.2.2.10 <u>Halogenation</u>. Halogenation is the process whereby a halogen (e.g., chlorine, fluorine, bromine, iodine) is used to introduce one or more halogen atoms into an organic compound. (Reactions in which the halogenating agent is halogen acid, such as hydrochloric acid, are included in a separate unit process called hydrohalogenation.) The chlorination process is the most widely used halogenation process in industry; fluorination is used exclusively in the manufacture of fluorocarbons. The major products of halogenation reactions are ethylene dichloride, phosgene, and chlorinated methanes and ethanes.

Reactor VOC emissions from halogenation reactions vary from no emissions to 51 kg/hr (112 lb/hr). Most chlorination reactors vent to scrubbers or condensers where HCl generated in the chlorination reaction is removed. Some VOC reduction occurs along with HCl removal by these devices. Also, some vent streams are combusted prior to discharge to the atmosphere. Purity of the feed materials (including chlorine) is a major factor affecting the amount of reactor VOC emissions vented to the atmosphere.

Ethylene dichloride can be produced by direct chlorination of ethylene or by oxychlorination of ethylene. Most ethylene dichloride is currently made by a "balanced" process that combines direct chlorination of ethylene and oxychlorination of ethylene. The direct chlorination

2-17

process reacts acetylene-free ethylene and chlorine in the liquid phase. The oxyhalogenation process using oxygen for the manufacture of ethylene dichloride is included in the reaction description for oxyhalogenation.

Reactor VOC emissions from ethylene dichloride production by direct chlorination vary according to process vent stream treatment. Hydrogen chloride is generated by the chlorination reaction and is typically removed from the process vent stream by a caustic scrubber. The vent stream following the scrubber may be discharged to the atmosphere, recycled to the reactor, or incinerated. The EDP contains information on three ethylene dichloride plants that use the direct chlorination process as part of the "balanced" process. The process vent stream characteristics for the three plants indicate a range of gas flow rates of 1.1 to 7.6 scm/min (39 to 268 scfm) and a range of heat contents of 1.5 to 46 MJ/scm (40 to 1,236 Btu/scf). The process vent stream with the highest heat content (i.e., 46 MJ/scm [1,236 Btu/scf]) is incinerated before venting to the atmosphere.

The fluorination reactions producing dichlorodifluoromethane and trichlorotrifluoroethane involve the replacement of a chlorine in carbon tetrachloride with fluorine. At two plants surveyed, no reactor VOC emissions are associated with these fluorination processes. The two plants report no process vent stream discharges to the atmosphere. Instead, process vent streams occur from distillation operations.

2.2.2.11 Hydrodealkylation. Hydrodealkylation is the process by which methyl groups, or larger alkyl groups, are removed from hydrocarbon molecules and replaced by hydrogen atoms. Hydrodealkylation is primarily used in the petrochemical industry to upgrade products of low value, such as heavy reformate fractions, naphthalenic crudes or recycle stocks from catalytic cracking. In particular, hydrodealkylation is used in the production of high purity benzene and naphthalene from alkyl aromatics such as toluene.

The EDP contains no information on emissions from hydrodealkylation processes. In the case of benzene production, the process vent stream containing unconverted toluene is recycled to the reactor, and no reactor VOC emissions are vented.[6]

2.2.2.12 <u>Hydrohalogenation</u>. Hydrohalogenation is the process in which a halogen atom is added to an organic compound using a halogen acid, such as HCl. The major chemical products of this reaction are methyl chloride and ethyl chloride.

The predominant share of methyl chloride is produced by the vapor-phase reaction of methanol and HCl.[7] In three process units the process vent stream is condensed to remove excess HCl; some VOC's are also removed by the condensers. Of the nine plants that manufacture methyl and ethyl chloride included in the EDP, five have no reactor process vent streams, one discharges the noncondensibles directly to the atmosphere, and three route the noncondensible stream to combustion devices. The VOC content of a methyl chloride vent stream is 76 kg/hr (168 lb/hr).

2.2.2.13 <u>Hydrolysis/Hydration</u>. Hydrolysis is the process in which water reacts with another substance to form two or more new substances. Hydration is the process in which water reacts with a compound without decomposition of the compound. These processes are a major route in the manufacture of alcohols and glycols, such as ethanol, ethylene glycols, and propylene glycols. Another major product of hydrolysis is propylene oxide.

Propylene oxide is produced by hydrolysis of propylene chlorohydrin with an alkali (usually sodium hydroxide [NaOH] or calcium hydroxide [CA(OH)$_2$]). The product vent stream is condensed to remove the propylene oxide product and the noncondensibles are discharged to the atmosphere. Data from a process unit that produces propylene oxide indicate the flow rate of the vent stream following the condenser to be about 2.8 scm/min (99 scfm) and the estimated VOC emissions to the atmosphere to be 0.05 kg/hr (0.1 lb/hr).

Sec-butyl alcohol is produced by absorbing n-butenes in sulfuric acid to form butyl hydrogen sulfate that is then hydrolyzed to sec-butyl alcohol and dilute sulfuric acid. The reactor product is steam stripped from the dilute acid solution and purified by distillation. Information on the sec-butyl alcohol production at one process unit does not indicate any specific process vents. All process vents at this process unit are reported to be flared so that any reactor VOC emissions would be combusted.

In general, production of chemicals by hydrolysis/hydration processes generate little or no reactor VOC emissions. Based on production information for ethylene glycol and propylene glycol, these hydration reactors do not have process vent streams associated with them. Ethylene glycol and propylene glycol are produced by hydrating ethylene oxide and propylene oxide, respectively. The reactions for both chemicals result in production of di- and tri-glycols as coproducts. Following the reactor, the glycols are separated and purified by distillation. No reactor VOC emissions are vented to the atmosphere from the glycol process units in the EDP.

2.2.2.14 <u>Hydrogenation</u>. Hydrogenation is the process in which hydrogen is added to an organic compound. The hydrogenation process can involve direct addition of hydrogen to the double bond of an unsaturated molecule, replacement of oxygen in nitro-containing organic compounds to form amines, and addition to aldehydes and ketones to produce alcohols. The major chemical products of hydrogenation reactions include cyclohexane, aniline, n-butyl alcohol, hexamethylene diamine, 1,4-butanediol, cyclohexanone, and toluene diamine.

In general, reactor VOC emissions from hydrogenation reactions appear to be small in comparison with other chemical reactions. However, combustion devices are typically associated with the vent streams of hydrogenation processes. Excess hydrogen in these vent streams makes them suitable for combustion in most cases.

Hexamethylene diamine is made by hydrogenation of adiponitrile. Reactor VOC emissions from hexamethylene diamine production are small according to information on three process units in the EDP. Excess hydrogen used in the reaction is recovered from the vent stream and recycled to the reactor. At two of these process units, the process vent streams are used as fuel in a plant boiler. The average vent stream flow rate following hydrogen recovery at the three process units is 14.0 scm/min (494 scfm) and the average heat content is 21 MJ/scm (564 Btu/scf). The VOC content of the noncombusted vent stream at the process unit that does not use combustion is approximately 3 kg/hr (6.6 lb/hr). The VOC content of the combusted streams at the other two process units is estimated to be negligible prior to combustion.

Cyclohexane is produced by the liquid-phase hydrogenation of benzene. In this process, both cyclohexane and hydrogen are recovered from the process vent stream. Information from one cyclohexane plant indicates that there is usually no flow in the vent stream following product and hydrogen recovery. The process vent stream after these recovery systems is discharged to the atmosphere only during emergencies, and the stream is vented to the flare system for VOC destruction during such upset conditions.

Cyclohexane, 1,4-butanediol, and toluene diamine production involve the hydrogenation of phenol, 2-butyne-1,4-diol, and 2,4-dinitrotoluene, respectively. The process vent stream for these hydrogenation reactions are ultimately combusted in incinerators, boilers, or flares. Precombustion vent stream characteristic data are available for only one of these vent streams--n-butyl alcohol.

2.2.2.15 <u>Isomerization</u>. During isomerization, organic compounds are converted by heat and a catalytic reaction that changes the arrangement of atoms in a molecule, but not the number of atoms. Catalysts include aluminum chloride, antimony chloride, platinum, and other metals. Temperatures range from 750 to 900 ^{o}C (400 to 480 ^{o}F), and pressures range from 7 to 50 atmospheres.[8]

Isomerization is used in petroleum refining to convert straight-chain hydrocarbons into branched-chain hydrocarbons. An example is the conversion of n-butane to isobutane.[9] Emissions from this process would be expected to be small, as with other high-temperature and high-pressure reactor processes in the EDP.

2.2.2.16 <u>Neutralization</u>. Neutralization is a process used to manufacture linear alkylbenzene; benzenesulfonic acid, sodium salt; dodecylbenzene sulfonic acid, sodium salt; and oil-soluble petroleum sulfonate, calcium salt. Diagrams of all of the production processes show no reactor process vent streams.[10]

2.2.2.17 <u>Nitration</u>. Nitration is the unit process in which nitric acid is used to introduce one or more nitro groups (NO_2) into organic compounds. Aromatic nitrations are usually performed with a mixture of nitric acid and concentrated sulfuric acid. Nitrobenzene and dinitrotoluene are the major products of nitration reactions.

Nitrobenzene production involves the direct nitration of benzene using a mixture of nitric acid and sulfuric acid. Only a small quantity of by-products, primarily nitrated phenols, are produced by the reaction. The reaction is normally blanketed with nitrogen gas to reduce fire and explosion hazards. At one process unit producing nitrobenzene, waste acid is removed from the reactor product stream by a separator followed by recovery of excess benzene by distillation. Vent streams from the reactor and separator are combined and discharged directly to the atmosphere. Industry information suggests that a new, but unnamed, process without reactor process vents is now in operation. No data, however, are available for this process. The main components of the combined vent streams are nitrogen and benzene. The EDP nitrobenzene nitration process has a combined vent stream flow rate estimated to be 0.38 scm/min (13 scfm) and an approximate heat content of 16 MJ/scm (430 Btu/scf). The VOC emissions to the atmosphere from the vent streams are 8.6 kg/hr (19 lb/hr).

Dinitrotoluene is produced by nitration of toluene in two stages using different acid mixtures. As in the case of nitrobenzene production, the waste acid is separated and recycled. Two process units producing dinitrotoluene operate scrubbers on the reactor vent streams to remove VOC. Following scrubbing, one plant discharges the vent stream to the atmosphere while the other incinerates the vent stream. No data are available on the characteristics of the incinerated vent stream. The flow rate of the nonincinerated vent stream following the scrubber is estimated to be 23 scm/min (812 scfm). Heat content of the vent stream is negligible. Estimated VOC emissions to the atmosphere are 0.05 kg/hr (0.1 lb/hr).

2.2.2.18 <u>Oligomerization</u>. In the oligomerization process, molecules of a single reactant are linked together to form larger molecules consisting of 2 to about 10 of the original molecules. Oligomerization is used to make several chemicals including alcohols, dodecene, heptene, nonene, and octene. Typically, it is a high-temperature, high-pressure process.[11,12] Diagrams for all of the chemical production processes show no reactor process vent streams.[13-15]

Other chemical unit processes with similar high-pressure characteristics, such as pyrolysis, emit little or no VOC's.

2.2.2.19 <u>Oxidation</u>. Oxidation of organic chemicals is the addition of one or more oxygen atoms into the compound. The oxidation processes considered here include pure oxygen oxidation and chemical oxidation. An example of pure oxygen oxidation is the production of ethylene oxide using pure oxygen and ethylene. The production of adipic acid from nitric acid is an example of chemical oxidation.

Ethylene oxide can be produced by oxidation using air or pure oxygen. In the pure oxygen process, ethylene, oxygen and recycled gas are reacted under pressures of 1 to 3 MPa (150 to 440 psia). Two reactor process vent streams are reported by one process unit that produces ethylene oxide by pure oxygen oxidation. At this plant, the reactor effluent is sent through an ethylene oxide absorber. The offgas from this absorber is routed to the carbon dioxide removal system. A portion of the vent stream from the carbon dioxide absorber system is recycled to the reactor, while the remainder is used as fuel in industrial boilers. The carbon dioxide absorber liquid is regenerated, and the removed carbon dioxide is vented to the atmosphere. The portion of the vent stream from the carbon dioxide absorber that is sent to a boiler has an approximate flow rate of 176 scm/min (6,200 scfm) and a heat content of 13 MJ/scm (350 Btu/scf). The estimated discharge rate to the atmosphere from the carbon dioxide absorber liquid regenerator vent is 345 scm/min (12,184 scfm), and the heat content is 0.15 MJ/scf (4 Btu/scf). Prior to combustion in the boiler, the VOC flow rate of the first vent stream is 0.59 kg/hr (1.3 lb/hr). For the uncontrolled vent stream, VOC emissions to the atmosphere are estimated to be 59 kg/hr (130 lb/hr).

In adipic acid production, an alcohol ketone mixture is oxidized using nitric acid. Adipic acid from the reactor is stripped of nitrogen oxides produced by the reaction and is then refined. Of the three process units producing adipic acid included in the EDP, two of the process unit discharge the stripper offgas to the atmosphere. Vent stream flow rates at the three process units are estimated to range from 24 to 132 scm/min (848 to 4,662 scfm). The heating values of all three vent streams are negligible, and there are no VOC emissions from any of these process units.

2-23

2.2.2.20 <u>Oxyacetylation</u>. Oxyacetylation is the process in which oxygen and an acetyl group are added to an olefin to produce an unsaturated acetate ester. Oxyacetylation is used in a new commercial process to make vinyl acetate.

Vinyl acetate is produced from ethylene, acetic acid, and oxygen. Reactor VOC emissions from one vinyl acetate production process unit are small. The estimated vent stream flow rate and heating values are 0.2 scm/min (7 scfm) and 15 MJ/scm (403 Btu/scf), respectively. The VOC flow rate prior to combustion is relatively low (0.05 kg/hr [0.1 lb/hr]).

2.2.2.21 <u>Oxyhalogenation</u>. In the oxyhalogenation process, a halogen acid is catalytically oxidized to the halogenated compound with air or oxygen. The main oxyhalogenation process is oxychlorination, in which HCl is catalytically oxidized to chlorine with air or oxygen. (Oxychlorination processes using air are included in the analyses for air oxidation processes.) The oxychlorination process is used in the production of ethylene dichloride.

As described previously, most ethylene dichloride is produced by the "balanced process" that combines oxychlorination and direct chlorination of ethylene. In the oxychlorination reaction, ethylene, HCl, and oxygen or air are combined. Emissions from air oxychlorination reactions used in ethylene dichloride production are regulated by the air oxidation processes new source performance standards (NSPS). Only emissions from oxygen oxychlorination reactions are considered here. At one process unit producing ethylene dichloride by oxychlorination using oxygen, the reactor effluent is condensed, and excess ethylene is recycled to the reactor. A small portion of the recycle stream is vented to prevent a buildup of impurities. The vent stream is incinerated in order to comply with State implementation plans (SIP's) and to reduce vinyl chloride emissions that are regulated under national emission standards for hazardous air pollutants (NESHAP). The vent stream flow rate prior to incineration is approximately 8.5 scm/min (300 scfm), and the estimated heat content is 27 MJ/scm (725 Btu/scf). The VOC flow rate in the vent stream is estimated to be 340 kg/hr (750 lb/hr). Following incineration, the estimated VOC emissions to the atmosphere are 6.8 kg/hr (15 lb/hr).

2.2.2.22 <u>Phosgenation</u>. Phosgenation is the process in which phosgene ($COCl_2$) reacts with an amine to form an isocyanate, or with an alcohol to form a carbonate. Toluene diisocyanate is the major chemical product of this chemical unit process.

Toluene diisocyanate is produced by phosgenating toluene diamine. At one process unit, the reactor vent is routed through distillation columns for product/by-product recovery and purification. Thus, no reactor VOC emissions are vented to the atmosphere from the process.[16]

2.2.2.23 <u>Pyrolysis</u>. Pyrolysis is a chemical reaction in which the chemical change of a substance occurs by heat alone. Pyrolysis includes thermal rearrangements into isomers, thermal polymerizations, and thermal decompositions. The major use of this process is in the production of ethylene by the steam pyrolysis of hydrocarbons. Other pyrolysis products include ketene (a captive intermediate for acetic anhydride manufacture) and by-products of ethylene production, such as propylene, bivinyl, ethylbenzene, and styrene.

Ethylene and other olefins can be produced from a variety of hydrocarbon feeds, including natural gas liquors, naphtha, and gas-oil. Maximum ethylene production is achieved by adjusting furnace temperature and steam-to-hydrocarbon ratios. Pyrolysis gases from the furnace are cooled, compressed, and separated into the desired products. As in refinery operations, the economics of olefins production make recovery of gaseous products desirable. Thus, process vent streams to the atmosphere are minimized. The ethylene process unit included in the EDP reports no process vent streams to the atmosphere.

The first step in the manufacture of acetic anhydride is production of ketene. Ketene and water are produced by pyrolysis of acetic acid. At two plants producing acetic anhydride, the pyrolysis products are cooled and separated prior to acetic anhydride formation. No process vent streams are associated with the pyrolysis reaction to produce ketene.

2.2.2.24 <u>Sulfonation</u>. Sulfonation is the process by which the sulfonic acid group (SO_2OH), or the corresponding salt, or sulfonyl halide is attached to a carbon atom. "Sulfonation" can also be used to mean treatment of any organic compound with sulfuric acid, regardless of the nature of products formed.

2-25

Isopropyl alcohol is made by sulfonation of propylene to isopropyl hydrogen sulfate and subsequent hydrolysis to isopropyl alcohol and sulfuric acid.

Many detergents are made by the sulfonation of mixed linear alkylbenzenes. These include benzenesulfonic acid and dodecylbenzene sulfonic acid. To manufacture these, the linear alkylbenzenes are sulfonated with sulfur trioxide or oleums of various strengths. One process uses diluted sulfur trioxide vapor in a continuous operation. The reaction and heat removal occurs in a thin film on a cooled reactor surface. The process forms almost entirely the p-sulfonic acid.[17]

The EDP contains emissions data on one sulfonation process unit controlled only with a caustic scrubber. It has extremely low uncombusted VOC emissions (0.05 kg/hr [0.1 lb/hr]), even though the vent stream flow rate is relatively large (52 scm/min [1,836 scfm]).

2.3 DISTILLATION OPERATIONS

Distillation is the most commonly used separation and purification procedure in refineries and large organic chemical manufacturing plants. The fundamental operating principles for a distillation column are the same regardless of the application. This section briefly discusses some of the fundamental principles involved in distillation to provide a better understanding of operating characteristics of distillation units and causes of VOC emissions from these units.

2.3.1 Types of Distillation

Distillation is an operation separating one or more feed stream(s)[b] into two or more product streams, each product stream having component concentrations different from those in the feed stream(s). The separation is achieved by the redistribution of the components between the liquid- and vapor-phase while the less volatile components(s) concentrate in the liquid-phase. Both the vapor- and liquid-phase originate predominantly by vaporization and condensation of the feed stream.

Distillation systems can be divided into subcategories according to the operating mode, the operating pressure, the number of distillation stages, the introduction of inert gases, and the use of additional

---

[b]For batch distillation, the word "charge" should be used in place of "stream", wherever applicable.

compounds to aid separation. A distillation unit may operate in a continuous or a batch mode. The operating pressures can be below atmospheric (vacuum), atmospheric, or above atmospheric (pressure). Distillation can be a single stage or a multistage process. Inert gas, especially steam, is often introduced to improve separation. Finally, compounds are often introduced to aid in distilling hard-to-separate mixture constituents (azeotropic and extractive distillation).

Single stage batch distillation is not common in large scale chemical production but is widely used in laboratories and pilot plants. Separation is achieved by charging a still with material, applying heat and continuously removing the evolved vapors. In some instances, steam is added or pressure is reduced to enhance separation.

Single stage continuous distillation is referred to as flash distillation (Figure 2-3). It is generally a direct separation of a component mixture based on a sudden change in pressure. Since flash distillation is a rapid process, steam or other components are not added to improve separation. A flash distillation unit is frequently the first separation step for a stream from the reactor. The heated products from a reaction vessel are pumped to an expansion chamber. The pressure drop across the valve, the upstream temperature, and the expansion chamber pressure govern the separation achieved. The light ends quickly vaporize and expand away from the heavier bottom fractions, which remain in the liquid-phase. The vapors rise to the top of the unit and are removed. Bottoms are pumped to the next process step.

Fractionating distillation is a multistage distillation operation. It is the most commonly used type of distillation unit in large organic chemical plants, and it can be a batch or a continuous operation. At times, inert carriers (such as steam) are added to the distillation column. Fractionating distillation is accomplished by using trays, packing, or other internals in a vertical column to provide multiple intimate contact of ascending vapor and descending liquid streams. A simplified block flow diagram of a fractionation column is shown in Figure 2-4. The light end vapors evolving from the column are condensed and collected in an accumulator tank. Part of the distillate is returned to the top of the column so it can fall countercurrent to the rising

Overheads (Gas) or
Light Ends

Pressure Control
Valve

Flash Distillation
Column

Feed

Bottoms (Liquid) or
Heavy Ends
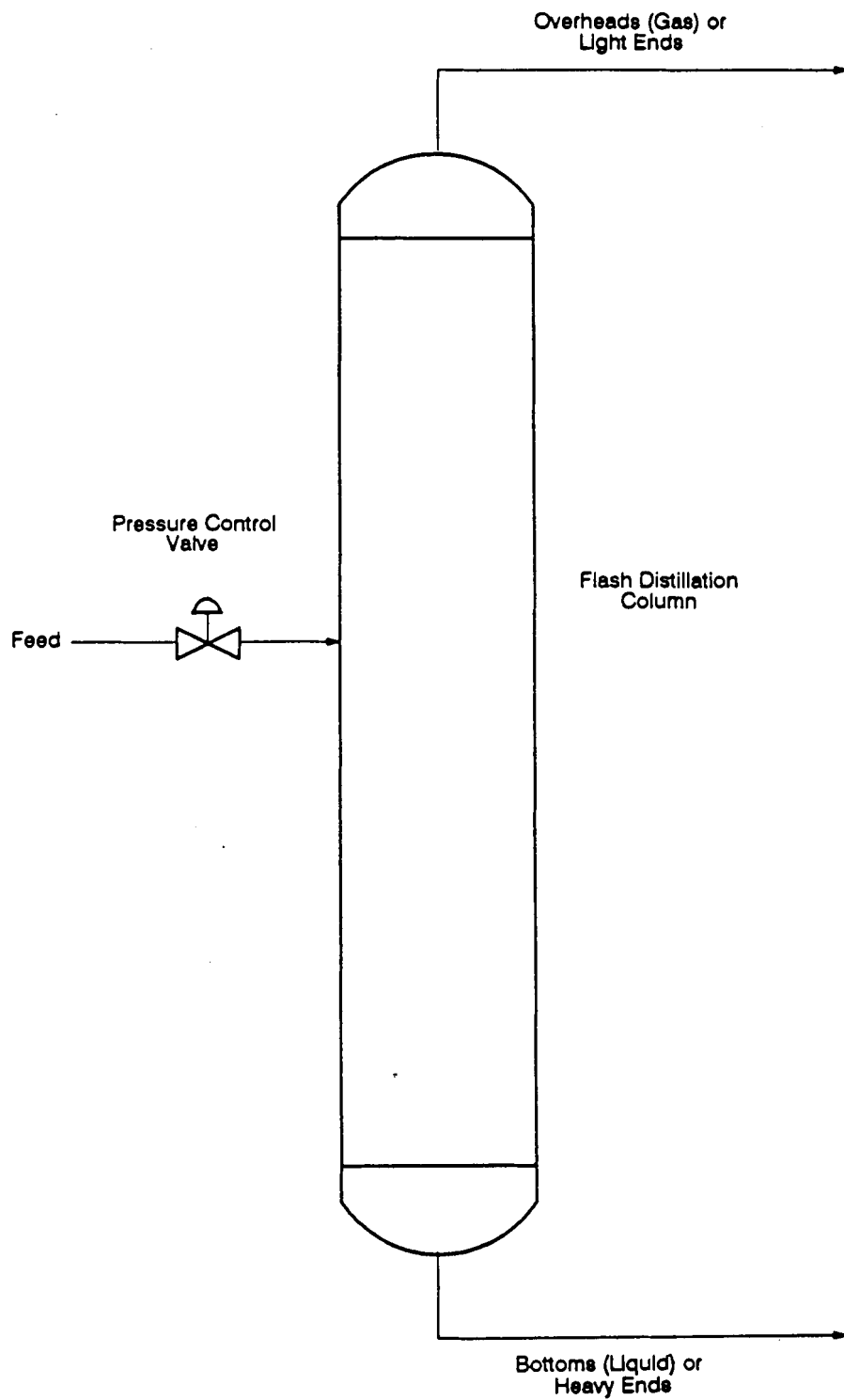
Figure 2-3.   Flash distillation.
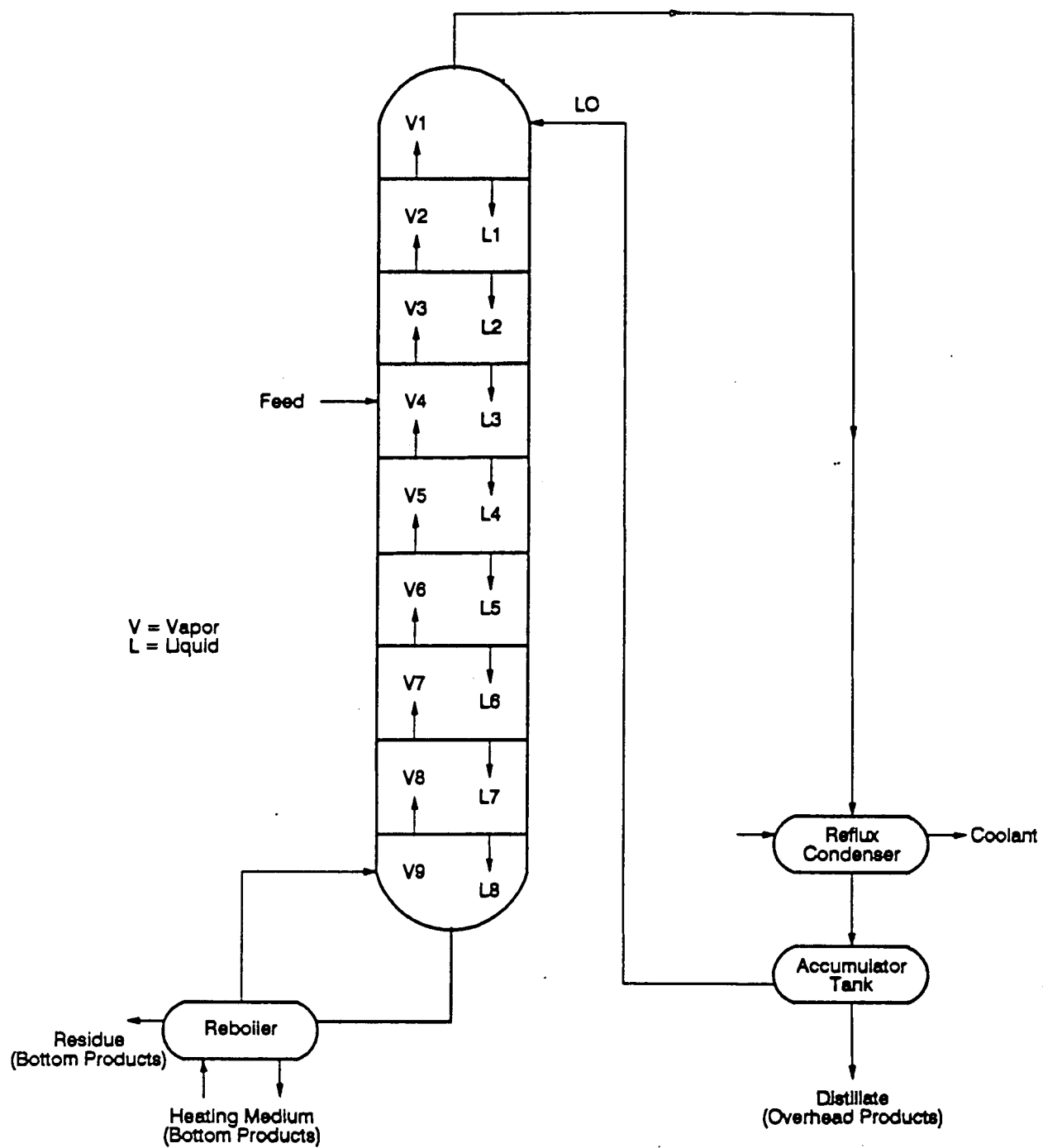
V = Vapor
L = Liquid

Figure 2-4. A conventional fractionating column.

vapors. For difficult separations, additional compounds may be added to achieve the desired separation. This is commonly referred to as extractive distillation and is typically used in lubricant oil refining. A desorption column is very similar to a fractionating distillation column except that it does not use a reflux condenser.

2.3.2 Fundamental Distillation Concepts

The emissions from distillation units are dependent on the size, operating conditions, and types of components present. Therefore, the design parameters and selection of operating conditions are discussed in this section to provide a better understanding of the emissions.

The separation of a mixture of materials into one or more individual components by distillation is achieved by selecting a temperature and pressure that allow the coexistence of vapor and liquid phases in the distillation column. Distillation is described as a mass-transfer operation involving the transfer of a component through one phase to another on a molecular scale. The mass transfer is a result of a concentration difference or gradient stimulating the diffusing substance to travel from a high concentration zone to one of lower concentration until equilibrium is reached. The maximum relative concentration difference between distillation materials in the vapor- and liquid-phases occurs when a state of equilibrium is reached. The equilibrium state is reached when the concentrations of components in the vapor-phase and liquid-phase, at a given temperature and pressure, do not change, regardless of the length of time the phases stay in contact.

For an ideal system, the equilibrium relationship is determined using the law of Dalton and Raoult. Dalton's Law states that the total pressure of a mixture of gases is equal to the sum of the partial pressures of each gas constituent:

$$P_t = \sum_1^n p_i \qquad (2.1)$$

where:

P_t = Total pressure,

p_i = Partial pressure of each gas constituent, and

n = Number of constituents.

Dalton's Law further states that the partial pressure of each ideal gas constituent is proportional to the mole fraction (relative percentage) of that gas in an ideal solution:

$$p_i = y_i \, P_t \qquad (2.2)$$

where:

y_i = Mole fraction.

Raoult's Law states the relationship for ideal solutions between the partial pressure of a mixture constituent in the vapor phase and its composition in the liquid-phase in contact. When the vapor phase is at equilibrium with the solution, the partial pressure of the evolved component is directly proportional to its vapor pressure (at the same temperature) and its mole fraction in the solution:

$$p_i = x_i \, p^*_i \qquad (2.3)$$

where:

x_i = Mole fraction in the solution.

p^*_i = Vapor pressure of the pure substance at the same temperature.

These statements may be combined to given an equilibrium vaporization ratio (K value). A simplified expression for this ratio is:

$$K_i = \frac{y_i}{x_i} \qquad (2.4)$$

This equilibrium constant is used to evaluate the properties that affect gas-liquid equilibrium conditions for individual components and mixtures. The K value represents the distribution ratio of a component between the vapor and liquid-phase at equilibrium. The K value for various materials may be calculated using thermodynamic equations of state or through empirical methods (suitably fitting data curves to experimental data). This constant is an extremely important tool for designing distillation units (determining required temperatures, pressures, and column size).

Another basic distillation concept is the separation factor or relative volatility (α_{ij}) of system components. This is the equilibrium

ratio of the mole fractions of component i to some component j in the vapor and liquid phase:

$$\sigma_{ij} = \frac{y_i}{x_i} \bigg/ \frac{y_j}{x_j} \qquad (2.5)$$

This is expressed as the ratio of the vapor pressures for an ideal mixture:

$$\sigma_{ij} = \frac{P_i}{P_j} \qquad (2.6)$$

The ratio is a measure of the separability of the two components to be separated and is very important in designing distillation equipment. In the case of a binary system, the two components to be separated are the two components present in the feed. In a multicomponent system, the components to be separated are referred to as "heavy key" and "light key." The "heavy key" is the most volatile component desired to be present in significant quantities in the bottom products or the residue. Similarly, "light key" is the least volatile compound desired to be present in significant quantities in the overhead products. Generally, separation by distillation becomes uneconomical when the relative volatility of the light key and heavy key is less than 1.05.[18]

The operating temperature and pressure in a distillation unit are interrelated. A decision made for the value of one of these parameters also determines the value of the other parameter. Essentially, the pressure and temperature are chosen so that the dew point[c] condition for

---

[c]The dew point temperature is the temperature at which the first droplet of liquid is formed as the vapor mixture is coiled at constant pressure, and the dew point pressure is that at which the first droplet of liquid is formed as the pressure is increased on the vapor at constant temperature.

Mathematically, the dew point is defined by:

$$\sum_1^n x_i = 1.0 = \sum \frac{y_i}{K_i} \qquad (2.7)$$

the overhead products and the bubble point[d] conditions for the bottom products can be present inside the distillation unit. The actual decision on these two conditions is predicated upon economic considerations and is made after evaluating the following items:

- The relative volatility, α_{ij}, of the components. A lower pressure in the column increases the value of α_{ij} and improves separation. This would result in a shorter fractionating column.

- The effect of pressure on vapor volume in the distillation unit. The vapor volume increases as the pressure decreases, requiring a larger diameter vessel.

- The effect of pressure on column wall thickness. Higher pressures require increased wall thickness and raise costs.

- Cost of achieving desired temperature and pressures. The cost of changing the pressure and that of changing the temperature are considered independently since these two costs are not proportional.

- The thermal stability limit of the compounds being processed. Many compounds decompose, polymerize, or react when the temperature reaches some critical value. In such cases it is necessary to reduce the design pressure so that this critical reaction temperature is not reached at any place in the distillation unit.

Data on the use of vacuum during distillation were compiled for a number of major chemicals to predict the use of vacuum for distillation. The physical properties of the compounds using vacuum during distillation

---

[d] The bubble-point temperature is the temperature at which the first bubble of vapor is formed on heating the liquid at constant pressure. The bubble-point pressure is the pressure at which the first bubble of vapor is formed on lowering the pressure on the liquid at constant temperature.

Mathematically, the bubble point is defined by:

$$\sum_{1}^{n} y_i = 1.0 = \sum K_i x_i \qquad (2.8)$$

were compared with those of compounds not using vacuum, with the following conclusions:

- Compounds with a melting point less than -10 °C (14 °F) and with a boiling point greater than 150 °C (302 °F) are likely to be distilled under vacuum.

- If the boiling point of a compound is less than 50 °C (122 °F) then it is likely to be distilled at or above atmospheric pressure.

- For the separation of compounds with boiling points between 50 and 150 °C (122 and 302 °F), the use of vacuum depends on the thermal operable limit of the compound (i.e., temperature range in which the compound does not decompose, polymerize, or react).[19]

In designing a distillation system, once the operating temperature and pressure are established, the type of distillation is considered. Flash distillation is preferred for separation of components with a high relative volatility. Steam is the most frequently used heat source for column distillation, since using a direct fired heater (although used in some instances) could create a dangerous situation. Steam is also used for distilling compounds that are thermally unstable or have high boiling points. Azeotropic and extractive distillation are used to separate compounds that are difficult to separate. For example, benzene is sometimes added in a distillation process to achieve separation of an alcohol-water mixture.

For a flash unit, the design of the flash vessel size is relatively straightforward. In the case of a fractionating unit design, once the column pressure and temperature are determined, the reflux ratio (fraction of total overhead condensate returned to column) is selected to ensure an adequate liquid phase in the distillation column for vapor enrichment. The number of trays (or weight of column packing), column diameter, and auxiliary equipment (e.g., pumps, condenser, boiler, and instruments) are then determined. The final decision on all these items is based on engineering judgment and economic trade offs. More detailed discussion on the design of distillation units is readily available in various chemical engineering texts.[20-22]

2.4 REACTOR VOLATILE ORGANIC COMPOUND EMISSIONS

Reactor VOC emissions include all VOC's in process vent streams from reactors and product recovery systems. Process product recovery equipment includes devices such as condensers, absorbers, and adsorbers, used to recover product or by-product for use, reuse, or sale. Not included in product recovery equipment are product purification devices involving distillation operations.

Reactor processes may be either liquid-phase reactions or gas phase reactions. Four potential atmospheric emissions points are shown in Figure 2-5 and include:

- Direct reactor process vents from liquid-phase reactors;

- Vents from recovery devices applied to vent streams from liquid phase reactors (raw materials, products, or by-products may be recovered from vent streams for economic or environmental reasons);

- Process vents from gas-phase reactors after either the primary or secondary product recovery device (gas-phase reactors always have primary product recovery devices); and

- Exhaust gases from combustion devices applied to any of the above streams.

Some chemical production processes may have no reactor process vents to the atmosphere, while others may have one or more vent streams. Specific examples of the first three vent types described above are presented in Figures 2-6, 2-7, and 2-8. Each figure represents one of the 173 reactor process chemicals covered within the scope of this document.

The production of nitrobenzene by a nitration process is shown in Figure 2-6 and is an example of a liquid reaction with an uncontrolled vent stream (Vent Type A). Benzene is nitrated at 55 °C (131 °F) under atmospheric pressure by a mixture of concentrated nitric and sulfuric acids in a series; reactor vents are the largest source of VOC's in nitrobenzene plants. It should be noted, however, that a new process without vents may now be in use.

The production of ethylbenzene is an example of a liquid-phase reaction of continuous stirred-tank reactions. The crude reaction mixture flows to a separator, where the organic phase is decanted from the aqueous

Liquid-Phase Reactor

Gas

Vent Type A

Product/By-product
Recovery Device

Gas

Vent Type B

Recovered
Product

R_x

Liquid

R_x

Liquid

Gas-Phase Reactor

Gas

Vent Type C

Liquid

R_x
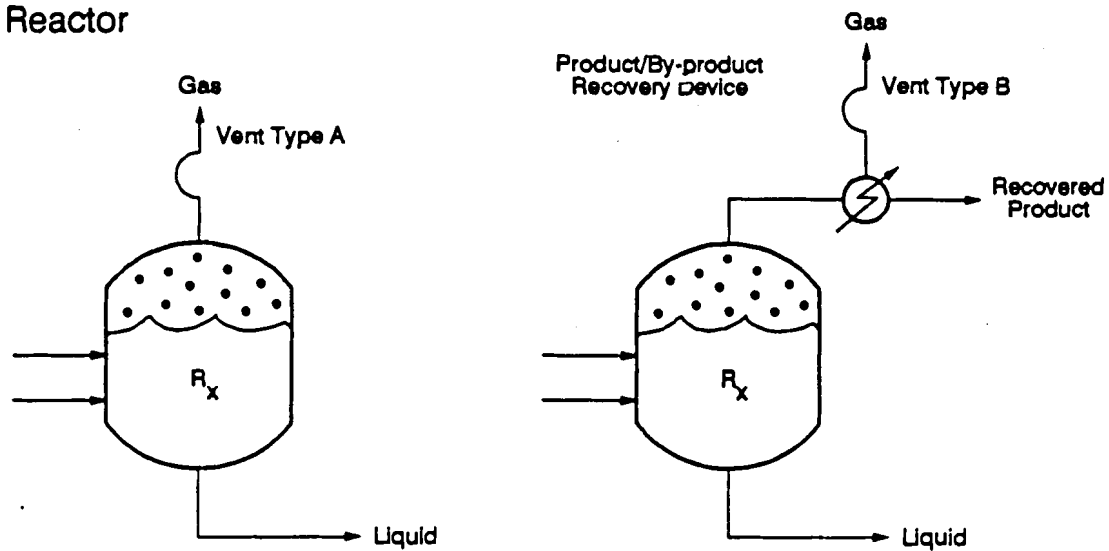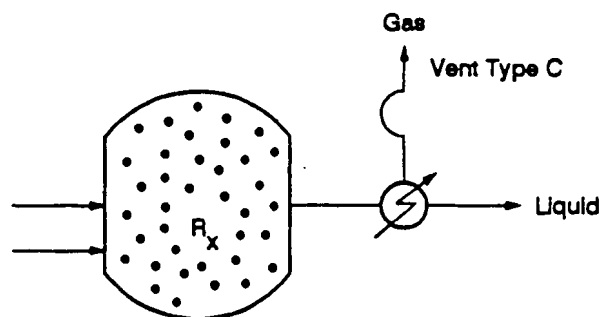
Process Vents Controlled by Combustion

Gas

Vent Type D

Process Vent Streams
from A, B, or C

Combustion
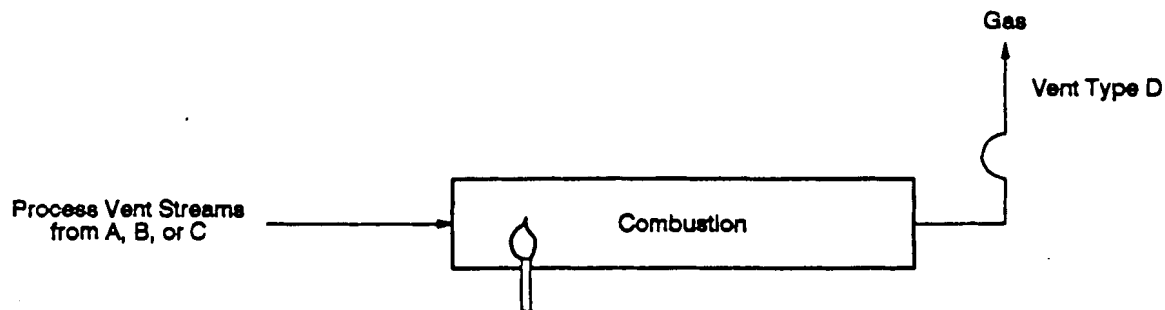
Figure 2-5. General examples of reactor-related vent streams.
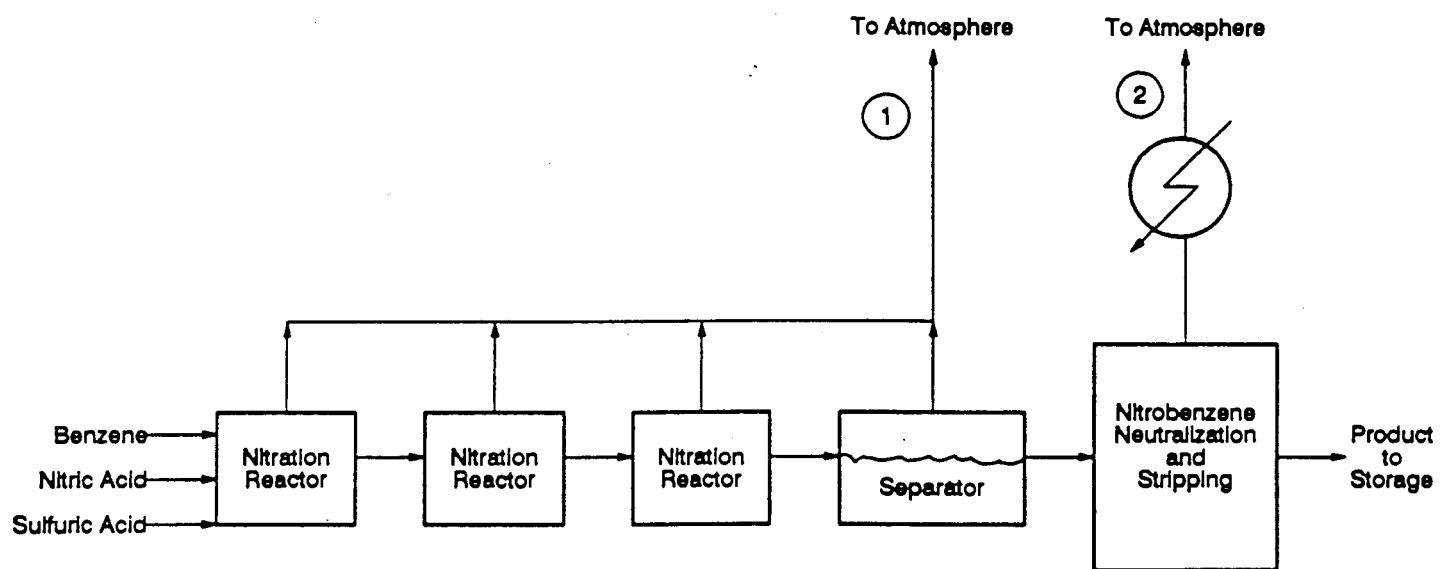
Figure 2-6. Process flow diagram for the manufacture of nitrobenzene.[7]
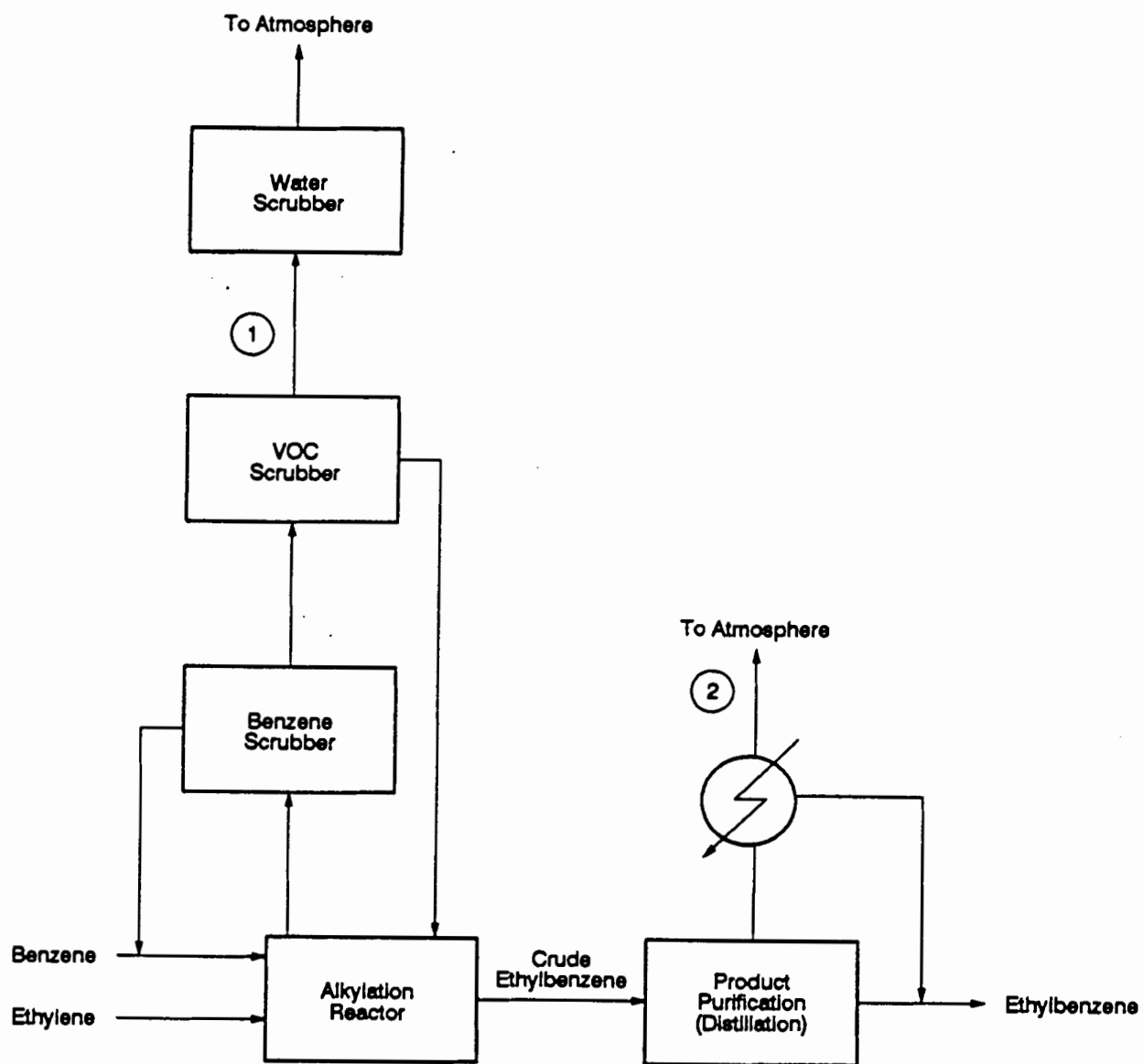
Figure 2-7.   Process flow diagram for the manufacture of ethylbenzene.
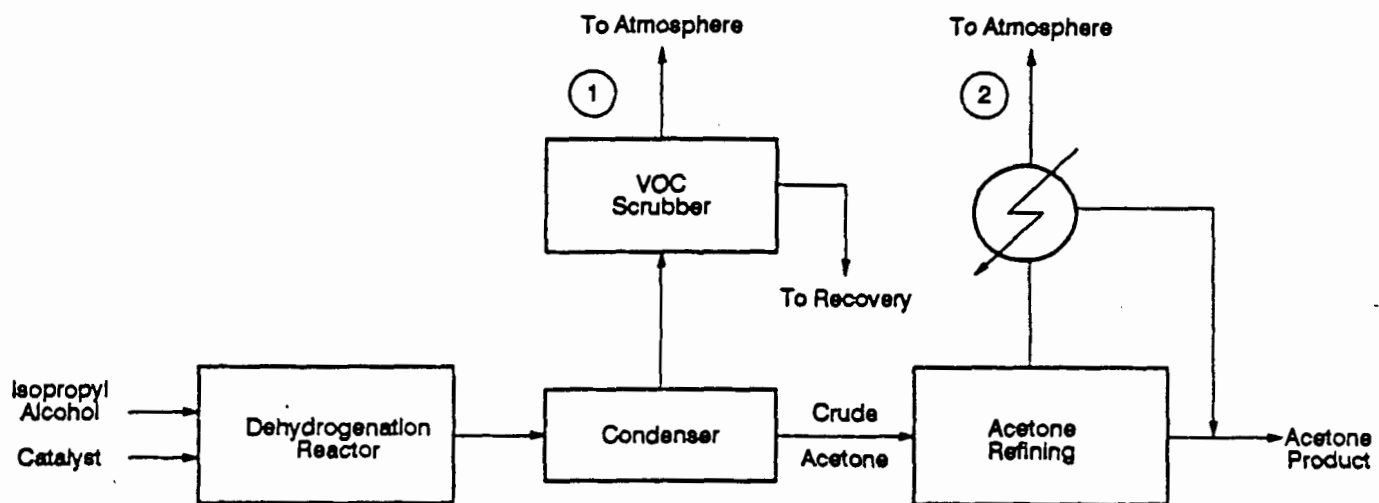
Figure 2-8. Process flow diagram for the manufacture of acetone.

waste acid. Emission streams from the reactors and separator are combined and emitted to the atmosphere without any control devices (Vent 1). Available data indicate that controls are not typically applied to this process, and that where the vent stream is passed through a VOC recovery device before it is discharged to the atmosphere (Type B). Figure 2-7 depicts an alkylation unit process used to produce ethylbenzene. Ethylene and benzene are combined in the alkylation reactor to form crude ethylbenzene. The process vent stream from the reactor goes through three types of scrubbers before discharging to the atmosphere. The first scrubber recovers the excess benzene reactant from the vent stream and recycles it to the reactor. The second scrubber removes any ethylbenzene product in the vent stream and recycles it to the reactor. Finally, traces of acidic catalyst in the vent stream are removed by a water scrubber before the vent stream is discharged to the atmosphere. Vent 1 in the figure designates the only reactor vent stream for this example. The crude ethylbenzene product stream from the reactor is purified by distillation. The vent stream from the product purifications operations (Vent 2) is associated with distillation operations and, therefore, is not considered to be a reactor-related vent stream.

Figure 2-8 shows a dehydrogenation process used to produce acetone. Although this is not the most widely used process to make acetone, it provides a good example of a vapor-phase reaction and its associated vent streams (Type C). In this process, isopropyl alcohol is catalytically dehydrogenated to acetone in a vapor-phase reaction to 400 to 500 $^{\circ}$C (750 to 930 $^{\circ}$F). The crude acetone then passes through a condenser or primary VOC recovery device. The overheads or process vent stream from the primary condenser then goes through a VOC scrubber and is released to the atmosphere (Vent 1). Acetone is further refined and emissions from the refining process (Vent 2) are again not considered to be reactor related. Other processes used to manufacture acetone have no reactor process vent streams to the atmosphere.

As indicated in Section 2.2, the characteristics of reactor vent streams (i.e., heat content, flow rate, VOC control) vary widely among the numerous chemicals and chemical reactions in the SOCMI. In addition, the numerous possible combinations of product recovery devices and reactors

introduce another source of variability among various process units using
the same reaction type.

Data included in the reactor processes emissions profile (see
Appendix B) have been grouped by chemical reaction type. Table 2-4
summarizes the VOC emission characteristics of reactor processes using
30 of the 35 chemical reactions considered here. These data represent the
process vent stream characteristics following the final gas treatment
device (i.e., condenser, absorber, or adsorber) but prior to any
combustion device.

There is a wide variability in the VOC emission characteristics
associated with the various chemical reactions. For example, VOC emission
factors range from 0 kilograms per gigagrams (kg/Gg) (0 lb/10^6 lb) of
product for pyrolysis reactions to 120,000 kg/Gg (120,000 lb/10^6 lb) of
product for hydroformylation reactions. Wide variability also exists in
the emission characteristics associated with process units using the same
chemical reaction. For example, process units using chlorination
reactions have VOC emission factors that range from 292 to 9,900 kg/Gg
(292 lb/10^6 lb to 9,900 lb/10^6 lb). The variability in process vent
stream flow rates and heating values is not as pronounced as the VOC
emission factors. Flow rates range from 0 to 537 scm/min (0 to
18,963 scfm) and heating values range from 0 to 58.8 MJ/scm (0 to
1,579 Btu/scf).

Although process vent stream characteristics are variable, there are
some general observations evident in Table 2-4. First, process units
using 11 of the 30 reaction types included in Table 2-4 were reported to
have no reactor process vents. These reactions include: ammination,
ammonolysis, cleavage, etherification, fluorination, hydration,
neutralization, oligomerization, phosgenation, pyrolysis, and
sulfurization.

A second general observation evident in Table 2-4 is that the
process units using six of the reaction types included in there were
reported to have the largest VOC emission factors. The reactions include:
hydroformylation, chlorination, dehydrogenation, condensation,
oxychlorination, and hydrochlorination. The vent streams from process

TABLE 2-4. SUMMARY OF REACTOR-RELATED VOLATILE ORGANIC COMPOUND EMISSION FACTORS, VENT STEAM HEAT CONTENTS, AND FLOW RATES PRIOR TO COMBUSTION

Chemical reaction type	Range (or single value) of reactor VOC emission factors[a,b] (kg/Gg)	Range (or single value) of vent stream VOC content[b,c] (g/scm)	Percent of process units with vent streams using combustion control	Range (or single value) of flow rates[b] (scm/min)	Range (or single value) of vent stream heat content[b] (MJ/scm)
Alkylation	5.95-78.1	3.07-252	33.3	0.24-0.48	0.15-6.74
Amination	0[d]	0[d]	0[d]	0[d]	0[d]
Ammonolysis	0[d]	0[d]	0[d]	0[d]	0[d]
Carbonylation	443	1.06	100	537	11.0
Chlorination	292-9,900	0.209-118	44.4	1.13-342	0-45.7
Cleavage	0[d]	0[d]	0[d]	0[d]	0[d]
Condensation	8,900	554	100	4.16	39.8
Dehydration	DNA[e]	DNA[e]	0	DNA[e]	DNA[e]
Dehydrogenation	11,400-12,600	36.5-75.0	85.7	16.3-147	10.4-11.2
Dehydrochlorination	4,790	1,097	100	0.283	22.3
Esterification	4.38-594	5.34-21.8	14.3	0.06-2.12	3.8
Etherification	0[d]	0[d]	0[d]	0[d]	0[d]
Fluorination	0[d]	0[d]	0[d]	0[d]	0[d]
Hydration	0[d]	0[d]	0[d]	0[d]	0[d]
Hydrogenation	0-943	0-1,638	83.3	0.09-36.9	12.0-58.8
Hydrochlorination	2,000-14,700	28.1-2,247	80	0.566	18.6-47.9
Hydroformylation	120,000	878	100	20.6	45.9
Hydrodimerization	1,310	6.69	0	30.6	2.61
Hydrolysis	2.5	0.27	33.3	2.80	0
Neutralization	0[d]	0[d]	0[d]	0[d]	0[d]
Nitration	9.95-1,350	0.03-390	33.3	0.37-23.3	0-16.2
Oligomerization	0[d]	0[d]	0[d]	0[d]	0[d]
Oxidation (Pure O2)	3,900	0-2.85	25	24-345	0-0.15
Oxyacetylation	2.20	3.82	0	0.198	15.2
Oxychlorination (Pure O2)	7,180	658	100	8.61	26.6
Phosgenation	0[d]	0[d]	0[d]	0[d]	0[d]
Pyrolysis	0[d]	0[d]	0[d]	0[d]	0[d]
Sulfonation	29.2	0.014	0	52.7	0
Sulfurization (Vapor Phase)	0[d]	0[d]	0[d]	0[d]	0[d]

[a]Emission factors are expressed in terms of kilogram of VOC emitted per gigagram of chemical produced and represent emissions to the atmosphere from the final gas treatment device (if used), but before combustion (if used).

[b]Ranges are due to: (1) different chemicals produced by the chemical process, and (2) different controls used at the process units.

[c]All values represent emission stream characteristics after the final product recovery device and before combustion (if used).

[d]No reactor vent streams are associated with chemicals manufactured by this chemical process.

[e]DNA = Data not available.

units using these reactions also tend to have both high heating values and a high percentage application of combustion devices.

2.5 VOLATILE ORGANIC COMPOUND EMISSIONS FROM DISTILLATION UNITS

The discussions on distillation column operating theory and design show the basic factors of column operation. Vapors separated from the liquid phase in a column rise out of the column to a condenser. The gases and vapors entering the condenser can contain VOC, water vapor, and noncondensibles such as oxygen, nitrogen, and carbon dioxide. The vapors and gases originate from vaporization of liquid feeds, dissolved gases in liquid feeds, inert carrier gases added to assist in distillation (only for inert carrier distillation), and air leaking into the column--especially in vacuum distillation. Most of the gases and vapors entering the condenser are cooled enough to be collected as a liquid-phase. The noncondensibles (oxygen, nitrogen, CO_2, and other organics with low boiling points), if present, are not usually cooled to the condensation temperature and are present as a gas stream at the end of the condenser. Portions of this gas stream are often recovered in devices such as scrubbers, adsorbers, and secondary condensers. Vacuum generating devices (e.g., pumps and ejectors), when used, might also affect the amount of noncondensibles. Some organics can be absorbed by condensed steam in condensers located after vacuum jets. In the case of oil-sealed vacuum pumps, the oil losses increase the VOC content of the noncondensibles exiting the vacuum pump. The noncondensibles from the last process equipment (e.g., condensers, pumps, ejectors, scrubbers, adsorbers, etc.) constitute the emissions from the distillation unit, unless they are controlled by combustion devises such as incinerators, flares, and boilers.

The most frequently encountered emission points from fractionation distillation operations are illustrated for several types of distillation units in Figures 2-9 to 2-12. These emission points are indicated by the numbers in parenthesis as follows: condenser (1), accumulator (2), hot wells (3), steam jet ejectors (4), vacuum pump (5), and pressure relief valve (6). Emissions of VOC's are created by the venting of noncondensible gases that concurrently carry out some hydrocarbons.

2-43

Vent to Atmosphere

Cooling Water

Vapor Phase

Condenser
(1)

Pressure Relief
Valve (6)

Accumulator
(2)

Liquid Reflux

Overhead Product

Distillation
Column
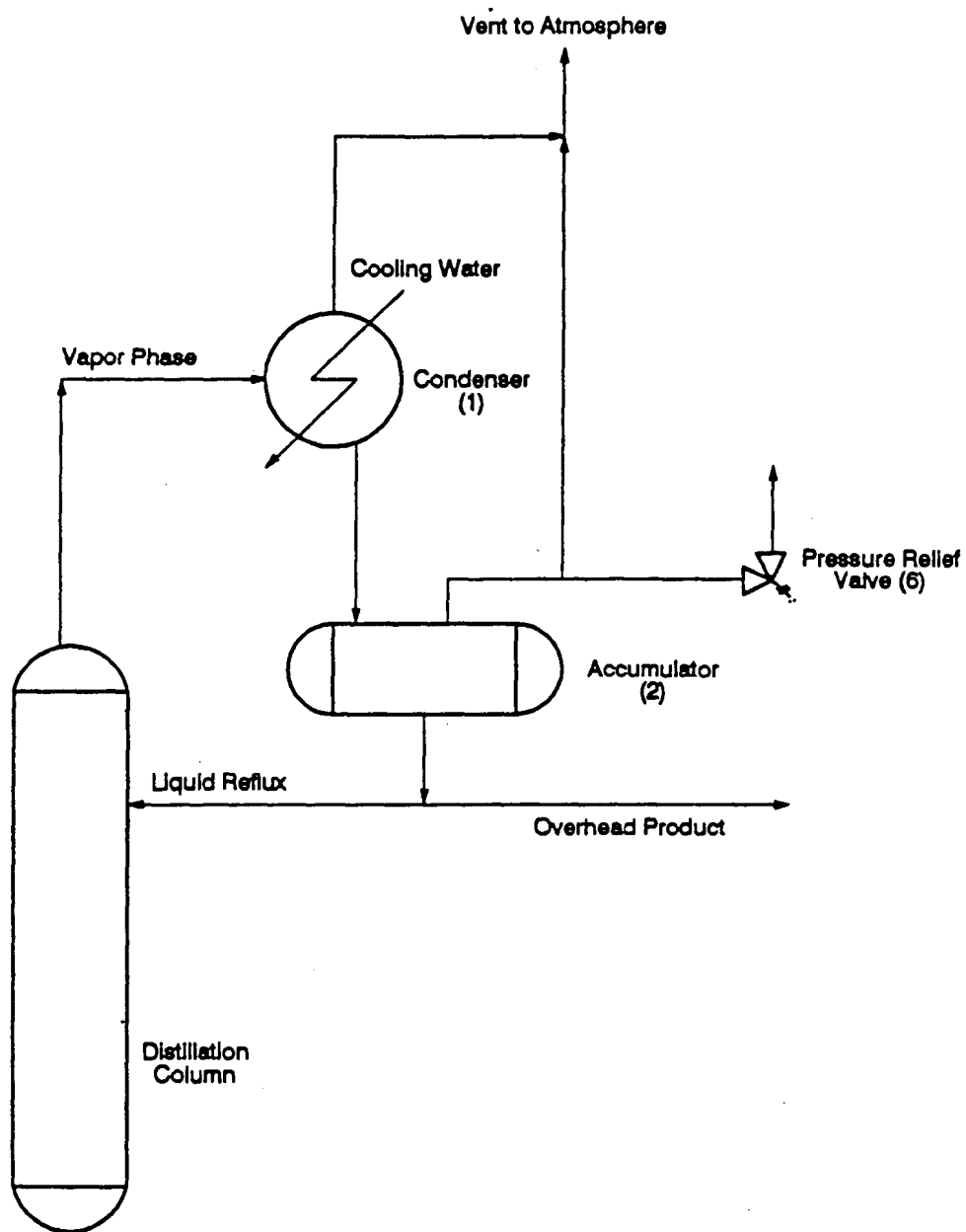
Figure 2-9.   Potential VOC emission points for a nonvacuum distillation
             column.
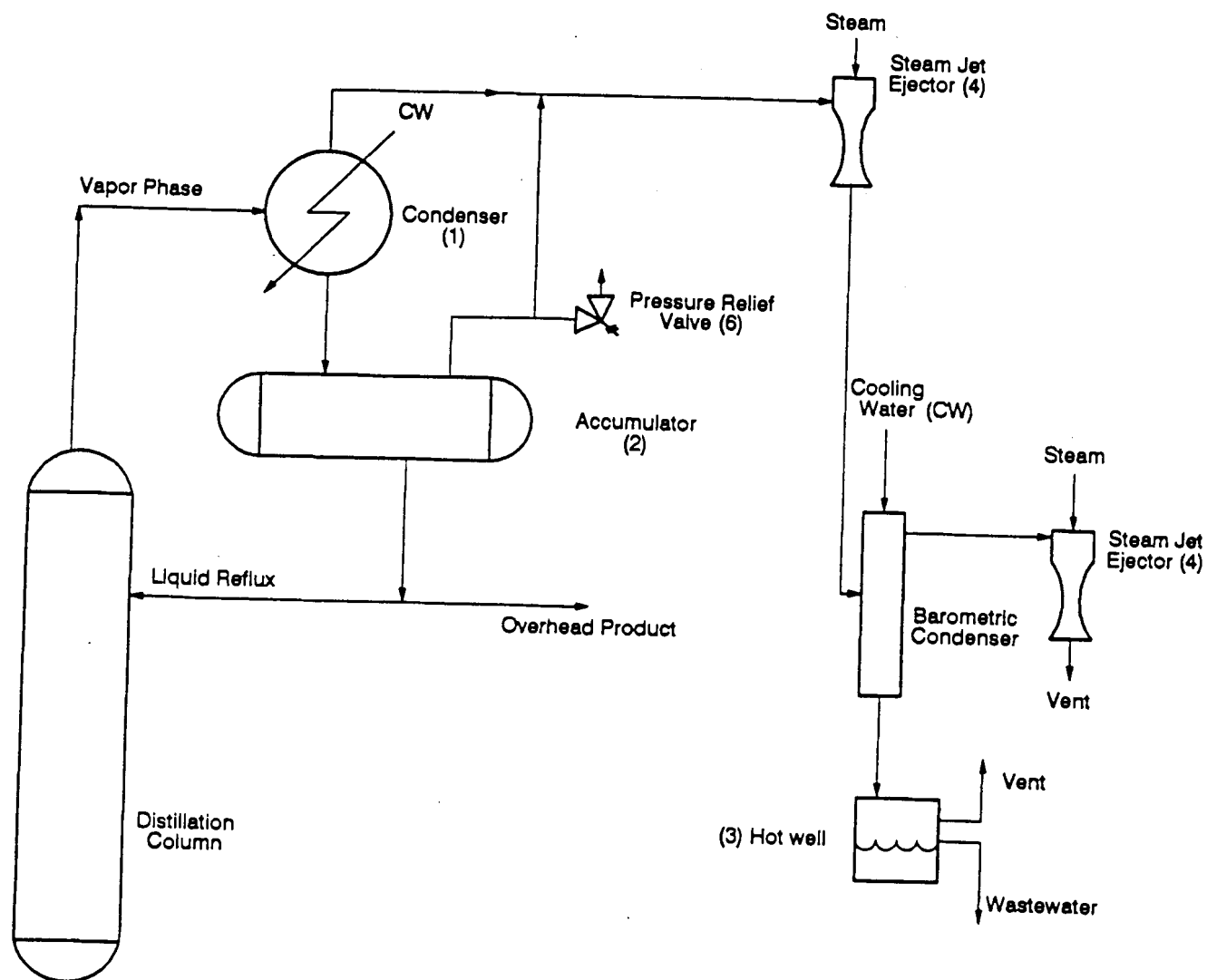
Figure 2-10.   Potential VOC emission points for a vacuum distillation
column using steam jet ejectors with barometric condenser.
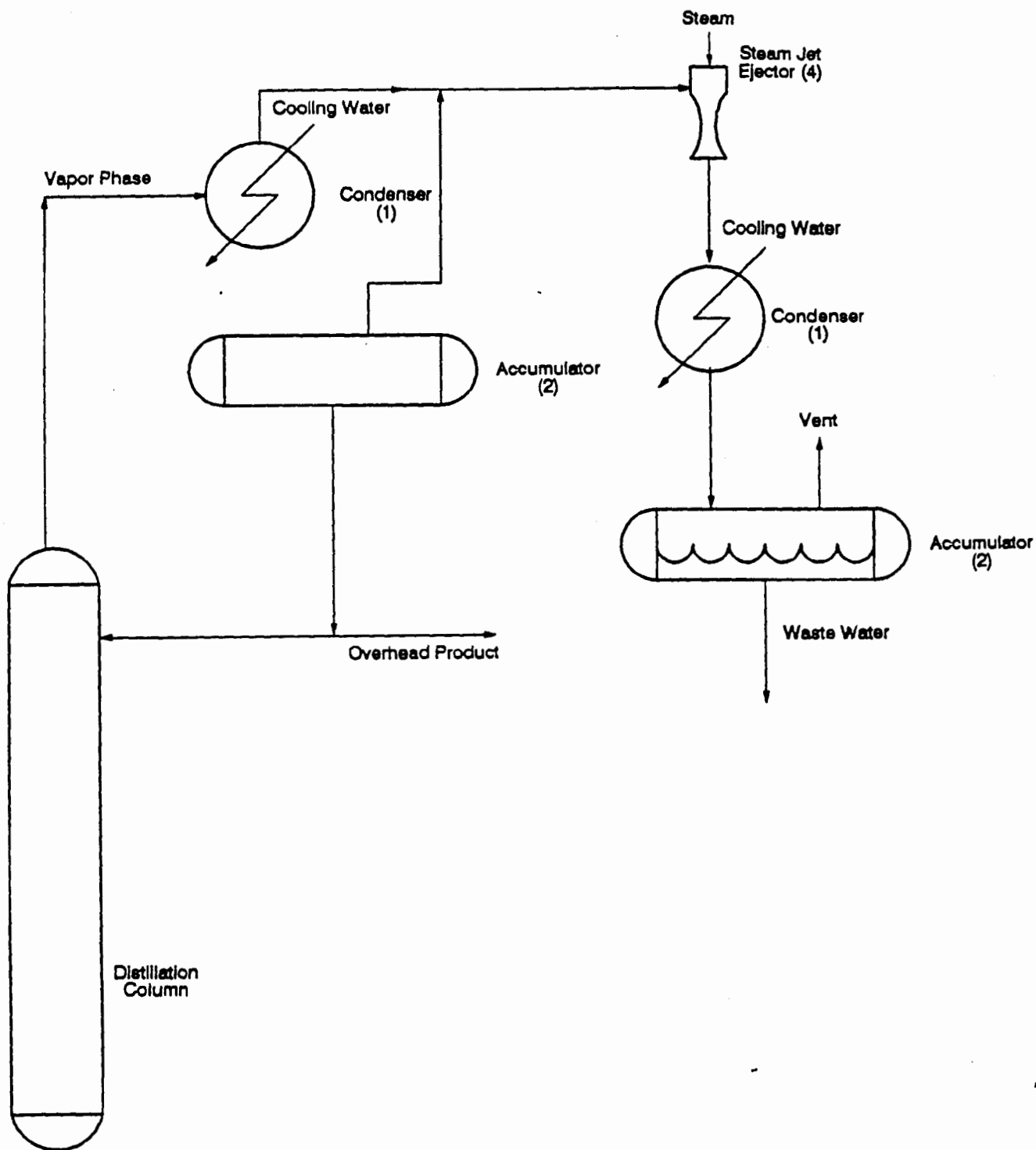
Figure 2-11. Potential volatile organic compound emission points for a
vacuum distillation column using steam jet ejectors.
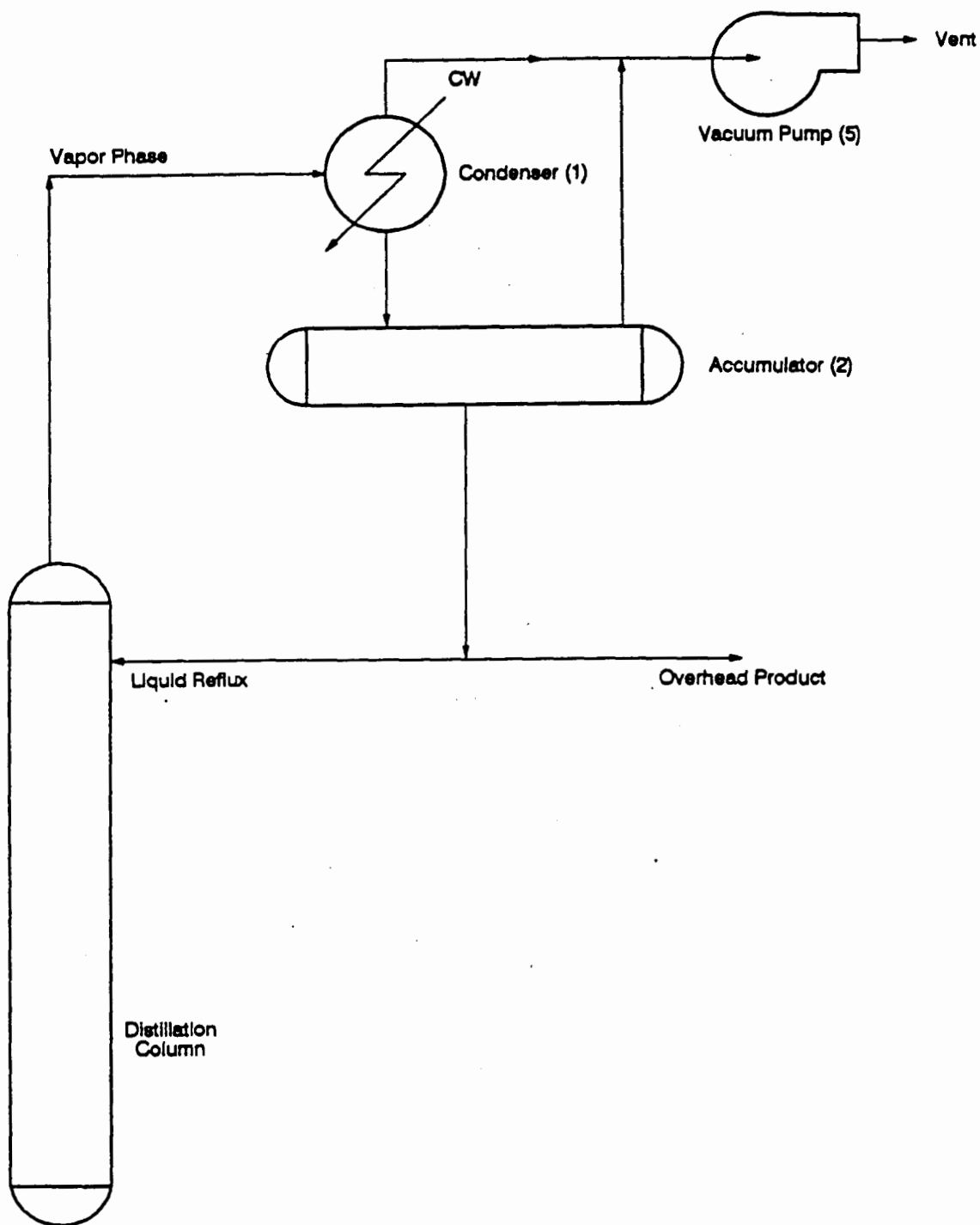
Figure 2-12. Potential VOC emission points for vacuum distillation column using a vacuum pump.

The total volume of gases emitted from a distillation operation depends upon air leaks into the vacuum column (reduced pressure increases leaks and increased size increases leaks), the volume of inert carrier gas used, gases dissolved in the feed, efficiency and operation conditions of the condenser and other process recovery equipment, and physical properties of the organic constituents. Knowledge of the quantity of air leaks and dissolved gases in the column in conjunction with information on organic vapor physical properties and condenser operating parameters allows estimation of the VOC emissions that may result from a given distillation unit operation.

The operating parameters for the industry vary to such a great extent that it is difficult to develop precise emission factors for distillation units. However, an extensive data base was gathered for organic chemical industry distillation units. The data base contains information on operating characteristics, emission controls, exit flows, and VOC emission characteristics.[23] This data base is presented in Appendix B.

The distillation emission profile contains information on the type of distillation involved, the produced recovery and VOC control equipment, the vent stream characteristics, and the other distillation units in the plant. The vent stream characteristics listed for each column in the profile (determined downstream of product recovery devices, but upstream of combustion devices) are: (1) volumetric flow rate, (2) heat content, (3) VOC emission rate, (4) VOC concentration, and (5) chlorine concentration. A summary of the distillation emissions profile is presented in Table 2-5.

TABLE 2-5.   OVERVIEW OF THE DISTILLATION OPERATIONS
EMISSIONS PROFILE

Operating Characteristics of the Distillation Emission Profile	
Average offgas flow rate, m^3/min (scfm)	1.0 (35)
Flow range, m^3/min (scfm)	0.001-18 (0.035-636)
Average VOC emission rate, kg/hr (lb/hr), precontrolled[a]	36 (79)
Average VOC emission rate, kg/hr (lb/hr), controlled[b]	5.9 (13)
VOC emission range, kg/hr (lb/hr), precontrolled	0-1,670 (0-3681)

[a]Calculated downstream of adsorbers, absorbers, and condensers, but upstream of combustion devices.

[b]Controlled VOC emission rates were estimated using a 98-percent destruction efficiency for flares, boilers, and incinerators (where it was indicated that control devices were being used).

2.6 REFERENCES

1. Synthetic Organic Chemicals, United States Production and Sales. U. S. International Trade Commission. USITC Publication 2219. Washington, D.C. U. S. Government Printing Office. 1989. p. 1, 3, and 4 through 7.

2. Memorandum from Lesh, S. A., Radian Corporation, to Evans, L. B., EPA/CPB. June 22, 1984. 13 pp. Revised list of high-volume reactor process chemicals.

3. Memorandum from Read, B. S., Radian Corporation, to Reactor Processes File. May 28, 1985. 12 pp. Summary of the emission data profile.

4. Memorandum from Fidler, K., Radian Corporation, to L. B. Evans, EPA/CPB. July 6, 1983. 66 pp. Identification of chemical production routes and unit processes expected to be used in the future to manufacture the chemicals considered in the Carrier Gas Project.

5. Urea Manufacturing Industry--Technical Document. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-81-001. January 1981. p. 3-8.

6. Faith, W., et al. Industrial Chemicals 4th Edition. New York, John Wiley & Sons. 1975. pp. 129 and 130.

7. Chemical Products Synopsis--Methyl Chloride. Mannsville Chemical Products. Cortland, New York. May 1984. 2 pp.

8. Herrick, E. C., et al, Mitre Corporation. Unit Process Guide to Organic Chemical Industries. Ann Arbor, Ann Arbor Science Publishers, Inc., 1979. pp. 111, and 120 and 121.

9. Ref. 8.

10. Ref. 3.

11. Waddams, A. L. Chemicals from Petroleum, 4th Edition. Houston, Gulf Publishing Company. 1978. p. 24, 145 and 146, 173 and 174, and 221 and 222.

12. Industrial Process Profiles for Environmental Use. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA- 600/2-77-023f. February 1977. pp. 6-637 through 6-641, and 6-667.

13. C_6-C_8 Olefins (Dimersol X). Hydrocarbon Processing. 60(11):192. November 1981.

14. Alpha Olefins. Hydrocarbon Processing. 58(11):128. November 1979.

15. C6-C$_8$ Olefins (Dimersol Process). Hydrocarbon Processing. 56(11):170. November 1977.

16. Organic Chemical Manufacturing, Volume 7: Selected Processes. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-80-028b. December 1980. Section 1-i, p. III-1 to III-4.

17. Ref. 8.

18. Van Winkle, M. Distillation. New York, McGraw-Hill, 1967.

19. Letter from Desai, T., Energy and Environmental Analysis (EEA) to Beck, D., U. S. Environmental Protection Agency. 12 pp. August 11, 1980.

20. King, C. J. Separation Processes, Second Edition. New York, McGraw-Hill, 1980.

21. Foust, A. S., et al. Principles of Unit Operations. New York, John Wiley & Sons, 1960.

22. Treybal, R. E. Mass Transfer Operations, Third Edition. New York, McGraw-Hill, 1980.

23. Distillation Operations in Synthetic Organic Chemical Manufacturing Industry--Background Information for Proposed Standards. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-83-005a. December 1983.

3.0 EMISSION CONTROL TECHNIQUES

This chapter discusses the volatile organic compound (VOC) emission control techniques that are applicable to distillation and reactor process vent streams. The control techniques discussed are grouped into two broad categories: (1) combustion control devices and (2) recovery devices. Combustion control devices are designed to destroy the VOC's in the vent stream prior to atmospheric discharge. Recovery devices limit VOC emissions by recycling material back through the process.

The design and operating efficiencies of each emission control technique are discussed in this chapter. The conditions affecting the VOC removal efficiency of each type of device are examined, along with an evaluation of their applicability for use to reduce emissions from distillation vents and reactor vents. Emphasis has been given to combustion control devices due to their wide applicability for the control of VOC's in Synthetic Organic Chemical Manufacturing Industry (SOCMI) vent streams.

3.1 COMBUSTION CONTROL DEVICES

Combustion control devices, unlike noncombustion control devices, alter the chemical structure of the VOC. Combustion is complete if all VOC's are converted to carbon dioxide and water. Incomplete combustion results in some of the VOC being totally unaltered or being converted to other organic compounds such as aldehydes or acids.

The combustion control devices discussed in the following four subsections are flares, thermal incinerators, catalytic incinerators, and boilers/process heaters. Each device is discussed separately with respect to its operation, destruction efficiency, and applicability to reactor process and distillation vent streams.

3.1.1 Flares

3.1.1.1 Flare Process Description. Flaring is an open combustion process in which the oxygen required for combustion is provided by the air around the flame. Good combustion in a flare is governed by flame temperature, residence time of components in the combustion zone, turbulent mixing of the components to complete the oxidation reaction, and the amount of oxygen available for free radical formation.

Flare types can be divided into two main groups: (1) ground flares and (2) elevated flares, which can be further classified according to the method to enhance mixing within the flare tip (air-assisted, steam-assisted, or nonassisted). The discussion in this chapter focuses on elevated flares, which are the most common type in the chemical industry. The basic elements of an elevated flare system are shown in Figure 3-1. The vent stream is sent to the flare through the collection header (1). The vent stream entering the header can vary widely in volumetric flow rate, moisture content, VOC concentration, and heat value. The knock-out drum (2) removes water or hydrocarbon droplets that could create problems in the flare combustion zone. Vent streams are also typically routed through a water seal (3) before going to the flare. This presents possible flame flashbacks, caused when the vent stream flow rate to the flare is too low and the flame front pulls down into the stack.[1]

Purge gas (nitrogen [N_2], carbon dioxide [CO_2], or natural gas) (4) also helps to prevent flashback in the flare stack (5) caused by low vent stream flow. The total volumetric flow to the flame must be carefully controlled to prevent low flow flashback problems and to avoid a detached flame (i.e., a space between the stack and flame with incomplete combustion), which is caused by an excessively high flow rate. A gas barrier (6) or a stack seal is sometimes used just below the flare head to impede the flow of air into the flare gas network.

The VOC stream enters at the base of the flame, where it is heated by already burning fuel and pilot burners (7) at the flare tip (8). Fuel flows into the combustion zone, where the exterior of the microscopic gas pockets is oxidized. The rate of reaction is limited by the mixing of the fuel and oxygen from the air. If the gas pocket has sufficient oxygen and
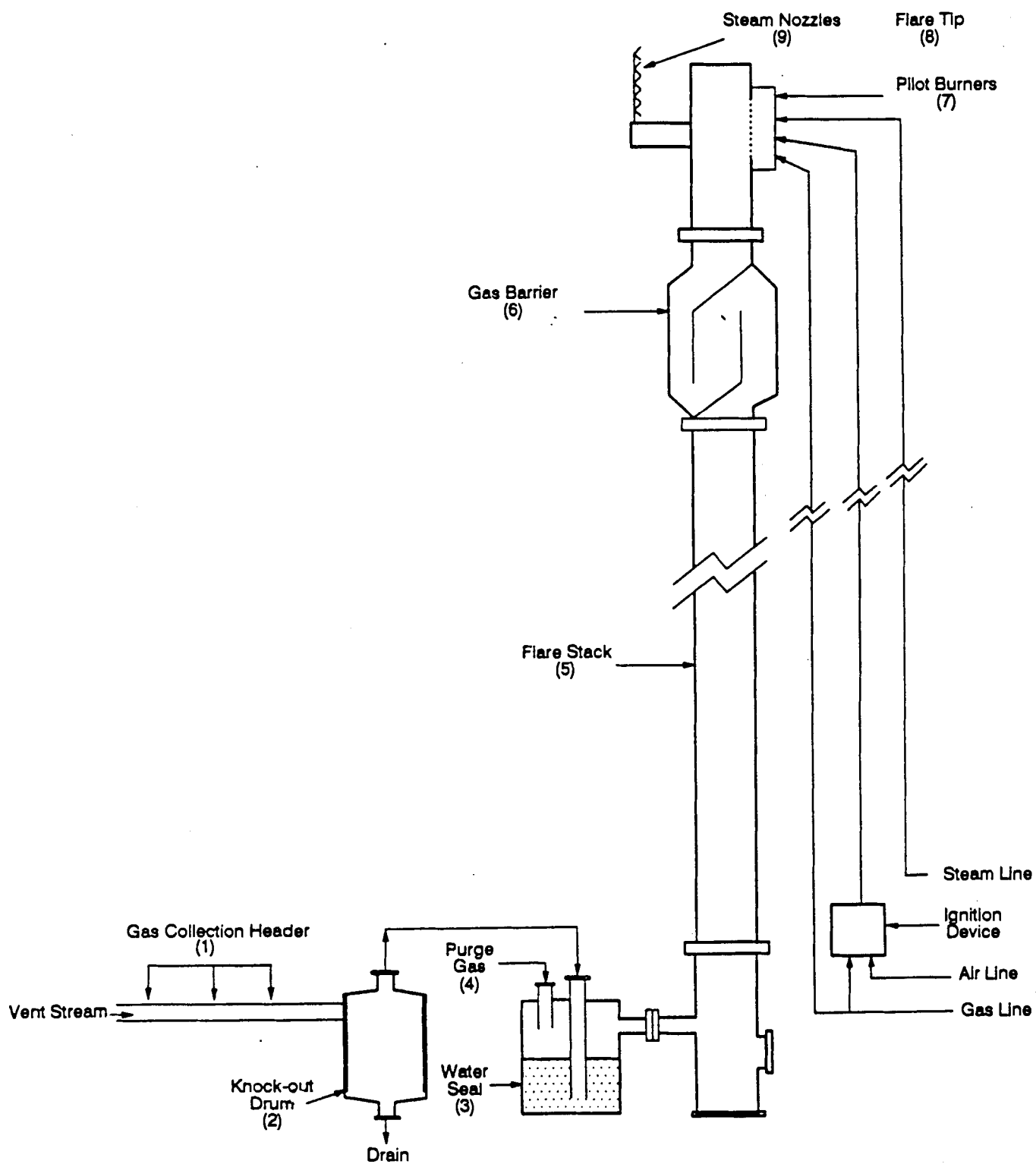
Figure 3-1.   Steam assisted elevated flare system.

residence time in the flame zone, it can be completely burned. A diffusion flame receives its combustion oxygen by diffusion of air into the flame from the surrounding atmosphere. The high volume of flue gas flow in a flare requires more combustion air at a faster rate than simple gas diffusion can supply. Thus, flare designers add high velocity steam injection nozzles (9) to increase gas turbulence in the flame boundary zones, thus drawing in more combustion air and improving combustion efficiency. This steam injection promotes smokeless flare operation by minimizing the cracking reaction that forms carbonaceous soot. Significant disadvantages of steam use are increased noise and cost. The steam requirement depends on the composition of the gas flared, the steam velocity from the injection nozzle, and the tip diameter. Although some gases can be flared smokelessly without any steam, typically 0.01 to 0.6 kilograms (kg) (0.02 to 1.33 pounds [lb]) of steam per kg of flare gas is required.

Steam injection is usually controlled manually by an operator who observes the flare (either directly or on a television monitor) and adds steam as required to maintain smokeless operation. Several flare manufacturers offer devices such as infrared sensors, which monitor flame characteristics and adjust the steam flow rate automatically to maintain smokeless operation.

Some elevated flares use forced air instead of steam to provide the combustion air and the mixing required for smokeless operation. These flares consist of two coaxial flow channels. The combustible gases flow in the center channel and the combustion air (provided by a fan in the bottom of the flare stack) flows in the annulus. The principal advantage of air-assisted flares is that they can be used where steam is not available. Air assist is rarely used on large flares because air flow is difficult to control when the gas flow is intermittent. About 67.7 kilowatts (90.8 horse power) of blower capacity is required for each 45.4 kilograms per hour (kg/hr) [100 pounds per hour (lb/hr)] of gas flared.[2]

Ground flares are usually enclosed and have multiple burner heads that are staged to operate based on the quantity of gas released to the flare. The energy of the gas itself (because of the high nozzle pressure

drop) is usually adequate to provide the mixing necessary for smokeless operation and air or steam assistance is not required. A fence or other enclosure reduces noise and light from the flare and provides some wind protection.

Ground flares are less numerous and have less capacity than elevated flares. Typically, they are used to burn gas continuously, while steam-assisted elevated flares are used to dispose of large amounts of gas released in emergencies.[3]

3.1.1.2 Factors Affecting Flare Efficiency.[4] Flare combustion efficiency is a function of many factors: (1) heating value of the gas, (2) density of the gas, (3) flammability of the gas, (4) auto-ignition temperature of the gas, and (5) mixing at the flare tip.

The flammability limits of the gases that are flared influence ignition stability and flame extinction. The flammability limits are defined as the stoichiometric composition limits (maximum and minimum) of an oxygen-fuel mixture that will burn indefinitely at given conditions of temperature and pressure without further ignition. In other words, gases must be within their flammability limits to burn. When flammability limits are narrow, the interior of the flame may have insufficient air for the mixture to burn. Fuels with wide limits of flammability (for instance, hydrogen) are, therefore, easier to combust.

The auto-ignition temperature of a fuel affects combustion because gas mixtures must be at high enough temperature and at the proper mixture strength to burn. A gas with a low auto-ignition temperature will ignite and burn more easily than a gas with a high auto-ignition temperature.

The heating value of the fuel also affects the flame stability, emissions, and flame structure. A lower heating value fuel produces a cooler flame that does not favor combustion kinetics and also is more easily extinguished. The lower flame temperature will also reduce buoyant forces, which reduces mixing.

The density of the gas flared also affects the structure and stability of the flame through the effect on buoyancy and mixing. By design, the velocity in many flares is very low; therefore, most of the flame structure is developed through buoyant forces as a result of combustion. Lighter gases, therefore, tend to burn better. In addition

3-5

to burner tip design, the density of the fuel also affects the minimum purge gas required to prevent flashback for smokeless flaring.

Poor mixing at the flare tip or poor flare maintenance can cause smoking (particulate). Fuels with high carbon to hydrogen ratios (greater than 0.35) have a greater tendency to smoke and require better mixing if they are to be burned smokelessly.

Many flare systems are currently operated in conjunction with baseload gas recovery systems. Such systems are used to recovery VOC's from the flare header system for reuse. Recovered VOC's may be used as a feedstock in other processes or as fuel in process heaters, boilers, or other combustion devices. When baseload gas recovery systems are applied, the flare is generally used to combust process upset and emergency gas releases that the baseload system is not designed to recover. In some cases, the operation of a baseload gas recovery system may offer an economic advantage over operation of a flare alone since sufficient quantities of useable VOC's can be recovered.

3.1.1.3 EPA Flare Specifications. The EPA has established flare combustion efficiency criteria in the Code of Federal Regulations (40 CFR 60.18) that specify that 98 percent combustion efficiency can be achieved provided that certain operating conditions are met: (1) the flare must be operated with no visible emissions and with a flame present; (2) the net heating value of the flared stream must be greater than 11.2 megajoules per standard cubic meter (MJ/scm) [300 British thermal units per standard cubic foot (Btu/scf)] for steam-assisted flares, and 7.45 MJ/scm (200 Btu/scf) for a flare without assist; and (3) steam assisted and nonassisted flares must have an exit velocity less than 18.3 meters per second (m/sec) [60 feet per second (ft/sec)]. Steam assisted and nonassisted flares having an exit velocity greater than 18.3 m/sec (60 ft/sec) but less than 122 m/sec (400 ft/sec) can achieve 98 percent control if the net heating value of the gas stream is greater than 37.3 MJ/scm (1,000 Btu/scf). Air-assisted flares, as well as steam-assisted and nonassisted flares with an exit velocity less than 122 m/sec (400 ft/sec) and a net heating value less than 37.3 MJ/scm (1,000 Btu/scf), can determine the allowable exit velocity by using an equation in 40 CFR 60.18.

3.1.1.4 <u>Applicability of Flares</u>. Most of the SOCMI plants are estimated to have a flare.[5] Flares are usually designed to control either the normal process vents or emergency upsets. The latter involves the release of large volumes of gases. Often, large diameter flares designed to handle emergency releases are used to control continuous vent streams from various process operations. In refineries, many process vents are usually combined in a common gas header that supplies fuel to boilers and process heaters. However, excess gases, fluctuations in flow in the gas line, and emergency releases are sometimes sent to a flare.

Flares have been found to be useful emission control devices. They can be used for almost any VOC stream, and can handle fluctuations in VOC concentration, flow rate, and inerts content. Some streams, such as those containing high concentrations of halogenated or sulfur-containing compounds, are not usually flared due to corrosion of the flare tip or formation of secondary pollutants (such as sulfur dioxide [SO_2]).

3.1.2 <u>Thermal Incinerators</u>

3.1.2.1 <u>Thermal Incinerator Process Description</u>. Any VOC heated to a high enough temperature in the presence of enough oxygen will be oxidized to CO_2 and water. This is the basic principle of operation of a thermal incinerator. The theoretical temperature required for thermal oxidation depends on the structure of the chemical involved. Some chemicals are oxidized at temperatures much lower than others. However, a temperature can be identified that will result in the efficient destruction of most VOC's. All practical thermal incineration processes are influenced by residence time, mixing, and temperature. An efficient thermal incinerator system must provide:

- A chamber temperature high enough to enable the oxidation reaction to proceed rapidly to completion;

- Enough turbulence to obtain good mixing between the hot combustion products from the burner, combustion air, and VOC; and

- Sufficient residence time at the chosen temperature for the oxidation reaction to reach completion.

A thermal incinerator is usually a refractory-lined chamber containing a burner (or set of burners) at one end. As shown in

Figure 3-2, discrete dual fuel burners (1) and inlets for the offgas (2) and combustion air (3) are arranged in a premixing chamber (4) to thoroughly mix the hot products from the burners with the process vent streams. The mixture of hot reacting gases then passes into the main combustion chamber (5). This chamber is sized to allow the mixture enough time at the elevated temperature for the oxidation reaction to reach completion (residence times of 0.3 to 1.0 second are common). Energy can then be recovered from the hot flue gases in a heat recovery section (6). Preheating combustion air or offgas is a common mode of energy recovery; however, it is sometimes more economical to generate steam. Insurance regulations require that if the waste stream is preheated, the VOC concentration must be maintained below 25 percent of the lower explosive limit to remove explosion hazards.

Thermal incinerators designed specifically for VOC incineration with natural gas as the auxiliary fuel may also use a grid-type (distributed) gas burner,[6] as shown in Figure 3-3. The tiny gas flame jets (1) on the grid surface (2) ignite the vapors as they pass through the grid. The grid acts as a baffle for mixing the gases entering the chamber (3). This arrangement ensures burning of all vapors at lower chamber temperature and uses less fuel. This system makes possible a shorter reaction chamber, yet maintains high efficiency.

Other parameters affecting incinerator performance are the vent stream heating value, the water content in the stream, and the amount of excess combustion air (i.e., the amount of air above the stoichiometric air needed for reaction). The vent stream heating value is a measure of the heat available from the combustion of the VOC in the vent stream. Combustion of the vent stream with a heating value less than 1.9 MJ/scm (50 Btu/scf) usually requires burning auxiliary fuel to maintain the desired combustion temperature. Auxiliary fuel requirements can be lessened or eliminated by the use of recuperative heat exchangers to preheat combustion air. Vent streams with a heating value above 1.9 MJ/scm (50 Btu/scf) may support combustion but may need auxiliary fuel for flame stability.

Other parameters affecting incinerator performance are the vent stream heating value, the water content in the stream, and the amount of
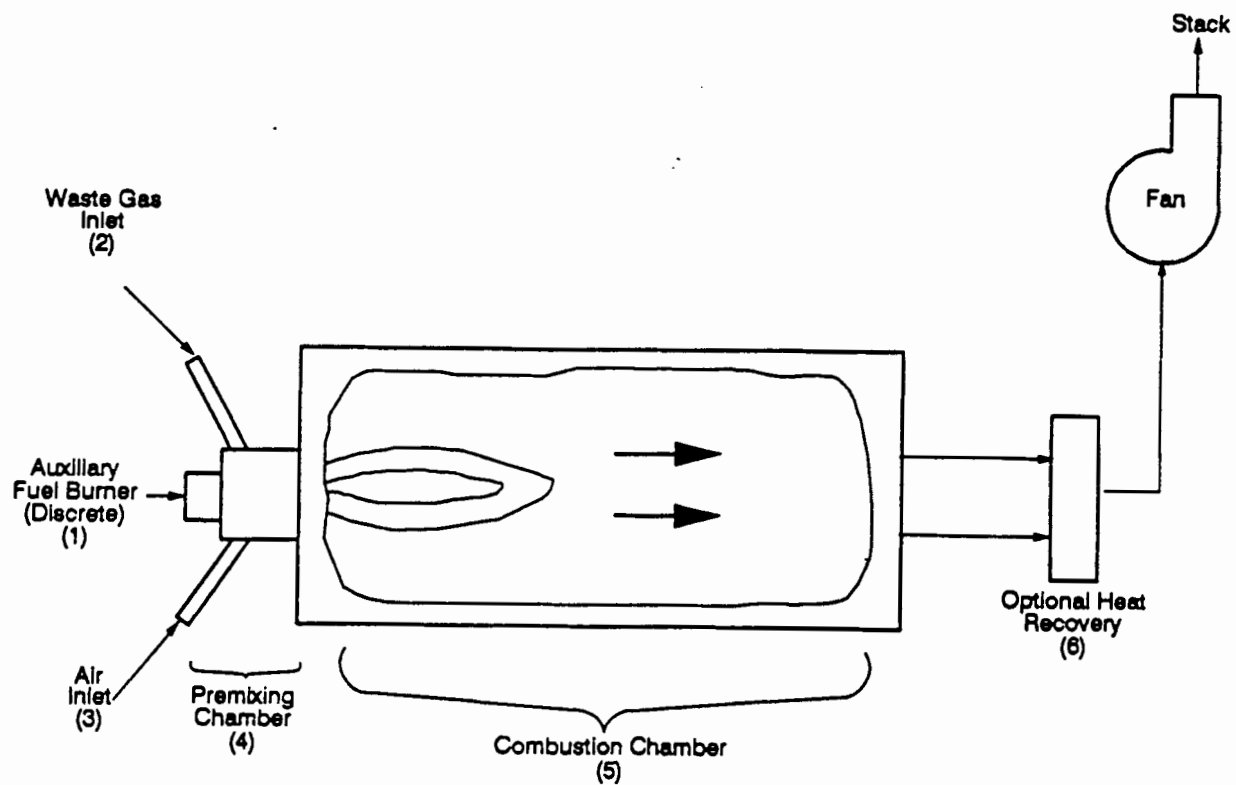
Figure 3-2. Discrete burner, thermal oxidizer.
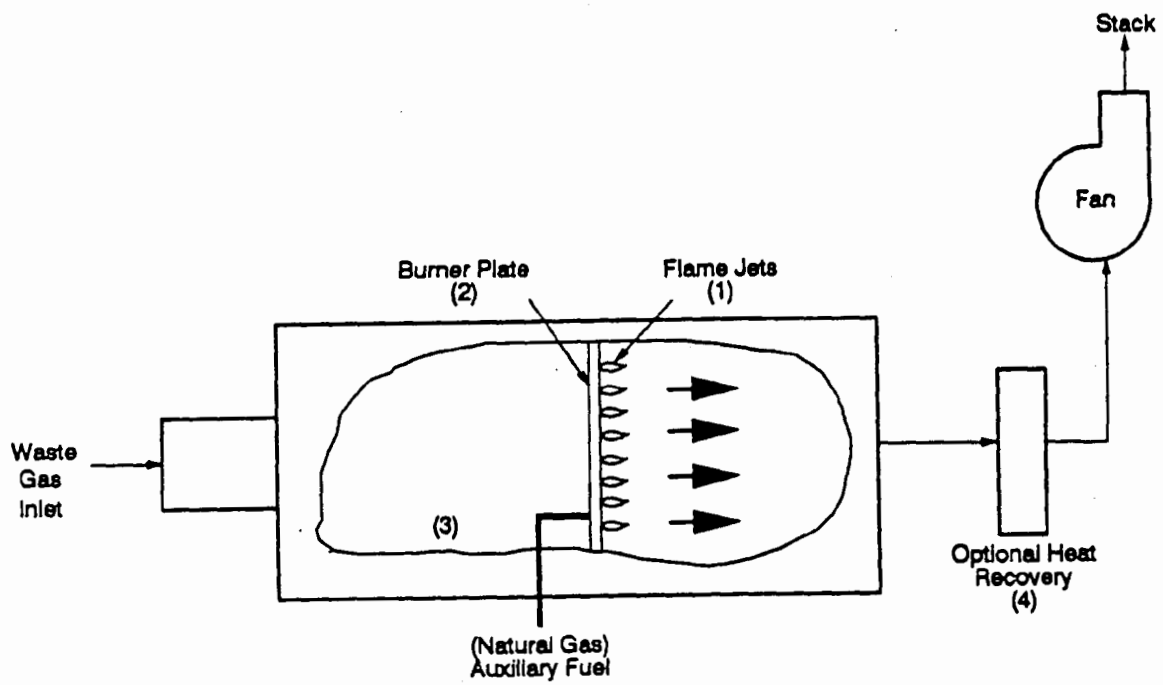
Figure 3-3. Distributed burner, thermal oxidizer.

excess combustion air (i.e., the amount of air above the stoichiometric air needed for reaction). The vent stream heating value is a measure of the heat available from the combustion of the VOC in the vent stream. Combustion of the vent stream with a heating value less than 1.9 MJ/scm (50 Btu/scf) usually requires burning auxiliary fuel to maintain the desired combustion temperature. Auxiliary fuel requirements can be lessened or eliminated by the use of recuperative heat exchangers to preheat combustion air. Vent streams with a heating value above 1.9 MJ/scm (50 Btu/scf) may support combustion but may need auxiliary fuel for flame stability.

A thermal incinerator, handling vent streams with varying heating values and moisture content, requires careful adjustment to maintain the proper chamber temperatures and operating efficiency. Since water requires a great deal of heat to vaporize, entrained water droplets in an offgas stream can increase auxiliary fuel requirements to provide the additional energy needed to vaporize the water and raise it to the combustion chamber temperature. Combustion devices are always operated with some quantity of excess air to ensure a sufficient supply of oxygen. The amount of excess air used varies with the fuel and burner type but should be kept as low as possible. Using too much excess air wastes fuel, because the additional air must be heated to the combustion chamber temperature. Large amounts of excess air also increases flue gas volume and may increase the size and cost of the system. Packaged, single-unit thermal incinerators can be built to control streams with flow rates in the range of 8.5 standard cubic meters per second (scm/sec) [300 standard cubic feet per minute (scfm)] to about 1,415 scm/sec (50,000 scfm).

Thermal oxidizers for halogenated VOC may require additional control equipment to remove the corrosive combustion products. The halogenated VOC streams are usually scrubbed to prevent corrosion due to contact with acid gases formed during the combustion of these streams. The flue gases are quenched to lower their temperature and are then routed through absorption equipment such as packed towers or liquid jet scrubbers to remove the corrosive gases.

3.1.2.2 Thermal Incinerator Efficiency. The VOC destruction efficiency of a thermal oxidizer can be affected by variations in chamber

temperature, residence time, inlet VOC concentration, compound type, and flow regime (mixing). Test results show that thermal oxidizers can achieve 98 percent destruction efficiency for most VOC's at combustion chamber temperatures ranging from 700 to 1,300 ^oC (1,300 to 2,370 ^oF) and residence times of 0.5 to 1.5 sec.[7] These data indicate that significant variations in destruction efficiency occurred for C_1 to C_5 alkanes and olefins, aromatics (benzene, toluene, and xylene), oxygenated compounds (methyl ethyl ketone and isopropanol), chlorinated organics (vinyl chloride), and nitrogen-containing species (acrylonitrile and ethylamines) at chamber temperatures below 760 ^oC (1,400 ^oF). This information, used in conjunction with kinetics calculations, indicates the combustion chamber parameters for achieving at least a 98-percent VOC destruction efficiency are a combustion temperature of 870 ^oC (1,600 ^oF) and a residence time of 0.75 sec (based upon residence in the chamber volume at combustion temperature). A thermal oxidizer designed to produce these conditions in the combustion chamber should be capable of high destruction efficiency for almost any nonhalogenated VOC.

At temperatures over 760 ^oC (1,400 ^oF), the oxidation reaction rates are much faster than the rate of gas diffusion mixing. The destruction efficiency of the VOC then becomes dependent upon the fluid mechanics within the oxidation chamber. The flow regime must ensure rapid, thorough mixing of the VOC stream, combustion air, and hot combustion products from the burner. This enables the VOC to attain the combustion temperature in the presence of enough oxygen for sufficient time so the oxidation reaction can reach completion.

Based on studies of thermal oxidizer efficiency, it has been concluded that 98 percent VOC destruction or a 20 parts per million volume (ppmv) compound exit concentration is achievable by all new incinerators. The maximum achievable VOC destruction efficiency decreases with decreasing inlet concentration because of the much slower combustion reaction rates at lower inlet VOC concentrations. Therefore, a VOC weight percentage reduction based on the mass rate of VOC exiting the control device versus the mass rate of VOC entering the device would be appropriate for vent streams with VOC concentrations above approximately 2,000 ppmv (corresponding to 1,000 ppmv VOC in the incinerator inlet

stream since air dilution is typically 1:1). For vent streams with VOC concentrations below approximately 2,000 ppmv, it has been determined that an incinerator outlet concentration of 20 ppmv (by compound), or lower, is achievable by all new thermal oxidizers.[8] The 98-percent efficiency estimate is predicated on thermal incinerators operated at 870 °C (1,600 °F) with 0.75 sec residence time.

3.1.2.3 <u>Applicability of Thermal Incinerators</u>. In terms of technical feasibility, thermal incinerators are applicable as a control device for most SOCMI vent streams. They can be used for vent streams with any VOC concentration and any type of VOC, and they can be designed to handle minor fluctuations in flows. However, excessive fluctuations in flow (i.e., process upsets) might not allow the use of incinerators and would require the use of a flare. Presence of elements such as halogens or sulfur might require some additional equipment, such as scrubbers for acid gas removal. Thermal incinerators are currently used to control VOC emissions from a number of process operations, including reactors and distillation operations.

3.1.3 <u>Industrial Boilers/Process Heaters</u>

Industrial boilers and process heaters can be designed to control VOC's by incorporating the reactor process or distillation vent stream with the inlet fuel or by feeding the stream into the boiler or heater through a separate burner. The major distinctions between industrial boilers and process heaters are that the former produces steam at high temperatures while the latter raises the temperature of process streams as well as superheating steam, typically at temperatures lower than with an industrial boiler. The process descriptions for an industrial boiler and a process heater are presented separately in the following two sections. The process descriptions focus on those aspects that relate to the use of these combustion devices as a VOC control method.

3.1.3.1 <u>Industrial Boiler/Process Description</u>. Surveys of industrial boilers show that the majority of industrial boilers used in the chemical industry are of watertube design. Furthermore, over half of these boilers use natural gas as a fuel.[9] In a water tube boiler, hot combustion gases contact the outside of heat transfer tubes, which contain hot water and steam. These tubes are interconnected by a set of drums

that collect and store the heated water and steam. The water tubes are of relatively small diameter, 5 centimeters (2.0 inches), providing rapid heat transfer, rapid response to steam demands, and relatively high thermal efficiency.[10] Energy transfer from the hot flue gases to water in the furnace water tube and drum system can be above 85 percent efficient. Additional energy can be recovered from the flue gas by preheating combustion air in an air preheater or by preheating incoming boiler feed water in an economizer unit.

When firing natural gas, forced or natural draft burners are used to thoroughly mix the incoming fuel and combustion air. If a SOCMI vent stream is combusted in a boiler, it can be mixed with the incoming fuel or fed to the furnace through a separate burner. In general, burner design depends on the characteristics of either the fuel mix (when the SOCMI vent stream and fuel are combined) or on the characteristics of the vent stream alone (when a separate burner is used). A particular burner design, commonly known as a high intensity or vortex burner, can be effective for vent streams with low heating values (i.e., streams where a conventional burner may not be applicable). Effective combustion of low heating value streams is accomplished in a high intensity burner by passing the combustion air through a series of spin vanes to generate a strong vortex.

Furnace residence time and temperature profiles vary for industrial boilers depending on the furnace and burner configuration, fuel type, heat input, and excess air level.[11] A mathematical model has been developed that estimates the furnace residence time and temperature profiles for a variety of industrial boilers.[12] This model predicts mean furnace residence times of from 0.25 to 0.83 second for natural gas-fired water tube boilers in the size range from 4.4 to 44 megawatts (MW) (15 to 150 x 10^{6} Btu/hr). Boilers at or above the 44 MW size have residence times and are generally operated at temperatures that ensure a 98-percent VOC destruction efficiency. Furnace exit temperatures for this range of boiler sizes are at or above 1,200 °C (2,200 °F) with peak furnace temperatures occurring in excess of 1,540 °C (2,810 °F).

3.1.3.2 <u>Process Heater Description</u>. A process heater is similar to an industrial boiler in that heat liberated by the combustion of fuels is transferred by radiation and convection to fluids contained in tubular

coils. Process heaters are used in chemical manufacturing to drive
endothermic reactions, such as natural gas reforming and thermal cracking.
They are also used as feed preheaters and as reboilers for some
distillation operations. The fuels used in process heaters include
natural gas, refinery offgases, and various grades of fuel oil. Gaseous
fuels account for about 90 percent of the energy consumed by process
heaters.[13]

There are many variations in the design of process heaters depending
on the application considered. In general, the radiant section consists
of the burner(s), the firebox, and a row of tubular coils containing the
process fluid. Most heaters also contain a convection section in which
heat is recovered from hot combustion gases by convective heat transfer to
the process fluid.

Process heater applications in the chemical industry can be broadly
classified with respect to firebox temperature: (1) low firebox
temperature applications, such as feed preheaters and reboilers;
(2) medium firebox temperature applications, such as stream superheaters;
and (3) high firebox temperature applications, such as pyrolysis furnaces
and steam-hydrocarbon reformers. Firebox temperatures within the chemical
industry can range from about 400 $^{\circ}$C (750 $^{\circ}$F) for preheaters and reboilers
to 1,260 $^{\circ}$C (2,300 $^{\circ}$F) for pyrolysis furnaces.

3.1.3.3 <u>Industrial Boilers and Process Heater Control Efficiency</u>. A
boiler or process heater furnace can be compared to an incinerator where
the average furnace temperature and residence time determines the
combustion efficiency. However, when a vent gas is injected as a fuel
into the flame zone of a boiler or process heater, the required residence
time is reduced due to the relatively high flame zone temperature. The
following test data, which document the destruction efficiencies for
industrial boilers and process heaters, are based on injecting the wastes
identified into the flame zone of each combustion control device.

A U. S. EPA-sponsored test was conducted to determine the destruction
efficiency of an industrial boiler for polychlorinated biphenyls
(PCB's).[14] The results of this test indicated that the PCB destruction

efficiency of an oil-fired industrial boiler firing PCB-spiked oil was greater than 99 percent for a temperature range of 1,361 to 1,520 °C (2,482 to 2,770 °F) and a range of residence time of 2 to 6 sec. This efficiency was determined based on the PCB content measured by a gas chromatograph in the fuel feed and flue gas.

As discussed in previous sections, firebox temperatures for process heaters show relatively wide variations depending on the application (see Section 3.1.3.2). Tests were conducted by the EPA to determine the benzene destruction efficiency of five process heaters firing a benzene offgas and natural gas mixture.[15-17] The units tested are representative of process heaters with low temperature fireboxes (reboilers) and medium temperature fireboxes (superheaters). Sampling problems occurred while testing one of these heaters, and, as a result, the data for that test may not be reliable and are not presented.[18] The reboiler and superheater units tested showed greater than a 98-percent overall destruction efficiency for C_1 to C_5 hydrocarbons.[19] Additional tests conducted on a second superheater and a hot oil heater showed that greater than 99 percent overall destruction of C_1 to C_5 hydrocarbons occurred for both units.[20]

3.1.3.4 <u>Applicability of Industrial Boilers and Process Heaters</u>. Industrial boilers and process heaters are currently used by industry to combust process vent streams from distillation operations, reactor operations, and general refinery operations. These devices are most applicable where high vent stream heat recovery potential exists.

Both boilers and process heaters are essential to the operation of a plant. As a result, only streams that are certain not to reduce the device's performance or reliability warrant use of a boiler or process heater as a combustion control device. Variations in vent stream flow rate and/or heating value could affect the heat output or flame stability of a boiler or process heater and should be considered when using these combustion devices. Performance or reliability may be affected by the presence of corrosive products in the vent stream. Because these compounds could corrode boiler or process heater materials, vent streams with a relatively high concentration of halogenated or sulfur-containing compounds are usually not combusted in boilers or process heaters. When

corrosive VOC's are combusted, the flue gas temperature must be maintained above the acid dew point to prevent acid deposition and subsequent corrosion from occurring.

The introduction of a vent stream into the furnace of a boiler or heater could alter the heat transfer characteristics of the furnace. Heat transfer characteristics are dependent on the flow rate, heating value, and elemental composition of the vent stream, and the size and type of heat generating unit being used. Often, there is no significant alteration of the heat transfer, and the organic content of the process vent stream can, in some cases, reduce the amount of fuel required to produce the desired heat. In other cases, the change in heat transfer characteristics after introduction of a vent stream may affect the performance of the heat-generating unit, and increase fuel requirements. For some vent streams, there may be potential safety problems associated with ducting reactor process or distillation vents to a boiler or process heater. Variation in the flow rate and organic content of the vent stream could, in some cases, lead to explosive mixtures within a boiler furnace. Flame fluttering within the furnace could also result from variations in the process vent stream characteristics. Precautionary measures should be considered in these situations.

When a boiler or process heater is applicable and available, they are excellent control devices providing at least 98 percent destruction of VOC's. In addition, near complete recovery of the vent stream heat content is possible. However, both devices must operate continuously and concurrently with the pollution source unless an alternate control strategy is available in the event that the heat generating capacity of either unit is not required and is shut down.

3.1.4 Catalytic Oxidizers

3.1.4.1 Catalytic Oxidation Process Description. Catalytic oxidation is the fourth major combustion technique examined for VOC emission control. A catalyst increases the rate of chemical reaction without becoming permanently altered itself. Catalysts for catalytic oxidation cause the oxidizing reaction to proceed at a lower temperature than is required for thermal oxidation. These units can also operate well at VOC concentrations below the lower explosive limit, which is a distinct

3-17

advantage for some process vent streams. Combustion catalysts include paladium and platinum group metals, magnesium oxide, copper oxide, chromium, and cobalt.[21] These are deposited in thin layers on inert substrates to provide for maximum surface area between the catalyst and the VOC stream. The substrate may be either pelletized or cast in a rigid honeycomb matrix.

A schematic of a catalytic oxidation unit is shown in Figure 3-4. The waste gas (1) is introduced into a mixing chamber (2), where it is heated to about 316 °C (600 °F) by contact with the hot combustion products from auxiliary burners (3). The heated mixture is then passed through the catalyst bed (4). Oxygen and VOC's migrate to the catalyst surface by gas diffusion and are adsorbed in the pores of the catalyst. The oxidation reaction takes place at these active sites. Reaction products are desorbed from the active sites and transferred by diffusion back into the waste gas.[22] The combusted gas may then be passed through a waste heat recovery device (5) before exhausting into the atmosphere.

The operating temperatures of combustion catalysts usually range from 260 to 427 °C (500 to 800 °F). Lower temperatures may slow down and possibly stop the oxidation reaction. Temperatures greater than 732 °C (1,350 °F) may result in shortened catalyst life and possible deterioration of the catalyst. Any accumulation of particulate matter, condensed VOC, or polymerized hydrocarbons on the catalyst could block the active sites and, therefore, reduce effectiveness. Some catalysts can also be deactivated by compounds containing sulfur, bismuth, phosphorous, arsenic, antimony, mercury, lead, zinc, tin, or halogens.[23] If the catalyst is exposed to any of these compounds, VOC's will pass through unreacted or be partially oxidized to form compounds such as aldehydes, ketones, and organic acids. Catalysts are now being marketed that are resistant to various poisons, specifically sulfur and halogenated compounds. Other designs incorporate a sacrificial bed to protect the catalyst. Materials accumulated on the catalyst can be removed by physical or chemical means, thus restoring the catalyst activity to its original (fresh) level. Condensed organics accumulated on the catalyst can be removed with thermal treatment.
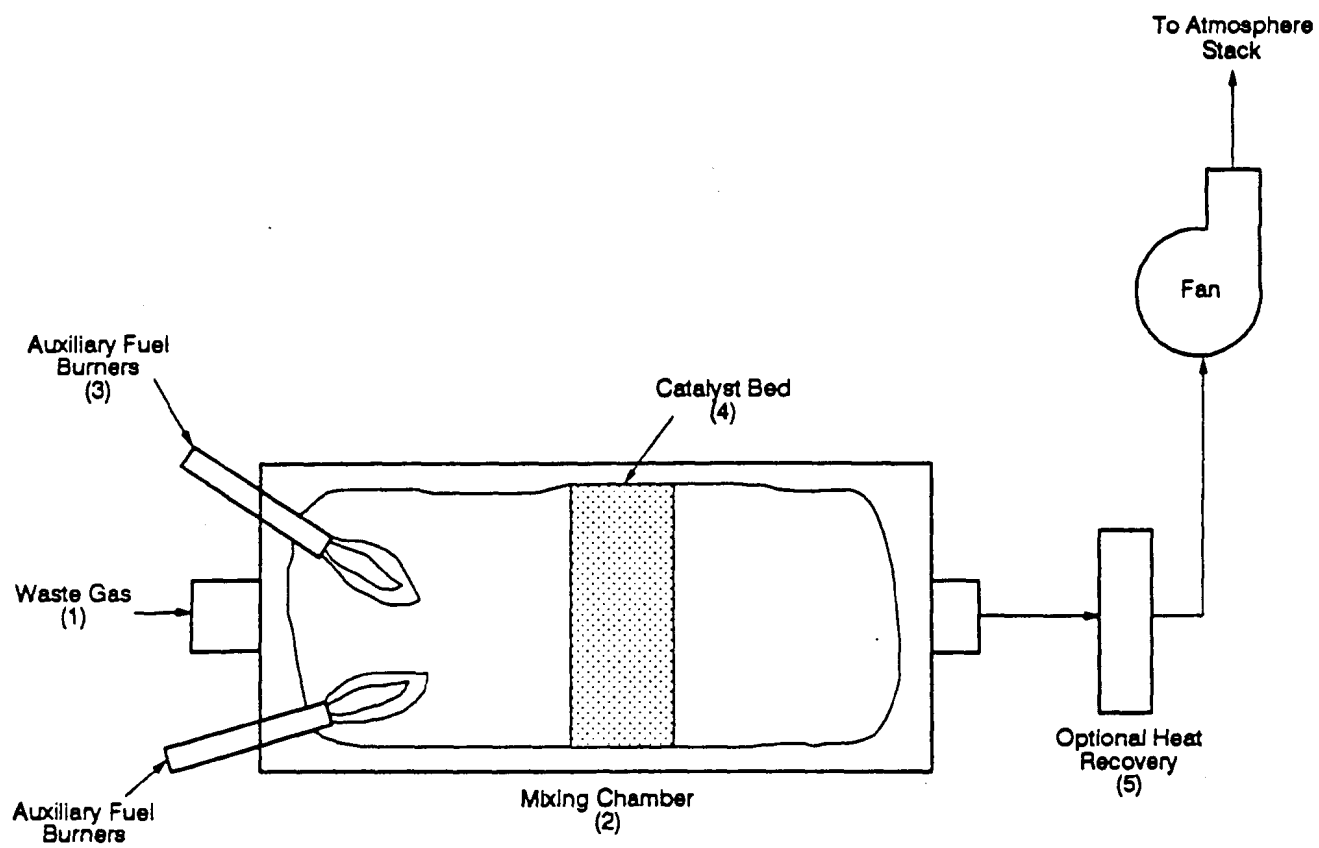
Figure 3-4. Catalytic oxidizer.

3-19

3.1.4.2 <u>Catalytic Oxidizer Control Efficiency</u>. Catalytic oxidizer destruction efficiency is dependent on the space velocity (i.e, the catalyst volume required per unit volume gas processed per hour), operating temperature, oxygen concentration, and waste gas VOC composition and concentration. A catalytic unit operating at about 450 °C (840 °F) with a catalyst bed volume of 0.014 to 0.057 cubic meters (0.5 to 2 cubic feet) per 0.47 scm/sec (1,000 scfm) of vent stream passing through the device can achieve 95 percent VOC destruction efficiency. However, catalytic oxidizers have been reported to achieve efficiencies of 99 percent or greater.[24] These higher efficiencies are usually obtained by increasing the catalyst bed volume-to-vent stream flow ratio.

3.1.4.3 <u>Applicability of Catalytic Oxidizers</u>. Catalytic oxidation has been successfully applied to a variety of SOCMI processes.[25] It is basically a chemical process that operates at a lower temperature than thermal oxidation, thereby reducing fuel consumption. In addition, catalytic oxidation produces smaller amounts of secondary air emissions such as nitrous oxides and carbon dioxide than thermal incinerators. High destruction efficiencies have been achieved through catalytic oxidation, partly because the SOCMI exhausts are generally very clean and suitable for this technology. The SOCMI industry has been accustomed to using a variety of process catalysts and is skilled in understanding and maintaining catalytic systems at maximum performance.

Periodic replacement of catalyst is required at intervals of 2 to 5 years due to thermal aging, masking, and poisoning processes. Thermal aging is caused by high temperatures damaging the active metal, sintering, or crystallizing the surface area. This results in permanent loss of surface area. Masking occurs when there is a loss of active sites due to a buildup of dust, carbons, or resins, which plug the catalyst's pores. This process is reversible; the catalyst can be cleaned off periodically with a caustic solution and restored. Poisoning occurs when an active site is taken up by contaminants and usually results in permanent loss of catalyst. Because of the sensitivity of catalytic oxidizers to VOC inlet stream flow conditions, the applicability of catalytic units for control of VOC's in the SOCMI industry is limited, particularly for halogenated streams.

3.2 RECOVERY DEVICES

The recovery devices discussed in this section include adsorbers, absorbers, and condensers. These devices are generally applied to recover reactant, product, or by-product VOC's from a vent stream for use as a product or to recycle a compound. The chemical structure of the VOC removed is usually unaltered.

3.2.1 Adsorption

3.2.1.1 Adsorption Process Description. Adsorption is a mass-transfer operation involving interaction between gaseous- and solid-phase components. The gas phase (adsorbate) is captured on the solid-phase (adsorbent) surface by physical or chemical adsorption mechanisms. Physical adsorption is a mechanism that takes place when intermolecular (van der Waals) forces attract and hold the gas molecules to the solid surface.[26] Chemisorption occurs when a chemical bond forms between the gaseous- and solid phase molecules. A physically adsorbed molecule can readily be removed from the adsorbent (under suitable temperature and pressure conditions), while the removal of a chemisorbed component is much more difficult.

The most commonly encountered industrial adsorption systems use activated carbon as the adsorbent. Activated carbon is effective in capturing certain organic vapors by the physical adsorption mechanism. In addition, the vapors may be released for recovery by regeneration of the adsorption bed with steam or nitrogen. Oxygenated adsorbents, such as silica gels, diatomaceous earth, alumina, or synthetic zeolites, exhibit a greater selectivity than activated carbon for capturing water vapor rather than organic gases. Thus, these adsorbents would be of little use for the high moisture gas streams characteristic of some SOCMI vents.[27]

The design of a carbon adsorption system depends on the chemical characteristics of the VOC's being recovered, the physical properties of the offgas stream (i.e., temperature, pressure, and volumetric flow rate), and the physical properties of the adsorbent. The mass quantity of VOC's that adhere to the adsorbent surface is directly proportional to the difference in VOC concentration between the gas-phase and the solid surface. In addition, the quantity of VOC's adsorbed is dependent on the adsorbent bed volume, the surface area of adsorbent available to capture

VOC's, and the rate of diffusion of VOC's through the gas film at the gas- and solid-phase interface. Physical adsorption is an exothermic operation that is most efficient within a narrow range of temperature and pressure.

A schematic diagram of a typical fixed bed, regenerative carbon adsorption systems is given in Figure 3-5. The process offgases are generally filtered and cooled (1) before entering the carbon bed. The inlet gases to an adsorption unit are filtered to prevent bed contamination. The gas is cooled to maintain the bed at optimum operating temperature and to prevent fires or polymerization of the hydrocarbons. Vapors entering the adsorber stage of the system (2) are passed through the porous activated carbon bed.

Adsorption of inlet vapors usually occurs until the outlet VOC concentration reaches some preset level (the "breakthrough" concentration). The dynamics of the process may be illustrated by viewing the carbon bed as a series of layers or mass-transfer zones (3a, b, c). Gases entering the bed are adsorbed first in zone (a). Because most of the VOC is adsorbed in zone (a), very little adsorption takes place in zones (b) and (c). Adsorption in zone (b) increases as zone (a) reaches equilibrium with organics and proceeds through zone (c). When the bed is completely saturated (breakthrough), the incoming VOC-laden offgases are routed to an alternate bed, while the saturated carbon bed is regenerated.

Regeneration of the carbon bed is accomplished by heating the bed or applying vacuum to draw off the adsorbed gases. Low pressure steam (4) is frequently used as a heat source to strip the adsorbent of organic vapor. After steaming, the carbon bed is cooled and dried typically by blowing air through it with a fan; the steam-laden vapors are routed to a condenser (5) and on to a solvent recovery system (6). The regenerated bed is put back into active service, while the saturated bed is purged of organics. The regeneration process may be repeated numerous times, but eventually the carbon must be replaced.

3.2.1.2 <u>Adsorption Control Efficiency</u>. Many modern, well-designed systems achieve 95 percent removal efficiency for some chemicals.[28] The VOC removal efficiency of an adsorption unit is dependent upon the physical properties of the compounds present in the offgas, the gas stream
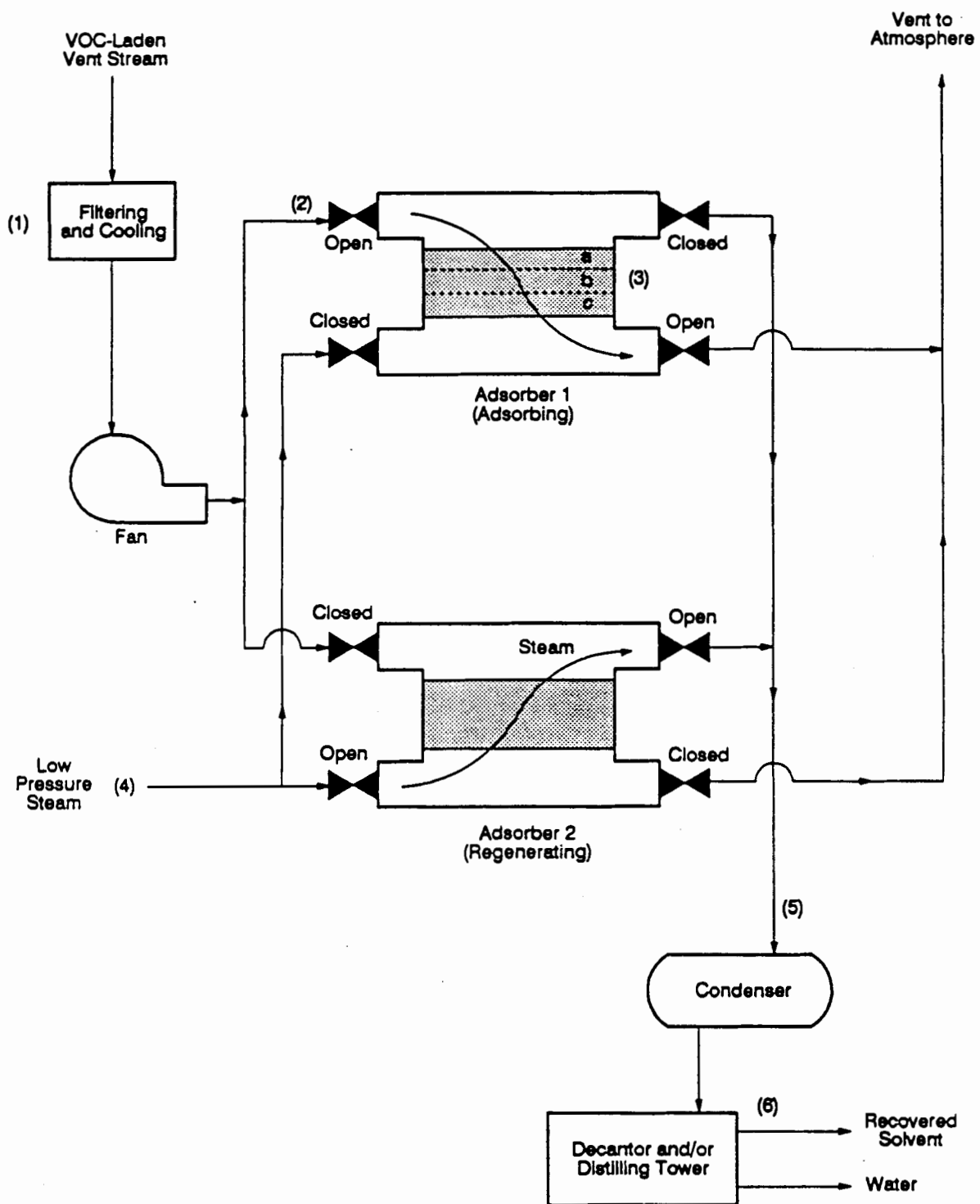
Figure 3-5. Two stage regenerative adsorption system.

characteristics, the physical properties of the adsorbent, and the condition of the regenerated carbon bed.

Gas temperature, pressure, and velocity are important in determining adsorption unit efficiency. The adsorption rate in the bed decreases sharply when gas temperatures are above 38 °C (100 °F).[29,30] High temperature increases the kinetic energy of the gas molecules, causing them to overcome van der Waals forces. Under these conditions, the VOC's are not retained on the surface of the carbon. Increasing vent stream pressure and temperature generally will improve VOC capture efficiency; however, care must be taken to prevent solvent condensation and possible fire.

3.2.1.3 <u>Applicability of Adsorption</u>. Although carbon adsorption is an excellent method for recovering some valuable process chemicals, it cannot be used as a universal control method for distillation or reactor process vent streams. The conditions where carbon adsorption is not recommended are present in many SOCMI vent streams. These include streams with: (1) high VOC concentrations, (2) very high or low molecular weight compounds, and (3) mixtures of high and low boiling point VOC's.

The range of organic concentrations to which carbon adsorption safely can be applied is from only a few parts per million to concentrations of several percent.[31] Adsorbing vent streams with high organic concentration may result in excessive temperature rise in the carbon bed due to the accumulated heat of adsorption of the VOC loading. However, streams with high organic concentrations can be diluted with air or inert gases to make a workable adsorption system.

The molecular weight of the compounds to be adsorbed should be in the range of 45 to 130 grams per gram-mole (gm/gm-mole) (45 to 130 pounds per pound-mole [lb/lb-mole]) for effective adsorption. Carbon adsorption may not be the most effective application for compounds with low molecular weights (below 45 gm/gm-mole [45 lb/lb-mole]) due to their smaller attractive forces, or for high molecular weight components (above 130 gm/gm-mole [130 lb/lb-mole]), which attach so strongly to the carbon bed that they are not easily removed.[32]

Properly operated adsorption systems can be very effective for homogenous offgas streams but can have problems with a multicomponent

system containing a mixture of light and heavy hydrocarbons. The lighter organics tend to be displaced by the heavier (higher boiling) components, greatly reducing system efficiency.[33]

3.2.2 Absorption

3.2.2.1 Absorption Process Description. The mechanism of absorption consists of the selective transfer of one or more components of a gas mixture into a solvent liquid. The transfer consists of solute diffusion and dissolution into a solvent. For any given solvent, solute, and set of operating conditions, there exists an equilibrium ratio of solute concentration in the gas mixture to solute concentration in the solvent. The driving force for mass transfer at a given point in an operating absorption tower is related to the difference between the actual concentration ratio and the equilibrium ratio.[34] Absorption may only entail the dissolution of the gas component into the solvent or may also involve chemical reaction of the solute with constituents of the solution.[35] The absorbing liquids (solvents) used are chosen for high solute (VOC) solubility and include liquids such as water, mineral oils, nonvolatile hydrocarbon oils, and aqueous solutions of oxidizing agents (e.g., sodium carbonate and sodium hydroxide).[36]

Devices based on absorption principles include spray towers, venturi and wet impingement scrubbers, packed columns, and plate columns. Spray towers require high atomization pressure to obtain droplets ranging in size from 500 to 100 micrometers (μm) (0.019 to 0.004 in.) in order to present a sufficiently large surface contact area.[37] Although they can remove particulate matter effectively, spray towers have the least effective mass transfer capability and, thus, are restricted to particulate removal and control of high-solubility gases such as sulfur dioxide and ammonia.[38] Venturi scrubbers have a high degree of gas-liquid mixing and high particulate removal efficiency but also require high pressure and have relatively short contact times. Therefore, their use is also restricted to high-solubility gases.[39] As a result, VOC control by gas absorption is generally accomplished in packed or plate columns.

Packed columns are mostly used for handling corrosive materials, liquids with foaming or plugging tendencies, or where excessive pressure drops would result from use of plate columns. They are less expensive

3-25

than plate columns for small-scale or pilot plant operations where the column diameter is less than 0.6 m (2 ft). Plate columns are preferred for large-scale operations, where internal cooling is desired or where low liquid flow rates would inadequately wet the packing.[40]

A schematic of a packed tower is shown in Figure 3-6. The gas to be absorbed is introduced near the bottom of the tower (1) and allowed to rise through the packing material (2). Solvent flows in from the top of the column, countercurrent to the vapors (3), absorbing the solute from the gas-phase and carrying the dissolved solute out of the tower (4). Cleaned gas exits at the top (5) for release to the atmosphere or for further treatment as necessary. The solute-rich liquid is generally sent to a stripping unit where the absorbed VOC's are recovered. Following the stripping operation, the absorbing solution is either recycled back to the absorber or sent to a water treatment facility for disposal.

The major tower design parameters to be determined for absorbing any substance are column diameter and height, system pressure drop, and liquid flow rate required. These parameters are derived by considering the waste gas solubility, viscosity, density, and concentration, all of which depend on column temperature; and also the total surface area provided by the tower packing material, and the quantity of gases to be treated.

3.2.2.2 Absorption Control Efficiency. The VOC removal efficiency of an absorption device is dependent on the solvent selected, and on proper design and operation. For a given solvent and solute, an increase in absorber size or a decrease in the operating temperature can increase the VOC removal efficiency of the system. It may be possible in some cases to increase VOC removal efficiency by a change in the absorbent.

Systems that use organic liquids as solvents usually include the stripping and recycling of the solvent to the absorber. In this case, the VOC removal efficiency of the adsorber is dependent on the solvent's stripping efficiency.

3.2.2.3 Applicability of Absorption. Absorption is an attractive control option if a significant amount of VOC's can be recovered for reuse. Although absorption is applicable for many SOCMI vent streams, it cannot be universally applied. It is usually not considered when the VOC concentration is below 200 to 300 ppmv.[41]
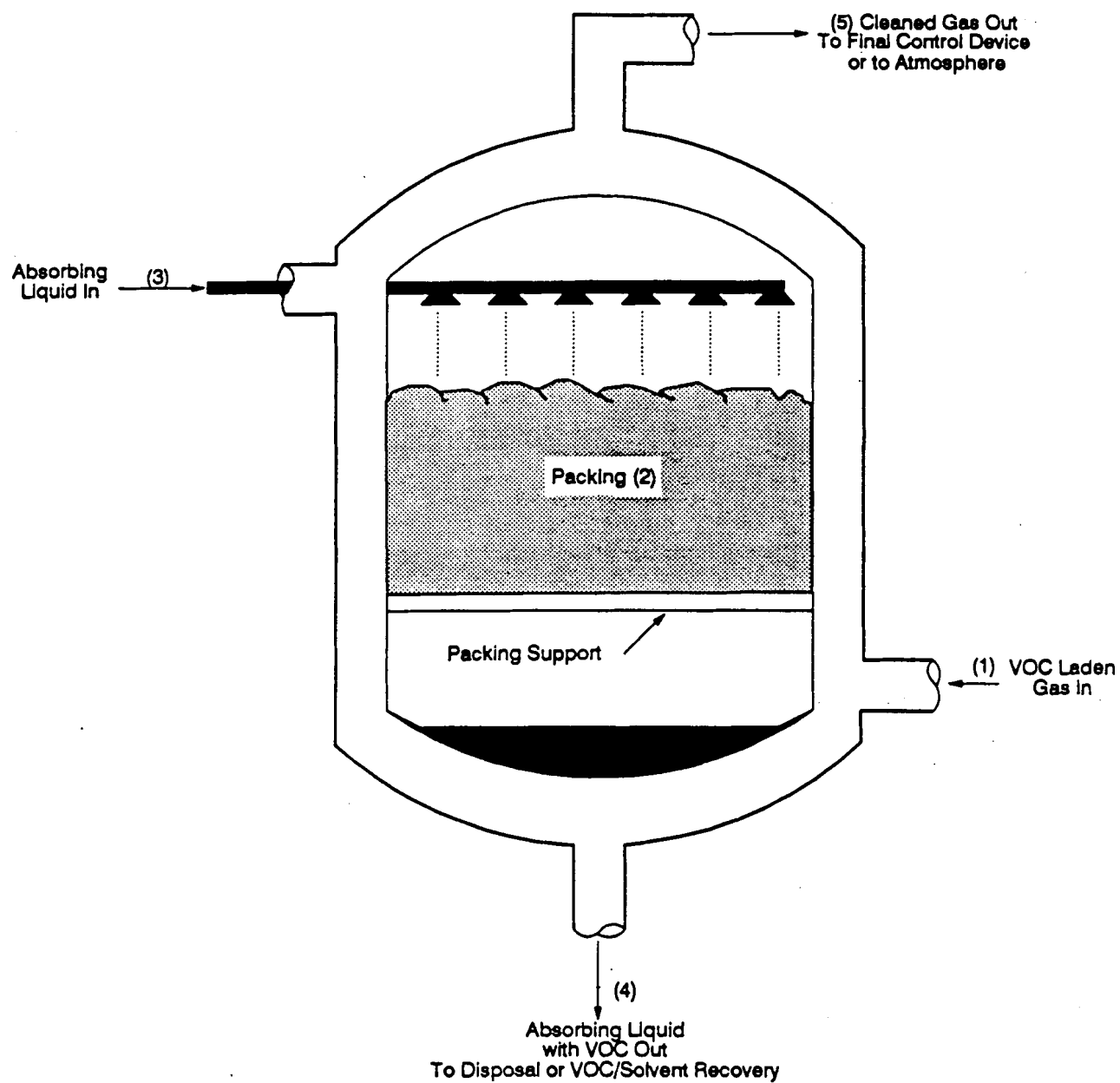
Figure 3-6.   Packed tower for gas absorption.

3.2.3 Condensation

3.2.3.1 Condensation Process Description. Condensation is a process of converting all or part of the condensable components of a vapor phase into a liquid phase. This is achieved by the transfer of heat from the vapor phase to a cooling medium. If only a part of the vapor phase is condensed, the newly formed liquid phase and the remaining vapor phase will be in equilibrium. In this case, equilibrium relationships at the operating temperatures must be considered. The heat removed from the vapor phase should be sufficient to lower the vapor-phase temperature to at or below its dew point temperature (i.e, temperature at which first drop of liquid is formed).

Condensation devices are of two types: surface condensers and contact condensers.[42] Surface condensers are typically shell-and-tube type heat exchangers. The coolant and the vapor phases are separated by the tube wall, and they never come in direct contact with each other. As the coolant passes through the tubes, the VOC vapors condense outside the tubes and are recovered. Surface condensers require more auxiliary equipment for operation but can recover valuable VOC's without contamination by the coolant, thus minimizing waste disposal problems. Only surface condensers are considered in the discussion of control efficiency and applicability since they are used more frequently in the chemical industry.

The major equipment components used in a typical surface condenser system for VOC removal are shown in Figure 3-7. This system includes a dehumidifier (1), surface condenser exchanger (2), refrigeration unit (3), and VOC storage tanks and operation pumps (4). Most surface condensers use a shell-and-tube type heat exchanger to remove heat from the vapor.[43] The coolant selected depends upon the saturation temperature of the VOC stream. Chilled water can be used down to 7 °C (45 °F), brines to -34 °C (-30 °F), and chlorofluorocarbons below -34 °C (-30 °F).[44] Temperatures as low as -62 °C (-80 °F) may be necessary to condense some VOC streams.[45]

3.2.3.2 Condenser Control Efficiency. The VOC removal efficiency of a condenser is dependent upon the type of vapor stream entering the condenser, and on condenser operating parameters. Efficiencies of condensers usually vary from 50 to 95 percent,[46] with higher efficiencies

VOC Laden
Gas

Dehumidification
Unit
To Remove Water
and
Prevent Freezing
In Main Condenser — (1)

Cleaned Gas Out
To Primary Control Flare,
Afterburner, Etc.

Main Condenser — (2)

Coolant
Return

Coolant

Condensed
VOC

Refrigeration
Unit — (3)

Storage Tanks — (4)

To Process
Or Disposal
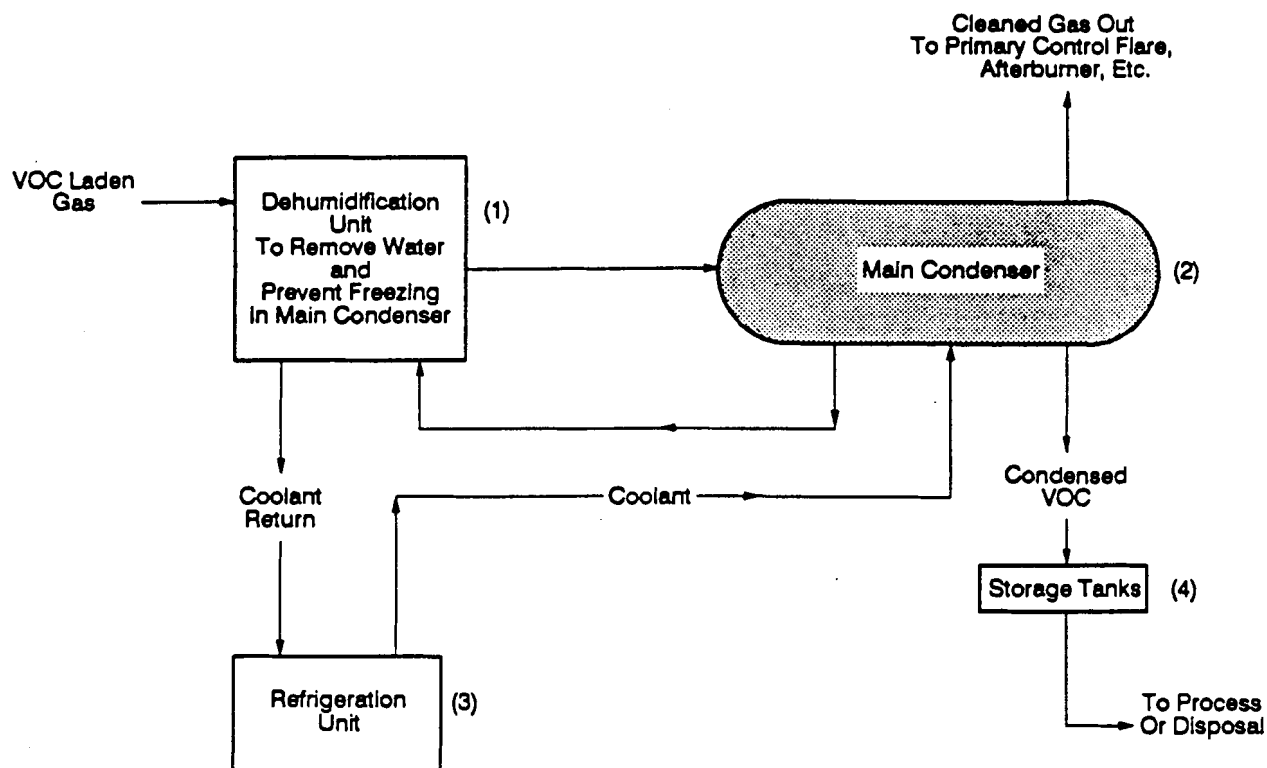
Figure 3-7. Condensation system.

expected for streams with low flow rates (less than 2,000 cubic feet per minute) and high VOC concentrations (greater than 5,000 ppmv).

3.2.3.3 <u>Applicability of Condensers</u>. A primary condenser system is usually an integral part of most distillation operations. Primary condensers are needed to provide reflux in fractionating columns and to recover distilled products. At times additional (secondary) condensers are used to recover more VOC's from the vent stream exiting the primary condenser. Condensers are sometimes present as accessories to vacuum generating devices (e.g., barometric condensers). Condensers are also commonly used product recovery devices on reactor process vent streams.

The use of a secondary condenser to control VOC emissions may not be applicable to some vent streams. Secondary condensers used as supplemental product recovery devices are not well suited for vent streams containing VOC's with low boiling points or for vent streams containing large quantities of inerts such carbon dioxide, air, and nitrogen. Low boiling point VOC's and inerts contribute significantly to the heat load that must be removed from the vent stream, resulting in costly design specifications and/or operating costs. In addition, some low boiling point VOC's cannot be condensed at normal operating temperatures. For example, process units producing chlorinated methanes have vent streams with substantial amounts of methane, methyl chloride, and methylene chloride. These compounds are not readily condensed and, as a result, are usually vented to the atmosphere or destroyed in a combustion device. However, some difficult-to-condense vapors can be compressed upstream of the condenser, thereby making them easier to recover in the condenser.

3.3 SUMMARY

The two general classifications of VOC control techniques discussed in the preceding sections are combustion and noncombustion control devices. This section summarizes the major points regarding control device applicability and performance.

The combustion control devices considered were flares, industrial boilers, process heaters, thermal incinerators, and catalytic oxidizers. With the exception of catalytic units, these devices are applicable to a wide variety of process vent stream characteristics and can achieve at least 98-percent destruction efficiency. Combustion devices are generally

capable of adapting to moderate changes in process vent stream flow rate and VOC concentration, while control efficiency is not greatly affected by the type of VOC's present. This is generally not the case with noncombustion control devices. In general, combustion control devices may require additional fuel, except in some cases where boilers or process heaters are applied and the energy content of the vent stream is recovered. Since boilers and process heaters are important in the operation of a chemical plant, only process vent streams that will not reduce boiler or process heater performance and reliability warrant use of these systems. Application of a scrubber prior to atmospheric discharge may be required when process vent streams containing high concentrations of halogenated or sulfonated compounds are combusted in an enclosed combustion device. The presence of high concentrations of corrosive halogenated or sulfonated compounds may preclude the use of flares because of possible flare tip corrosion and may preclude the use of boilers and process heaters because of potential internal boiler corrosion.[47] The presence of a halogen acid, such as hydrogen chloride, in the atmosphere may cause adverse health effects and equipment corrosion.

The noncombustion control devices discussed include adsorbers, absorbers, and condensers. In general, although noncombustion devices are widely applied in the industry, no one device is universally applicable to SOCMI vent streams because of the many restrictions applying these devices across a broad category of reactor process and distillation operation vent streams. For example, adsorbers may not always be applicable to vent streams with: (1) high VOC concentrations, (2) low molecular weight, and (3) mixtures of low and high molecular weight compounds. These conditions exist in many reactor process vent streams. Absorbers are generally not applied to streams with VOC concentrations below 200 to 300 ppmv, while condensers are not well suited for application to vent streams containing low boiling point VOC's or to vent stream with large inert concentrations. Even though these restrictions exist, many condensers and absorbers are applied to distillation and reactor process vent streams in the SOCMI to recover VOC's. Control efficiencies for the noncombustion devices considered vary from 50 to 95 percent for condensers and absorbers and up to 95 percent for adsorbers.

3.4 REFERENCES

1. Blackburn, J. W., et al. (IT Enviroscience, Inc.). Organic Chemical Manufacturing Series Volume 4: Combustion Control Devices. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-80-026. December 1980. 67 pp.

2. Klett, M. G. and J. B. Galeski (Lockheed Missiles and Space Co., Inc.). Flare Systems Study. Prepared for U. S. Environmental Protection Agency. Huntsville, AL. Publication No. EPA-600/2-76-079. March 1976. pp. ia, 22, 27, and 71 through 75.

3. D. Joseph, et al. (Energy and Environmental Research Corporation). Evaluation of the Efficiency of Industrial Flares: Background- Experimental Design-Facility. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-600/2-83-070. August 1983. Abstract page only.

4. Ref. 1.

5. Letter from Matey, J. S., Chemical Manufacturers Association, to Beck, D., U. S. Environmental Protection Agency. 14 pp. November 25, 1981.

6. North American Manufacturing Company. North American Combustion Handbook, Second Edition. Cleveland, Ohio. 1979. p. 269.

7. Memorandum and attachments from Farmer, J. R., EPA/ESD to Distribution. 30 pp. August 22, 1980. Thermal incinerators and flares.

8. Ref. 7.

9. Devitt, T., et al. (PEDCo Environmental, Inc.). Population and Characteristics of Industrial Boilers in the U.S. Prepared for the U. S. Environmental Protection Agency, Washington, D.C. Publication No. EPA-600/7-79-178a. August. 1979.

10. Fossil Fuel Fired Industrial Boilers - Background Information Document, Volume 1: Chapters 1 - 9. Draft EIS. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-82-006a. March 1982. p. 3-27 and technical report data sheet.

11. C. Castaldini, et al. (Acurex Corporation). A Technical Overview of the Concept of Disposing of Hazardous Wastes in Industrial Boilers. Prepared for the U. S. Environmental Protection Agency. Cincinnati, Ohio. EPA Contract No. 68-03-2567. October 1981. pp. 44 and 73.

12. Ref. 11, p. 73.

13. Hunter, S. C. and S. C. Cherry (KVB.) NO_x Emissions from Petroleum Industry Operations. Washington, D.C. API Publication No. 4311. October 1979. p. 83.

14. J. Hall, et al. (GCA Technology Division). Evaluation of PCB Destruction Efficiency in an Industrial Boiler. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-600/2-81-055a. April 1981. pp. 4 through 10, 117 through 128, and 161.

15. M. W. Hartman and C. W. Stackhouse (TRW Environmental Engineering Division). Benzene--Organic Chemical Manufacturing Emission Test Report, Ethylbenzene/Styrene, Amoco Chemicals Company, Texas City, Texas. Prepared for U. S. Environmental Protection Agency. Research Triangle Park, N.C. EMB Report No. 79-OCM-13. August 1979.

16. W. Kelly (TRW Environmental Engineering Division). Benzene Organic Chemical Manufacturing Ethylbenzene/Styrene Test Report, El Paso Products Company, Odessa, Texas. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. EMB Report No. 79-OCM-15. April 1981.

17. W. Kelly (TRW Environmental Engineering Division). Benzene--Organic Chemical Manufacturing Ethylbenzene/Styrene Emission Test Report, USS Chemicals, Houston, Texas. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. EMB Report No. 80-OCM-19. August 1980.

18. Ref. 15.

19. Ref. 16.

20. Ref. 17.

21. Ref. 1.

22. Control Techniques for Volatile Organic Emissions from Stationary Sources. U. S. Environmental Protection Agency. Research Triangle Park, N.C. EPA Publication No. EPA-450/2-78-002. May 1978. pp. 32 and 33, 53, 72, 76, and 83 and 84.

23. Control of Volatile Organic Emissions. MetPro Corp., Systems Division. Harleysville, Pennsylvania. 1981. 8 pp.

24. Letter from Connor, R. J., Manufacturers of Emission Controls Association, to Rosensteel, R. E., EPA. May 4, 1992.

25. Ref. 24, p. 6.

26. Ref. 22, p. 53.

27. Stern, A. C. Air Pollution, Volume IV, Third Edition, New York, Academic Press. 1977. pp. vii through xii, 22 through 27, 336 and 337, and 354 through 359.

28. Barnett, K. W. (Radian Corporation). Carbon Adsorption for Control of VOC Emissions: Theory and Full Scale System Performance. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. EPA Contract No. 68-02-4378. June 6, 1988. p. 3-52.

29. Ref. 27, p. 356.

30. Ref. 28.

31. H. S. Basdekis, et al (IT Enviroscience, Inc.). Organic Chemical Manufacturing Volume 5: Adsorption, Condensation, and Absorption Devices. Report 2. Prepared for the U. S. Environmental Protection Agency. Publication No. EPA-450/3-80-027. Research Triangle Park, N.C. December 1980. 336 pp.

32. Ref. 31, p. I-4.

33. Staff of Research and Education Association. Modern Pollution Control Technology: Volume I. New York, Research and Education Association. 1978. pp. 22-20 through 22-25.

34. Ref. 31, p. II-15.

35. Perry, R.H., and Chilton, C.H. Eds. Chemical Engineers Handbook. 6th Edition. New York, McGraw-Hill. 1984. pp. 14-1 through 14-2.

36. Ref. 22, p. 76.

37. Ref. 27, p. 24.

38. Ref. 22, p. 72.

39. Ref. 31, p. II-1.

40. Ref. 35, p. 14-1.

41. Ref. 31, p. III-5.

42. Ref. 31, Report 2, p. II-1.

43. Ref. 22, p. 84.

44. Ref. 31, Report 2, p. IV-1.

45. Ref. 31, Report 2, pp. II-3.

46. Ref. 31, Report 2, p. III-5.

47. Ref. 1.

4.0 ENVIRONMENTAL IMPACTS

The environmental impacts associated with applying reasonably available control technology (RACT) to synthetic organic chemical manufacturing industry (SOCMI) distillation and reactor process vent streams are analyzed in this chapter. As discussed further in Chapter 6.0, the recommended RACT is based on the combustion of certain SOCMI reactor and distillation process vent streams to achieve a 98 weight-percent volatile organic compound (VOC) reduction. The requirements of RACT can be achieved at distillation and reactor process facilities by either thermal incinerators or flares; therefore, the environmental impacts analysis assumes that RACT is represented by thermal incineration and flaring.

The environmental impacts analysis considers effects on air quality, water quality, solid waste, and energy consumption. Ten model vent streams derived from the emissions profiles presented in Appendix B are used to assess these impacts. The model vent streams represent the range of flow rates and heating values typical of SOCMI distillation and reactor process vent streams. Table 4-1 presents the environmental impacts for the 10 model vent streams. Calculated impacts are based on the lowest cost control technique (thermal incineration versus flares) for nonhalogenated streams, and on a thermal incinerator/scrubber system for halogenated streams.

4.1 AIR POLLUTION IMPACTS

Section 4.1.1 presents the uncontrolled VOC emissions from each model vent stream and the expected VOC emission reductions from the application of RACT. Section 4.1.2 discusses additional air quality impacts that may be observed in applying RACT to specific reactor and distillation process vents. Also included is discussion on possible impacts from the

4-1

TABLE 4-1. ENVIRONMENTAL IMPACTS FOR DISTILLATION AND REACTOR MODEL VENT STREAMS

Model vent stream type[a]	Air Impacts				Energy Impacts		Water Impacts
	Uncontrolled VOC emissions[b] (Mg/yr)	Controlled VOC emissions[b] (Mg/yr)	Secondary NO_x emissions[b,c] (Mg/yr)	Secondary CO emissions[b,d] (Mg/yr)	Auxiliary fuel use[b] (MMBtu/yr)	Electrical demand per vent[b] (Kw-hr/yr)	Scrubber wastewater flow[b] (gal/yr)
Distillation							
LFLH	5.16	0.10	0.043	0.001	1,126	1,131	404,367
LFHH	8.14	0.16	0.006	0.002	620	0	0
HFLH	24.41	0.49	0.531	0.121	6,997	6,508	0
HFHH	605.30	12.11	1.789	1.347	3,163	46,836	16,719,531
Average	79.25	1.58	0.074	0.030	620	0	0
Reactor							
LFLH	14.29	0.29	0.035	0.010	289	902	325,728
LFHH	33.34	0.67	0.032	0.024	56	836	297,661
HFLH	5.36	0.11	7.165	0.369	1,083	10,246	0
HFHH	802.97	16.06	47.82	19.128	34,653	315,639	0
Average	31.95	0.64	2.05	0.820	1,485	12,377	0

[a]LFLH   - low flow low heating value
LFHH   - low flow high heating value
HFLH   - high flow low heating value
HFHH   - high flow high heating value
Average - average flow, average heating value

[b]Impacts are based on the lower cost control technique (thermal incineration versus flaring) for nonhalogenated streams and on a thermal incinerator/scrubber system for halogenated streams.

[c]NO_x emission factors used:
  Incinerators: 200 ppm in exhaust for streams containing nitrogen compounds, and 21.5 ppm NO_x on all other streams (based on test data).
    Flares: 0.05 lb/MMBtu (based on EPA 600/2-83-052)

[d]CO emissions based on 20 lb/MMscf (AP-42).

4-3

inefficient operation of the control devices used to meet RACT requirements.

4.1.1 <u>Volatile Organic Compound Emission Impacts</u>

The VOC emissions (megagrams per year) for the distillation and reactor model vent streams in Table 4-1 were estimated using an assumption of 8,760 working hours per year. Controlled emissions were calculated using a 98 weight-percent VOC reduction efficiency.

Uncontrolled VOC emissions from the distillation vent streams range from about 5 megagrams per year (Mg/yr) (5.5 tons/yr) for the Low Flow Low Heat (LFLH) model, to 600 Mg/yr (661 tons/yr) for the High Flow High Heat (HFHH) model. Uncontrolled VOC emissions from the average distillation vent stream are 80 Mg/yr (88 tons/yr). The controlled VOC emissions from the distillation vent streams range from 0.10 Mg/yr (0.11 ton/yr) (LFLH) to 12 Mg/yr (13 tons/yr) (HFHH), with 2 Mg/yr (2.2 ton/yr) representing the average.

Uncontrolled VOC emissions from the reactor model vent streams range from 5 Mg/yr (5.5 tons/yr) (HFLH) to 800 Mg/yr (882 tons/yr) (HFHH), with 32 Mg/yr (35 tons/yr) representing the average model vent stream. The controlled VOC emissions from the reactor model streams range from 0.11 Mg/yr (0.12 tons/yr) (HFLH) to 16 Mg/yr (17.6 tons/yr) (HFHH), with 0.6 Mg/yr (0.66 tons/yr) representing the average.

4.1.2 <u>Secondary Air Impacts</u>

Other air quality impacts from the application of incinerator or flare control technologies include secondary pollutants produced from the combustion of vent streams containing VOC's. Possible by-product emissions from VOC combustion include nitrogen oxides, sulfur dioxide, carbon monoxide, particulate matter. Generally, the only combustion-related secondary pollutants of any potential concern are nitrogen oxides and carbon monoxide. Data are not available on carbon monoxide emissions from thermal incinerators and flares. However, a reasonable estimate can be made using the AP-42 factor for natural gas combustion. Test data on nitrogen oxides emissions from thermal incinerator and flares are available as discussed below.

Incinerator outlet concentrations of nitrogen oxides are generally below 100 ppm, except for cases where the vent stream contains nitrogenous

compounds. Test data for a toluene diisocyanate process unit in the reactor processes emissions profile showed a nitrogen oxide concentration of 84 per million by volume (ppmv).[1] Testing at a polymer and resin process unit using an incinerator for VOC control measured nitrogen oxide ranging from 20.2 to 38.6 ppmv.[2] The fuels tested were mixtures of natural gas, waste gas, and/or atactic waste; incineration temperatures ranged from 980 to 1,100 °C (1,800 to 2,000 °F). In a series of seven tests conducted at three air oxidation process units, incinerator outlet nitrogen oxide concentrations ranged from 8 to 200 ppmv.[3] The maximum outlet nitrogen oxide concentration was measured at an acrylonitrile (air oxidation) process unit, which has a vent stream containing nitrogenous compounds. The nitrogen oxide concentration measured at the other process units, where the vent streams do not contain nitrogenous compounds, ranged from 8 to 30 ppmv, with a median value of 21.5 ppm.

The use of flares for combustion may also produce nitrogen oxide secondary air pollution impacts. Concentrations of nitrogen oxide were measured at two flares used to control hydrocarbon emissions from refinery and petrochemical processes. One flare was steam-assisted and the other air-assisted, and the heat content of the fuels ranged from 5.5 to 81 megajoule per standard cubic meter (148 to 2,175 British thermal units per standard cubic feet). The measured nitrogen oxide concentrations were somewhat lower than those for incinerators, ranging from 0.4 to 8.2 ppmv. The ranges of relative NO_x emissions per unit of heat input are 7.8 to 90 gram per gigajoule (0.018 to 0.208 lb/MMBtu) for flares.[4]

Table 4-1 presents the secondary air impacts for the 10 model vent streams. As shown, nitrogen oxide emissions range from 0.006 Mg/yr (0.007 tons/yr) for the LFHH distillation vent stream to 48 Mg/yr (52.9 tons/yr) for the HFHH reactor vent stream. The carbon monoxide emissions range from 0.001 Mg/yr (0.0011 tons/yr) for the LFLH reactor vent stream to 19 Mg/yr (20.9 tons/yr) for the HFHH reactor vent stream.

In addition to nitrogen oxide and carbon monoxide emissions, combustion of halogenated VOC emissions may result in the release of halogenated combustion products to the environment. Generally, streams containing halogenated VOC would not be controlled by a flare. Incinerators are generally more capable of tolerating the corrosive

4-4

effects of halogenated VOC and its combustion by-products. In addition, scrubbing is used to remove these halogenated compounds from an incinerator's flue gas. Generally, incineration temperatures greater than 870 °C (1,600 °F) are required to ensure 98-percent destruction of halogenated VOC. For example, when incinerating chlorinated VOC's at temperatures of 980 to 1,100 °C (1,800 to 2,000 °F), almost all chlorine present exists in the form of hydrogen chloride. The hydrogen chloride emissions generated by thermal oxidation at these temperatures can be efficiently removed by wet scrubbing.[5] As discussed further in Chapter 5.0, the cost of the scrubber was added to the overall thermal incinerator system cost.

4.2 WATER POLLUTION IMPACTS

Control of VOC emissions using combustion does not typically result in any significant increase in wastewater discharge; that is, no water effluents are generated by the combustion device. However, the use of an incinerator/scrubber system for control of vent streams with halogenated VOC does result in slightly increased water consumption. In this type of control system, water is used to remove the acid gas contained in the incinerator outlet stream. In most cases, any increase in total process unit wastewater would be relatively small and would not affect plant waste treatment or sewer capacity. Table 4-1 presents the water pollution impacts for the 10 model vent streams. Scrubber wastewater flow ranges from less than 0.001 million gallons per day (Mgal/d) for the LFLH reactor vent stream to 0.05 Mgal/d for the HFHH distillation vent stream.

The absorbed acid gas may cause the water leaving the scrubber to have a low pH. This acidic effluent could lower the pH of the total plant effluent if it is released into the plant wastewater system. The water effluent guidelines for individual States may require that industrial sources maintain the pH of water effluent within specified limits. To meet these guidelines, the water used as a scrubbing agent would have to be neutralized prior to discharge to the plant effluent system. The scrubber effluent can be neutralized by adding caustic sodium hydroxide to the scrubbing water. The amount of caustic needed depends on the amount of acid gas in the waste gas. For example, approximately 1.09 kilograms

(kg) (2.4 lb) of caustic (as sodium hydroxide) are needed to neutralize
1 kg (2.2 lb) of hydrogen chloride.

The salt formed in the neutralization step must be purged from the
system for proper disposal. The methods of disposal include direct
wastewater discharge into sewer systems, salt water bodies, brackish
streams, freshwater streams, deep well injection, and evaporation. Use of
the latter disposal method is not widespread, and data show that most
plants currently incinerating halogenated streams have State permits to
dump the brine or use on-site wells to dispose of salty wastewater at a
relatively low cost.[7] The increased water consumption and caustic costs
were included in the projected operating costs for control of halogenated
vent streams using an incinerator/scrubber system. The costs associated
with the disposal of the salty wastewater were judged not to be
significant in comparison to the control costs and, therefore, were not
included in the projected cost impacts presented in Chapter 5.0.[7]

An alternative to brine disposal is to use the brine as feed to
chlorine production. Such a use would be site specific, where there was a
need for the chlorine in subsequent syntheses, and where quantities of
brine either alone or in combination with other brine sources were
adequate for economical production.

The use of scrubbers to remove hydrogen chloride from the incinerator
flue gas also has the potential to result in small increases in the
quantities of organic compounds released into plant wastewater. However,
only small amounts of organics are released into the scrubber wastewater;
the flow of wastewater from the scrubber is small compared to total plant
wastewater, especially in installations where there are multiple chemical
processing units using a central wastewater treatment facility.
Therefore, the increase in the generation of organics in plant wastewater
is not likely to be significant.

4.3 SOLID WASTE DISPOSAL IMPACTS

There are no significant solid wastes generated as a result of
control by thermal oxidation. A small amount of solid waste for disposal
could result if catalytic oxidation, instead of thermal oxidation, were
used by a facility to achieve RACT requirements. The solid waste would
consist of spent catalyst.

used by a facility to achieve RACT requirements. The solid waste would consist of spent catalyst.

4.4 ENERGY IMPACTS

The use of incineration to control VOC's from reactor and distillation process vent streams requires fuel and electricity. Supplemental fuel is frequently required to support combustion. Electricity is required to operate the pumps, fans, blowers and instrumentation that may be necessary to control VOC's using an incinerator or flare. Fans and blowers are needed to transport vent streams and combustion air. Pumps are necessary to circulate absorbent through scrubbers that treat corrosive offgases from incinerators combusting halogenated VOC's. Fuel and energy usage requirements for incinerators and flares are discussed in detail as part of the overall cost methodology in Chapter 5.0.

Table 4-1 presents the estimated energy impacts associated with each model vent stream from reactor and distillation units. These energy values include both fuel and electricity usage estimates. As shown, auxiliary fuel use ranges from 56 MMBtu/year for the LFHH reactor vent streams to 34,653 MMBtu/yr for the HFHH reactor vent stream. Electrical demand per vent ranges from zero for two vent streams to 315,639 kilowatt-hour per year for the HFHH reactor vent stream. Electricity generally accounts for a small fraction of the total energy impacts, while fuel use accounts for the remainder. Heat recovery systems may substantially affect fuel usage requirements for incinerators.

4.5 REFERENCES

1. Reactor Processes in Synthetic Organic Chemical Manufacturing Industry-- Background Information for Proposed Standards. Draft EIS. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-90-016a. June 1990.

2. Lee, K. W., et al (Radian Corporation). Polymers and Resins, Volatile Organic Compound Emissions from Incineration, Emissions Test Report, ARCO Chemical Company, LaPorte Plant, Deer Park, Texas. Volume I: Summary of Results. Prepared for the U. S. Environmental Protection Agency. Research Triangle Park, N.C. EMB Report No. 81-PMR-1. March 1982. pp. 12 through 15.

3. Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry--Background Information for Proposed Standards. Draft EIS. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-82-001a. October 1983. pp. ii, 7-5, C-22, and technical report data sheet.

4. McDaniel, M. (Engineering Science). Flare Efficiency Study. Prepared for the U. S. Environmental Protection Agency. Washington, D.C. Publication No. EPA-600/2-83-052. July 1983. p. 134 and technical report data sheet.

5. Ref. 4.

6. Memorandum from Piccot, S. D., and Lesh, S. A., Radian Corporation, to Reactor Processes NSPS file. June 25, 1985. Disposal of brine solutions from wet scrubbers.

7. Memorandum from Stelling, J. H. E., Radian Corporation, to Distillation Operations NSPS file. September 2, 1982. Caustic and salt disposal requirements for incineration. 1 p.

5.0 COST ANALYSIS

5.1 INTRODUCTION

This chapter presents the costs associated with control options for reducing volatile organic compound (VOC) emissions from distillation column and reactor process vents. Control system elements, design assumptions, and costing equations are provided for incinerator and flare control systems. For streams containing halogenated VOC's, the incinerator control system cost includes a packed tower scrubber system to remove acidic vapors from the incinerator flue gas.

Since synthetic organic compound manufacturing industry (SOCMI) processes encompass a wide range of emission parameters, a model stream approach was used to present example control system costs. Ten model systems were selected from the distillation and reactor process emission profiles to represent a broad spectrum of possible vent streams. The model vent stream characteristics are presented in Appendix B. Because flow rates, heating values, and VOC concentrations of the model streams vary considerably, there is a large variation in system costs and cost effectiveness values.

5.2 COST METHODOLOGY FOR INCINERATOR SYSTEMS

This section presents the methodology used to develop VOC control system costs for incinerators and scrubbers. Incinerator costs were developed using Chapters 2 and 3 of the EPA's Control Cost Manual (OCCM).[1] Scrubber costs were based on the procedure outlined in the EPA's Handbook on Control Technologies for Hazardous Air Pollutants,[2] with equipment costs updated from recent technical journal information.[3]

5.2.1 Thermal Incinerator Design Considerations

The thermal incinerator system consists of the following equipment: combustion chamber, instrumentation, recuperative heat exchanger, blower,

collection fan and ductwork, quench/scrubber system (if applicable), and stack. The OCCM contains further discussion of incinerator control system design. Control system elements and design assumptions specific to SOCMI vent streams are discussed below. General incinerator design specifications are presented in Table 5-1.

    5.2.1.1 Combustion Air Requirements. The amount of oxygen in the waste gas or that provided by the VOC's is important because it establishes the auxiliary combustion air required, which has an impact on both the capital and operating costs of the thermal oxidizer. This cost analysis assumes that the waste gas does not contain free oxygen and that, therefore, auxiliary combustion air must be added. (In other words, the vent stream is essentially a mixture of VOC's and an inert gas such as nitrogen.) After combustion, the design excess oxygen content in the incinerator flue gas is assumed to be 3 mole percent, which is based on commonly accepted operating practice.

    In order to calculate the amount of combustion air required to ensure a flue gas oxygen concentration of 3 mole percent, a complete stoichiometric equation must be balanced for each compound present in the waste gas stream. In many cases, the complete chemical composition of the waste stream is not known. Thus, for the purpose of costing incinerator systems for typical vent streams encountered in the SOCMI, a design molecule approach was used for halogenated and nonhalogenated waste gas streams.

    The design molecule was based on a survey of typical values for carbon, hydrogen, oxygen, sulfur and chloride ratios for group of 219 organic compounds.[4] For nonhalogenated streams, the average VOC molecular composition of 68.3 percent carbon, 11.4 percent hydrogen, and 20.3 percent oxygen was used to calculate combustion air requirements. These weight ratios correspond to a molecular formula of $C_{2.88}H_{5.7}O_{0.63}$. For halogenated streams, component averages of 34.3 percent carbon, 4.7 percent hydrogen, and 6.1 percent chlorine were used to predict combustion air requirements. This corresponds to a molecular formula of $C_{2.86}H_{4.7}Cl_{1.71}$. In both cases, assuming zero percent oxygen in the waste

TABLE 5-1.   INCINERATOR GENERAL DESIGN SPECIFICATIONS

Item	Specification
Emission control efficiency	98 percent destruction
Minimum incinerator capacity[a]	500 scfm
Maximum incinerator capacity	50,000 scfm
Incinerator temperature	
- nonhalogenated vent streams	870 °C (1,600 °F)
- halogenated vent streams[b]	1,100 °C (2,000 °F)
Chamber residence times	
- nonhalogenated vent streams	0.75 sec
- halogenated vent streams[b]	1.00 sec
Auxiliary fuel requirement	Natural gas required to maintain incinerator temperature with 3 mole percent excess oxygen in flue gas
Scrubber system	Used when halogenated VOC is present to remove corrosive combustion by-products
- type	Packed tower
- packing type	2-inch rings, carbon steel
- scrubbing liquid	Water
- scrubber gas temperature	100 °C (212 °F)

[a]For capital cost purposes. A minimum flow rate of 50 scfm was used for determining operating costs.

[b]Used when halogenated VOC are present due to the difficulty of achieving complete combustion of halogenated VOC at lower temperatures.

stream, a dilution ratio (mole of air per mole of VOC) of approximately 18:1 is required to achieve 3 percent oxygen in the incinerator flue gas.

5.2.1.2 <u>Dilution Air Requirements</u>. After the required combustion air is calculated and added to the total vent stream flow, the overall heat value megajoules per standard cubic meter (MJ/scm) of the stream is recalculated. Addition of combustion air will effectively dilute the stream and lower the heat content of the combined stream fed to the incinerator. However, if the heat content of the vent stream is still greater than 3,648 kilojoules per standard cubic meters (KJ/scm) [98 British thermal units per standard cubic feet (Btu/scf)] for nonhalogenated streams or greater than 3,536 KJ/scm (95 Btu/scf) for halogenated streams, then additional dilution air must be added to ensure these maximum heat content levels are not exceeded. The imposition of a maximum heat content level prevents the temperature in the incinerator from exceeding the design specifications.

The minimum flow rate to the incinerator is 1.42 standard cubic meter per minute (scmm) (50 scfm). It is assumed that vent streams smaller than 1.42 scmm (50 scfm) will be mixed with air to achieve this minimum flow rate. The maximum incinerator flow rate is 1,416 scmm (50,000 scfm). Flow rates greater than this will be handled by multiple incinerators in this cost analysis.

5.2.1.3 <u>Recuperative Heat Recovery</u>. Halogenated vent streams are not considered candidates for heat recovery systems, and are costed assuming zero percent heat recovery. This conservative design assumption is imposed because of the potential for corrosion in the heat exchanger and incinerator. If the temperature of the flue gas leaving the heat exchanger, T_{fo}, were to drop below the acid dew temperature, condensation of acid gases would result. Significant corrosion can lead to shortened equipment life, higher maintenance costs, and potentially unsafe working conditions.

Nonhalogenated vent streams are considered candidates for recuperative heat recovery. The extent of heat recovery depends on the heat value of the vent stream after dilution. Four different heat recovery scenarios are evaluated for nonhalogenated streams. The cost algorithm includes systems with 0, 35, 50 and 70 percent heat recovery.

The extent of heat exchange to be utilized is decided by an economic optimization procedure with the following restrictions. No heat recovery is allowed for vent streams with a heat value greater than 25 percent of the lower explosive limit (LEL), due to the possibility of explosion or damaging temperature excursions within the heat exchanger. This limit typically corresponds to a heat content of 484 KJ/scm (13 Btu/scf). Therefore, if the heat content of the total vent stream--even after addition of required combustion and dilution air--is still greater than 484 KJ/scm (13 Btu/scf), no heat recovery for the entire stream is allowed. For streams with a heat content less than 484 KJ/scm (13 Btu/scf), the entire stream is preheated in the recuperative heat exchanger, allowing for maximum energy recovery. However, for streams with a heat content greater than 484 KJ/scm (13 Btu/scf), the flammable vent gas stream cannot be preheated, but the combustion/dilution air stream can. In this case, the cost optimization procedure evaluates the option of preheating only the air stream, and combines the VOC stream with the preheated air stream in the incinerator.

All allowable heat recovery percentages are evaluated and the calculated total capital and annual costs are based on the most cost-effective configuration. The tradeoff between the capital cost of the equipment and the operating cost (fuel) of the system determines the optimum level of energy recovery.

5.2.1.4 Incinerator Design Temperature. The destruction of VOC's is a function of incinerator temperature and residence time in the combustion chamber. The design VOC destruction efficiency is 98 weight-percent, which can be met by well-designed and well-operated thermal incinerator systems. Previous studies by the EPA show that 98 weight-percent destruction efficiency can be met in a thermal incinerator operated at a temperature, T_{fi}, of 871 °C (1,600 °F) and a residence time of 0.75 second. Thermal oxidation of halogen-containing VOC's requires higher temperature oxidation to convert the combustion product to a form that can be more readily removed by flue gas scrubbing. For instance, chloride-containing waste gases are burned at high temperature to convert the chlorine to hydrogen chloride instead of to chlorine, since hydrogen chloride is more easily scrubbed. Available data indicate that a

temperature of 1,093 °C (2,000 °F) and residence time of 1 second are necessary to achieve 98 weight-percent VOC destruction efficiency for halogen-containing waste gas streams. Chapter 3.0 contains additional details on thermal incinerator performance.

5.2.2 Thermal Incinerator Capital Costs

The costing analysis follows the methodology outlined in the OCCM. Equipment cost correlations are based on data provided by various vendors; each correlation is valid for incinerators in the 14.2 scmm to 1,416 scmm (500 to 50,000 scfm) range.[5] Thus, the smallest incinerator size used for determining equipment costs was 14.2 scmm (500 scfm) and for flow rates above 1,416 scmm (50,000 scfm) additional incinerators were costed.

Purchased equipment costs (PEC's) for thermal incinerators are given as a function of total volumetric throughput, Q_{tot}, in scfm. Four equations were used in the costing analysis, each pertaining to a different level of heat recovery (HR):

$$PEC = 10294\ Q_{tot}^{0.2355} \qquad HR = 0\%$$

$$PEC = 13149\ Q_{tot}^{0.2609} \qquad HR = 35\%$$

$$PEC = 17056\ Q_{tot}^{0.2502} \qquad HR = 50\%$$

$$PEC = 13149\ Q_{tot}^{0.2500} \qquad HR = 70\%$$

The cost of ductwork (not included in PEC) was calculated based on 1/8 inch (in.) carbon steel with two elbows per 100 feet (ft), using the equation in Reference 6. The length of duct was assumed to be 300 feet. Collection fan costs were developed using methods in Reference 7. The duct and fan costs are added to the total equipment cost and installation factors applied to this total.

Installation costs are estimated as a percentage of total equipment costs. Table 5-2 lists the values of direct and indirect installation factors for thermal incinerators.

5.2.3 Thermal Incinerator Annualized Cost

Annualized costs for the thermal incinerator system include direct operating and maintenance costs, as well as annualized capital charges. It should be pointed out that vendor contacts indicate that an incinerator turndown ratio of 10/1 is available.[8] Consequently, the minimum flow rate

TABLE 5-2. CAPITAL COST FACTORS FOR THERMAL INCINERATORS[a]

Cost item	Factor
Direct Costs	
Purchased equipment costs	
Incinerator (EC) + auxiliary equipment[b]	As estimated, A
Instrumentation[c]	0.10 A
Sales taxes	0.03 A
Freight	0.05 A
Purchased equipment cost, PEC	B = 1.18 A
Direct installation costs	
Foundations and supports	0.08 B
Handling and erection	0.14 B
Electrical	0.04 B
Piping	0.02 B
Insulation for ductwork[d]	0.01 B
Painting	0.01 B
Direct installation cost	0.30 B
Site preparation	As required, SP
Buildings	As required, Bldg.
Total direct costs, DC	1.30 B + SP + Bldg.
Indirect Costs (Installation)	
Engineering	0.10 B
Construction and field expenses	0.05 B
Contractor fees	0.10 B
Start-up	0.02 B
Performance test	0.01 B
Contingencies	0.03 B
Total indirect cost, IC	0.31 B
Total Capital Investment = DC + IC	1.61 B + SP + Bldg.

[a]Reference 1.

[b]Ductwork and any other equipment normally not included with unit furnished by incinerator vendor.

[c]Instrumentation controls often furnished with the incinerator, and thus often included in the EC.

[d]If ductwork dimensions have been established, cost may be estimated based on $10 to $12 per ft^2 of surface area for field application. Fan housings and stacks may also be insulated.

5-7

for determining operating costs is assumed to be 1.42 scmm (50 scfm). Additional dilution air is added where necessary to raise the fuel-waste gas-air mixture to 1.42 scmm (50 scfm). The bases for determining thermal incinerator annualized costs are presented in Table 5-3. Each cost parameter is reviewed below.

5.2.3.1 Labor Costs. The operating labor requirements vary depending on the components of the overall system. Incinerator systems not employing a scrubber require the least amount of operating labor [548 hours per year (hr/yr) or 0.5 hours per 8-hour shift]. Systems employing a scrubber require an additional 548 hr/yr operating labor. Maintenance labor requirements are assumed to be identical to operating labor requirements--that is 548 hr/yr for the incinerator and 548 hr/yr for the scrubber. Supervisory cost is estimated to be 15 percent of the operating labor cost. The maintenance labor hourly rate is assumed to be 10 percent higher than the operating labor hourly rate.

5.2.3.2 Capital Charges. Return on investment for the incinerator system is not included, but the cost of the capital investment is accounted for in evaluating total annual costs. The capital recovery factor (0.163) is based on a 10-percent interest rate and a 10-year life for the equipment. Taxes, insurance, and administrative costs are assumed to be 4 percent of the total capital investment. Overhead is estimated to be 60 percent of the total labor and maintenance costs.

5.2.3.3 Utility Costs. The utilities considered in the annual cost estimates include natural gas and electricity. The procedures for estimating electricity and supplemental fuel requirements are described in Chapter 3 of the OCCM.

5.2.3.4 Maintenance Costs. Maintenance labor costs are discussed above. Maintenance material costs are assumed to be equal to maintenance labor costs.

5.3 COST METHODOLOGY FOR FLARE SYSTEMS

This section presents the methodology used to develop VOC control system costs for flares. Flare design aspects and costs are based on Chapter 7 of the OCCM.

TABLE 5-3. ANNUAL OPERATING COST BASIS FOR THERMAL INCINERATORS

Direct Operating Cost Factors

Hours of operation (hrs/yr)   8,760

Operating labor (manhours)

   Incinerator (0.5 hrs/8 hr shift)   548
   Incinerator with scrubber (1 hr/8 hr shift)   1,096

Maintenance labor (manhours) per incinerator

   Incinerator (0.5 hr/8 hr shift)   548
   Incinerator with scrubber (1 hr/8 hr shift)   1,096

Labor rates ($/hr) based on 1990 data

   Operating labor   15.64
   Maintenance labor   17.21

Supervisory cost   15% of Operating Labor
                                                                            Cost

Maintenance materials cost   100% of Maintenance
Labor Cost

   Utilities (1990 $)

      Electricity ($/1,000 kWh)   59
      Natural Gas ($/$10^6$ Btu)   3.30

Indirect Operating Cost Factors

   Equipment life (years)   10
   Interest rate (percent)   10

   Capital recovery factor   0.163

   Taxes, insurance, administration   4
      (percent of total installed cost)

   Overhead   60% of Total Labor and
                                                                  Maintenance Costs

5.3.1 Flare Design Considerations

The flare design consists of an elevated, steam-assisted, smokeless flare. Elements of the flare system include knock-out drum, liquid seal, stack, gas seal, burner tip, pilot burners, and steam jets. For flare system sizing, correlations were developed relating process vent stream flow rate and heat content value to the flare height and tip diameter. The general design specifications used in developing these correlations are discussed below and presented in Table 5-4.

Flare height and tip diameter are the basic design parameters used to determine the installed capital cost of a flare. The tip diameter selected is a function of the combined vent stream and supplemental fuel flow rates, and the assumed tip velocity. Supplemental fuel requirements and tip velocity values are shown in Table 5-4. Determination of flare height is based on worker safety requirements. The flare height is selected so the maximum ground level heat intensity including solar radiation is 2,525 watts per square meter (W/m^2) [800 Btu/hr per foot squared (ft^2)]. Vendor contacts indicate the smallest elevated flare commercially available is 30 ft high and 1 in. in diameter. For vent streams requiring smaller flare systems, this is the minimum flare size used.

After flare tip diameter (D) and flare height (H) are determined, the natural gas required for pilots and purge, and the mass flow rate of steam required are calculated. Pilot gas consumption is a function of the number of pilots and, in turn, of the tip diameter as shown in Table 5-4. The number of pilots is selected based on the tip diameter. The pilot gas consumption is calculated based on an energy-efficient model of 1.98 scm/hr (70 scf/hr) per pilot burner. The purge gas requirement is also a function of the tip diameter and the minimum design purge gas velocity of 0.012 meters per second (m/s) [0.04 ft/second (sec)] at the tip, as shown in Table 5-4. A design flare tip velocity 14.6 mps (48 ft/sec) equal to 80 percent of the maximum smokeless velocity is used in the costing equations. Steam use is that flow which maintains a steam to flare gas ratio of 0.4 pound (1b) steam/1b vent gas [kilogram (kg) steam/kg vent gas].

TABLE 5-4. FLARE GENERAL DESIGN SPECIFICATIONS

Item	Specification
Emission control efficiency	98 percent destruction
General flare design	Elevated, steam assisted Smokeless flare
- minimum net heating valve	300 Btu/scf of gas being combusted
- minimum flare tip diameter	2.5 cm (1.0 inch)
- minimum flare height	9.1 m (30 ft)
- maximum ground level heat intensity[a]	2,525 W/m^2 (800 Btu/hr ft^2)
- flare tip velocities[b]	HV $\leq$ 11.2 (300): V = 18.3 m/s (60 ft/s) + natural gas to 11.2 MJ/Nm^3 (300 Btu/scf) 11.2 (300) < HV < 37.3 (1,000): log(V) = (HV + 1,214)/852 HV > 37.3 (1,000): V = 122 m/s (400 ft/s)
- emissivity	0.3
- number of pilots[c]	(see table below)

Number of Pilots	Tip Diameter	
1	D $\leq$ 25	(D $\leq$ 10)
2	25 < D $\leq$ 61	(10 < D $\leq$ 24)
3	61 < D $\leq$ 152	(24 < D $\leq$ 60)
4	D > 152	(D > 60)

Item	Specification
- pilot gas requirement	2.0 m^3/hr (70 scf/hr) of natural gas per pilot
- steam requirement	0.4 kg steam/kg vent gas
- purge gas requirement	Natural gas added to maintain a minimum flare tip velocity of 0.01 m/s (0.04 ft/s)
Supplemental fuel requirement[d]	Natural gas required to maintain vent stream HV of 11.2 MJ/Nm^3 (300 Btu/scf for V 18.3 m/s (60 ft/s)

[a] Including solar radiation of 300 Btu/hr ft^2.

[b] HV = Heat content value of process vent stream, MJ/m^3 (Btu/scf). A flare tip velocity equal to 80 percent of the maximum smokeless velocity (18.3 m/s [60 ft/s]) is used in the costing equations.

[c] D = tip diameter, cm (inch).

[d] V = flare tip velocity, m/s (ft/s).

5-11

5.3.2 Development of Flare Capital Costs

The capital cost of a flare is based on vendor supplied information as described in the OCMM cost equations are developed from a regression analysis of the combined data set over a range of tip diameters and flare heights. Flare equipment costs (C_F) are calculated based on stack height, H (ft) and tip diameter, D (in.) according to support type as follows:

- Self Support Group:

$$C_F = [78.0 + 9.14(D) + 0.749(H)]^2$$

- Guy Support Group:

$$C_F = [103 + 8.68(D) + 0.470(H)]^2$$

- Derrick Support Group:

$$C_F = [76.4 + 2.72(D) + 1.64(H)]^2$$

The flare equipment cost includes the flare tower (stack) and support, burner tip, pilots, utility piping from base, utility metering and control, water seal, gas seal, and galvanized caged ladders and platforms as required. The material of construction basis is carbon steel, except for the upper 4 ft and burner tip, which is 310 stainless steel.

Vent stream piping costs, C_p, are a function of pipe, or flare, diameter, D, and length of piping.

- $C_p = 508 (D)^{1.21}$ (where 1" < D < 24")

- $C_p = 556 (D)^{1.07}$ (where 30" < D < 60")

These costs include 400 ft of straight piping and are directly proportional to the distance required.

Knock-out drum costs C_K, are a function of drum diameter, d (in.) and drum thickness, t (in.).

- $C_K = 14.2 [(d)(t)(h + 0.812(d)]^{0.737}$

Total flare system equipment cost is the sum of flare, piping, and knock-out drum costs.

$$EC = C_F + C_K + C_p$$

Purchased equipment cost, PEC, is equal to equipment cost, EC, plus factors for ancillary equipment (i.e., instrumentation at 0.10, sales

taxes at 0.03, and freight at 0.05). Installation costs are estimated as a percentage of total equipment costs. The total capital investment, TCI, is obtained by multiplying PEC by an installation factor of 1.61.

5.3.3 Development of Flare Annualized Costs

The annualized costs include direct operating and maintenance costs, and annualized capital charges. The assumptions used to determine annualized costs are presented in Table 5-5, and are given in first quarter 1990 dollars. Direct operating and maintenance costs include operating and maintenance labor, replacement parts, and utilities.

5.3.3.1 _Labor Costs_. The operating labor requirements are 500 hrs/yr for typical flare systems. Supervisory labor is estimated to be 15 percent of the operating labor cost. Maintenance labor is assumed to be 10 percent higher than the operating labor cost.

5.3.3.2 _Capital Charges_. The capital recovery factor (0.1314) is based on a 10-percent interest rate and a 15-year life for the equipment. Taxes, insurance and administrative costs are assumed to be 5 percent of the total capital investment.

5.3.3.3 _Utility Costs_. The utilities considered in the annual cost estimates include natural gas and electricity. The procedures for estimating electricity and supplemental fuel requirements are described in Chapter 4 of the OAQPS Cost Manual.

5.3.3.4 _Maintenance Costs_. Maintenance labor costs are discussed above. Maintenance material costs are assumed to be equal to maintenance labor costs.

5.4 COMPARISON OF CONTROL SYSTEM COSTS

This section presents and discusses the capital costs, annualized costs, average cost effectiveness, and natural gas costs for the application of incinerators or flares to representative SOCMI vent streams. These costs are determined by applying the costing methodology, developed in the previous sections, to the 10 model vent streams described in Appendix B.

For a specific combustion control system, capital and annualized costs vary with vent stream flow rate and heat content. Therefore, five reactor process vent streams and five distillation vent streams are used as examples to show how the costs of control vary for vent streams with a

TABLE 5-5. ANNUAL OPERATING COSTS FOR FLARE SYSTEMS

Direct Annual Costs	Factor/Basis
Operating Labor	630 manhours/yr
Supervision	15% of operating labor
Maintenance Labor	1/2 hour per shift
Maintenance Materials	equal to maintenance labor

Natural Gas - Pilot Gas
          - Auxiliary Fuel
          - Purge Gas
	}
	 }
	 } All utilities equal to:
	)consumption rate * hours/yr *

Steam Electricity	) unit cost)(Natural Gas = $330/10^6$ Btu))(Electricity = \$59.0/1,000 kWh))(Steam = \$5.30/1,000 lb)

Indirect Annual Costs	
Overhead	60% of total labor costs
Capital Recovery Factor	0.1314 (assuming 15 year life at 10%)
General and Administrative, Taxes, and Insurance	(4% of total installed capital)

wide range of vent stream characteristics. These example cases are
selected from the emission profiles in Appendix B and represent the range
of vent stream characteristics found. Stream characteristics for the
10 example cases are as follows:

Case 1 - reactor process - low flow rate, high heat content -
     (R-LFHH);

Case 2 - reactor process - low flow rate, low heat content - (R-LFH);

Case 3 - reactor process - high flow rate, high heat content -
     (R-HFHH);

Case 4 - reactor process - high flow rate, low heat content -
     (R-HFLH);

Case 5 - reactor process - medium flow rate and medium heat content -
     (R-AVG);

Case 6 - distillation - low flow rate, high heat content - (D-LFHH);

Case 7 - distillation - low flow rate, low heat content - (D-LFLH);

Case 8 - distillation - high flow rate, high heat content - (D-HFHH);

Case 9 - distillation - high flow rate, low heat content - (D-HFLH);

Case 10 - distillation - medium flow rate and medium heat content -
     (D-AVG);

Table 5-6 presents the results of the costing analysis for the
10 example SOCMI vent streams. The values presented are the lower cost
control option (thermal incineration versus flaring) for nonhalogenated
streams. For halogenated streams, the values in the table represent the
cost of a thermal incineration/scrubber system.

Table 5-6 shows that average cost effectiveness for each control
system varies with the vent stream characteristics. The lowest
cost-effectiveness values shown occur for those vent streams with the
highest vent stream energy flow (i.e., (flow rate) x (heat content) in
megajoules per minute); Cases 3 and 8. The cost effectiveness for Case 3
is about $300/megagram (Mg) ($272/ton), while the cost effectiveness for
Case 8 is about $270/Mg ($245/ton). In general, the low cost
effectiveness values for high-energy content vent streams are a result of
the large mass of VOC's available to support combustion and, subsequently,

TABLE 5-6. COST RESULTS FOR MODEL SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY VENT STREAMS

Source ID	Halogenation status	Control device	Total inlet flow (scfm)	Inlet VOC flow rate (lb/hr)	Inlet heat value (Btu/scf)	Total emissions reduction (Mg/yr)	Natural gas cost ($/yr)	Capital cost ($)	Annual cost ($/yr)	Cost effectiveness ($/Mg removed)
R-LFHH	H	Incin + Scrubber	3.8	8.4	1,286	32.7	186	114,450	115,323	3,529
R-LFLH	H	Incin + Scrubber	40	3.6	40	14	953	115,506	116,314	8,306
R-HFHH	NH	Thermal Incineration	5,090	202.3	776	786.9	114,355	292,118	238,743	303
R-HFLH	NH	Thermal Incineration	1,078	1.4	70	5.3	3,575	109,698	72,348	13,778
D-LFHH	NH	Thermal Incineration	564	8.1	300	31.3	4,902	114,284	74,736	2,387
R-AVG	NH	Flare	0.2	2.1	2,870	8	2,046	28,991	52,936	6,638
D-LFLH	H	Incin + Scrubber	2.6	1.3	62	5.1	3,715	115,318	119,068	23,546
D-HFHH	H	Incin + Scrubber	344	152.5	804	593.2	10,438	243,020	158,061	266
D-HFLH	NH	Thermal Incineration	632	6.2	19	23.9	23,089	100,786	89,828	3,758
D-AVG	NH	Flare	13.8	20	449	77.7	2,046	29,836	54,087	696

the low supplemental fuel costs. Also, relatively large VOC emission reductions occur for these streams, which greatly decreases the cost per megagram of VOC removed/destroyed.

Table 5-6 also shows the highest cost effectiveness occurs for vent streams with a low energy flow (Case 7). This occurs even though this type of stream does not have extremely high annualized costs. For Case 4, cost effectiveness is $13,778/Mg ($12,497/ton) with incineration. Application of controls to this low heat content stream results in moderately low annual costs but very low emissions reductions. A relatively small amount of VOC's are controlled because of the low VOC content associated with this vent stream.

5.5 REFERENCES

1. OAQPS Control Cost Manual. Fourth Edition. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-90-006. January 1990. pp. 1-1 through 1-7, 2-1 through 2-32, 3-1 through 3-66, 4-1 through 4-44, 5-1 through 5-54, 6-1 through 6-74, and 7-1 through 7-43.

2. Handbook: Control Technologies for Hazardous Air Pollutants. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-625/6-86-014. September 1986. 176 pp.

3. W. M. Vatavuk. Pricing Equipment for Air Pollution Control. Chemical Engineering. May 1990. pp 126 through 130.

4. Organic Chemical Manufacturing Series. Volume 4: Combustion Control Devices. U. S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-450/3-80-026. December 1990.

5. Ref. 1.

6. Richardson Engineering Services, Inc. The Richardson Rapid System Process Plant Cost Estimating Standards. Volume 3, p. 16-0.2 and Volume 4, pp. 100-110.4 and 100-653.13 and 100-653.14, 1988.

7. Telecon. Stone, D. K., Radian Corporation with E. Dowd, ARI Technology. January 18, 1990. Incinerator sizes and turndown. 1 p.

6.0 SELECTION OF REASONABLY AVAILABLE
CONTROL TECHNOLOGY

This chapter provides State and local regulatory authorities with guidance on the selection of reasonably available control technology (RACT) for volatile organic compound (VOC) emissions from synthetic organic chemical manufacturing industry (SOCMI) reactor processes and distillation operations. Background on the regulatory authority and goals for establishment of RACT is discussed in Section 6.1. The technical basis for RACT is discussed in Section 6.2, while the approach for applying RACT is described in Section 6.3. Section 6.4 presents the impacts of RACT on example vent streams. Finally, Section 6.5 provides an overall summary of RACT for this source category.

6.1 BACKGROUND

The Clean Air Act Amendments of 1990 mandate that State implementation plans (SIP's) for ozone nonattainment areas be revised to require the implementation of RACT to limit VOC emissions from sources for which the EPA has already published a control techniques guideline (CTG), or for which it will publish a CTG between the date the amendments are enacted and the date an area achieves attainment status.

Section 172(c)(1) requires that nonattainment area SIP's provide for the adoption of RACT for existing sources. As a starting point for ensuring that these SIP's provide for the required emissions reduction, the EPA has defined RACT as "...the lowest emission limitation that a particular source is capable of meeting by the application of control technology that is reasonably available considering technological and economic feasibility. The RACT for a particular source is determined on a case-by-case basis, considering the technological and economic circumstances of the individual source category."[1] The EPA has elaborated in subsequent notices on how RACT requirements should be applied.[2,3]

The CTG documents are intended to provide State and local air pollution authorities with an information base for proceeding with their own analysis of RACT to meet statutory requirements. These documents review existing information and data concerning the technical capability and cost of various control techniques to reduce emissions. Each CTG document contains a recommended "presumptive norm" for RACT for a particular source category, based on the EPA's current evaluation of capabilities and problems general to the source category. Where applicable, the EPA recommends that regulatory authorities adopt requirements consistent with the presumptive norm level, but authorities may choose to develop their own RACT requirements on a case-by-case basis, considering the economic and technical circumstances of the individual source category.

6.2 TECHNICAL BASIS FOR REASONABLY AVAILABLE CONTROL TECHNOLOGY

The technology underlying RACT for SOCMI reactor process and distillation operations is combustion via either thermal incineration or flaring. These techniques are applicable to all SOCMI reactor processes and distillation operations and can generally achieve the highest emission reduction among demonstrated VOC control technologies. Thermal incinerators can achieve at least 98 weight-percent reduction of VOC emissions (or reduction to 20 parts per million by volume [ppmv] dry basis, corrected to 3 percent oxygen) for any vent stream if the control device is well operated and maintained. Likewise, the EPA has presumed that flares can achieve at least 98 weight-percent control of VOC emissions if the design and operating specifications given in the Code of Federal Regulations (40 CFR 60.18) are met. (Chapter 3.0 contains more detail on the performance capabilities of thermal incinerators and flares as applied to SOCMI vent streams.) Although the control level representing RACT is based on the application of thermal incineration or flaring, it does not specify these techniques as the only VOC control methods that may be used. Any device can be used to comply with RACT requirements as long as the 98 weight-percent destruction or 20 ppmv dry basis, corrected to 3 percent oxygen emission limit is met.

Other VOC control technologies were considered in the RACT evaluation, including catalytic incinerators, carbon adsorbers, condensers

and absorbers. However, for several reasons, these technologies were rejected as the basis for the recommended presumptive norm for RACT. Catalytic incinerators are difficult to apply one costing model to, because different catalysts are required depending on the feed stream characteristics. Thus, it would be difficult to evaluate the cost impacts of RACT options based on this technology. Carbon adsorbers cannot achieve 98 weight-percent control in all cases and may not be applicable to certain vent streams (i.e., streams containing sulfur compounds or heavy metals) due to problems with carbon bed fouling. Finally, refrigerated condensers and absorbers, while effective for certain SOCMI vent streams, cannot achieve 98 weight-percent control in all cases because they are highly dependent on the type and concentration of organic compounds present in the vent stream. As explained in Section 6.5, recovery devices, such as adsorbers, absorbers, and condensers, can be used as pollution prevention techniques to meet the cutoffs described in Section 6.3.

In summary, the control level for RACT is represented by a VOC emission reduction of 98 weight-percent or reduction to 20 ppmv dry basis, corrected to 3 percent oxygen. Section 6.3 discusses how to determine which vent streams should apply control.

6.3 REASONABLY AVAILABLE CONTROL TECHNOLOGY SIZE CUTOFFS

Vent streams from reactor processes and distillation operations can vary widely in flow rate, VOC concentration, heating value, and VOC emission rate. Therefore, the uncontrolled emissions, emission reductions, and control costs can also vary considerably for different vent streams. Accordingly, it may not be reasonable from a technical or economic standpoint to apply controls to all distillation and reactor vent streams.

Important vent stream parameters in determining the emission reduction and cost impacts of control are flow rate, heating value, and VOC emission rate. Flow rate determines control device sizing and, therefore, equipment cost. Vent stream heating value determines how much supplemental fuel is necessary to support combustion. The VOC emission rate determines the amount of emissions that can potentially be reduced. It should be noted that heating value is closely related to VOC

concentration. Similarly, VOC emission rate is dependent on the flow rate and VOC concentration. In general, as flow rate and VOC concentration increase, the VOC emission reduction achievable by controlling these streams increases and they become more cost effective to control. Alternatively, if the flow rate and VOC concentration are low, the achievable VOC emissions reduction is low and the cost effectiveness of control is high.

The total resource effectiveness (TRE) index was chosen as the applicability approach to be adopted for this CTG. The TRE index is a decision tool used to determine if the annual cost of controlling a given vent gas stream is acceptable when considering the emission reductions achieved. The TRE index equation is a measure of the cost per unit of VOC emissions reduction and is normalized so that the decision point has a defined value of 1.0. The variables in the TRE index equation are the stream characteristics (i.e., flow rate, heat value, VOC emission rate and maximum cost effectiveness). If the result for plugging in the characteristics of a specific vent stream is less than or equal to 1.0, the stream could effectively be controlled further using a combustion device (flare or incinerator). If the result of the TRE index equation is greater than 1.0, the stream would not be controlled further without incurring an unreasonable cost burden. The Radian memorandum, "Total Resource Effectiveness Derivation," explains the TRE development and results.[4]

6.4 IMPACTS OF APPLYING VARIOUS COST EFFECTIVENESS CUTOFFS

This section describes the impacts of applying various stream parameters and cost-effectiveness value cutoffs to SOCMI reactor process and distillation vent streams. Options for the recommended presumptive norm for RACT have been identified using a TRE index less than or equal to 1.0. Thus, the impacts analysis assumes that any vent stream with a calculated TRE index of less than or equal to 1.0 would be required to reduce emissions by 98 weight-percent (or to 20 ppmv) via thermal incineration or flaring.

Table 6-1 summarizes the impacts of various options for the recommended presumptive norm for RACT. These options are based on the different maximum cost-effectiveness values for the model streams

TABLE 6-1. SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY REASONABLY AVAILABLE CONTROL TECHNOLOGY IMPACTS--HALOGENATED AND NONHALOGENATED VENT STREAMS[a]

Option	Maximum Cost effectiveness ($/Mg)	Stream controlled[b] (%)	National VOC emission reduction[c] (Mg/yr)	National secondary emissions of NO_x (Max)[d] (Mg/yr)	National secondary emissions of CO[e] (Mg/yr)	National cost impacts[c,f] ($ x 10^6/yr)	Average CE[f] ($ x 10^3/Mg)	Incremental CE[f] ($ x 10^3/Mg)	Average emission reduction per vent in increment controlled[g] (Mg/yr)	Average cost per vent in increment controlled[h] ($/yr)
1	All	100	4,800	153 (48)	69	6 - 13	1.2 - 2.6			
								> 31 - 64	1.5	93,000
2	20,000	63	4,700	100 (48)	40	3.4 - 7.3	0.7 - 1.5			
								> 5.9 - 15	5.2	80,000
3	10,000	41	4,500	84 (8)	38	2.3 - 4.5	0.5 - 1			
								> 4.3 - 9	9.5	85,000
4	8,000	36	4,450	83 (8)	38	2.0 - 3.9	0.45 - 0.9			
								> 1.7 - 6.9	10.2	70,000
5	5,000	23	4,300	80 (2)	36	1.7 - 2.5	0.4 - 0.6			
								> 0.5 - 3.4	17.5	59,000
6	3,000	16	4,100	79	36	1.6 - 1.9	0.39 - 0.46			
								> 1.4 - 2.6	21.3	55,000
7	2,500	15	4,000	79	36	1.5 - 1.8	0.38 - 0.44			
								> 1.9 - 2.3	26.6	62,000
8	2,000	12	3,900	74	34	1.3 - 1.5	0.34 - 0.39			
								> 0.34 - 0.39	206	80,000

[a]It is assumed that 95 percent control on all streams >5 lbs/hr reflects current level of control due to State regulations; based on first quarter 1990 dollars.

[b]Represents the number of vent streams controlled at a particular cutoff level divided by the total number of model vent streams in the data base.

[c]It is assumed that 60 percent of the facilities are nonattainment areas.

[d]NO_x emission factors used:
   Incinerators: 200 ppm in exhaust for streams containing nitrogen compounds, and 21.5 ppm NO_x on all other streams (based on test data).
       Flares: 0.05 lb/10^6 Btu (Based on EPA 600/2-83-052).

[e]CO emissions based on 20 lb/10^6 scf (AP-42).

[f]Impacts shown for two cases: (1) utilization of existing controls for streams below 27 scfm, while streams above 27 scfm are costed with a dedicated device; and (2) all streams costed with dedicated devices.

[g]Represents the additional emission reduction divided by the additional number of vent streams controlled at a particular cutoff level relative to the next least stringent cutoff level.

[h]Represents the additional cost divided by the additional number of vent streams controlled at a particular cutoff level relative to the next least stringent cutoff level.

controlled by each option. These impacts were calculated for a population of model vent streams that represents a subset of SOCMI reactor process and distillation facilities. National impacts were calculated by scaling up impacts that would be incurred by a typical population of facilities for this source category.[a] A discussion of the procedure for estimating impacts incurred by the model vent stream population is contained in the Radian memorandum, "Reasonably Available Control Technology (RACT) Impacts for the SOCMI CTG."[5]

After reviewing the impacts in Table 6-1, the EPA has selected option number 7 as the recommended presumptive norm for RACT. This control level would reduce an estimated 83 percent of the available VOC emissions and would require controls on an estimated 15 percent of the vent streams for a typical population of facilities. At the recommended cutoff level, there are no technical reasons why controls could not be applied. In fact, many facilities with reactor process and distillation operations are already controlling streams of this size. The EPA recognizes that the impacts estimation procedure includes certain average assumptions for variables that affect emission reduction and cost. For example, assumptions have been made regarding the piping distance to the control device, and availability of space within existing facilities to accommodate new control devices. However, it is the EPA's judgment that even if the characteristics of any individual facility were to deviate somewhat from the assumed characteristics, the feasibility and costs of control would remain reasonable.

6.5 REASONABLY AVAILABLE CONTROL TECHNOLOGY SUMMARY

The recommended presumptive norm for RACT is the reduction of VOC emissions by 98 weight-percent or to 20 parts per million by volume (ppmv) on a dry basis, corrected to 3 percent oxygen in any vent stream that has both a calculated TRE index less than or equal to 1.0. When calculating

---

[a]To avoid "double-counting," national impacts include only those impacts resulting from control after the implementation of the Hazardous Organic National Emission Standard for Hazardous Air Pollutants (HON) has occurred. The SOCMI CTG and HON process vents regulatory actions will affect many of the same vents at SOCMI plants. In addition, only facilities in nonattainment areas are considered subject to the CTG.

the TRE index, the standardized TRE equation should be used with the plant specific characteristics, not quoted values from vendors or manufacturers.

Several additional considerations in applying RACT warrant mention. First, it is recommended that any vent stream for which an existing combustion device is employed to control VOC emissions should not be required to meet the 98 weight-percent destruction or 20 ppmv emission limit until the combustion device is replaced. In other words, it is recommended that facilities not be required to upgrade or replace existing combustion devices. This approach would avoid penalizing those facilities which have already undertaken efforts to control VOC emissions through combustion, but whose control device is not designed to achieve the 98 weight-percent/20 ppmv level of control.

Second, it is important to note that the presumptive norm for RACT provides incentives for pollution prevention by letting each facility consider the trade-offs between process modifications and add-on controls. Specifically, as an alternative to installing an add-on control device, facilities can choose to improve product recovery equipment so that the calculated TRE index falls above the cutoff value of 1.0. In this manner, the facility would be limiting VOC emissions via process changes and would thereby avoid having to install an add-on combustion device.

Another important consideration in applying RACT is emissions of pollutants such as carbon monoxide and nitrogen oxides from combustion-based control devices. The potential consequences of emission from control devices are twofold. First, depending on the VOC's-to-nitrogen oxides ratio in the ambient air, nitrogen oxides emissions from control devices may cause more ozone to be formed than could be eliminated through the VOC reductions. Second, emissions from control devices may be enough to trigger New Source Review. (Table 6-1 shows expected national emissions of nitrogen oxides and, in parentheses, the maximum annual emissions of nitrogen oxides at a single facility.) Whether the VOC emission decreases are worth the increases in other pollutants from the VOC control device is highly dependent on air quality and meteorological conditions in each specific geographical area. Therefore, States may select a less stringent level of control as RACT based on these considerations.

6-7

Finally, other regulatory initiatives under Title I (Nonattainment) and Title III (Air Toxics) provisions of the Clean Air Act Amendments of 1990 may result in the application of controls to vent streams with a TRE index above the cutoff value of 1.0. For example, maximum achievable control technology (MACT) requirements for the process vents portion of the proposed HON may impact SOCMI vents more stringently than would the presumptive norm for RACT as described above. Furthermore, all revised ozone SIP's (except for "marginal" areas) must demonstrate a total net reduction in VOC emissions in accordance with a specified percentage reduction schedule. This requirement could also result in more stringent control of SOCMI reactor process and distillation vents than would be required by the presumptive norm for RACT.

6.6 REFERENCES

1. <u>Federal Register</u>. State Implementation Plans; General Preamble for Proposed Rulemaking on Approval of Plan Revisions for Nonattainment Areas - Supplement (on Control Techniques Guidelines). 44 FR 53761-53763. September 17, 1979.

2. <u>Federal Register</u>. Emissions Trading Policy Statement; General Principles for Creation, Banking and Use of Emission Reduction Credits. 51 FR 43814-43860. December 4, 1986.

3. <u>Federal Register</u>. Approval and Promulgation of Implementation Plan; Illinois. 53 FR 45103-45106. November 8, 1988.

4. Memorandum from Barbour, W. J., Radian Corporation, to L. Evans, EPA/CPB. July 19, 1993. Total resource effectiveness equation development.

5. Memorandum from Quincey, K. and Pring, M., Radian Corporation, to L. Evans, EPA/CPB. November 17, 1992. Reasonably available control technology (RACT) impacts for the SOCMI CTG.

7.0 REASONABLY AVAILABLE CONTROL TECHNOLOGY IMPLEMENTATION

7.1 INTRODUCTION

This chapter presents information on factors State agencies should consider when developing an enforceable rule limiting volatile organic compound (VOC) emissions from synthetic organic chemical manufacturing industry (SOCMI) reactor processes and distillation operations. Information is provided on important definitions, rule applicability, emission limit format, performance testing, monitoring, and reporting/recordkeeping. Where several options exist for implementing a certain aspect of the rule, each option is discussed along with its relative advantages and disadvantages. In some cases, there may be other equally valid options. The State or other implementing agency can exercise its prerogative to consider other options provided the options meet the objectives prescribed in this chapter.

For each aspect of the rule, one option is identified as the preferred option. This guidance is for instructional purposes only and, as such, is not binding. Appendix D contains an example rule that incorporates the guidance provided in this document. The example rule provides an organizational framework and sample regulatory language specifically tailored for reactor processes and distillation operations. As with the preferred option, the example rule is for instructional purposes and is not intended to be binding. The State or other implementing agency should consider all information presented in this control techniques guideline (CTG), together with additional information about specific sources to which the rule will apply. The reasonable available control technology (RACT) rule should address all the factors listed in this chapter to ensure that the rule is enforceable and has reasonable provisions for demonstrating compliance.

7.2 DEFINITIONS

The RACT rule should accurately describe the types of sources that would be affected and clearly define terms used to describe the SOCMI industry or applicable control methods. This section offers guidance to agencies in selecting terms that need clarification when used in a regulatory context. This section presents example definitions of pertinent terms (or cites sources where definitions may be found) the agency may refer to when drafting RACT regulations for these source categories.

Two important terms that should be defined are "reactor processes" and "distillation operations." An example definition of the first term might be "unit operations in which one or more chemicals or reactants other than air are combined or decomposed in such a way that their molecular structures are altered and one or more new organic compounds are formed." An example definition of the second term might read as: "an operation separating one or more feed streams into two or more exit streams, each exit stream having component concentrations different from those in the feed streams. The separation is achieved by the redistribution of the components between the liquid- and vapor-phase as they approach equilibrium within the distillation unit." A detailed discussion of these terms can be found in Sections 2.2 and 2.3 of this document.

Certain types of equipment associated with reactor processes may need further clarification, such as the terms "process unit" or "product." Certain descriptors for reactor processes or distillation operations may be helpful to define, such as "batch reactor process," "batch distillation operation," "vent stream," or "halogenated vent stream." A discussion of these terms is found in Chapter 2.0 of this document.

Other terms requiring definition are those used to describe emission control techniques such as "recovery device," "incinerator," "flare," "boiler," and "process heater." A discussion of flares and incinerators is presented in Section 3.1. A discussion of recovery devices is found in Section 3.2. A description of boilers is given in Section 3.2.3.1 and a description of process heaters is given in Section 3.2.3.2.

Terms pertaining to equipment used in monitoring and recording emissions which may also require further clarification are "continuous recorder," "flow indicator," and "temperature monitoring device." An example definition of continuous recorder might be "a data recording device recording an instantaneous data value at least once every 15 minutes." An example definition of flow indicator might be "a device which indicates whether gas flow is present in a line." Finally, an example definition of temperature monitoring device might be "a unit of equipment used to monitor temperature and having an accuracy of ± 1 percent of the temperature being monitored expressed in degrees Celsius or ± 0.5 degrees Celsius, whichever is greater."

7.3 REGULATORY SUMMARY

The EPA has published one CTG, promulgated two New Source Performance Standards (NSPS), and proposed a third NSPS for SOCMI. These regulatory actions are summarized in the following subsections. Table 7-1 presents the list of chemicals affected by the proposed and promulgated SOCMI NSPS and air oxidation CTG. The marks alongside the chemicals indicate which NSPS or CTG apply to that specific chemical.

7.3.1 Air Oxidation Control Techniques Guidelines

The air oxidation CTG published in December, 1984, was written in response to the Clean Air Act Amendment of 1977. The purpose of the CTG was to provide State and local air quality management agencies with an initial information base for proceeding with their own assessment of RACT for specific stationary sources. The cutoff total resource effectiveness index (TRE) of 1.0 was based on a cutoff cost effectiveness value of 1,600 ($/megagram). Table 7-1 lists the chemicals affected by this CTG.

7.3.2 Air Oxidation Processes New Source Performance Standard

The NSPS for Volatile Organic Compound Emissions from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) Air Oxidation Processes (55 FR 26912, June 29, 1990: 40 CFR 60, Subpart III) was promulgated on June 29, 1990. This NSPS regulates SOCMI air oxidation processes constructed, reconstructed, or modified after October 21, 1983, that produce any of the affected

7-3

TABLE 7-1. CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING
INDUSTRY RULES AND GUIDELINE

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
Acetaldehyde	75-07-0	X	X	X
Acetaldol	107-89-1		X	
Acetic acid	64-19-7	X	X	X
Acetic anhydride	108-24-7	X	X	
Acetone	67-64-1	X	X	X
Acetone cyanohydrin	75-86-5	X	X	
Acetylene	74-86-2	X	X	
Acrylic acid	79-10-7	X	X	
Acrylonitrile	107-13-1	X	X	X
Adipic acid	124-04-9	X	X	
Adiponitrile	111-69-3	X	X	
Alcohols, C-11 or lower, mixtures	-	X	X	
Alcohols, C-12 or higher, mixtures	-	X	X	
Alcohols, C-12 or higher, unmixed	-	X	X	
Allyl chloride	107-05-1	X	X	
Amylene	513-35-9	X	X	
Amylenes, mixed	-	X	X	
Aniline	62-53-3	X	X	
Anthraquinone	84-65-1			X
Benzaldehyde	100-52-7			X
Benzene	71-43-2	X	X	
Benzenesulfonic acid	98-11-3	X	X	
Benzenesulfonic acid C_{10-16}-alkyl derivatives, sodium salts	68081-81-2	X	X	
Benzoic acid tech	65-85-0		X	X
Benzyl chloride	100-44-7	X	X	
Bisphenol A	80-05-7	X	X	
Brometone	76-08-4	X	X	
1,3-Butadiene	106-99-0	X	X	X
Butadiene and butene fractions	-	X	X	
n-Butane	106-97-8	X	X	
1,4-Butanediol	110-63-4	X	X	
Butanes, mixed	-	X	X	
1-Butene	106-98-9	X	X	
2-Butene	25167-67-3	X	X	

7-4

TABLE 7-1. CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING
INDUSTRY RULES AND GUIDELINE (CONTINUED)

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
Butenes, mixed	-	X	X	
n-Butyl acetate	123-86-4	X	X	
Butyl acrylate	141-32-2	X	X	
n-Butyl alcohol	71-36-3	X	X	
sec-Butyl alcohol	78-92-2	X	X	
tert-Butyl alcohol	75-65-0	X	X	
p-1 Butyl benzoic acid	98-73-7			X
Butylbenzyl phthalate	85-86-7	X	X	
tert-Butyl hydroperoxide	75-91-2	X	X	
2-Butyne-1,4-diol	110-65-6	X	X	
Butyraldehyde	123-72-8	X		X
n-Butyric acid	107-92-6			X
Butyric anhydride	106-31-0	X	X	
Caprolactam	105-60-2	X	X	
Carbon disulfide	75-15-0	X	X	
Carbon tetrabromide	558-13-4		X	
Carbon tetrachloride	56-23-5	X	X	
Chloroacetic acid	79-11-8	X		
Chlorobenzene	108-90-7	X	X	
Chlorodifluoromethane	75-45-6	X		
Chloroform	67-66-3	X	X	
p-Chloronitrobenzene	100-00-5	X	X	
Chloro-4-(ethylamino)-(isopropylamino)-s-triazine	1912-24-9		X	
Chloroprene	126-99-8		X	
Citric acid	77-92-9	X	X	
Crotonaldehyde	4170-30-0		X	
Crotonic acid	3724-65-0			X
Cumene	98-82-8	X	X	
Cumene hydroperoxide	80-15-9	X	X	X
Cyanuric chloride	108-77-0	X	X	
Cyclohexane	110-82-7	X	X	
Cyclohexane, oxidized	68512-15-2	X	X	
Cyclohexanol	108-93-0	X	X	X
Cyclohexanone	108-94-1	X	X	X

7-5

TABLE 7-1. CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY RULES AND GUIDELINE (CONTINUED)

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
Cyclohexanone oxime	100-64-1	X	X	
Cyclohexene	110-83-8	X	X	
1,3-Cyclopentadiene	110-83-8		X	
Cyclopropane	75-19-4	X	X	
Diacetone alcohol	123-42-2	X	X	
Dibutanized aromatic concentrate	-		X	
1,4-Dichlorobutene	110-57-6	X	X	
3,4-Dichloro-1-butene	64037-54-3	X	X	
Dichlorodifluoromethane	75-71-8	X	X	
Dichlorodimethylsilane	75-78-5	X	X	
Dichlorofluoromethane	75-43-4	X	X	
Diethanolamine	111-42-2	X		
Diethylbenzene	25340-17-4	X		
Diethylene glycol	111-46-6	X	X	
Di-isodecyl phthalate	26761-40-0	X		
Diisononyl phthalate	28553-12-0		X	
Dimethylamine	124-40-3		X	
Dimethyl terephthalate	120-61-6	X	X	
2,4-(and 2,6)-dinitrotoluene	121-14-2	X	X	
	606-20-2	X	X	
Dioctyl phthalate	117-81-7	X	X	
Dodecene	25378-22-7	X	X	
Dodecylbenzene, nonlinear	-	X	X	
Dodecylbenzenesulfonic acid	27176-87-0	X	X	
Dodecylbenzenesulfonic acid, sodium salt	25155-30-0	X	X	
Epichlorohydrin	106-89-8	X	X	
Ethanol	64-17-5	X	X	
Ethanolamine	141-43-5	X	X	
Ethyl acetate	141-78-6	X	X	
Ethyl acrylate	140-88-5	X	X	
Ethylbenzene	100-41-4	X	X	
Ethyl chloride	75-00-3	X	X	
Ethyl cyanide	107-12-0		X	
Ethylene	74-85-1	X	X	
Ethylene dibromide	106-93-4	X	X	X

TABLE 7-1. CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING
INDUSTRY RULES AND GUIDELINE (CONTINUED)

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
Ethylene dichloride	107-06-2	X	X	X
Ethylene glycol	107-21-1	X	X	
Ethylene glycol monobutyl ether	111-76-2	X	X	
Ethylene glycol monoethyl ether acetate	111-15-9	X	X	
Ethylene glycol monomethyl ether	109-86-4	X	X	
Ethylene oxide	75-21-8	X	X	
2-Ethylhexyl alcohol	104-76-7	X	X	
(2-Ethylhexyl) amine	104-75-6	X	X	
6-Ethyl-1,2,3,4-tetrahydro-9,10-antracenedione	15547-17-8	X	X	
Formaldehyde	50-00-0	X	X	X
Formicacid	64-18-6			X
Glycerol	56-81-5	X	X	
Glyoxal	107-22-2			X
n-Heptane	142-82-5	X	X	
Heptenes (mixed)	-	X	X	.
Hexamethylene diamine	124-09-4	X	X	
Hexamethylene diamine adipate	3323-53-3	X	X	
Hexamethylenetetramine	100-97-0	X	X	
Hexane	110-54-3	X	X	
2-Hexenedinitrile	13042-02-09		X	
3-Hexenedinitrile	1119-85-3		X	
Hydrogen cyanide	74-90-8		X	X
Isobutane	75-28-5	X	X	
Isobutanol	78-83-1	X	X	
Isobutylene	115-11-7	X	X	
Isobutyric acid	79-31-2			X
Isobytyraldehyde	78-84-2	X	X	
Isodecyl alcohol	25339-17-7		X	
Isooctyl alcohol	26952-21-6		X	
Isopentane	78-78-4	X	X	X
Isoprene	78-79-5	X	X	
Isopropanol	67-63-0	X	X	
Ketene	463-51-4	X	X	
Linear alcohols, ethoxylated, mixed	-	X	X	

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
Linear alcohols, ethoxylated, and sulfated, sodium salt, mixed	-	X	X	
Linear alcohols, sulfated, sodium salt, mixed	-	X	X	
Linear alkylbenzene	123-01-3	X	X	
2-Methyl pentane	107-83-5		X	
1-Methyl-2-pyrrolidone	872-50-4		X	
Magnesium acetate	142-72-3		X	
Maleic anhydride	108-31-6	X	X	X
Melamine	108-78-1		X	
Mesityl oxide	141-79-7	X	X	
Methacrylonitrile	126-98-7	X		
Methanol	67-56-1	X	X	
Methylamine	74-39-5	X	X	
ar-Methylbenzenediamine	25376-45-8	X	X	
Methyl chloride	74-87-3	X	X	
Methylene chloride	75-09-2	X	X	
Methyl ethyl ketone	78-93-3	X	X	X
Methyl isobutyl ketone	108-10-1	X	X	
Methyl methacrylate	80-62-6	X	X	
1-Methyl-2-pyrrolidone	872-50-4	X		
a-Methyl styrene	98-83-9			X
Methyl tert-butyl ether	-	X	X	
Naphthalene	91-20-3	X	X	
Nitrobenzene	98-95-3	X	X	
1-Nonene	27215-95-8	X	X	
Nonyl alcohol	143-08-08	X	X	
Nonylphenol	25154-52-3	X	X	
Nonylphenol, ethoxylated	9016-45-9	X	X	
Oil-soluble petroleum sulfonate, sodium salt	-		X	
Octene	25377-83-7	X	X	
Oil-soluble petroleum sulfonate, calcium salt	-	X	X	
n-Petane	109-66-0		X	
Pentaerythritol	115-77-5	X	X	

TABLE 7-1. CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING
INDUSTRY RULES AND GUIDELINE (CONTINUED)

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
3-Pentenenitrile	4635-87-4	X	X	
Pentenes, mixed	109-67-1	X	X	
Perchloroethylene	127-18-4	X	X	
Phenol	108-95-2	X	X	X
1-Phenylethyl hydroperoxide	3071-32-7	X	X	
Phenylpropane	103-65-1	X	X	
Phosgene	75-44-5	X	X	
Phthalic anhydride	85-44-9	X	X	X
Propane	74-98-6	X	X	X
Propionic acid	79-09-4		X	X
Propionaldehyde	123-38-6	X	X	
Propyl alcohol	71-23-8	X	X	
Propylene	115-07-1	X	X	
Propylene chlorohydrin	78-89-7		X	
Propylene glycol	57-55-6	X	X	
Propylene oxide	75-56-9	X	X	X
Sodium cyanide	143-33-9		X	
Sorbitol	50-70-4	X	X	
Styrene	100-42-5	X	X	X
Terephthalic acid	100-21-0	X	X	X
Tetraethyl lead	78-00-2	X	X	
Tetrahydrofuran	109-99-9	X	X	
Tetra (methyl-ethyl) lead	-	X	X	
1,1,2,2-Tetrachloroethane	79-34-5		X	
Tetraethyl lead	78-00-2		X	
Tetramethyl lead	75-74-1	X	X	
Toluene	108-88-3	X	X	
Toluene-2,4-diamine	95-80-7	X	X	
Toluene-2,4-(and, 2,6)-diisocyanate (80/20 mixture)	26471-62-5	X	X	
Tribromomethane	75-25-2		X	
1,1,1-Trichloroethane	71-55-6	X	X	
1,1,2-Trichloroethane	79-00-5	X	X	
Trichloroethylene	79-01-6	X	X	
Trichlorofluoromethane	75-69-4	X	X	

TABLE 7-1.   CHEMICALS AFFECTED BY SYNTHETIC ORGANIC CHEMICAL MANUFACTURING
INDUSTRY RULES AND GUIDELINE (CONTINUED)

Chemical	CAS number[a]	Reactor NSPS	Distillation NSPS	Air oxidation CTG/NSPS
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	X	X	
Triethanolamine	102-71-6	X	X	
Triethylene glycol	112-27-6	X	X	
Vinyl acetate	108-05-4	X	X	
Vinyl chloride	75-01-4	X	X	
Vinylidene chloride	75-35-4	X	X	
m-Xylene	108-38-3	X	X	
o-Xylene	95-47-6	X	X	
p-Xylene	106-42-3	X	X	
Xylenes (mixed)	1330-20-7	X	X	
m-Xylenol	576-26-1		X	

[a]CAS numbers refer to the Chemical Abstracts Registry numbers assigned to specific chemicals, isomers, or mixtures of chemicals. Some isomers or mixtures that are covered by the standards do not have CAS numbers assigned to them. The standards apply to all of the chemicals listed, whether CAS numbers have been assigned or not.

chemicals listed in Table 7-1 as a product, co-product, by-product, or intermediate.

7.3.3 Distillation Process New Source Performance Standard

The NSPS for Volatile Organic Compound Emissions from the Synthetic Organic Chemical Manufacturing Industry Distillation Operations (55 FR 26931, June 29, 1990; 40 CFR 60, Subpart NNN) was also promulgated on June 29, 1990. This NSPS covers SOCMI distillation operations constructed, reconstructed, or modified after December 30, 1983, that produce any of the affected chemicals listed in Table 7-1 as a product, co-product, or intermediate.

7.3.4 Reactor Process New Source Performance Standard

Standards of performance for SOCMI reactor process operations were proposed in the Federal Register on June 29, 1990 (55 FR 26953),[1] but have not yet been promulgated. The proposed standards apply to reactor processes operating as part of a process unit that produces any of the affected chemicals listed in Table 7-1 as a product, by-product, co-product, or intermediate.

7.4 APPLICABILITY

Because most industrial plants are comprised of numerous pieces or groups of equipment that may be viewed as "sources" of air pollutant emissions, it is helpful to define the specific source or "affected facility" that will be regulated. A possible definition for affected facility is "an individual reactor or distillation column with its own individual recovery system (if any) or the combination of two or more reactors or distillation columns and the common recovery system they share." Reactors or distillation units operated in a batch mode are excluded from this definition since this CTG focuses on reactor processes and distillation operations that are continuous. Also excluded from this definition are distillation operations that are a part of polymer manufacturing processes.

Other facilities to consider exempting from RACT requirements include reactor or distillation processes in plants with very low capacities. Most research and development facilities or laboratory-scale facilities are not designed to produce more than 1 gigagram (2.2×10^6 pounds) of chemicals per year. These facilities generally operate on an intermittent

basis making control techniques that apply to industry-scale production
facilities inappropriate for these operations. For these same reasons, it
may also be appropriate to exempt facilities with vent stream flow rates
or VOC concentrations below a specified level. It would be appropriate,
however, to require initial measurements or engineering assessments and
reports of the low flow rate to verify that these facilities are entitled
to the exemption. It may also prove valuable to require owners and
operators of both low capacity and low flow rate facilities to report if a
process or equipment change occurs that increases the production capacity
or flow rate above the specified cutoff levels.

7.5 FORMAT OF THE STANDARDS

Several formats are available for RACT regulations covering these
source categories. Because emissions can be measured from reactor process
and distillation operation vents and from applicable control devices, an
emission limitation (performance) standard, rather than an equipment
standard, is recommended.

Possible emission limitation formats would include a mass emission
rate limit, a concentration limit, or a percent reduction level. A
percent reduction format best represents performance capabilities of
control devices used to comply with the RACT regulation. Alternate
formats (such as mass emission rate or concentration limit) could cause
greater control than is required by RACT at some sources versus others and
less control than is required by RACT at others. For example, under a
mass emission rate or concentration format, the required control
efficiency is greater for streams with higher emission rates or higher
vent stream concentrations. Furthermore, the required control level for
vent streams with a low mass emission rate or concentration would not
reflect the capabilities of RACT.

A weight-percent reduction standard is feasible when applied to
incinerators, boilers, and process heaters because emission rates can be
measured readily from the control device inlet and outlet. As discussed
in Chapter 3.0 of this document, new incinerators can achieve at least
98 weight-percent reduction in total organics (minus methane and ethane),
provided that the total organic (minus methane and ethane) concentration
of the process vent stream is greater than approximately 2,000 parts per

million by volume (ppmv). For vent streams with organics concentrations below 2,000 ppmv, a 98 weight-percent reduction may be difficult to achieve, but an incinerator outlet concentration of 20 ppmv dry basis, corrected to 3 percent oxygen is achievable. Therefore, the recommended option is an emission limitation format based on a combination weight-percent reduction standard and a volume concentration standard. This recommended standard would demonstrate a 98 weight-percent reduction in total organic compounds (minus methane and ethane) or a reduction to 20 ppmv total organic compounds (minus methane and ethane) dry basis, corrected to 3 percent oxygen, whichever is less stringent.

Available data indicate that boilers and process heaters with design heat input capacity greater than 150 million British thermal unit per hour (MMBtu/hr) can achieve at least a 98 weight-percent reduction provided the waste stream is introduced into the flame zone where temperatures are highest 1,538 to 1,649 °C (2,800 to 3,000 °F). Therefore, vent stream combustion in a boiler or a process heater of this size makes performance testing unnecessary. However, to ensure sufficient destruction of the VOC, the regulation must require that the vent stream be introduced into the flame zone.

Flares differ from boilers, process heaters, and incinerators because combustion occurs in the open atmosphere rather than in an enclosed chamber. For this reason, it is difficult to measure the emissions from a flare to determine flare efficiency. However, the EPA test data indicate that if certain design and operating condition are met, flares can be presumed to be in compliance with the 98 percent/20 ppmv dry basis, corrected to 3 percent oxygen, emission limit. These conditions are found in Section 118 of Part 60 of Chapter 40 of the Code of Federal Regulations (40 CFR 60).[1]

7.6 PERFORMANCE TESTING

When the owner or operator of an affected facility conducts either an initial or subsequent performance test, it is recommended that the facility be running at full operating conditions and flow rates. Performance tests needed to achieve the specified RACT requirements are an initial test for a facility demonstrating either compliance with the 98-percent/20 ppmv emission limit, or maintenance of vent stream flow

rates and VOC concentrations at levels that assume a TRE value greater than 1.0. Specific recommendations pertaining to performance and compliance testing are provided in Appendix D of this document.

The best available procedure recommended for determining concentrations from reactor process and distillation vents is EPA Method 18. This method has the advantage of being able to detect and measure individual organic compounds. Details concerning the use of this method, including sampling, analysis, preparation of samples, calibration procedures, and reporting of results are discussed in Appendix D of this document. All of the reference methods mentioned in this section are found in Appendix A of 40 CFR 60.

7.6.1 Incinerators

For the owner or operator of a facility using an incinerator to achieve the suggested RACT emission limit, Reference Method 18 is recommended for determining compliance during any performance test. Reference Method 1 or 1A is recommended for selecting the sampling site. To determine the reduction efficiency, it is recommended that the control device inlet sampling site be located prior to the control device inlet and following the product recovery device. Reference Methods 2, 2A, 2C, or 2D are recommended for determining the volumetric flow rate, and Reference Method 3 is recommended for determining the air dilution correction, based on 3 percent oxygen in the emission sample.

7.6.2 Flares

The recommended compliance test for a flare includes measuring exit velocity and stream heat content to verify compliance with the operating specifications listed in 40 CFR 60.18.

7.6.3 Boiler or Process Heater

The performance test requirements for a small boiler or process heater (less than 150 MMBtu/hr) are identical to those for incinerators. For a large boiler or process heater, the initial performance test could be waived. It is the EPA's judgment that a boiler or process heater of this size would be able to meet the 98 percent/20 ppmv dry basis, corrected to 3 percent oxygen emission limit provided that the vent stream is introduced into the flame zone of the boiler or process heater.

7.6.4 Recovery Devices

A facility may choose to comply with RACT requirements by maintaining its product recovery system in such a manner that the vent stream flow rate and VOC concentration are below the cutoff points. Calculation of flow rate and VOC concentration must be immediately downstream of all product recovery equipment and prior to the introduction of any nonaffected stream. It is recommended that the volumetric flow rate be determined according to Reference Methods 2, 2A, 2c, or 2D, as appropriate. Molar composition of the vent stream should be measured via Reference Method 18.

7.7 COMPLIANCE MONITORING REQUIREMENTS

Note: The monitoring requirements need to be consistent with the Enhanced Monitoring Rule, once it is promulgated. The Hazardous Organic National Emission Standard for Hazardous Air Pollutants (HON) can be used as guidance in the interim. If a facility is covered by the HON, the HON monitoring requirements would also satisfy the RACT compliance determination requirements, and no additional monitoring is necessary.

7.7.1 Thermal Incinerators

There are two possible monitoring methods for facilities with an incinerator to determine compliance with the suggested RACT emission limit. They are continuous emission monitoring and continuous combustion control device monitoring. Continuous combustion control device inlet and outlet monitoring is preferred because it would give a continuous, direct measurement of actual emissions. However, no continuous monitor measuring total organics has been demonstrated for incinerators because each of the many diverse types of compounds in process vent streams would have to be identified separately and the concentrations of each determined. Continuous monitoring of all the individual compounds would be too expensive to be practical.

The other possible monitoring method is continuous combustion control device measurement. Certain parameters, such as temperature and flow rate, when measured, can reflect the level of achievable control device efficiency. It has been demonstrated that a decrease in combustion temperatures from the design value can cause significant decreases in control device efficiency. Because temperature monitors are relatively

inexpensive and easy to operate, it is recommended that the owner or operator of an affected facility should be required to install, calibrate, maintain, and operate a temperature measurement device according to manufacturer's instructions.

Flow indicators are also relatively inexpensive and easy to operate. Flow indicators determine control device efficiency by indicating whether or not organic-laden streams are being routed for destruction. It is recommended that the owner or operator of an affected facility should be required to install, calibrate, maintain, and operate a flow indicator according to the manufacturer's specifications. It is recommended that the flow indicator be installed at the entrance to any bypass line that could divert the stream away from the combustion device to that atmosphere.

7.7.2 Flares

In order comply with the recommended RACT requirements (see Section 7.5), flares must be operated in accordance with 40 CFR 60.18. Visual inspection is one method of determining whether a flame is present; however, if the flare is operating smokelessly, visual inspection would be difficult. An inexpensive heat sensing device, such as an ultra-violet beam sensor or a thermocouple, is recommended for use at the pilot light to indicate continuous presence of a flame. Measuring combustion parameters (as recommended for incinerators), such as temperature and flow rate, is not feasible for flares because these parameters are more variable in an unenclosed combustion zone.

It is also recommended that flow rate and heat content of the flared stream be determined by a flow indicator in the vent stream of the affected facility. This should be performed at a point closest to the flare and before the stream is joined with any other vent stream.

7.7.3 Boiler or Process Heater

To ensure that a boiler or process heater is operating properly as a combustion control device, it is recommended that the owner or operator maintain steam production (or equivalent) records. The owner or operator should also install and operate a flow indicator that provides a record of vent stream flow to the boiler (or process heater). It is recommended that temperature be monitored for boilers and process heaters of less than

150 MMBtu/hr design heat input capacity. Any boiler or process heater in which all vent streams are introduced with primary fuel is exempt from this requirement.

7.7.4 Recovery Devices

Facilities using product recovery devices to determine compliance with the recommended RACT, should ensure that the measured flow rate and VOC concentration have not changed since the time of the initial performance test. To accomplish this the facility owner or operator should monitor product recovery device parameters that correlate with proper operation of the device. The type of parameters to be monitored depends on the final device in the product recovery system.

For an absorber, two operating parameters are recommended as adequate determinants of performance: the specific gravity of the absorbing liquid and the flow rate of the absorbing liquid. For a condenser, the exit stream temperature is recommended as the main determinant of performance. For a carbon adsorber, the carbon bed temperature (after regeneration and completion of any cooling cycle) and the quantity of steam used to regenerate the carbon bed are recommended as the main determinants of performance.

As an alternative to monitoring the above parameters, the EPA recommends that a vent stream (post-recovery system) organic monitoring device with a continuous recorder be allowed.

7.8 REPORTING/RECORDKEEPING REQUIREMENTS

Each facility subject to the RACT requirements should keep records of certain key parameters that would indicate compliance. First, the facility should identify the control method selected to meet the RACT requirements. Next, the results of any performance testing results (discussed in Section 7.6) should be recorded. Further, the facility should record all parameters monitored on a routine basis to determine continued compliance with the RACT emission limit. These parameters (listed in Section 7.7) differ depending on the means by which the RACT requirements are met. Any deviations of the monitored parameters listed in Section 7.7 should also be recorded along with any corrective actions.

7.9 REFERENCES

1. _Federal_ _Register_. Standards of Performance for New Stationary
   Sources; Volatile Organic Compound (VOC) Emissions from the Synthetic
   Organic Chemical Manufacturing Industry (SOCMI) Distillation
   Operations. Final rule. 55 FR 26931-26952. June 29, 1990.

2. U. S. Environmental Protection Agency. Code of Federal Regulations.
   Chapter 40, Part 60. Washington, D.C. Office of the Federal
   Register. July 1, 1990. pp. 630 through 633.

APPENDIX A

LIST OF SYNTHETIC ORGANIC CHEMICAL
MANUFACTURING INDUSTRY CHEMICALS

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
83-32-9	Acenaphthene (POM)	X		X			
105-57-7	Acetal	X		X			
107-89-1	Acetaldol	X		X			
60-35-5	Acetamide	X		X			
103-84-4	Acetanilide	X		X			
108-24-7	Acetic acid, anhydride	X	X		X	X	
123-86-4	Acetic acid, butyl ester	X			X	X	
108-05-4	Acetic acid, ethenyl ester	X	X		X	X	
141-78-6	Acetic acid, ethyl ester	X			X	X	
142-72-3	Acetic acid, magnesium salt	X			X		
102-01-2	Acetoacetanilide	X		X			
---	Acetoamides	X		X			
---	Acetyl chloride	X		X			
---	Acetylene tetrabromide	X		X			
79-06-1	Acrylamide	X		X			
---	Alcohols, C-11 or lower, mixtures	X			X	X	
---	Alcohols, C-12 or higher, mixtures	X			X	X	
72-48-0	Alizarin (POM)	X		X			
00-8	Alkyl anthraquinones	X		X			
---	Alkyl naphthalenes sulfonates	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
107-18-6	Allyl alcohol	X		X			
---	Allyl bromide	X		X			
109-75-1	Allyl cyanide	X .		X			
---	Aluminum acetate	X		X			
---	Aluminum formates	X		X			
---	Aminobenzoic acid (p-)	X		X			
141-43-5	2-Aminoethanol	X			X	X	
---	Aminoethylethanolamine	X		X			
0-01-0	Aminophenol sulfonic acid	X		X			
123-30-8	Aminophenol (p-isomer)	X		X			
---	Amino-3,4,6-trichlorophenol (2-)	X		X			
---	Ammonium acetate	X		X			
---	Ammonium thiocyanate	X		X			
---	Amyl acetates	X		X			
---	Amyl alcohol (n-)	X		X			
---	Amyl alcohol (tert-)	X		X			
---	Amyl alcohols (mixed)	X		X			
---	Amyl chloride (n-)	X		X			
---	Amyl chlorides (mixed)	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Amyl ether	X		X			
---	Amylamines	X		X			
142-04-1	Aniline hydrochloride	X		X			
90-04-0	Anisidine (o-isomer)	X		X			
---	Anisole	X		X			
120-12-7	Anthracene (POM)	X		X			
---	Anthranilic acid	X		X			
103-33-7	Azobenzene	X		X			
---	Barium acetate	X		X			
---	Benzamide	X		X			
62-53-3	Benzenamine	X	X		X	X	
71-43-2	Benzene	X	X		X	X	
98-48-6	Benzenedisulfonic acid	X		X			
121-91-5	1,3-Benzenedicarboxylic acid	X	X		X	X	
100-21-0	1,4-Benzenedicarboxylic acid	X	X		X	X	X
117-81-7	1,2-Benzenedicarboxylic acid, bis (2-ethylhexyl) ester	X	X				
85-68-7	1,2-Benzenedicarboxylic acid butyl, phenylmethyl ester	X	X		X	X	
---	1,2-Benzenedicarboxylic acid di-n-heptyl-n-nonyl undecyl ester	X					

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
26761-40-0	1,2-Benzenedicarboxylic acid diisodecyl ester	X	X			X	X
---	1,2-Benzenedicarboxylic acid diisononyl ester	X					X
120-61-6	1,4-Benzenedicarboxylic acid, dimethyl ester	X	X		X	X	X
98-48-6	Benzenedisulfonic acid	X		X			
98-11-3	Benzenesulfonic acid	X	X			X	
---	Benzenesulfonic acid, mono-C_{10-16}-alkyl derivatives, sodium salts	X				X	X
---	Benzidine	X		X			
134-81-6	Benzil (POM)	X		X			
76-93-7	Benzilic acid (POM)	X		X			
---	Benzoguanamine	X		X			
119-53-9	Benzoin (POM)	X		X			
100-47-0	Benzonitrile (POM)	X		X			
119-61-9	Benzophenone (POM)	X		X			
98-07-7	Benzotrichloride	X		X			
96-88-4	Benzoyl chloride	X		X			
---	Benzoyl perioxide	X		X			
140-11-4	Benzyl acetate	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS (CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
100-51-6	Benzyl alcohol	X		X			
120-51-4	Benzyl benzoate (POM)	X		X			
98-87-3	Benzyl dichloride	X		X			
---	Benzylamine	X		X			
---	Benzylideneacetone	X		X			
92-52-4	1,1-Biphenyl	X	X			X	
542-88-1	Bis (chloromethyl) ether (dichloromethyl ether)	X		X			
115-77-5	2,2-Bis (hydroxymethyl)- 1,3-propanediol	X	X			X	X
108-86-1	Bromobenzene	X		X			
27497-51-4	Bromonaphthalene (POM)	X		X			
---	Butadiene and butene fractions	X				X	X
123-72-8	Butanol	X				X	X
106-97-8	Butane	X				X	X
---	Butanes, mixed	X				X	X
584-03-2 107-88-0	1,2 (and 1,3) Butanediol	X	X			X	
110-63-4	1,4-Butanediol	X	X			X	X
106-31-0	Butanoic acid, anhydride	X				X	X
71-36-3	1-Butanol	X				X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
78-92-3	2-Butanol	X				X	X
78-93-3	2-Butanone	X	X		X	X	X
123-73-9	2-Butenal	X	X			X	
106-98-91	1-Butene	X					
---	2-Butene	X				X	X
---	Butenes, mixed	X				X	X
3724-65-0	2-Butenoic acid	X			X	X	
111-76-2	2-Butoxyethanol	X					
---	Butyl acetate (sec-)	X		X			
---	Butyl acetate (tert-)	X		X			
---	Butyl chloride (tert-)	X		X			
---	Butyl benzoate	X		X			
---	Butyl hydroperoxide (tert-)	X		X			
---	Butyl mercaptan (2-Methyl-2-propanethiol) (tert-)	X		X			
---	Butyl mercaptan (n-)	X		X			
---	Butyl methacrylate (n-)	X		X			
---	Butyl methacrylate (tert-)	X		X			
---	Butyl phenol (tert-)	X		X			
---	Butylamine (n-isomer)	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Butylamine (s-isomer)	X		X			
---	Butylamine (t-isomer)	X		X			
---	Butylbenzene (tert-)	X		X			
---	tert-Butylbenzene	X				X	
---	Butylbenzoic acid (p-tert-)	X		X			
85-68-7	Butylbenzyl phthalate	X		X			
---	p-tert-Butyl toluene	X		X			
110-65-6	2-Butyne-1,4-diol	X					X
---	Butyrolactone	X		X			
---	Butyronitrile	X		X			
---	Calcium acetate	X		X			
---	Calcium propionate	X		X			
---	Caproic acid	X		X			
---	Carbamic acid, monoammonium salt	X					
63-25-2	Carbaryl	X		X			
86-74-8	Carbazole	X		X			
75-73-0	Carbon tetrafluoride	X		X			
75-15-0	Carbon disulfide	X	X			X	X
75-44-5	Carbonic dichloride	X	X			X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
75-87-6	Chloral	X		X			
---	Chloranil	X		X			
79-11-8	Chloroacetic acid	X		X			
532-27-4	Chloroacetophenone (2-)	X		X			
---	Chloroaniline (m-isomer)	X		X			
---	Chloroaniline (o-isomer)	X		X			
106-47-8	Chloroaniline (p-isomer)	X		X			
---	Chlorobenzaldehyde	X		X			
108-90-7	Chlorobenzene	X	X			X	X
---	Chlorobenzoic acid	X		X			
---	Chlorobenzotrichloride (o-)	X		X			
---	Chlorobenzotrichloride (p-)	X		X			
---	Chlorobenzoyl chloride (o-)	X		X			
---	Chlorobenzoyl chloride (p-)	X		X			
126-99-8	2-Chloro-1,3-butadiene	X	X			X	
25497-29-4	Chlorodifluoroethane	X		X			
75-45-6	Chlorodifluoromethane	X		X			
75-00-3	Chloroethane	X	X			X	X
108-05-4	Chloroethene	X	X			X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
1912-24-9	6-Chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine	X				X	
---	Chlorofluorocarbons	X		X			
---	Chlorohydrin	X		X			
74-87-3	Chloromethane	X					
100-00-5	(Chloromethyl) benzene	X	X			X	X
106-89-8	(Chloromethyl) oxirane	X	X			X	X
25586-43-0	Chloronaphthalene (POM)	X		X			
121-73-3	Chloronitrobenzene (1,3-)	X		X			
88-73-3	Chloronitrobenzene (o-isomer)	X		X			
109-69-3	1-Chloro-4-nitrobenzene	X	X			X	X
---	Chlorophenols (all isomers)	X		X			
78-89-7	2-Chloro-1-propanol	X				X	
107-05-1	3-Chloro-1-propene	X	X			X	X
---	Chlorosulfonic acid	X		X			
108-41-8	Chlorotoluene (m-isomer)	X		X			
95-49-8	Chlorotoluene (o-isomer)	X		X			
106-43-4	Chlorotoluene (p-isomer)	X		X			
---	Chlorotrifluoroethylene	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
75-72-9	Chlorotrifluoromethane	X		X			
---	Choline chloride	X		X			
218-01-9	Chrysene (POM)	X		X			
---	Cinnamic acid	X		X			
---	Cobalt acetate	X		X			
---	Coconut oil acids, sodium salt	X					
---	Copper acetate	X		X			
108-39-4	Cresol (m-isomer)	X		X			
1319-77-3	Cresols/cresylic acid (mixed)	X		X			
95-48-7	Cresols (o-isomer)	X		X			
106-44-5	Cresols (p-isomer)	X		X			
---	Cyanamide	X		X			
372-09-8	Cyanoacetic acid (CN compound)	X		X			
0-01-1	Cyanoformamide	X		X			
---	Cyanogen chloride (CN compound)	X		X			
---	Cyanuric acid	X		X			
110-82-7	Cyclohexane	X	X			X	X
---	Cyclohexane, oxidized	X				X	X
---	Cyclohexanone oxime	X				X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
110-83-8	Cyclohexene	X				X	X
108-91-8	Cyclohexylamine	X		X			
111-78-4	Cyclooctadiene	X		X			
1552-12-1	Cyclooctadiene (1,5-isomer)	X		X			
542-92-7	1,3-Cyclopentadiene	X					
75-19-4	Cyclopropane	X				X	X
91-17-8	Decahydronaphthalate	X		X			
0-01-2	Diacetoxy-2-Butene (1,4-)	X		X			
---	Diallyl isophthalate	X		X			
131-17-9	Diallyl phthalate	X		X			
---	Diaminobenzoic acids	X		X			
137-09-7	Diaminophenol hydrochloride	X		X			
117-83-9	Dibutoxyethyl phthalate	X·		X			
106-93-4	1,2-Dibromoethane	X	X			X	X
---	Dibutanized aromatic concentrate	X				X	
27134-27-6	Dichloroaniline (all isomers)	X		X			
106-46-7	Dichlorobenzene (1,4-isomer) (p-isomer)	X		X			
541-73-1	Dichlorobenzene (m-isomer)	X		X			
95-50-1	Dichlorobenzene (o-isomer)	X		X			

A-11

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
91-94-1	Dichlorobenzidine (3,3'-)	X		X			
760-23-6	Dichloro-1-butene (3,4-isomer)	X		X			
764-41-0	Dichloro-2-butene (1,4-isomer)	X.		X			
111-44-4	Dichloroethyl ether (bis(2-chloroethyl)ether)	X		X			
540-59-0	Dichloroethylene (1,2-isomer)	X		X			
---	Dichloronitrobenzenes	X		X			
---	Dichloropane (1,1-)	X		X			
---	Dichloropentanes	X		X			
---	Dichlorophenol (2,4-isomer)	X		X			
---	Dichloropropane (1,1-)	X		X			
542-75-6	Dichloropropene (1,3-isomer)	X		X			
---	Dichloropropene/dichloropropane (mixed)	X		X			
---	Dichlorotetrafluoroethane	X		X			
764-41-0	1,4-Dichloro-2-butene	X					X
---	3,4-Dichloro-1-butene	X					
75-71-8	Dichlorodifluoromethane	X	X			X	X
75-78-5	Dichlorodimethylsilane	X				X	X
107-06-2	1,2-Dichloroethane	X	X				
75-35-4	1,1-Dichloroethene	X	X			X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS (CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
75-43-4	Dichlorofluoromethane	X				X	X
75-09-2	Dichloromethane	X	X			X	X
96-23-1	1,3-Dichloro-2-propanol	X				X	
---	Dicyanidiamide	X		X			
---	Dicyclohexylamine	X		X			
---	Dicyclopentadiene	X		X			
25340-17-4	Diethylbenzene	X				X	X
84-66-2	Diethyl phthalate	X		X			
64-67-5	Diethyl sulfate	X		X			
109-89-7	Diethylamine	X		X			
579-66-8	Diethylaniline (2,6-isomer)	X		X			
121-69-7	Diethylaniline (N,N-)	X		X			
112-73-2	Diethylene glycol dibutyl ether	X		X			
112-36-7	Diethylene glycol diethyl ether (glycol ether)	X		X			
111-96-6	Diethylene glycol dimethyl ether (glycol ether)	X		X			
124-17-4	Diethylene glycol monobutyl ether acetate (glycol ether)	X		X			
112-34-5	Diethylene glycol monobutyl ether (glycol ether)	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
112-15-2	Diethylene glycol monoethyl ether acetate (glycol ether)	X		X			
111-90-0	Diethylene glycol monoethyl ether (glycol ether)	X		X			
629-38-9	Diethylene glycol monomethyl ether acetate (GE)	X		X			
111-77-3	Diethylene glycol monomethyl ether (glycol ether)	X		X			
---	Difluoroethane (1,1-)	X		X			
---	Diisobutylene	X		X			
584-84-9 91-08-07	1,3-Diisocyanato-2-(and 4-) methylbenzene (80/20 mixture)						
27554-26-3	Diisooctyl phthalate	X		X			
---	Diisopropyl amine	X		X			
---	Diketene	X		X			
---	Dimethyl acetamide	X		X			
119-93-7	Dimethyl benzidine (3,3-isomer)	X		X			
115-10-6	Dimethyl ether - N,N	X		X			
68-12-2	Dimethyl formamide (NN-isomer) (DMF)	X		X			
57-14-7	Dimethyl hydrazine (1,1-isomer)	X		X			
131-11-3	Dimethyl phthalate	X		X			
77-78-1	Dimethyl sulfate	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS (CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Dimethyl sulfide	X		X			
---	Dimethyl sulfoxide	X		X			
108-01-0	Dimethylaminoethanol (2-isomer)	X		X			
121-69-7	Dimethylaniline - N,N (N,N Diethylaniline)	X		X			
95-47-6	1,2-Dimethylbenzene	X	X			X	X
108-38-3	1,3-Dimethylbenzene	X				X	X
106-42-3	1,4-Dimethylbenzene	X	X			X	X
1330-20-7	Dimethylbenzenes (mixed)	X	X			X	X
75-91-2	1,1-Dimethylethyl hydroperoxide	X					X
1300-71-6	2,6-Dimethylphenol	X					
25154-54-5	Dinitrobenzenes	X		X			
---	Dinitrobenzoic acid (3,5-)	X		X			
51-28-5	Dinitrophenol (2,4-isomer)	X		X			
---	Dinitrotoluene (2,3-)	X		X			
---	Dinitrotoluene (3,4-)	X		X			
123-91-1	Dioxane (1,4-Diethyleneoxide)	X		X			
646-06-0	Dioxolane	X		X			
101-81-5	Diphenyl methane	X		X			
101-84-8	Diphenyl oxide (POM)	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
102-08-9	Diphenyl thiourea (POM)	X		X			
122-39-4	Diphenylamine (POM)	X		X			
110-98-5	Dipropylene glycol	X		X			
117-82-8	Di(2-methoxyethyl) phthalate	X		X			
97-39-2	Di-o-tolyguanidine	X		X			
6842-15-5	1-Dodecene	X					
---	Dodecylbenzene, linear	X					
123-01-3	Dodecylbenzene, nonlinear	X				X	X
---	Dodecylbenzenesulfonic acid	X				X	X
25155-30-0	Dodecylbenzenesulfonic acid, sodium salt	X					
---	Dodecene (branched)	X		X			
---	Dodecyl mercaptan (branched)	X		X			
---	Dodecyl phenol (branched)	X		X			
28675-17-4	Dodecylaniline	X		X			
27193-86-8	Dodecylphenol	X		X			
74-84-0	Ethane	X		X			
107-21-1	1,2-Ethanediol	X	X			X	X
112-27-6	2,2'-(1,2-Ethanediylbis (oxy)) bisethanol	X	X			X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS (CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
64-17-5	Ethanol	X				X	X
74-85-1	Ethene	X				X	X
463-51-4	Ethenone	X				X	X
100-42-5	Ethenylbenzene	X	X		X	X	X
110-80-5	2-Ethoxyethanol	X	X			X	
111-15-9	2-Ethoxyethyl acetate acetate	X	X			X	X
---	Ethyl acetoacetate	X		X			
---	Ethyl bromide	X		X			
---	Ethyl caproate	X		X			
105-39-5	Ethyl chloroacetate	X		X			
---	Ethyl ether	X		X			
---	Ethyl hexanol (2-)	X		X			
---	Ethyl mercaptan (ethanethiol)	X		X			
---	Ethyl orthoformate	X		X			
---	Ethyl oxalate	X		X			
---	Ethyl sodium oxalacetate	X		X			
75-04-7	Ethylamine	X		X			
103-69-5	Ethylaniline (N-isomer)	X		X			
578-54-1	Ethylaniline (o-isomer)	X		X			

A-17

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
100-41-4	Ethylbenzene	X	X				
9004-57-3	Ethylcellulose	X		X			
105-56-6	Ethylcyanoacetate	X		X			
96-49-1	Ethylene carbonate	X		X			
---	Ethylene chlorohydrin	X		X			
106-93-4	Ethylene dibromide (dibromoethane) (EDB)	X		X			
111-55-7	Ethylene glycol diacetate	X		X			
112-48-1	Ethylene glycol dibutyl ether (GE)	X		X			
629-14-1	Ethylene glycol diethyl ether	X		X			
110-71-4	Ethylene glycol dimethyl ether (glycol ether)	X		X			
542-59-6	Ethylene glycol monoacetate	X		X			
112-07-2	Ethylene glycol monobutyl ether acetate (glycol ether)	X		X			
111-76-2	Ethylene glycol monobutyl ether (glycol ether)	X		X			
111-15-9	Ethylene glycol monoethyl ether acetate (glycol ether)	X		X			
110-49-6	Ethylene glycol monomethyl ether acetate (glycol ether)	X		X			
109-86-4	Ethylene glycol monomethyl ether (glycol ether)	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
00-2	Ethylene glycol monooctyl ether (GE)	X		X			
122-99-6	Ethylene glycol monophenyl ether (glycol ether)	X		X			
2807-30-9	Ethylene glycol monopropyl ether (glycol ether)	X		X			
---	Ethylene imine (aziridine)	X		X			
107-15-3	Ethylenediamine	X		X			
60-00-4	Ethylenediamine tetraacetic acid	X		X			
151-56-4	Ethyleneimine (aziridine)	X		X			
123-05-7	2-Ethylhexanal	X				X	
---	Ethylhexanoic acid	X		X			
104-76-7	2-Ethyl-1-hexanol	X					
103-11-7	Ethylhexyl acrylate (2-isomer)	X		X			
104-75-6	(2-Ethylhexyl) amine	X				X	X
---	Ethylhexyl succinate (2-)	X		X			
---	Ethylmethylbenzene	X				X	
---	Ethylnaphthalene (2-isomer) (alkyl naphthalene)	X		X			
---	6-Ethyl-1,2,3,4-tetrahydro-9,10-anthracenedione	X				X	X
74-86-2	Ethyne	X				X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Fatty acids, tall oil, sodium salt	X					
206-44-0	Fluoranthene (POM)	X		X			
75-12-7	Formamide	X		X			
110-17-8	Fumaric acid	X		X			
108-31-6	2,5-Furandione	X	X		X	X	X
50-70-4	D-Glucitol	X					X
111-30-8	Glutaraldehyde	X		X			
367-47-5	Glyceraldehyde	X		X			
---	Glycerol dichlorohydrin	X		X			
---	Glycidol	X		X			
56-40-6	Glycine	X		X			
---	Glycol ethers (other than those presented)	X		X			
---	Guanidine	X		X			
---	Guanidine nitrate	X		X			
142-82-5	Heptane	X				X	X
---	Heptenes (mixed)	X				X	X
118-74-1	Hexachlorobenzene	X		X			
87-68-3	Hexachlorobutadiene	X		X			
---	Hexachlorocyclopentadiene	X		X			

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
67-72-1	Hexachloroethane	X		X			
---	Hexadecyl alcohol (cetyl alcohol)	X				X	
592-45-0	Hexadiene (1,4-isomer)	X				X	
105-60-2	Hexahydro-2H-azepin-2-one	X	X			X	X
110-53-3	Hexane	X				X	X
124-09-4	1,6-Hexanediamine	X				X	X
---	1,6-Hexanediamine adipate	X				X	X
111-69-3	Hexanedinitrile	X	X			X	X
124-04-9	Hexanedioic acid	X				X	X
106-69-4	Hexanetriol (1,2,6-isomer)	X				X	
---	2-Hexenedinitrile	X				X	
---	3-Hexenedinitrile	X				X	
---	Hexyl alcohol	X				X	
---	Hexylene glycol	X				X	
---	Higher glycols	X				X	
74-90-8	Hydrocyanic acid	X	X		X	X	
123-31-9	Hydroquinone	X				X	
0-01-6	Hydroxyadipaldehyde	X				X	
---	Hydroxybenzoic acid (p-)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	3-Hydroxybutyraldehyde	X	X				X
123-42-2	4-Hydroxy-4-methyl-2-pentanone	X	X			X	X
75-86-5	2-Hydroxy-2-methylpropanenitrile	X	X			X	X
---	2-Hydroxy-1,2,3-propanetricarboxylic acid	X				X	X
11-42-2	2,2'-Iminobisethanol	X	X			X	X
111-42-2	Iminodiethanol (2,2-)	X				X	
74-88-4	Iodo-methane	X				X	
---	Isoamyl alcohol	X				X	
---	Isoamyl chloride (mixed)	X				X	
---	Isoamylene	X				X	
85-44-9	1,3-Isobenzofurandione	X	X		X	X	X
---	Isobutanol	X				X	
---	Isobutyl acetate	X				X	
106-63-8	Isobutyl acrylate	X				X	
---	Isobutyl methacrylate	X				X	
---	Isobutyl vinyl ether (vinyl isobutyl ether)	X				X	
25339-17-7	Isodecanol	X					
---	Isohexyldecyl alcohol	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Isononyl alcohol	X				X	
78-59-1	Isophorone	X				X	
0-01-7	Isophorone nitrile	X				X	
---	Isopropanol	X				X	
---	Isopropyl acetate	X				X	
---	Isopropyl chloride	X				X	
---	Isopropyl ether	X				X	
---	Isopropylamine	X				X	
25168-06-3	Isopropylphenol	X				X	
---	Lactic acid	X				X	
---	Lauryl dimethylamine oxide	X				X	
---	Lead acetate	X				X	
0-01-8	Lead phthalate	X				X	
---	Lead subacetate	X				X	
---	Linear alcohols, ethoxylated, mixed	X				X	X
---	Linear alcohols, ethoxylated and sulfated, sodium salt, mixed	X				X	X
---	Linear alcohols, sulfated, sodium salt, mixed	X				X	
---	Linear alkylbenzene (linear dodecylbenzene)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Maleic acid	X				X	
123-33-1	Maleic hydrazide	X				X	
6915-15-7	Malic acid	X				X	
---	Mercuric acetate	X				X	
---	Mesityl oxide	X				X	
121-47-1	Metanilic acid	X				X	
79-41-4	Methacrylic acid	X				X	
---	Methallyl alcohol	X				X	
---	Methallyl chloride	X				X	
74-89-5	Methanamine	X	X			X	X
---	Methane	X				X	
67-56-1	Methanol	X	X			X	X
63-68-3	Methionine	X				X	
109-86-4	2-Methoxyethanol	X	X			X	X
79-20-9	Methyl acetate	X				X	
---	Methyl acetoacetate	X				X	
96-33-3	Methyl acrylate	X				X	
74-83-9	Methyl bromide (bromomethane)	X				X	
---	Methyl butenols	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Methyl butynol	X				X	
107-31-3	Methyl formate	X				X	
60-34-4	Methyl hydrazine	X				X	
108-11-2	Methyl isobutyl carbinol	X				X	
108-10-1	Methyl isobutyl ketone (hexone)	X				X	
624-83-9	Methyl isocyanate	X				X	
74-93-1	Methyl mercaptan	X				X	
98-85-1	Methyl phenyl carbinol (methyl benzyl alcohol)	X				X	
---	Methyl salicylate	X				X	
100-61-8	Methylaniline (n-isomer)	X				X	
108-88-3	Methylbenzene	X	X			X	X
95-80-7	4-Methyl-1,3-benzenediamine	X	X			X	X
---	ar-Methylbenzenediamine	X					X
78-79-5	2-Methyl-1,3-butadiene	X				X	
---	Methylbutanol (2-)	X				X	
78-78-4	2-Methylbutane	X				X	X
513-35-9	2-Methyl-2-butene	X				X	X
---	2-Methylbutenes, mixed	X				X	X
1634-04-4	Methyl tert-butyl ether	X	X				

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
606-20-2	1-Methyl-2,4-dinitrobenzene (and 2-Methyl-1,3-dinitrobenzene)	X					
121-14-2	1-Methyl-2,4-dinitrobenzene	X	X			X	X
98-82-8	(1-Methylethyl) benzene	X	X			X	X
80-05-7	4,4'-(1-Methylethylidene) bisphenol	X	X			X	X
26952-21-6	6-Methyl-heptanol	X				X	
108-87-2	Methylcyclohexane	X				X	
25639-42-3	Methylcyclohexanol	X				X	
1331-22-2	Methylcyclohexanone	X				X	
101-77-9	Methylene dianiline (4,4-isomer) (MDA)	X				X	
101-68-8	Methylene diphenyl diisocyanate (MDI)	X				X	
79-69-6	Methylionones (a-isomer)	X				X	
124-40-3	N-Methylmethanamine	X	X			X	
---	Methylnaphthalene (1-isomer) (alkyl naphthalene)	X				X	
---	Methylnaphthalene (2-isomer) (alkyl naphthalene)	X				X	
75-56-9	Methyloxirane	X	X		X	X	X
107-83-5	2-Methylpentane	X				X	
108-10-1	4-Methyl-2-pentanone	X	X			X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
141-79-7	4-Methyl-3-penten-2-one	X					
80-15-9	1-Methyl-1-phenylethyl hydroperoxide	X	X		X	X	X
78-84-2	2-Methylpropanal	X				X	X
75-28-5	2-Methylpropane	X				X	X
78-83-1	2-Methyl-1-propanol	X					
75-65-0	2-Methyl-2-propanol	X	X			X	X
115-11-7	2-Methyl-1-propene	X	X			X	X
126-98-7	2-Methyl-2-propenenitrile	X					
80-62-6	2-Methyl-2-propenoic acid, methyl ester	X					
872-50-4	1-Methyl-2-pyrrolidinone	X					X
---	Methyl-1-pentene (2-)	X				X	
77-75-8	Methylpentynol	X				X	
---	Morpholine	X				X	
91-20-3	Naphthalene	X	X			X	X
85-47-2	Naphthalene sulfonic acid (a-isomer) (POM)	X				X	
120-18-3	Naphthalene sulfonic acid (b-isomer) (POM)	X				X	
---	Naphthenic acids	X				X	
90-15-3	Naphthol (a-isomer) (POM)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
135-19-3	Naphthol (b-isomer) (POM)	X				X	
567-18-0	Naphtholsulfonic acid (1-) (POM)	X				X	
84-86-6	Naphthylamine sulfonic acid (1,4-) (POM)	X				X	
81-16-3	Naphthylamine sulfonic acid (2,1-) (POM)	X				X	
134-32-7	Naphthylamine (1-) (POM)	X				X	
91-59-8	Naphthylamine (2-) (POM)	X				X	
---	Neohexane	X				X	
---	Neopentanoic acid (trimethylacetic acid)	X				X	
---	Neopentyl glycol	X				X	
---	Nickel formate	X				X	
---	Nitriloacetic acid	X				X	
102-71-6	2,2,2-Nitrilotrisethanol	X	X			X	X
99-09-2	Nitroaniline (m-isomer)	X				X	
88-74-4	Nitroaniline (o-isomer)	X				X	
---	Nitroaniline (p-isomer)	X				X	
91-23-6	Nitroanisole (o-isomer)	X				X	
100-17-4	Nitroanisole (p-isomer)	X				X	
98-95-3	Nitrobenzene	X	X			X	X
---	Nitrobenzoic acid (m-)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Nitrobenzoic acid (o-)	X				X	
---	Nitrobenzoic acid (p-)	X				X	
---	Nitrobenzoyl chloride (p-)	X				X	
---	Nitroethane	X				X	
---	Nitroguanidine	X				X	
---	Nitromethane	X				X	
86-57-7	Nitronaphthalene (1-) (POM)	X				X	
100-02-7	Nitrophenol (4-) (p-)	X				X	
88-75-5	Nitrophenol (o-isomer) (2-Nitrophenol)	X				X	
79-46-9	Nitropropane (1-)	X				X	
79-46-9	Nitropropane (2-)	X				X	
13211-12-6	Nitrotoluene	X				X	
88-72-2	Nitrotoluene (2-isomer) (o-)	X				X	
99-08-1	Nitrotoluene (3-isomer) (m-)	X				X	
99-99-0	Nitrotoluene (4-isomer) (p-)	X				X	
25168-04-1	Nitroxylene	X				X	
143-08-8	1-Nonanol	X					X
124-11-8	1-Nonene	X				X	X
---	Nonene (nonylene)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
1081-77-2	Nonylbenzene (branched)	X				X	
15154-52-3	Nonylphenol	X	X			X	X
---	Nonylphenol, ethoxylated	X					X
25154-52-3	Nonylphenol (branched)	X				X	
88-12-0	N-Vinyl-2-Pyrrolidine	X				X	
---	Octane	X				X	
111-66-0	Octene-1	X	X			X	X
---	Octylamine (tert-)	X				X	
27193-28-8	Octylphenol	X				X	
---	Oil-soluble petroleum sulfonate, calcium salt	X					X
---	Oil-soluble petroleum sulfonate, sodium salt	X				X	
---	Oxalic acid	X				X	
---	Oxamide	X				X	
75-21-8	Oxirane	X	X		X	X	X
---	Oxo chemicals	X				X	
11-46-6	2,2'-Oxybisethanol	X	X				X
30525-89-4	Paraformaldehyde	X				X	
123-63-7	Paraldehyde	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
87-86-5	Pentachlorophenol	X				X	
---	Pentaerythritol tetranitrate	X				X	
109-66-0	Pentane	X				X	
---	Pentanethiol	X				X	
---	Pentanol (2-)	X				X	
---	Pentanol (3-)	X				X	
---	Pentene (2-)	X				X	
79-21-0	Peracetic acid	X				X	
594-42-3	Perchloromethyl mercaptan	X				X	
---	3-Penetenenitrile	X					X
---	Pentenes, mixed	X				X	
---	Phenacetin (acetophenetidin)	X				X	
85-01-8	Phenanthrene (POM)	X				X	
---	Phenetidine (o-)	X				X	
156-43-4	Phenetidine (p-isomer)	X				X	
---	Phenolphthalein	X				X	
---	Phenolsufonic acids (all isomers)	X				X	
---	Phenylanthranilic acid	X				X	
---	Phenylenediamine (m-)	X				X	

TABLE A-1.   LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Phenylenediamine (o-)	X				X	
106-50-3	Phenylenediamine (p-isomer)	X				X	
---	Phenylmethylpyrazolone (methylhenylpyrazolinone)	X				X	
---	1-Phenylethyl hydroperoxide	X					X
108-73-6	Phloroglucinol	X				X	
88-99-3	Phthalic acid	X				X	
85-41-6	Phthalimide	X				X	
91-15-6	Phthalonitrile	X				X	
---	Picoline (a-)	X				X	
108-99-6	Picoline (b-isomer)	X				X	
---	Picramic acid	X				X	
---	Picric acid	X				X	
110-85-0	Piperazine	X				X	
---	Piperylene	X				X	
25322-68-3	Polyethylene glycol	X				X	
25322-69-4	Polypropylene glycol	X				X	
---	Potassium acetate	X				X	
123-38-6	Propanal	X	X			X	X
74-98-6	Propane	X				X	X

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
57-55-6	1,2-Propanediol	X	X		X	X	
107-12-0	Propanenitrile	X					
56-81-5	1,2,3-Propanetriol	X	X		X	X	
71-23-8	1-Propanol	X	X			X	X
67-63-0	2-Propanol	X				X	X
67-64-1	2-Propanone	X	X		X	X	X
115-07-1	1-Propene	X				X	X
107-13-1	2-Propenenitrile	X	X		X	X	X
79-10-7	2-Propenoic acid	X	X		X	X	X
141-32-2	2-Propenoic acid, butyl ester	X	X			X	X
140-88-5	2-Propenoic acid, ethyl ester	X	X			X	X
57-57-8	Propiolacetone (b-isomer)	X				X	
---	Propyl acetate (n-)	X				X	
---	Propyl carbonate	X				X	
---	Propyl chloride	X				X	
---	Propylamine	X				X	
103-65-1	Propylbenzene	X					X
78-87-5	Propylene dichloride (1,2-Dichloropropane)	X				X	
107-98-2	Propylene glycol monomethyl ether	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS (CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Pseudocumene	X				X	
---	Pseudocumidine	X				X	
129-00-0	Pyrene (POM)	X				X	
110-86-1	Pyridine	X				X	
---	Pyrrolidone (2-)	X				X	
106-51-4	Quinone	X				X	
108-46-3	Resorcinol	X				X	
69-72-7	Salicylic acid	X				X	
---	Sebacic acid	X				X	
---	Sodium acetate	X				X	
---	Sodium benzoate	X				X	
---	Sodium chloroacetate	X				X	
143-33-9	Sodium cyanide	X				X	
---	Sodium dodecyl benzene sulfonate	X				X	
---	Sodium formate	X				X	
124-41-4	Sodium methooxide	X				X	
---	Sodium oxalate	X				X	
139-02-6	Sodium phenate	X				X	
---	Sodium propionate	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Sorbic acid	X				X	
588-59-0	Stilbene	X				X	
110-15-6	Succinic acid	X				X	
110-61-2	Succinonitrile	X				X	
121-57-3	Sulfanilic acid	X				X	
126-33-0	Sulfolane	X				X	
---	Synthesis gas	X				X	
---	Tallow acids, potassium salt	X					
---	Tallow acids, sodium salt	X					
526-83-0	Tartaric acid	X				X	
---	Terephthaloyl chloride	X				X	
---	Tetra (methyl-ethyl) plumbane	X					X
100-97-0	1,3,5,7-Tetraazatricyclo (3,3,1,13,7)-decane	X	X			X	X
558-13-4	Tetrabromomethane	X	X			X	
632-79-1	Tetrabromophthalic anhydride	X				X	
95-94-3	Tetrachlorobenzene (1,2,4,5-)	X				X	
---	Tetrachlorobenzene (1,2,3,5-isomer)	X				X	
117-08-8	Tetrachlorophthalic anhydride	X				X	
79-34-5	1,1,2,2-Tetrachloroethane	X	X			X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
127-18-4	Tetrachloroethene	X	X			X	X
56-23-5	Tetrachloromethane	X	X			X	X
112-60-7	Tetraethylene glycol	X				X	
112-57-2	Tetraethylenepentamine	X				X	
78-00-2	Tetraethylplumbane	X	X			X	X
---	Tetrafluoroethylene	X				X	
109-99-9	Tetrahydrofuran	X				X	X
119-64-2	Tetrahydronapthalene (tetralin) (POM)	X				X	
85-43-8	Tetrahydrophthalic anhydride	X				X	
110-60-1	Tetramethylenediamine	X				X	
110-18-9	Tetramethylethylenediamine	X				X	
75-74-1	Tetramethylplumbane	X					X
102-08-9	Thiocarbanilide	X				X	
---	Thiourea	X				X	
26741-62-5	Toluene diisocyanates (mixture)	X				X	
---	Toluene sulfonamides (o- and p-)	X				X	
104-15-4	Toluenesulfonic acids (all isomers)	X				X	
98-59-9	Toluenesulfonyl chloride	X				X	
95-53-4	Toluidine (o-isomer)	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
108-78-1	1,3,5-Triazine-2,4,6-triamine	X				X	
75-25-2	Tribromomethane	X	X				
---	1,1,1-Tribromo-2-methyl-2-propanol	X				X	X
108-77-0	2,4,6-Trichloro-1,3,5-triazine	X				X	X
76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane	X	X		X	X	
---	Trichloroacetic acid	X				X	
634-93-5	Trichloroaniline (2,4,6-isomer)	X				X	
87-61-6	Trichlorobenzene (1,2,3-)	X				X	
---	Trichlorobenzene (1,2,4-isomer)	X				X	
120-82-1	Trichlorobenzene (1,3,5-)	X				X	
71-55-6	1,1,1-Trichloroethane	X	X			X	X
79-00-5	1,1,2-Trichloroethane	X	X			X	X
79-01-6	Trichloroethene	X	X			X	X
75-69-4	Trichlorofluoromethane	X	X			X	X
67-66-3	Trichloromethane	X	X			X	X
95-95-4	Trichlorophenol (2,4,5-)	X				X	
---	Trichloropropane (1,2,3-)	X				X	
---	Tricresyl phosphate	X				X	
---	Tridecyl alcohol	X				X	

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONTINUED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
121-44-8	Triethylamine	X				X	
112-49-2	Triethylene glycol dimethyl ether (glycol ether)	X				X	
---	Triethylene glycol monoethyl ether	X				X	
112-35-6	Triethylene glycol monomethyl ether	X				X	
---	Triisobutylene	X				X	
---	Trimellitic anhydride	X				X	
---	Trimethyl pentanol	X				X	
75-50-3	Trimethylamine	X				X	
80-56-8	2,6,6-Trimethylbicyclo (3,1,1) hept-2-ene	X					
---	Trimethyl-1,3-pentanediol (2,2,4-)	X				X	
933-48-2	Trimethylcyclohexanol	X				X	
2408-37-9	Trimethylcyclohexanone	X				X	
00-7	Trimethylcyclohexylamine	X				X	
77-99-6	Trimethylopropane	X				X	
540-84-1	Trimethylpentane (2,2,4-)	X				X	
24800-44-0	Tripropylene glycol	X				X	
57-13-6	Urea	X					
---	Urea ammonium nitrate	X					

TABLE A-1. LIST OF SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY CHEMICALS
(CONCLUDED)

CAS number	Chemical	Reactor and distillation CTG	Included in-HON impacts analysis	SOCMI list	Air oxidation processes NSPS	Distillation operations NSPS	Reactor processes NSPS
---	Vinyl toluene	X				X	
25013-15-4	Vinyl toluene	X				X	
100-40-3	Vinylcyclohexene (4-isomer)	X				X	
---	Xanthates (potassium ethyl xanthate)	X				X	
25321-41-9	Xylene sulfonic acid	X				X	
---	Xylenol (2,3-)	X				X	
---	Xylenol (2,4-)	X				X	
---	Xylenol (2,5-)	X				X	
---	Xylenol (2,6-)	X				X	
---	Xylenol (3,4-)	X				X	
---	Xylenol (3,5-)	X				X	
---	Xylidine (2,3-)	X				X	
---	Xylidine (2,4-)	X				X	
---	Xylidine (2,5-)	X				X	
---	Xylidine (2,6-)	X				X	
---	Xylidine (3,4-)	X				X	
---	Xylidine (3,5-)	X				X	
---	Zinc acetate	X				X	

APPENDIX B

EMISSION DATA PROFILES

PRODUCT PROCESS	PROCESS DESCRIPTION	FLOWRATE (SCFM)	HEAT CONTENT (BTU/SCF)	VOC FLOWRATE LB/HR)
Butyl Acetate	Esterification	2	102	0.1
Dioctyl phthalate	Esterification	5	102	0.1
Vinyl Acetate	Oxyacetylation	7	407	0.1
Ethyl Acetate	Esterification	7	102	0.5
Ethylene Glycol Monoethyl ether acetate	Esterification	8	102	NR[b]
Ethylbenzene	Alkylation	8.7	4	0.1
Butynediol	Ethynylation	9.2	747	19.8
Vinylidene Chloride	Dehydrochlorination	10	600	41
Nitrobenzene	Nitration	13	434	19
Ethylbenzene	Alkylation	17	181	16
Ethyl Chloride	Hydrochlorination	20	1286	168
Methyl Chloride	Hydrochlorination	20	500	2.1
Ethylene Dichloride	Chlorination	40	40	3.6
Chlorobenzene	Chlorination	55	0	4
Hexamethyl diamine	Hydrogenation	70	323	6.6
Ethyl Acrylate	Esterification	75	102	6.1
Propylene Oxide	Hydrolysis	99	0	0.1
Hexamethyl diamine	Hydrogenation	113	900	0
Acetic Anhydride	Condensation	147	1069	305
Ethylene Dichloride	Chlorination	167	163	74
Ethylene Dichloride	Chlorination	267	1228	113
Ethylene Dichloride	Oxychlorination	304	713	748
Styrene	Dehydrogenation	574	300	161
Butyraldehyde	Hydroformylation	729	1233	2394
Dinitrotoluene	Nitration	822	0	0.1
Adipic Acid	Oxidation	848	0	0
Adiponitrile	Hydrodimerization	1080	70	27
Benzene	Catalytic Reforming	1289	205	8.3
Hexamethylene Diamine	Hydrogenation	1304	462	0
Dodecylbenzene sulfonic acid	Sulfonation	1863	0	0.1
Adipic Acid	Oxidation	2800	0	0
Adipic Acid	Oxidation	4653	0	0
Styrene	Dehydrogenation	5208	280	711
n-Butyl Alcohol	Hydrogenation	5429	776	4046
1,4-Dichloride	Chlorination	9195	0	7.2
Ethylene Oxide	Oxidation	12187	4	130
Methanol	Carbonylation	18950	295	75

[a] Emissions data taken from Appendix C of Reactor Processes in Synthetic Organic Chemical Manufacturing Industry - Background Information for Proposed Standards (EPA 450/3-85-005a).

[b] Data not reported.

TABLE B-2 DISTILLATION EMISSION DATA PROFILE[a]

PRODUCT PROCESS	NUMBER OF COLUMNS AND OPERATING CONDITIONS	FLOWRATE (SCFM)	HEAT CONTENT (BTU/SCF)	VOC FLOWRATE (LB/HR)
Chlorobenzene	1 NV	0.005	133	0.004
Aniline	1 V	0.007	3752	0.11
Chlorobenzene	1 NV	0.012	374	0.025
Chlorobenzene	1 NV	0.015	755	0.034
Aniline	1 V	0.02	3047	0.29
Chlorobenzene	1 NV	0.02	432	0.031
Terephthalic Acid	1 NV	0.02	169	0.02
Confidential	1 CO	0.02	0	0
Ethylbenzene	1 NV	0.063	7	0
Methyl Methacrylate	1 NV	0.1	1056	0.4
84	2 NV	0.1	834	0.25
Acetone	1 V	0.1	360	0.2
Acetone	2 NV	0.1	36	0.2
Acetic ACid	1 NV	0.18	207	0.08
Chloroprene	1 NV	0.2	2778	2
Malic Anhydride	3 V	0.2	0	0
Confidential	1 CO	0.26	1375	1.83
Dimethyl Terephthalate	1 V	0.3	4978	4.9
Chloroprene	1 V	0.4	2224	4.9
Acetic Anhydride	1 CO	0.48	1024	1.53
Phthalic Anhydride	1 V	0.5	3602	11.5
Ethylacetate	1 NV	0.7	680	0.4
Ethyldichloride	1 V	0.9	1024	14
Alkyl Benzene	1 NV	1.2	3643	15
Acetic Anhydride	1 CO	1.2	1024	3.81
Perchloroethylene	1 NV	1.3	143	3.4
Acetone	1 NV	1.39	966	6.04
Acetone	1 V	1.39	966	6.04
Acetic Acid	1 NV	1.45	903	1.6
Acetone	1 NV	1.5	1225	10.4
Nitrobenzene	1 V	1.5	352	1.8
Methyl Methacrylate	1 NV	1.7	1483	13.6
Chloroprene	2 V	1.8	858	4.9
Dichlorobenzene	1 V	1.8	651	8.1
Acetic Acid	1 CO	1.94	68	0.8
Diphenylamine	1 V	2	0	0.003
Methyl Ethyl Ketone	1 NV	2.2	1183	10
Ethylene Oxide	1 NV	2.3	1191	13.8
Ethylacetate	1 NV	2.3	1012	6.4
Vinyl Acetate	1 NV	2.3	781	5.2
Ethyldichloride	1 NV	2.4	1024	38
Phthalic Anhydride	1 V	2.4	260	4
Terephthalic Acid	1 NV	2.5	114	1.9
Methyl Methacrylate	1 V	2.6	2870	41
Dichlorobenzene	1 V	2.6	62	1.3
86	1 NV	3.3	90	28.8
Acetic Anhydride	1 CO	3.66	1024	11.61
Dimethyl Terephthalate	1 NV	4.2	180	5
Ethanolamines	1 V	2.3	0	0
Acetone Cyanonydride	1 NV	4.4	190	4
Ethyldichloride	1 V	4.8	53	3.9
Methyl Ethyl Ketone	1 NV	4.9	2003	32.68
Acetic Anhydride	1 CO	4.98	1024	15.81
Ethyldichloride	2 NV	6	727	63.9
Malic Anhydride	1 V	6.5	0	0
Ethylbenzene	1 NV	6.5	1286	3
Ethyldichloride	1 NV	6.94	727	55
Dimethyl Terephthalate	1 NV	7	0	10
Methyl Methacrylate	1 NV	7.4	439	12
Acrylic Acid	1 V	7.4	0	0
Ethyldichloride	1 NV	8.1	91	6.6
Acetic Anhydride	4 CO	8.16	1024	25.88

PRODUCT PROCESS	NUMBER OF COLUMNS AND OPERATING CONDITIONS	FLOWRATE (SCFM)	HEAT CONTENT (BTU/SCF)	VOC FLOWRATE (LB/HR)
Dimethyl Terephthalate	1 NV	8.4	236	13
Dimethyl Terephthalate	2 V	8.9	47	2.2
Vinyl Acetate	1 NV	9	1308	34.8
Phthalic Anhydride	1 V	9.5	690	42.7
Chlorobenzene	1 V	9.9	177	6
Dichlorobenzene	1 V	9.9	177	2
Chloroprene	1 V	10	3	0.2
Acrylonitrile	1 NV	10.2	379	15.8
Vinyl Acetate	1 NV	10.5	74	15.2
Chloroprene	2 V	11.0	30	1.1
Acetone	1 V	12.15	0	0
Ethyldichloride	1 NV	12.5	727	98.8
Formaldehyde	2 V	12.5	9	0.8
Ethyldichloride	1 V	13	183	32.3
Phthalic Anhydride	1 V	13.2	979	84.1
Acrylic Acid	2 V	13.2	8	0.6
Perchloroethylene	1 NV	13.6	6	2.1
Dimethyl Terephthalate	1 NV	15	236	12
Vinyl Acetate	1 NV	15	149	6.6
Dimethyl Terephthalate	2 V	15	47	5
85	4 NV	16.7	1464	0.1
Dimethyl Terephthalate	1 NV	17.4	1282	120.5
Phthalic Anhydride	1 V	17.9	69	8
Acetone	1 NV	18	0	0
Methyl Methacrylate	1 V	18.3	2870	289
Ethanolaimines	3 V	19.5	0	0
Ethylbenzene	1 V	19.7	0	0
Acrylic Acid	2 V	20	0	0
Acetone	1 NV	21.13	2592	170.2
Butadiene	1 NV	22.5	1453	100.5
Acrylic Acid	1 V	22.6	92	10.5
Acrylonitrile	1 V	22.7	439	44
Cyclohexanone/cyclohexanol	3 V	22.701	18	15
Chloroprene	1 NV	23.6	0	0
Acrylonitrile	1 V	25.6	346	37.9
Chlorobenzene	1 V	26.1	346	43.1
Phthalic Anhydride	2 V	27	505	100
Ethyl Acrylate	2 V	27.2	69	5.6
Acrylic Acid	2 V	27.6	400	55.8
Acetone Cyanohydride	1 NV	31.5	1916	289
Acrylic Esters	3 V	33.9	168	15.7
Chlorobenzene	1 NV	34.9	495	59
85	7 V	36.701	123	15.498
Acetone Cyanohydride	1 V	39.2	4	0.18
Confidential	3 CO	40.59	0	0.09
Confidential	4 CO	49.6	0	0.56
Acetic Acid	3 NV	50	4	1.1
Acetone	1 NV	50.4	70	16.9
Dimethyl Terephthalate	2 V	54.6	47	17
Methanol	1 NV	63.4	449	399.3
Cyclohexanone/cyclohexanol	1 V	68.7	72	26.3
Methyl Methacrylate	1 V	72.9	66	26.5
Adiponitrile	9 V	75	0	0
Ethylene Glycol	6 V	75.1	0	0
Confidential	1 CO	77.32	6	1.36
Dimethyl Terephthalate	1 NV	79.3	1453	601
86	1 NV	80	9	19.6
Hexamethylene Diamine	7 V	81.1	0	0
Alkyl Benzene	1 V	85.9	104	30.6
Methyl Methacrylate	1 V	96.2	295	148.8

TABLE B-2 DISTILLATION EMISSION DATA PROFILE[a] (Continued)

PRODUCT PROCESS	NUMBER OF COLUMNS AND OPERATING CONDITIONS	FLOWRATE (SCFM)	HEAT CONTENT (BTU/SCF)	VOC FLOWRATE (LB/HR)
Ethyldichloride	1 NV	100	6	8.3
Acetone Cyanohydride	2 V	101.2	4	1.8
Dimethyl Terephthalate	1 NV	123.8	768	628.2
Methyl Methacrylate	2 NV	126.4	155	116.2
ChloropreneMethyl	3 V	145	12	7.2
Methacrylate	1 V	152	13	9.8
Dimethyl Trephthalate	2 V	176	47	57
Methyl Methacrylate	1 NV	178.5	1316	1300
Ethyl Acrylate	2 V	219	45	454
Dimethyl Terephthalate	1 NV	281	768	1426
Acetic Acid	1 NV	358	333	375
Acrylic Acid	1 NV	364	150	289
Ethyldichloride	1 NV	535.5	804	3050
Methanol	1 NV	560	1258	3668
Acetic Acid	1 NV	575	380	600
Isophthalic Acid	1 NV	637	19	123
Acetaldehyde	2 NV	647.3	293	183
84	6 NV	656	6	19

[a] Emissions data taken from Appendix C of Distillation Operations in Synthetic Organic Manufacturing - Background Information for Proposed Standards (EPA-450/3-83-005a).

APPENDIX C
COST CALCULATIONS

APPENDIX C

COST CALCULATIONS

C.1 SIZING CALCULATIONS FOR THERMAL INCINERATOR

Hand Calculations for the VENTCOST Program - Incineration Procedure

- Used to assess control equipment costs for the SOCMI CTG for Reactor Process and Distillation Vents.

- Calculations based on OAQPS Control Cost Manual, Chapter 3.

- The stream costed in this example is model stream R-LFHH. Its characteristics are as follows:

  VOC to be controlled: Ethyl Chloride*
  MW   : 64.5 lb/lb mole
  Flow rate (total)   : 3.839 scfm
  VOC flow rate   : 8.4 lb/hr
  Heat value   : 1,286 Btu/scf
  Oxygen content   : 0%
  Inert content   : Assume all N_2

  *Most of the following calculations are based on the actual compound in the SOCMI Profile. However, the combustion and dilution air calculations are based on the design molecule $C_{2.85}H_{5.7}O_{0.63}$, which represents the average ratio of carbon, hydrogen, and oxygen for streams in the SOCMI profile. The molecular weight of this "design molecule" is 50 lb/lb·mole.

A. Check to see if the stream to be controlled is halogenated--yes, ethyl chloride contains chlorine. Since the stream is halogenated, the following applies.

  1. No heat recovery is allowed for halogenated streams.

  2. A scrubber will be required to remove acidic vapors from the flue gas following combustion. Scrubber sizing and costing calculations for this vent stream immediately follow the incinerator calculations (see Section C.2).

B. Calculate total moles of the vent stream, and quantify moles of VOC, O_2 and inerts.

1. VOC moles only:

VOC moles = (8.4 lb/hr)(hr/60 min)(lb·mole/64.5 lb)
= 0.0022 lb·moles/min

2. Total vent stream moles:

Vent moles = (3.839 scfm)(lb·mole/392 scf)
= 0.0098 lb·moles/min

3. Oxygen moles:

O_2 moles = 0

4. Inert moles:

Inert moles = Vent moles - VOC moles - O_2 moles
= (0.0098 - 0.0022 - 0) lb·mole/min
= 0.0076 lb·mole/min

C. Calculation of Molar Ratio of Air to VOC

Please note that the combustion and dilution air calculations are based on the design molecule $C_{2.85}H_{5.7}O_{0.63}$, which represents the average ratio of carbon, hydrogen, and oxygen. The molecular weight of this "design molecule" is 50 lb/lb·mole.

Assume 3.96 moles of O_2 are required for each VOC mole.

1. Since no oxygen is present in the stream, additional combustion air must be added, to insure proper combustion.

2. Calculate the ratio of O_2 to VOC required for combustion.

O_2 theory = 3.96 - O_2 ratio already in stream*

*Additional air is not required if sufficient oxygen is already present in the vent stream.

3. Since air is 21% O_2 the necessary ratio of air to VOC is:

Air ratio = (3.96)/0.21 = 18.86 moles air/mole VOC

D. Calculation of molar ratios of inert moles to moles VOC

1, Inert ratio = inert moles/VOC moles
= 0.0076/0.0022
= 3.4545 moles inert/mole VOC

E. In order to ensure sufficient O_2 is present in the combustion chamber, enough air must be added to provide 3% O_2 in the exhaust (flue) gas stream after combustion. The O_2 material balance is :

(Initial O_2%)(vent stream) + (0.21)(dilution air) =
     (0.03)(exhaust)

Initial O_2% = 0; therefore,

(0.21)(Dilution air) = (0.03)(exhaust stream)

(0.21)(Dilution air) = (0.03)(dilution air + vent stream)*

*Assume no increase in moles after combustion

(0.21)(Dilution air) = (0.03)(dilution air) +
     (0.03)(vent stream)

Dilution air = (0.03)/(0.21 - 0.03) (Vent stream flow)

*This factor will be used later.

F. Exhaust gas consists of noncombustibles (N_2) + CO_2 + H_2O (see "Combustion Stoichiometry Memo")

1. Exhaust ratio = (0.79)(air ratio) + 2.85 + 2.85
                  = 20.6 moles exhaust/mole VOC

2. Dilution ratio = 0.03/(0.21 - 0.03)
                     (Inert ratio + Exhaust ratio)

G. Calculate flows of stream components based on calculated ratios

1. Dilution ratio = Factor * (Inert ratio - Exhaust ratio)
                   = (0.1667)(3.4545 + 20.6)
                   = 4.009

2. Dilution air flow = (Dilution air ratio)(VOC moles)
                        (392 scf/lb·mole)

    Dilution air flow = (4.009)(0.0022)(392)
                      = 3.457 scfm

3. Combustion air flow = (Air ratio)(VOC moles)(392)
                        = (18.86)(0.0022)(392)
                        = 16.26 scfm

    Combined air flow = Combustion air + Dilution air
                      = (16.26 + 3.4545)
                      = 19.7 scfm

4. Inert gas flow = (Inert ratio)(VOC moles)(392)
= (3.4545)(0.0022)(392)
= 2.98 scfm

5. Total flow = Combined air flow + Initial vent stream flow
+ Inert gas flow
= 19.7 + 3.839 scfm

New flow = 26.519 scfm

H. Recalculate heat value of the stream after adding air streams
(prior to combustion)

1. Heatval = (Initial flow * Initial heatval)/New flow
= (3.839 * 1.286)/26.519
= 186.2 Btu/scf

I. Check the heat value of the precombustion vent stream, to see if
it is acceptable from a safety perspective

1. Streams containing halogens must have a heat value
< 95 Btu/scf, nonhalogens < 98 Btu/scf.

186.2 > 95

2. Dilute stream to have a heat value < 95 Btu/scf.

Dilution air = [New flow * (Heatval - 95)]/95
= [26.5 * (186.2 - 95)]/95
= 25.5 scfm

Heatval = 95 Btu/scf

New flow = 26.5 + 25.5
= 52.0 scfm

J. Minimum incinerator flow is 50 scfm. Streams less than 50 scfm
will be increased by addition of air.

52 scfm > 50 scfm

K. Establish temperature that incinerator operates:

Halogenated: 2,000°F

Nonhalogenated: 1,600°F

L. Nonhalogenated streams are potential candidates for heat recovery.

If addition of air flows results in lowering the heat value of the entire vent stream below 13 Btu/scf ($\approx$25% LEL), then the entire vent stream is eligible for heat (energy) recovery in a heat exchanger.

High heat value streams cannot be heated in a preheater because of combustion/explosion concerns, but the VENTCOST program will calculate economic options that allow preheating of the air stream only.

The energy recovery equations are weighted to account for the mass of the heated streams since the flows being preheated may be smaller than the exhaust (flue) gas flows.

No calculations are presented here since the example stream is halogenated, and, therefore, heat recovery is not allowed.

M. Calculate the auxiliary fuel (Q_{af}) requirement

Q_{af} = [0.0739 * new flow * [0.255 * (1.1 * incinerator temperature - temperature gas - 0.1 * 77) - (heatval/0.0739))] $\div$ [0.0408 * [21,502 - (1.1 * .255 * (incinerator temperature - 77))]

$\rightarrow$ Incinerator Temperature = 2,000 °F

*See OAQPS Control Cost Manual, Incinerator Chapter for Derivation and Assumptions.

$$Q_{af} = \frac{[.0739 * 52 * [.255 * (1.1 * 2,000 - 77 - 0.1 * 77) - (209/.0739)]]}{[0.0408 * [21,502 - (1.1 * .255 * (2,000 - 77))]]}$$

$$Q_{af} = \frac{[.0739 * 52 * (-2288)]}{855.27}$$

Q_{af} = -10.3 scfm

Negative value indicates no auxiliary fuel is theoretically needed. Therefore, set Q_{af} = 0.

N. Calculate sufficient auxiliary fuel to stabilize flame (5% of TEI).

1. Thermal Energy Input (TEI) = 0.0739 * (new flow + Q_{af}) * (0.255 * (incinerator temperature - 77)

TEI = 0.0739 * (52 + 0) * 0.255 * (2,000 - 77)
    = 1,884

2. Q_{af} = (0.05 • 1,884)/(0.0408 • 21,502)
   = 0.107 ≈ 0.1 scfm

O. Calculate the total volumetric flow rate of gas through the incinerator, Q_{fi}. Include auxiliary air for the natural gas.

1. Q_{fi} = new flow + Q_{af} + combustion air for fuel

2. Assuming the fuel is methane, CH_4, the combustion reaction is:

$$CH_4 + 2O_2 = CO_2 = CO_2 + 2H_2O$$
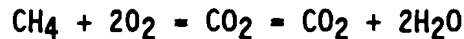
So two moles of O_2 are required for each mole of fuel. Since air is 21% O_2.

2/0.21 = 9.5 moles air/mole of fuel

Combustion air for fuel = (Q_{af} • 9.5)

3. Q_{fi} = New flow + Q_{af} + (Q_{af} * 9.5)
   = 52 + 0.107 + (0.107 • 9.5)
   = 53 scfm

C.2 COST ANALYSIS - ESTIMATING INCINERATOR TOTAL CAPITAL INVESTMENT

A. The equipment cost algorithms are only good for the range of 500 scfm to 50,000 scfm. The minimum design size is 500 scfm, so capital costs are based on 500 scfm, and annual operating costs are based on calculated Q_{fi}.

1. Design Q = 500 scfm

B. For 0% heat recovery, equipment cost, EC, is:

EC = 10,294 * (Design $Q^{.2355}$) * (# incinerators) • (CE INDEX/340.1)

EC = 10,294 * ($500^{.2355}$) * 1 * (355.6/340.1)

EC = $46,510.

C. Add duct cost. Based on an article in <u>Chemical Engineering</u> (5/90) and assuming 1/8-in. carbon steel and 24-in. diameter with two elbows per 100 feet.

Ductcost = [(210 * $24^{0.839}$) + (2 * 4.52 * $24^{1.43}$) * (length/100) * (CE INDEX/352.4)]

Ductcost = $11,722.52 (for length of 300 ft)

D.   Add auxiliary collection fan cost, based on 1988 Richardson manual.

Fancost = (96.96418 * Initial $Q^{0.5472}$) • 355.6/342.5
= 210.18

E.   Total Equipment Cost, EC_{TOT}, is given by:

EC_{TOT} = EC + Ductcost + Fancost
= 46,510 + 11,723 + 210.18
= $58,443

F.   Purchased Equipment Cost, PCE, is:

PCE = 1.18 • EC_{TOT}
= $68,963

G.   Estimate Total Capital Investment, TCI

if Design Q > 20,000, installation factor = 1.61
if Design Q < 20,000, installation factor = 1.25

TCI = 1.25 • PCE
= 1.25 • $68,963
= $86,203

C.3 CALCULATING ANNUAL COSTS FOR INCINERATORS

A.   Operating labor including supervision (15%)

1.   Assume operating labor rate = $15.64/hr (1/2 hour per shift)

Op labor = (0.5 • Op hours)/8 • ($15.64/hr)(1.15)
(Op hours = 8,760)
Op labor = $9,847.34/yr

B.   Maintenance labor and materials

M labor = (0.5/8 • 8,760) * ($17.21/hr)
= $9,422.48
Materials = M labor = $9,422.48

C.   Utilities = Natural Gas & Electrical Costs
Assume value of natural gas = $3.30/1,000 scf

1.   Natural gas = (3.30/1,000) • Q_{af} • 60 min/hr • Op hours
Natural gas = (3.30/1,000) • 0.107 scfm • 60 * 8,760
= $186/yr

2.   Power = (1.17 • 10^{-4} • Q_{fi} • 4)/0.60
Power = (1.17 • 10^{-4} • 53 • 4)/0.60
= 0.0413 kW

3. ElecCost = (0.061 $/kWh) * (0.0413) * (8,760)
             = $22.07

D. Calculate total direct costs, TDC

    TDC = Op_Labor + M_Labor + Material + NatGas + ElecCost
        = (9,847 + 9,422 + 9,422 + 186 + 22.07)
        = $28,899/yr

E. Overhead = 0.60 * (Op_Labor + M_Labor + Material)
             = $17,214.6/yr

F. Administrative = 2% of TCI

    Admin = (0.02)(86,203)
          = $1,724/yr

G. Tax = 1% of TCI
    Tax = $862/yr

H. Insurance = 1% of TCI

    Ins = 0.01 * TCI
        = $862/yr

I. Annualized Capital Recovery Costs, Anncap, is:

    AnnCap = 0.16275 * $86,203
           = $14,029.54/yr

J. Total Indirect Capital Cost, IC, is:

    IC = overhead + administrative + tax + insurance + Anncap
       = (17,215 + 1,724 + 862 + 862 + 14,029) $/yr
       = 34,692 $/yr

K. Total Annual Cost, TAC, is:

    TAC = IC + DC
        = 34,692 + 28,899
        = 63,591 $/yr

C.4 SIZING CALCULATIONS FOR SCRUBBER

Hand Calculations for the Ventcost Program Scrubber Procedure

*   Stream to be costed is R-LFHH as it exists after combustion in incinerator

- Calculate stream parameters after combustion. Assume 98 percent VOC destruction

  → Ethyl chloride is the VOC in stream R-LFHH. There is one mole of Cl for every mole of VOC. Therefore, for every mole of VOC destroyed, one mole of HCl is created.

  VOC destroyed = (initial VOC flow-lb/hr)(0.98) ÷ VOC MW
  $\quad\quad\quad\quad\quad\quad$ = (8.4 lb/hr)(0.98)/(64.5 lb/lb·mole)
  $\quad\quad\quad\quad\quad\quad$ = 0.13 lb·mole/hr

  HCl created = 0.13 lb·mole/hr

  HCl (lb/hr) = (0.13 lb·mole/hr)(36.5 lb/lb·mole)
  $\quad\quad\quad\quad\quad$ = 4.66 lb/hr

- Calculate inlet halogen concentration

  HCl (scfm) = (4.66 lb/hr)(lb·mole/36.5 lb) * 392 scf/lb·mole *
  $\quad\quad\quad\quad\quad\quad$ 1 hr/60 min
  $\quad\quad\quad\quad\quad$ = 0.83 scfm/min

  HCl (ppm) = (0.83 scfm)/Q_{fi} * 10^6
  $\quad\quad\quad\quad\quad$ = (0.83/53) * 10^6
  $\quad\quad\quad\quad\quad$ = 15,660 ppm (inlet concentration)

- The halogen is chlorine, therefore

  Molecular weight (Hal_MW) = 35.5

  Slope of operating curve (slope) = 0.10

  Schmidt No. for HCl in air (SCG) = 0.809

  Schmidt No. for HCl in water (SCL) = 381.0

- Calculate the solvent flow rate.

  New flow = 53 scfm

  Gas moles = (53 scfm)(.075 lb/ft^3)(lb·mole/29 lb)(60 min/hr)
  $\quad\quad\quad\quad$ = (53)(0.155)
  $\quad\quad\quad\quad$ = 8.22 lb·mole/hr

  Assume L/g = 17 gpm/1,000 scfm

  Convert to unitless ratio

  L/G = 17 * (8.34 * 60)/[(1,000/392) * 60 * 29] = 1.916

Absorption factor (AF) = (L/G)/slope

AF = 1.916/0.1
AF = 19.16

Liquid moles = (slope of operating curve)(adsorption factor AF)
 (gas moles)
  = (0.1)(19.16)(8.22)
  = 15.75 lb·mole/hr

Liquid flow (gal/min) = (15.75 lb·mole/hr)(18 lb/lb·mole)/
 (62.43 lb/ft^3)/60 min/hr * 7.48 gal/ft^3

Liquid flow = 0.57 gal/min

Liquid flow (lb/hr) = (0.57 gal/min)(8.34 lb/gal)(60 min/hr)
 = 283.3 lb/hr

- Calculate Column Diameter

Density of air = 0.0739 lb/ft^3 (from ideal gas law)

Density of liquid = 62.2 lb/ft^3

MW of gas stream = MW HCL x Volume Fraction + MW Air x Volume
 Fraction

MW stream = 36.5 * (15,660/10^6) + 29 * [(10^6-15,880)/10^6]
 = 36.5 * 0.0157 + 29 * 0.98434
 = 29.12 lb/lb·mole

→ Column diameter based on correlation for flooding rate in
 randomly packed towers (see HAP manual)

 ABSCISSA = (liquid lb/hr)/(gas lb/hr) *
 (density of gas/density of liquid)^0.5
 ABS = [283.3/[8.22 * 29]] * (0.0739/62.2)^0.5
 ABS = 0.0410

ORD = 0.9809237 * (ABS)^(-0.0065226 * log [ABS]) +
 (ABS)^(-0.021897)
 = 0.9809237*(0.0410)^(-0.0065226 * log[0.0410]) +
 (0.0410)^(-0.012897)
ORD = 0.15

- Calculate G_Area (lb/ft^2·sec) based on column cross sectional
area at flooding conditions.

G_Area = F * (ORD * density of gas * density of liquid *
 32.2/69.1 * 0.85^0.2)^0.5
 = 0.6 * (0.15 * 0.0739 * 62.2 * 32.2/69.1 * 0.85^0.2)^0.5
 = 0.34

C-10

- Calculate the Area of the Column

  Area of column = (MW stream * gas moles)/(3,600 * G_Area)

  $\quad$ Area (ft^2) = (29.12 * 8.22)/(3,600 * 0.34)

  $\quad$ Area (ft^2) = 0.19 ft^2 .

- Calculate Diameter of Column

  D_col = [(4/π) Area]$^{0.5}$

  $\quad$ = 1.27 (Area)$^{0.5}$

  $\quad$ = 0.5 ft

- Calculate liquid flux rate

  LL (lb/hr·ft^2) = (liquid flow lb/hr)/Area

  $\quad$ LL = (283.3)/(0.19)

  $\quad$ = 1,491

- Calculate the number of gas transfer units (NOG) (Assume 98% removal efficiency)

  NOG = ln [(Hal concentration/(0.02 * Hal concentration)) * (1-(1/AF)) + (1/AF)]/(1-(1/AF))]

  = ln [(15,660/(0.02 * 15,660))* (1-1/19.16) + (1/19.16)]/(1-1/19.16)

  NOG = 4.07

- Calculate the height of the overall gas transfer unit (HOG) using:

  HOG = Hg + (1/AF) H_L

  where

  $\quad$ H_G = Height of a single gas transfer unit (ft)

  $\quad$ H_L = Height of a liquid transfer unit (ft)

  Based on generalized correlations:

  H_G = [b * (3,600 * G_Area)^c/(LL^d)](SCG)$^{0.5}$

  H_L = Y * (LL/liquid viscosity)^S * (SCL)$^{0.5}$ assuming 2-in. ceramic raschig rings for packing

  b = 3.82

  c = 0.41

  d = 0.45

s = 0.22

Y = 0.0125

→ To convert from centipoise to lb/hr * ft^2

Liquid viscosity = 0.85 * 2.42

                g = 11.13

                r = 0.00295

Therefore,

H_G = [3.82 * (3,600 * 0.34)^0.41/(1,491^0.45)] * $SCG^{0.5}$
    = 2.63 x 0.809^0.5 = 2.37

H_L = (0.0125) * (1,491/2.05)^0.22 * $SCL^{0.5}$
    = 0.051 * 381^0.5 = 1.0

Solving for HOG:

HOG = HG + (1/AF) * H_L
    = 2.37 + (1/19.16) * 1.0
    = 2.42

● Calculate the height of the packed column from HOG and NOG. Allow for 2 ft of freeboard above and below the packing for gas disentanglement, and additional height based on column.

Height (Ht) = (NOG)(HOG) + 2 + 0.25 * Diam. Col
            = (4.07)(2.42) + 2 + 0.25 * 0.5
            = 12 ft

● Calculate Volume of Packing

Volume = (π/4) * (D)^2 * (NOG * HOG)
      = (π/4) * (.5)^2 * (4.07 * 2.42)
      = 1.93 ft^3

● Calculate Volume of Column

Volume = (π/4)(Diam col)^2 x Ht
      = (0.785)(0.5)^2 x 12
      = 2.36 ft^3

● Calculate Pressure Drop

DelPa = (g x 10^{-8}) * [10^(r * LL/liquid density)] *
      [(3,600 * G_Area)^2]/gas density

- DelPa = $(11.13 \times 10^{-8}) * (10^{(0.00295 * 1,491/62.2)}) * ((3600 * 0.34)^2)/0.0739$

  DelPa = 2.66

  Del Ptot = DelPa * (NOG + HOG)/5.2
  = 2.66 * (4.07 * 2.42)/5.2
  = 5.09

C.5 COST ANALYSIS--ESTIMATING SCRUBBER TOTAL CAPITAL INVESTMENT

- Total Cost of Tower is:

  wt = (48 * Diam * ht) + 39 * Diam^2
  = (48 * 0.5 * 12) + 39 * (0.5)^2
  wt = 297.8 lbs

  TCost = [1.900604 * (wt/1,000)$^{0.93839}$] * 1,000 * (355.6/298.2)

  TCost = [1.900604 * (297.8/1,000)$^{0.93839}$] * 1,000 * (355.6/298.2)
  = 727

- Cost of Packing

  Packcost = Volume of packing * 20
  = 1.93 * 20
  = 38.6

- Assume Cost of Duct Work and Fan

  Duct cost = 3,907.5

  Fan cost = 488.9

- Calculate Platform Cost. For columns less than 3 ft in diameter design diam (DD) = 3.

  Platform Cost = 10$^{(0.78884 * \ln (\text{diam}) + 3.325)}$ * (355.6/298.2)
  = 10$^{(0.7884 * \ln (0.5) + 3.325)}$ * (355.6/298.2)
  = 715.6

- Assume Stackcost = 5,000

- Calculate Total Capital Investment (TCI)

  TCI = (towercost + packcost + ductcost + fancost + platform cost + stackcost) * 1.18 * 2.2

$$TCI = (727 + 38.6 + 3,907 + 488.9 + 715.6 + 5,000) * \\ 1.18 * 2.2$$

$$= \$28,237$$

C.6 CALCULATING ANNUAL COSTS FOR SCRUBBERS

- Calculate Water Costs

Water = (liquid flow lb/hr)/8.34 lb/gal * price per 1,000 gal * 8,760 hr/yr

Water = (283.4)/(8.34) * 0.22/1,000 * 8,760

Water = 65.49

- Calculate Electrical Costs Based on Pressure Drop

Elec = 0.0002 * new flow * DelPtot * 8,760 * elec_cost \$/KW·Hr

= 0.0002 * 53 * 5.09 * 8,760 * 0.061

= 29 \$/yr

- Calculate Cost of Labor, Supervision, Maintenance

Op labor = (1/2 hour per 8 hour shift) * (Annual operating hours) * (Op labor rate)

Op labor = 0.5/8 * 8,760 * 15.64

Op labor = 8,563 \$/yr

Supervision = 0.15 * Op_Labor

Supervision = 0.15 * 8,563 = 1,284.44

Maintenance labor = 0.5/8 * 8,760 * 17.21

Maintenance labor = 9,422.48 \$/yr

Maintenance materials = 9,428.48 \$/yr

- Calculate Direct Operating Costs

Dir Op Cost = Water + electric + op_labor + supervision + main labor + maintenance materials

Dir Op Cost = 65.49 + 29 + 8,563 + 1,284.44 + 9,422.5 + 9,422.5

Dir Op Cost = 28,786 \$/yr

- Calculate cost of overhead, tax, insurance, administrative, and capital recovery costs

$$\text{Tax} = 0.01 * \text{TCI} = 282.4$$

$$\text{Insurance} = 0.01 * \text{TCI} = 282.4$$

$$\text{Administrative} = 0.02 * \text{TCI} = 564.7$$

$$\text{CRC} = 0.16275 * \text{TCI} = 4,596$$

$$\text{Overhead} = 0.6 * (\text{op\_labor} + \text{supervision} + \text{main\_La} + \text{maint})$$

$$\text{Overhead} = 17,215$$

- Calculate indirect operating costs

$$\begin{aligned}\text{Ind Op Cost} &= \text{Overhead} + \text{Tax} + \text{Insurance} + \text{Administrative} + \text{CRC} \\ &= 17,215.44 + 282.4 + 282.4 + 564.7 + 4,596 \\ &= 22,940\end{aligned}$$

- Annual Operating Cost, Anncost

$$\text{Anncost} = 28,786 + 22,940$$

$$\text{Anncost} = 51,726 \ \$/\text{yr}$$

C.7 SIZING CALCULATIONS FOR FLARES

Hand Calculations for the VENTCOST Program - Flare Procedure

- Used to assess control equipment cost for the SOCMI CTG

- Calculations based on OAQPS Control Cost Manual, Chapter 7.

- The stream costed in this example is model stream D-HFLH. Its characteristics are the following:

```
VOC to be controlled:  Isophthalic acid
MW                  :  166 lb/lb mole
Flow rate (total)   :  632.401 scfm
VOC flow rate       :  6.15 lb/hr
Heat value          :  19 Btu/scf
Oxygen content      :  0%
```

A. Flare tip diameter is generally sized on a velocity basis. Flare tip sizing is governed by EPA rules defined in the Federal Register. For flares with a heat value less than 300 Btu/scf the maximum velocity is 60 ft/sec.

1. The net heating value of vent stream = 19 Btu/scf

2. Thus maximum velocity (V_{max}), = 60 ft/sec. (It is standard practice to size flares at 80 percent of V_{MAX}).

3. Calculate the heat released by combustion of the vent stream

   Heatrel (Btu/hr) = Vent Flow * heat value * 60 min/hr
   = 632.401 scfm * 19 Btu/scf * 60
   = 720,937 Btu/hr

4. Flare height (ft) is determined using Equation 7-3 in OAQPS SOCMI flares chapter.

   Height = $(TFQ/r\pi k)^{0.5}$

   where

   T = Fraction of heat intensity transmitted

   F = Fraction of heat radiated

   Q = Heat release (Btu/hr) = 720,937 Btu/hr

   k = allowable radiation, (500 Btu/hr-ft^2)

   Assuming (a) no wind effects, (b) center of radiation at the base of the flare, and (c) thermal radiation limited at base of the flare.

   T = 1

   F = 0.2

   k = 500

   Substituting and simplifying,

   Height = $((heatrel)^{0.5})./177.24$

   (Note that this assumes allowable radiation = 500 Btu/hr·ft^2)

   Height = 4.79 ft

   The minimum flare height is 30 ft. Therefore,

   Height = 30 ft

5. Calculate the auxiliary fuel flow required to sustain a stable flame. A minimum heat value of 300 Btu/scf is required by 40 CFR, Section 60.18. Therefore, the auxiliary fuel flow, Q_{af} (scfm) is:

$$Q_{af} = \text{Vent flow} * (300 - \text{heat value})/(1000-300)$$
$$= 632 * (300-19)/(1000-300)$$
$$= 253.70 \text{ scfm}$$

6. Calculate total stream flow, Q_{Tot} (scfm):

$$Q_{tot} = \text{Vent flow} + Q_{af}$$
$$= 632 + 253.7$$
$$= 886 \text{ scfm}$$

7. Calculate minimum flare tip diameter, D, (in.) by

$$D = 12[4/\pi * (Qtot/60)/0.8 \ V_{MAX}]^{0.5}$$
$$= 12[4/\pi * (886/60)]^{0.5}$$
$$= 12(0.392)^{0.5}$$
$$= 7.51 \text{ in.}$$

Since the calculated diameter is rounded up to the next commercially available size, available in 2-in. increments, the diameter would be D = 8 in.

B. Purge Gas Requirement - Purge gas is used to maintain a minimum required constant flow through the system. Using the conservative value of 0.04 ft/sec (gas velocity) and knowing the flare diameter, the annual P volume can be calculated.

1. $$P(\text{scfm/yr}) = (0.04) * ((\pi)/4) * (D^2)/144 * 60$$
$$= 0.006 \text{ scfm}$$

C. Pilot Gas Requirement

1. Since the number of pilot burners (n) is based on flare size (flare diameter 1 to 10 in. = 1 pilot burner) this stream would require 1 burner (our flare tip is 8 in.)

2. Pilot gas flow (fp)

$$Fp = (70 \text{ scf/hr}) * N * (\text{hr/60 min})$$
$$= 1.167 \text{ scfm}$$

D. Steam Requirement

The steam requirement depends on the composition of the vent gas being flared, the steam velocity from the injection nozzle, and the flare tip diameter.

1. The steam requirement can be calculated based on steam - CO_2 weight ratio of 0.68 (see Equation 7-7, OCCM flares chapter).

$$W_{steam} = flow * (0.075 * 60) * 0.4$$
$$= 632 * (0.075 * 60) * 0.4$$
$$= 1,137 \text{ lb/hr}$$

E. Knockout Drum

The dropout velocity, U, of a particle in a stream, or the maximum design vapor velocity, is calculated by:

1. $U = K \times ((p_1 - p_v)/p_v)^{0.5}$ ft/sec

   where

   k = design vapor velocity factor = .2 assumed as representative of the k range of 0.15 to 0.25

   $P_1 = 37$ = liquid density, assumed

   $P_v = 0.1125$ vapor density, assumed

   $U = 3.62$

F. The maximum vessel cross-sectional area, A, can be calculated by:

$A = Q$ (ft^3/min)/(60 x U (ft/sec), ft^2

$Q = 632$ scfm

$A = 632/(60 \times 3.62)$

$A = 2.91$

G. Calculate vessel diameter

1. The vessel diameter, d_{min}, is calculated by:

   $d_{min} = 12$ (in/ft) x (4 x A (ft^2)/π)$^{0.5}$, in.

   $d_{min} = 12 \times (4 \times 2.91/\pi)^{0.5}$

   $d_{min} = 23.1$ in.

2. In accordance with standard head sizes, drum diameters in 6-in. increments are assumed so:

   $d = d_{min}$ to the next largest 6 in.

   $d = 24$ in.

3. The vessel height, h, is determined by:

    h = 3 x d, in.
    h = 3 x 24 = 72 in.

C.8 COST ANALYSIS - ESTIMATING TOTAL CAPITAL INVESTMENT FOR FLARES
     (*Assuming March 1990 Dollars)

A. Flare costs (C_f) are calculated as a function of stack height,
    H (ft) and tip diameter, D, (in), and are based on support type.
    Derrick support group was not considered since the stack height
    is < 100 ft.

    1. Self Support Group

        $C_f = [78 + 9.14 (D) + .75 (H)]^2$

        $C_f = [78 + 9.14 (8) + .75 (30)]^2$

        $C_f = 30,144$

    2. Guy Support Group:

        $C_f = [103.17 + 8.68(8) + .47 (30)]^2$

        $C_f = 34,861$

        Since Self Support is < Guy Support, the cheaper is chosen.

B. Cost for 100 ft of transfer and header pipe, C_p, assuming
    400 length needed.

    $C_p = (127.4 \times D^{1.121}) \times 4$

    $C_p = (127.4 \times 8^{1.121}) \times 4$

    $C_p = 5,243$

C. Cost for knockout drum, C_k, is a function of drum diameter,
    d (ft) and height (ft)

    $C_k = 14.2 \times [d \times t \times (h + 0.0812 \times d)]^{0.737}$

    where

        t = vessel thickness (in.)

vessel thickness is determined based on drum diameter. Since

Drum diameter, d = 24 in. = 2.0 ft and

Drum height, h = 90 in. = 7.5 ft,

Drum thickness, t = 0.25 in.

C_k = 14.2 x [24 x 0.25 x (90 + 0.0812 x 24)]$^{0.737}$

C_k = 1,484

D. Collection Fan Cost

C_{fan} = (96.96418 x 632 scfm$^{0.5471969}$) x 355.6/342.5
     = 3,431

Collection Fan Cost based on 1988 Richardson Manual; see Chris Bagley's March 9, 1990, calculation placed in the polystyrene file.

E. Flare system equipment cost, EC, is the total of the calculated flare, knockout drum, manifold piping, and collection fan cost.

E_c = [C_f + C_k + C_p) * 355.6/354.6] + C_{fan}

E_c = [30,144 + 1,484 + 5,243) * 355.6/354.6] + 3,431

E_c = 41,712

F. Purchased equipment cost, PEC, is equal to equipment cost, EC, plus factors for instrumentation (.10), sales taxes (0.03), and freight (0.05) or

PEC = EC x (1 + 0.10 + 0.03 + 0.05)

PEC = 1.18 x 41,712

PEC = 49,220

G. Installation Costs: The total capital investment, TCI, is obtained by multiplying the purchased equipment costs, PEC, by an installation factor of 1.92

TCI = 1.92 x PEC

TCI = 1.92 x 48,916

TCI = 94,502

C.9 CALCULATING ANNUAL COST FOR FLARES

A. Direct Annual Cost

1. Total natural gas cost, C_f, to operate a flare system includes pilot, C_p, auxiliary fuel, C_a, and purge cost C_{pu}:

$$C_f = C_p + C_a + C_{pu}$$

where C_p is equal to the annual volume of pilot gas, f_p, multiplied by the cost per scf

$$C_p \text{ (\$/yr)} = \text{Flow} * 60 * 8,760$$
$$= f_p \text{ (scf/yr)} \times \text{(\$/scf)}$$

Assume price of natural gas = 3.30 \$/Mscf

$$C_p = 1.167 \text{ scfm} * 60 * 8,760 \times (3.30 \text{ \$/Mscf})$$

$$C_p = \$2,024/yr$$

2. Annual Purge gas cost $C_{pu} = 247.68 \times D^2 \text{ (Mscf/yr)} * (3.3 \text{ \$/Mscf})$

Annual $C_{pu} = \$817.3/yr$

3. Auxiliary Gas Cost C_a

133,350 Mscf/yr x 3.3 \$/Mscf = \$440,055/yr

4. $C_f = 2,024 + 817.3 + 440,055 = \$442,896/yr$

B. Calculate Steam Cost (C_s) required to eliminate smoking

$$C_s \text{ (\$/yr)} = 8,760 \text{ (hr/yr)} \times \text{steam use (lb/hr)} \times \text{(\$/lb)}$$

$$C_s = 8,760 \times 1,137 \times 4.65 \times 10^{-3}$$

$$C_s = \$46,315$$

C. Calculate operating labor cost, based on 630 manhours/yr

Operator labor = 0.5/8 * 8,760 * \$15.64 = 8,562
Supervisor labor 8,572 x .15 = <u>1,286</u>
Total labor =   9,848

D. Maintenance labor cost and materials

Maintenance labor (\$/yr) = (1/2 hr/8 hrs shift) x 8,760 hr/yr x \$17.21/hr = \$9,422/yr

Materials assumed equal to maintenance labor = \$9,422/yr

APPENDIX D

SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY
CONTROL TECHNIQUES GUIDELINE EXAMPLE RULE

APPENDIX D

SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY
CONTROL TECHNIQUES GUIDELINE EXAMPLE RULE

D.1 INTRODUCTION

This appendix presents an example rule limiting volatile organic compound (VOC) emissions from reactor processes and distillation operations. The example rule is for informational purposes only and, as such, is not legally binding. The purpose of the example rule is to provide a model containing information on the sections and typical issues that need to be considered in writing a rule to ensure clarity and enforceability of the standards.

Two points concerning implementation of the recommended reasonably available control technology (RACT) in Chapter 6.0 warrant consideration in drafting a regulation. First, Chapter 6.0 recommended that any reactor process or distillation vent stream for which an existing combustion device is employed to control VOC emissions should not be required to meet the 98 percent destruction or 20 parts per million by volume emissions limit until the combustion device is replaced for other reasons. Second, Chapter 6.0 recommended that the total resource effectiveness index limit be applied on an individual process vent stream basis for a given process unit.

An additional point warranting consideration when drafting a regulation pertains to the reporting requirements. Section 7.8 stated that reporting frequency is left to the discretion of State air quality management agencies; however, this model rule provides example

E. Overhead Cost

    = 0.60 x (op labor + supervisor + labor + materials)
    = 0.60 x (8,572 + 1,286 + 9,422 + 9,422)
    = 17,221

F. Capital Recovery Factor: Assume 15 year life and 10% interest
                              so CRF = 0.1314

    Capital recovery cost = 0.1314 x TCI
                          = 0.1314 x 94,502
                          = $12,418

G. General and Administrative, Taxes, and Insurance Costs

    Assume 4% of total capital investment

    4% of 94,502

    = 3,780

H. Utilities--Power consumption based on actual minimum flow

    Pressure drop = $[1.238 * 10^{-6} * \text{flow} - (1.15 * 10^{-4})]$ *
                    length of pipe
                  = $[1.238 * 10^{-6} * 632 - 1.15 * 10^{-4}]$ * 400
                  = 0.27 in. H_2O

    Power = $(1.17 * 10^{-4} * \text{flow} * \text{pressure drop})/0.6$
          = $[1.17 * 10^{-4} * 632 * 0.27)/0.6$
          = 0.03 kW

I. Elec cost = Power x op hours x elec price ($/1000 kW·hrs)
              = (0.03)(8,760)(0.061)
              = 16.03

J. Calculating total Annual Costs (Indirect and Direct)

    1. Direct Annual Cost

        Direct Cost = Cost electricity + materials +
                      maintenance labor + supervisors +
                      operation labor + steam cost + fuel cost

        Direct cost = 16.03 + 9,422 + 9,422 + 1,286 + 8,562 +
                      46,315 + 443,162

                    = 518,383

C-22

2. Indirect Annual Cost

IAC = general + capital recovery cost + overhead

IAC = 3,757 + 12,341 + 17,221

IAC = 33,320

K. Annual Cost = Direct cost + Indirect Cost
                = 518,383 + 33,320
                = 551,702

(iii) Any boiler or process heater in which all vent streams are introduced with primary fuel are exempt from these requirements.

(3) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with D.4(a)(2) through use of a smokeless flare; flare design (i.e., steam-assisted, air-assisted, or nonassisted), all visible emission readings, heat content determinations, flow rate measurements, and exit velocity determinations made during the performance test, continuous records of the flare pilot flame monitoring, and records of all periods of operations during which the pilot flame is absent.

(4) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with D.4(b):

(i) Where an absorber is the final recovery device in the recovery system, the exit specific gravity (or alternative parameter which is a measure of the degree of absorbing liquid saturation, if approved, by the permitting authority), and average exit temperature of the absorbing liquid measured at least 15 minutes and averaged over the same time period of the performance testing (both measured while the vent stream is normally routed and constituted), or

(ii) Where a condenser is the final recovery device the recovery system, the average exit (product side) temperature measured at least every 15 minutes and averaged over the same time period of the performance testing while the vent stream is routed and constituted normally, or

(iii) Where a carbon adsorber is the final recovery device in the recovery system, the total stream mass or volumetric flow measured at least every 15 minutes and averaged over the same time period of the performance test (full carbon bed cycle), temperature of the carbon bed after regeneration (and within 15 minutes of completion of any cooling cycle(s)), and duration of the carbon bed steaming cycle (all measured while the vent stream is routed and constituted normally), or

(iv) As an alternative to D.7(a)(4)(i), (a)(4)(ii) or (a)(4)(iii), the concentration level or reading indicated by the organics monitoring device at the outlet of the absorber, condenser, or carbon adsorber, measured at least every 15 minutes and averaged over the same time period

as the performance testing while the vent stream is normally routed and constituted.

(v) All measurements and calculations performed to determine the flow rate, and volatile organic compound concentration, heating value, and TRE index value of the vent stream.

(b) Each reactor process or distillation operation subject to this guideline will also be subject to the exceedance reporting requirements of the draft Enhanced Monitoring Guideline. The specifics of the requirements will be added to this document when the Enhanced Monitoring Guideline is quotable.

(c) Each reactor process or distillation operation seeking to comply with D.4(b) shall also keep records of the following information:

(1) Any changes in production capacity, feedstock type, or catalyst type, or of any replacement, removal, and addition of recovery equipment or reactors and distillation units.

(2) Any recalculation of the flow rate, TOC concentration, or TRE value performed according to D.5(g).

(d) Each reactor process or distillation operation seeking to comply with the flow rate or concentration exemption level in D.2(b)(4) shall keep records to indicate that the stream flow rate is less than 0.0085 standard cubic meters per minute or the concentration is less than 500 parts per million by volume.

(e) Each reactor process or distillation operation seeking to comply with the production capacity exemption level of 1 gigagrams per year shall keep records of the design production capacity or any changes in equipment or process operation that may affect design production capacity of the affected process unity.

(d)   The owner or operator of an affected facility that seeks to demonstrate compliance with the total resource effectiveness index limit specified under D.4(b) shall install, calibrate, maintain, and operate according to manufacturer's specifications the following equipment:

(1)   Where an absorber is the final recovery device in the recovery system:

(i)   A scrubbing liquid temperature monitor equipped with a continuous recorder.

(ii)   Specific gravity monitor equipped with continuous recorders.

(2)   Where a condenser is the final recovery device in the recovery system, a condenser exit (product side) temperature monitoring device equipped with a continuous recorder and having an accuracy of ±1 percent of the temperature being monitored expressed in degrees Celsius or ±0.5 $^{\circ}$C, whichever is greater.

(3)   Where a carbon adsorber is the final recovery device unit in the recovery system, an integrating regeneration stream flow monitoring device having an accuracy of ±10 percent, capable of recording the total regeneration stream mass flow for each regeneration cycle; and a carbon bed temperature monitoring device having an accuracy of ±1 percent of the temperature being monitored expressed in degrees Celsius of ±0.5 $^{\circ}$C, capable of recording the carbon bed temperature after each regeneration and within 15 minutes of completing any cooling cycle.

(4)   Where an absorber scrubs halogenated streams after an incinerator, boiler, or process heater, the following monitoring equipment is required for the scrubber.

(i)   A pH monitoring device equipped with a continuous recorder.

(ii)   Flow meters equipped with a continuous recorders to be located at the scrubber influent for liquid flow and the scrubber inlet for gas stream flow.

(e)   The owner or operator of a process vent using a vent system that contains bypass lines that could divert a vent stream away from the combustion device used shall either:

(1)   Install, calibrate, maintain, and operate a flow indicator that provides a record of vent stream flow at least once every 15 minutes. The

flow indicator shall be installed at the entrance to any bypass line that could divert the vent stream away from the combustion device to the atmosphere; or

(2) Secure the bypass line valve in the closed position with a car-seal or a lock-and-key type configuration. A visual inspection of the seal or closure mechanism shall be performed at least once every month to ensure that the valve is maintained in the closed position and the vent stream is not diverted through the bypass line.

D.7 REPORTING/RECORDKEEPING REQUIREMENTS

(a) Each reactor process or distillation operation subject to this rule shall keep records of the following parameters measured during a performance test or TRE determination required under D.5, and required to be monitored under D.6.

(1) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with D.4(a)(1) through use of either a thermal or catalytic incinerator:

(i) The average firebox temperature of the incinerator (or the average temperature upstream and downstream of the catalyst bed for a catalytic incinerator), measured at least every 15 minutes and averaged over the same time period of the performance testing, and

(ii) The percent reduction of TOC determined as specified in D.5(c) achieved by the incinerator, or the concentration of TOC (parts per million by volume, by compound) determined as specified in D.5(c) at the outlet of the control device on a dry basis corrected to 3 percent oxygen.

(2) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with D.4(a)(1) through use of a boiler or process heater:

(i) A description of the location at which the vent stream is introduced into the boiler or process heater, and

(ii) The average combustion temperature of the boiler or process heater with a design heat input capacity of less than 44 megawatt measured at least every 15 minutes and averaged over the same time period of the performance testing.

(i) For the purpose of demonstrating that a process vent stream has a VOC concentration below 500 parts per million by volume, the following to set procedures shall be followed:

(1) The sampling site shall be selected as specified in D.5(c)(1).

(2) Method 18 or Method 25A of Part 60, Appendix A shall be used to measure concentration; alternatively, any other method or data that has been validated according to the protocol in Method 301 of Part 63, Appendix A may be used.

(3) Where Method 18 is used, the following procedures shall be used to calculate parts per million by volume concentration:

(i) The minimum sampling time for each run shall be 1 hour in which either an integrated sample or four grab samples shall be taken. If grab sampling is used, then the samples shall be taken at approximately equal intervals in time, such as 15 minute intervals during the run.

(ii) The concentration of TOC (minus methane and ethane) shall be calculated using Method 18 according to D.5(c)(4).

(4) Where Method 25A is used, the following procedures shall be used to calculate parts per million by volume TOC concentration:

(i) Method 25A shall be used only if a single VOC is greater than 50 percent of total VOC, by volume, in the process vent stream.

(ii) The process vent stream composition may be determined by either process knowledge, test data collected using an appropriate EPA Method or a method of data collection validated according to the protocol in Method 301 of Part 63, Appendix A. Examples of information that could constitute process knowledge include calculations based on material balances, process stoichiometry, or previous test results provided the results are still relevant to the current process vent stream conditions.

(iii) The VOC used as the calibration gas for Method 25A shall be the single VOC present at greater than 50 percent of the total VOC by volume.

(iv) The span value for Method 25A shall be 50 parts per million by volume.

(v) Use of Method 25A is acceptable if the response from the high-level calibration gas is at least 20 times the standard deviation of

the response from the zero calibration gas when the instrument is zeroed on the most sensitive scale.

(vi) The concentration of TOC shall be corrected to 3 percent oxygen using the procedures and equation in D.5(c)(3).

(5) The owner or operator shall demonstrate that the concentration of TOC including methane and ethane measured by Method 25A is below 250 parts per million by volume with VOC concentration below 500 parts per million by volume to qualify for the low concentration exclusion.

D.6 MONITORING REQUIREMENTS

(a) The owner or operator of an affected facility that uses an incinerator to seek to comply with the TOC emission limit specified under D.4(a)(1) shall install, calibrate, maintain, and operate according to manufacturer's specifications: a temperature monitoring device equipped with a continuous recorder and having an accuracy of ±0.5 °C, whichever is greater.

(1) Where an incinerator other than a catalytic incinerator is used, a temperature monitoring device shall be installed in the firebox.

(2) Where a catalytic incinerator is used, temperature monitoring devices shall be installed in the gas stream immediately before and after the catalyst bed.

(b) The owner or operator of an affected facility that uses a flare to seek to comply with D.4(a)(2) shall install, calibrate, maintain, and operate according to manufacturer's specifications, a heat-sensing device, such as a ultraviolet beam sensor or thermocouple, at the pilot light to indicate continuous presence of a flame.

(c) The owner or operator of an affected facility that uses a boiler or process heater with a design heat input capacity less than 44 megawatts to seek to comply with D.4(a)(1) shall install, calibrate, maintain, and operate according to the manufacturer's specifications, a temperature monitoring device in the firebox. The monitoring device should be equipped with a continuous recorder and having an accuracy of ±1 percent of the temperature being measured expressed in degrees Celsius or ±0.5 °C, whichever is greater. Any boiler or process heater in which all vent streams are introduced with primary fuel is exempt from this requirement.

Q_S = Vent stream flow rate standard cubic meters per minute at a standard temperature of 20 °C.

H_T = Vent stream net heating value (megajoules per standard cubic meter), as calculated in D.5(e)(6).

E_{TOC} = Hourly emission rate of TOC (minus methane and ethane), (kilograms per hour) as calculated in paragraph D.5(e)(4).

a,b,c,d = Coefficients presented in Table D-1.

(2) The owner or operator of a vent stream shall use the applicable coefficients in Table D-1 to calculate the TRE index value based on a flare, a thermal incinerator with 0 percent heat recovery, and a thermal incinerator with 70 percent heat recovery, and shall select the lowest TRE index value.

(3) The owner or operator of a unit with a halogenated vent stream, determined as any stream with a total concentration of halogen atoms contained in organic compounds of 200 parts per million by volume or greater, shall use the applicable coefficients in Table D-1 to calculate the total resource effectiveness index value based on a thermal incinerator and scrubber.

(g) Each owner or operator of an affected facility seeking to comply with D.4(b) shall recalculate the flow rate and TOC concentration for that affected facility whenever process changes are made. Examples of process changes include changes in production capacity, feedstock type, or catalyst type, or whenever there is replacement, removal, or addition of recovery equipment. The flow rate and VOC concentration shall be recalculated based on test data, or on best engineering estimates of the effects of the change to the recovery system.

(h) Where the recalculated values yield a total resource effectiveness index ≤ 1.0, the owner or operator shall notify the State air quality management agency within 1 week of the recalculation and shall conduct a performance test according to the methods and procedures required by D.5.

TABLE D-1. COEFFICIENTS FOR TOTAL RESOURCE EFFECTIVENESS FOR
NONHALOGENATED AND HALOGENATED VENT STREAMS

Type of stream	Control device basis	Values of Coefficients			
		a	b	c	d
Nonhalogenated	Flare	2.129	0.183	-0.005	0.359
	Thermal incinerator 0 Percent heat Recovery	3.075	0.021	-0.037	0.018
	Thermal incinerator 70 Percent heat Recovery	3.803	0.032	-0.042	0.007
Halogenated	Thermal incinerator and scrubber	5.470	0.181	-0.040	0.004

attributable to the reactor or distillation vent stream. The resulting organic compound concentrations are then used to perform the calculations outlined in D.5(e)(4).

(2) The molar composition of the vent stream shall be determined as follows:

(i) Method 18 to measure the concentration of organic compounds including those containing halogens.

(ii) ASTM D1946-77 to measure the concentration of carbon monoxide and hydrogen.

(iii) Method 4 to measure the content of water vapor.

(3) The volumetric flow rate shall be determined using Method 2, 2A, 2C, or 2D, as appropriate.

(4) The emission rate of TOC (minus methane and ethane) (E_{TOC}) in the vent stream shall be calculated using the following equation:

$$E_{TOC} = K_2 \sum_{j=1}^{n} C_j M_j \quad Q_s$$

where:

E_{TOC} = Emission rate of TOC (minus methane and ethane) in the sample, kilograms per hour.

K_2 = Constant, 2.494×10^{-6} (liters per parts per million)(gram-moles per standard cubic meter)(kilogram per gram)(minute per hour), where standard temperature for (gram-mole per standard cubic meter)(g-mole/scm) is 20 °C.

C_j = Concentration of compound j, on a dry basis, in parts per million as measured by Method 18, as indicated in D.5(c)(3).

M_j = Molecular weight of sample j, grams per gram-mole.

Q_s = Vent stream flow rate (standard cubic meters per minute) at a temperature of 20 °C.

(5) The total process vent stream concentration (by volume) of compounds containing halogens (parts per million by volume, by compound) shall be summed from the individual concentrations of compounds containing halogens which were measured by Method 18.

(6) The net heating value of the vent stream shall be calculated using the equation:

$$H_T = K_1 \sum_{j=1}^{n} C_j H_j (1 - B_{ws})$$

where:

H_T = Net heating value of the sample (megajoule per standard cubic meter), where the net enthaply per mole of vent stream is based on combustion at 25 °C and 760 millimeters of mercury, but the standard temperature for determining the volume corresponding to one mole is 20 °C, as in the definition of Q_S (vent stream flow rate).

K_1 = Constant, 1.740 x 10^{-7} (parts per million)$^{-1}$ (gram-mole per standard cubic meter), (megajoule per kilocalorie), where standard temperature for (gram-mole per standard cubic meter) is 20 °C.

B_{ws} = Water vapor content of the vent stream, proportion by volume; except that if the vent stream passes through a final stream jet and is not condensed, it shall be assumed that B_{ws} = 0.023 in order to correct to 2.3 percent moisture.

C_j = Concentration on a dry basis of compound j in parts per million, as measured for all organic compounds by Method 18 and measured for hydrogen and carbon monoxide by the American Society for Testing and Materials D1946-77.

H_j = Net heat of combustion of compound j, kilocalorie per gram-mole, based on combustion at 25 °C and 760 millimeters of mercury. The heats of combustion of vent stream components shall be determined using American Society for Testing and Materials D2382-76 if published values are not available or cannot be calculated.

(f)(1) The total resource effectiveness index value of the vent shall be calculated using the following equation:

$$TRE = \frac{1}{E_{TOC}} [a + b (Q_S) + c (H_T) + d (E_{TOC})]$$

where:

TRE = TRE index value.

E_{TOC} = Hourly emission rate of TOC (kilograms per hour) as calculated in D.5(e)(4).

(iii) The mass rates of TOC (E_i, E_0) shall be computed using the following equations:

$$E_i = K_2 \left(\sum_{j=1}^{n} C_{ij}M_{ij} \right) Q_i$$

$$E_0 = K_2 \left(\sum_{j=1}^{n} C_{oj}M_{oj} \right) Q_0$$

where:

C_{ij}, C_{oj} = Concentration of sample component "j" of the gas stream at the inlet and outlet of the control device, respectively, dry basis, parts per million by volume.

M_{ij}, M_{oj} = Molecular weight of sample component "j" of the gas stream at the inlet and outlet of the control device, respectively, grams per gram-mole.

Q_i, Q_0 = flow rate of gas stream at the inlet and outlet of the control device, respectively, dry standard cubic meters per minute.

K_2 = 2.494 x 10^{-6} (liters per minute)(gram-mole per standard cubic meter)(kilogram per gram)(minute per hour), where standard temperature for (gram-mole per standard cubic meter) is 20 °C.

(iv) The TOC concentration (C_{TOC}) is the sum of the individual components and shall be computed for each run using the following equation:

$$C_{TOC} = \sum_{j=1}^{n} C_j$$

where:

C_{TOC} = Concentration of TOC (minus methane and ethane), dry basis, parts by million by volume.

C_j = Concentration of sample component "j", dry basis, parts per million by volume.

n = Number of components in the sample.

(5) When a boiler or process heater with a design heat input capacity of 44 megawatts or greater, or a boiler or process heater into which the process vent stream is introduced with the primary fuel, is used to comply with the control requirements, an initial performance test is not required.

(d) When a flare is used to comply with the control requirements of this rule, the flare shall comply with the requirements of 40 CFR 60.18.

(e) The following test methods shall be used to determine compliance with the TRE index value.

(1) Method 1 or 1A, as appropriate, for selection of the sampling site.

(i) The sampling site for the vent stream molar composition determination and flow rate prescribed in D.5(e)(2) and (e)(3) shall be, except for the situations outlined in paragraph (e)(1)(ii) of this section, after the final recovery device, if a recovery system is present, prior to the inlet of any control device, and prior to any post-reactor or post-distillation unit introduction of halogenated compounds into the process vent stream. No traverse site selection method is needed for vents smaller than 10 centimeters in diameter.

(ii) If any gas stream other than the reactor or distillation vent stream is normally conducted through the final recovery device:

(A) The sampling site for vent stream flow rate and molar composition shall be prior to the final recovery device and prior to the point at which any nonreactor or nondistillation stream or stream from a nonaffected reactor or distillation unit is introduced. Method 18 shall be used to measure organic compound concentrations at this site.

(B) The efficiency of the final recovery device is determined by measuring the organic compound concentrations using Method 18 at the inlet to the final recovery device after the introduction of all vent streams and at the outlet of the final recovery device.

(C) The efficiency of the final recovery device determined according to D.5(e)(1)(ii)(B) shall be applied to the organic compound concentrations measured according to D.5(e)(1)(ii)(A) to determine the concentrations of organic compounds from the final recovery device

D-11

properties. Examples for analytical methods include, but are not limited to:

(A) Use of material balances based on process stoichiometry to estimate maximum VOC concentrations.

(B) Estimation of maximum flow rate based on physical equipment design such as pump or blower capacities.

(C) Estimation of TOC concentrations based on saturation conditions.

(D) Estimation of maximum expected net heating value based on the stream concentration of each organic compound, or, alternatively, as if all TOC in the stream were the compound with the highest heating value.

(v) All data, assumptions, and procedures used in the engineering assessment shall be documented.

(b) For the purpose of demonstrating compliance with the control requirements of this rule, the process unit shall be run at representative operating conditions and flow rates during any performance test.

(c) The following methods in 40 CFR 60, Appendix A, shall be used to demonstrate compliance with the emission limit or percent reduction efficiency requirement listed in D.4(a)(1).

(1) Method 1 or 1A, as appropriate, for selection of the sampling sites. The control device inlet sampling site for determination of vent stream molar composition or TOC (less methane and ethane) reduction efficiency shall be located after the last recovery device but prior to the inlet of the control device, prior to any dilution of the process vent stream, and prior to release to the atmosphere.

(2) Method 2, 2A, 2C, or 2D, as appropriate, for determination of gas stream volumetric flow rate.

(3) The emission rate correction factor, integrated sampling, and analysis procedure of Method 3 shall be used to determine the oxygen concentration (% O_{2d}) for the purpose of determining compliance with the 20 parts per million by volume limit. The sampling site shall be the same as that of the TOC samples, and samples shall be taken during the same

time that the TOC samples are taken. The TOC concentration corrected to 3 percent oxygen (C_c) shall be computed using the following equation:

$$C_c = C_{TOC} \times \frac{17.9}{20.9 - \% \, O_{2d}}$$

where:

C_c = Concentration of TOC (minus methane and ethane) corrected to 3 percent O_2, dry basis, parts per million by volume.

C_{TOC} = Concentration of TOC (minus methane and ethane), dry basis, parts per million by volume.

$\% \, O_{2d}$ = Concentration of oxygen, dry basis, percent by volume.

(4) Method 18 to determine the concentration of TOC (less methane and ethane) at the outlet of the control device when determining compliance with the 20 parts per million by volume limit, or at both the control device inlet and outlet when the reduction efficiency of the control device is to be determined.

(i) The minimum sampling time for each run shall be 1 hour in which either an integrated sample or four grab samples shall be taken. If grab sampling is used then the samples shall be taken at 15-minute intervals.

(ii) The emission reduction (R) of TOC (less methane and ethane) shall be determined using the following equation:

$$R = \frac{E_i - E_o}{E_i} \times 100$$

where:

R = Emission reduction, percent by weight.

E_i = Mass rate of TOC (minus methane and ethane) entering the control device, kilogram TOC per hour.

E_o = Mass rate of TOC (minus methane and ethane) discharged to the atmosphere, kilogram TOC per hour.

negligible photochemical reactivity. The Administrator has designated the following organic compounds as negligibly reactive: methane; ethane; 1,1,1-trichloroethane; methylene chloride, trichlorofluoromethane; dichlorodifluoromethane; chlorodifluoromethane; trifluoromethane; trichlorotrifluoroethane; dichlorotetrafluoroethane; and chloropentafluoroethane.

Total resource effectiveness index value or "TRE index value" means a measure of the supplemental total resource requirement per unit reduction of organic hazardous air pollutants associated with a process vent stream, based on vent stream flow rate, emission rate of volatile organic compound, net heating value, and corrosion properties (whether or not the vent stream contains halogenated compounds) as quantified by the given equations. The TRE index is a decision tool used to determined if the annual cost of controlling a given vent gas stream is acceptable when considering the emissions reduction achieved.

Vent stream means any gas stream discharge directly from a distillation operation or reactor process to the atmosphere or indirectly to the atmosphere after diversion through other process equipment. The vent stream excludes relief valve discharges and equipment leaks including, but not limited to, pumps, compressors, and valves.

D.4 CONTROL REQUIREMENTS

(a) For individual vent streams within a process unit with a TRE index value less than or equal to 1.0, the owner or operator shall comply with paragraphs (1) or (2) of this section.

(1) Reduce emission of TOC (less methane and ethane) by 98 weight-percent, or to 20 parts per million by volume, on a dry basis corrected to 3 percent oxygen, whichever is less stringent. If a boiler or process heater is used to comply with this paragraph, then the vent stream shall be introduced into the flame zone of the boiler or process heater.

(2) Combust emissions in a flare. Flares used to comply with this paragraph shall comply with the requirements of 40 CFR 60.18. The flare operation requirement does not apply if a process, not subject to this CTG, vents an emergency relief discharge into a common flare header and

causes the flare servicing the process subject to this CTG to be out of compliance with one or more of the provisions of the flare operation rule.

(b) For each individual vent streams within a process unit with a TRE index value greater than 1.0, the owner or operator shall maintain vent stream parameters that result in a calculated total resource effectiveness greater than 1.0 without the use of a volatile organic compound control device. The TRE index shall be calculated at the outlet of the final recovery device.

D.5 TOTAL RESOURCE EFFECTIVENESS DETERMINATION, PERFORMANCE TESTING, AND EXEMPTION TESTING

(a) For the purpose of demonstrating compliance with the TRE index value in D.4(b), engineering assessment may be used to determine process vent stream flow rate, net heating value, and TOC emission rate for the representative operating condition expected to yield the lowest TRE index value.

(1) If the TRE value calculated using such engineering assessment and the TRE equation in paragraph D.5(f)(1) is greater than 4.0, then it is not recommended that the owner or operator perform the measures specified in Section D.5(e).

(2) If the TRE value calculated using such engineering assessment and the TRE equation in paragraph D.5(f)(1) is less than or equal to 4.0, then it is recommended that the owner or operator perform the measurements specified in Section D.5(e).

(3) Engineering assessment includes, but is not limited to, the following:

(i) Previous test results proved the test are representative of current operating practices at the process unit.

(ii) Bench-scale or pilot-scale test data representative of the process under representative operating conditions.

(iii) Maximum flow rate specified or implied within a permit limit applicable to the process vent.

(iv) Design analysis based on accepted chemical engineering principles, measurable process parameters, or physical or chemical laws or

D.3 DEFINITIONS

Batch mode means a noncontinuous operation or process in which a discrete quantity or batch of feed is charged into a process unit and distilled or reacted at one time.

Boiler means any enclosed combustion device that extracts useful energy in the form of steam.

By compound means by individual stream components, not carbon equivalents.

Continuous recorder means a data recording device recording an instantaneous data value at least once every 15 minutes.

Distillation operation means an operation separating one or more feed stream(s) into two or more exit stream(s), each exit stream having component concentrations different from those in the feed stream(s). The separation is achieved by the redistribution of the components between the liquid and vapor-phase as they approach equilibrium within the distillation unit.

Distillation unit means a device or vessel in which distillation operations occur, including all associated internals (such as trays or packing) and accessories (such as reboiler, condenser, vacuum pump, stream jet, etc.), plus any associated recovery system.

Flame zone means the portion of the combustion chamber in a boiler occupied by the flame envelope.

Flow indicator means a device that indicates whether gas flow is present in a vent stream.

Halogenated vent stream means any vent stream determined to have a total concentration of halogen atoms (by volume) contained in organic compounds of 200 parts per million by volume or greater determined by Method 18 of 40 CFR 60, Appendix A, or other test or data validated by Method 301 of 40 CFR 63, Appendix A, or by engineering assessment or process knowledge that no halogenated organic compounds are present. For example, 150 parts per million by volume of ethylene dichloride would contain 300 parts per million by volume of total halogen atoms.

Incinerator means any enclosed combustion device that is used for destroying organic compounds. Auxiliary fuel may be used to heat waste

gas to combustion temperatures. Any energy recovery section present is not physically formed into one section; rather, the energy recovery system is a separate section following the combustion section and the two are joined by ducting or connections that carry fuel gas.

Primary fuel means the fuel that provides the principal heat input to the device. To be considered primary, the fuel must be able to sustain operation without the addition of other fuels.

Process heater means a device that transfers heat liberated by burning fuel to fluids contained in tubes, including all fluids except water that is heated to produce steam.

Process unit means equipment assembled and connected by pipes or ducts to produce, as intermediates or final products, one or more SOCMI chemicals (see Appendix A of this document). A process unit can operate independently if supplied with sufficient feed or raw materials and sufficient product storage facilities.

Product means any compound or SOCMI chemical (see Appendix A of this document) that is produced as that chemical for sale as a product, by-product, co-product, or intermediate or for use in the production of other chemicals or compounds.

Reactor processes mean unit operations in which one or more chemicals, or reactants other than air, are combined or decomposed in such a way that their molecular structures are altered and one or more new organic compounds are formed.

Recovery device means an individual unit of equipment, such as an adsorber, carbon adsorber, or condenser, capable of and used for the purpose of recovering chemicals for use, reuse, or sale.

Recovery system means an individual recovery device or series of such devices applied to the same vent stream.

Total organic compounds or "TOC" means those compounds measured according to the procedures of Method 18 of 40 CFR 60, Appendix A. For the purposes of measuring molar composition as required in D.5(c)(4); hourly emissions rate as required in D.5(e)(4) and D.4(b); and TOC concentration as required in D.7(a)(4) and D.7(b). The definition of TOC excludes those compounds that the Administrator designates as having

requirements to make the example rule more complete. These requirements may also be revised by the State agencies.

The remainder of this appendix constitutes the example rule. Sections are provided on the following rule elements: applicability, definitions, control requirements, performance testing, monitoring requirements, and reporting/recordkeeping requirements.

D.2 APPLICABILITY

(a) The provisions of this rule apply to any vent stream originating from a process unit in which a reactor process or distillation operation is located. A decision tree is provided (Figure D.1) to facilitate determination of applicability to this guideline on a per vent basis.

(b) Exemptions from the provisions of this guideline are as follows:

(1) Any reactor process or distillation operation that is designed and operated in a batch mode is not subject to the provisions of this rule.

(2) Any reactor process or distillation operation that is part of a polymer manufacturing operation is not subject to the provisions of this guideline.

(3) Any reactor process or distillation operation operating in a process unit with a total design capacity of less than 1 gigagram per year for all chemicals produced within that unit is not subject to the provisions of this guideline except for the reporting and recordkeeping requirements listed in D.7(e).

(4) Any vent stream for a reactor process or distillation operation with a flow rate less than 0.0085 standard cubic meter per minute or a total VOC concentration less than 500 parts per million by volume is not subject to the provisions of this guideline except for the performance testing requirement listed in D.5(c)(2), D.5(i) and the reporting and recordkeeping requirements listed in D.7(d).
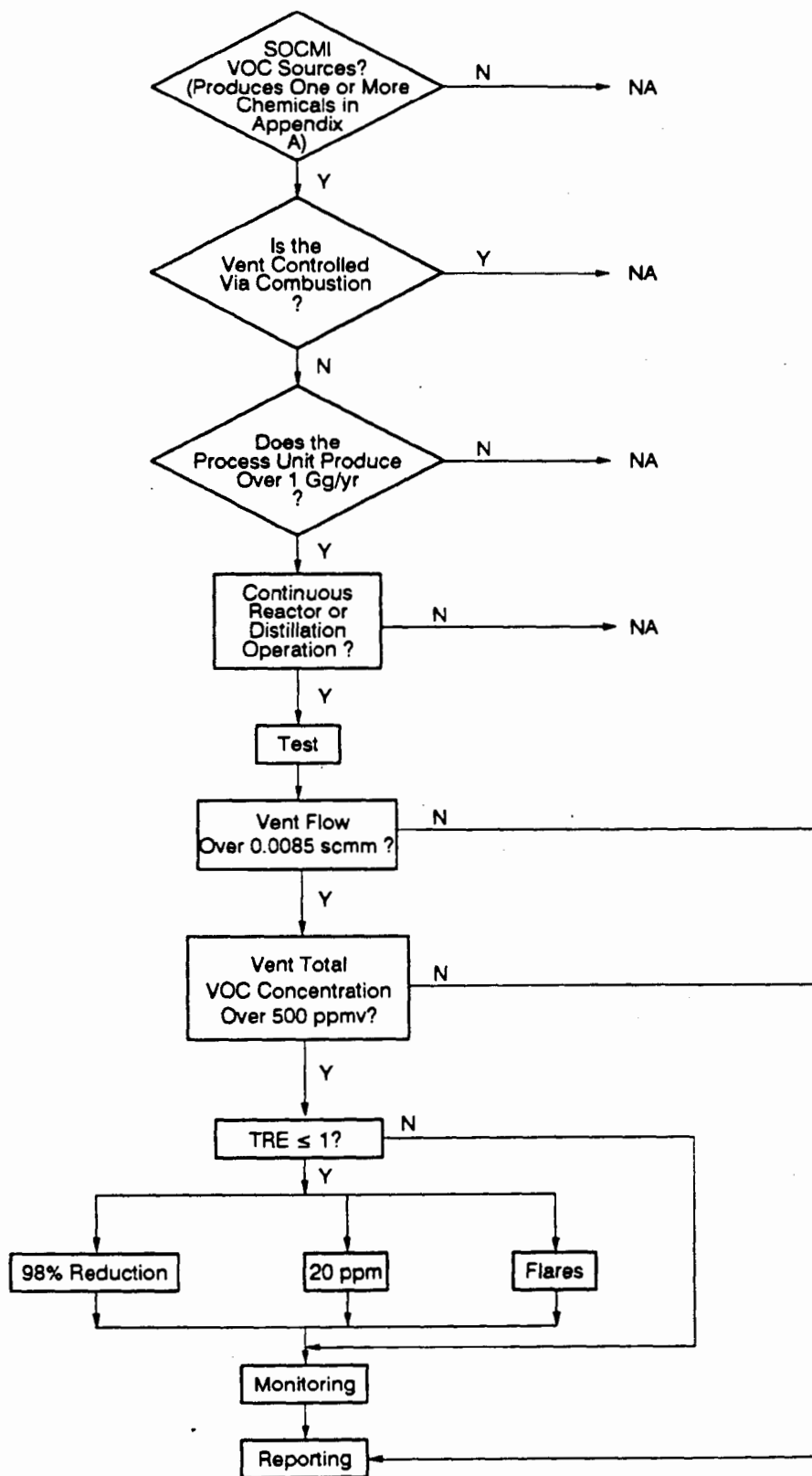
Figure D.1. Synthetic organic chemical manufacturing industry reactor/distillation control techniques guideline logic diagram per vent.

D-3

APPENDIX E

ENVIRONMENTAL IMPACTS CALCULATIONS

APPENDIX E

ENVIRONMENTAL IMPACTS CALCULATIONS

E.1 CALCULATION OF SECONDARY AIR IMPACTS

Calculations will be based on model stream R-LFHH, the same stream used as an example in Appendix C.

E.2 ESTIMATING CARBON MONOXIDE EMISSIONS

Calculate total heat input of the stream to be combusted.

(1) H_1 = Initial heat input of waste stream
H_1 = (flow rate)(heat value)
   = (23.54 scfm)(209.7 Btu/scf)
   = 4,936 Btu/min x (60 min/hr) x (8,760 hr/yr) x (MMBtu/10^6 Btu)
   = 2,595 MMBtu/yr

(2) H_2 = Heat input from auxiliary fuel
H_2 = (flow rate)(heat value)
   = (0.1 scfm)(1,000 Btu/scf)
   = 100 Btu/min
   = 52.5 MMBtu/yr

(3) Total heat input = H_1 + H_2
               = (2,595 + 52.5) MMBtu/yr
               = 2,648 MMBtu/yr

Calculate carbon monoxide (CO) emissions using AP-42 factor of 20 lb CO/MMscf of fuel.

(1) Convert MMBtu/yr to equivalent fuel flow (Q_F)
Q_F = (2,698 MMBtu/yr)(scf/1,000 Btu)
   = 2.6 MMscf/yr

(2) CO_{em} = (2.6 MMscf/yr)(20 lb/MMscf)(Mg/2,207 lb)
       = 0.02 Mg/yr of CO

E.3 ESTIMATING NITROGEN OXIDES EMISSIONS

Determine method of control (flare or incinerator). Model stream R-LFHH is cheapest to control using incinerator with scrubber (see Appendix C for costing analysis).

For incinerators, two nitrous oxide (NO_x) emission factors are used: one for streams containing nitrogen compounds, and one for streams without nitrogen compounds. Inert nitrogen gas (N_2) is not included. The NO_x factors for incinerators are as follows:

        with nitrogen compounds: 200 ppm in exhaust
        without nitrogen compounds: 21.5 ppm in exhaust

The model stream R-LFHH has no nitrogen, so 21.5 ppm will be used. These factors reflect testing data that was gathered for the Air Oxidation Reactor processes CTG and the Polymers and Resins CTG.

Calculate total outlet flow, as explained in Appendix C. As shown in Section C.4, the total outlet flow exiting the incinerator/scrubber system is 53 scfm.

(1) NO_x emissions = (53 scfm)(21.5/10^6)/(392 scf/lb·mole) x (46 lb/lb·mole)

       NO_x emissions = (0.000134 lb/min) x (60 min/hr) x (8,760 hr/yr) x (Mg/2,207 lb)
                 = 0.032 Mg/yr

(2) If the total outlet flow rate from the incinerator is not known, the following emission factors may be used to calculate NO_x emissions:

        with nitrogen compounds: 0.41 lb NO_x/MMBtu
        without nitrogen compounds: 0.08 lb NO_x/MMBtu

As calculated in E.2 (3), the total heat input is 2,648 MMBtu/yr. Therefore, the NO_x emissions estimated using this factor are calculated by:

   NO_x emissions = (2,648 MMBtu/yr)(0.08 lb NO_x/MMBtu) x (Mg/2,207 lb)
                 = 0.10 Mg/yr

APPENDIX F

RESPONSE TO PUBLIC COMMENTS RECEIVED ON THE DRAFT SYNTHETIC
ORGANIC CHEMICAL MANUFACTURING INDUSTRY REACTOR PROCESSES
AND DISTILLATION OPERATIONS CONTROL TECHNIQUES GUIDELINE

APPENDIX F

RESPONSE TO PUBLIC COMMENTS RECEIVED ON THE DRAFT SYNTHETIC
ORGANIC CHEMICAL MANUFACTURING INDUSTRY REACTOR PROCESSES
AND DISTILLATION OPERATIONS CONTROL TECHNIQUES GUIDELINE

F.1 INTRODUCTION

On December 12, 1991, the U. S. Environmental Protection Agency (EPA) announced the availability of a draft control techniques guideline (CTG) document for "The Control of Volatile Organic Compound Emissions from Reactor Processes and Distillation Operations Processes in the Synthetic Organic Chemical Manufacturing Industry" (56 FR 64785). Public comments were requested on the draft CTG in that Federal Register notice. Thirteen comments were received. Table F.1-1 lists the commenters, their affiliations, and the EPA docket number assigned to their correspondence. The major topics of the comments were: the recommendation to incorporate a total resource effectiveness (TRE) index approach for determining applicability; the recommendation for less stringent flow cutoffs; and a concern that the cost of complying with the recommended control level is too high. The comments that were submitted, along with responses to these comments, are summarized in this appendix. The summary of comments and responses serve as the basis for the revisions made to the CTG between the draft and final document.

F.2 SUMMARY OF CHANGES TO THE DRAFT CONTROL TECHNIQUES GUIDELINE

Several changes and clarifications were made in the CTG as a result of review of public comments. These changes and clarifications were made in the following areas: (1) use of the TRE index equations; (2) aggregation of vent streams to a control device; (3) location of flow indicators; (4) definition of total organic compounds (TOC's); (5) description of catalytic incinerators; (6) applicable chemicals;

TABLE F.1-1. LIST OF COMMENTERS AND AFFILIATIONS

Docket item number[a]	Commenter and affiliation
IV-D-1	Mr. Charles D. Malloch Director, Regulatory Management Environment, Safety and Health Monsanto Company 800 N. Lindbergh Boulevard St. Louis, Missouri 63167
IV-D-2	Mr. R.L. Arscott, General Manager Health, Environmental and Loss Protection Chevron Corporation Post Office Box 7924 San Francisco, California 94120-7924
IV-D-3	Mr. David W. Gustafson Environmental Quality Mr. Sam P. Jordan Environmental Law The Dow Chemical Company Midland, Michigan 48667
IV-D-4	Mr. John A. Dege CAA Issue Manager DuPont Chemicals Wilmington, Delaware 19898
IV-D-5	V.M. McIntire Environmental Affairs Eastman Chemical Company Post Office Box 511 Kingsport, Tennessee 37662
IV-D-6	Ms. Sherry L. Edwards, Manager Government Relations Synthetic Organic Chemical Manufacturers Association, Incorporated 1330 Connecticut Avenue, N.W., Suite 300 Washington, D.C. 20036-1702
IV-G-2	M.L. Mullins Vice President, Regulatory Affairs Chemical Manufacturers Association 2501 M Street, N.W. Washington, D.C. 20037

TABLE F.1-1. LIST OF COMMENTERS AND AFFILIATIONS
(CONCLUDED)

Docket item number[a]	Commenter and affiliation
IV-G-3	Mr. E. G. Collier Chairman, Control Techniques Guidelines Subcommittee Texas Chemical Council
IV-G-4	Mr. B.L. Taranto Environmental Affairs Department Exxon Chemical Americas Post Office Box 3272 Houston, Texas 77253-3272
IV-G-5	Ms. Regina M. Flahie Chief Division of Interagency and International Affairs U. S. Department of Labor, Occupational Safety and Health Administration Washington, D.C. 20210
IV-G-6	Mr. G. E. Addison Manager, Planning and Development ARI Technologies, Incorporated 600 N. First Bank Drive Palatine, Illinois 60067
IV-G-7	Mr. Raymond J. Connor Technical Director Manufacturers of Emission Controls Association 1707 L Street, N.W., Suite 570 Washington, D.C. 20036-4201
IV-G-8	Mr. Kevin Ewing Market Manager Thermotron Industries 291 Kollen Park Drive Holland, Michigan 49423

[a]The docket number for this project is SOCMI CTG A-91-38. Dockets are on file at the EPA Air Docket in Washington, D.C.

(7) definition of product; (8) definition of halogenated stream;
(9) exemption of streams with a flow rate or concentration below a cutoff
value; and (10) definition of affected facility.

The comments summarized in this appendix have been organized into the
following categories: Applicability of the Control Techniques Guideline;
Recommendation of Reasonably Available Control Technology; Cost
Effectiveness, Monitoring and Testing, and Editorial.

F.3 APPLICABILITY OF THE CONTROL TECHNIQUES GUIDELINE

F.3.1 <u>Comment</u>: One commenter (IV-G-4) disagreed with the assertion on
pages 6-7 and 6-8 of the draft CTG that the recommended applicability
criteria provide an incentive for pollution prevention. The commenter
stated that since control by combustion (or equivalent control) would be
required for the residual emissions from virtually any recovery device, the
incentive to install such a device would be diminished. The commenter
suggested that an incentive could be provided for control of vent emissions
by combusting the residuals as primary fuel.

<u>Response</u>: The incentive referred to on pages 6-7 and 6-8 of the
draft CTG pertains to an incentive for any pollution prevention or
recycling practice that lowers emissions below the cutoff level. Pollution
prevention and recycling can include any process change--including the
addition of recovery devices--that significantly reduces the amount of
pollutants that are emitted from the process unit. In the case of this
CTG, the recommended presumptive norm for reasonably available control
technology (RACT) would allow an affected facility to avoid having to
install an add-on combustion control device if the affected facility lowers
emissions below the cutoff. The EPA believes that this provision
encourages pollution prevention and recycling.

F.3.2 <u>Comment</u>: One commenter (IV-D-5) requested that the EPA include in
this CTG a statement that distillation operations that are part of polymer
manufacturing processes are not covered by this CTG. The commenter
reasoned that this would be consistent with the applicability criteria for
the new source performance standards (NSPS) for distillation operations
(40 CFR Part 60 Subpart NNN).

<u>Response</u>: It is not the intent of this CTG to provide guidance for
process vents that are subject to regulations for the polymer manufacturing

industry. To clarify that these facilities are not subject to this CTG, an exemption statement has been added to this document (see Section 7.4).

F.3.3 Comment: Two commenters (IV-D-2, IV-G-2) suggested that the CTG provide a more detailed discussion of the overlap between the source categories and chemicals covered under this CTG, and the source categories and hazardous air pollutants (HAP's) covered under Title III of the Clean Air Act (CAA), as amended in 1990.

One commenter (IV-G-2) further stated that the EPA should strive for consistency between Title I RACT and Title III maximum achievable control technology (MACT) with respect to the application of control standards, testing, monitoring, and reporting requirements.

Response: The EPA understands that more clarification is needed to explain which chemicals within the SOCMI source category are applicable to this CTG and which are subject to Title III of the CAA. The SOCMI is a broad source category that includes any manufacturer of synthetic organic chemicals. Appendix A of this CTG has been revised to present the organic chemicals that are subject to this CTG. Appendix A also indicates which chemicals in this list are listed as part of the SOCMI source category and which chemicals are subject to the proposed Hazardous Organic National Emission Standard for Hazardous Air Pollutants (HON), or any of the following regulations: the air oxidation processes NSPS; distillation operations NSPS; and the reactor processes NSPS. The regulations' and rules' applicability criteria is based on the chemical manufactured. For example, hexanedioic acid is manufactured using a reactor and distillation unit and is subject to this CTG, the distillation NSPS, and the reactor process NSPS. However, hexanedioic acid is not manufactured using an air oxidation process and, therefore, is not subject to the air oxidation process NSPS.

Although there are appropriate differences with respect to applicability, the EPA wants to eliminate duplicate performance testing, reporting and recordkeeping, and monitoring requirements. The EPA is considering options to deal with the interface between regulations promulgated under Section 112 of the Clean Air Act and RACT rules. Specifically, the EPA is developing a policy statement for emission points that will be affected both by the HON and RACT rules. This policy statement will be published in the Federal Register when completed.

Pursuant to the CTG, recordkeeping and reporting requirements have been left to the discretion of the State air quality management agencies as stated in Section 7.7 (Reporting/Recordkeeping Requirements) of the CTG document; however, emission points subject to the HON would be subject to the recordkeeping and reporting requirements of the HON.

The controls required to comply with the SOCMI NSPS, CTG's and the HON are the same and are based on the same control technology--that is, combustion. The cutoff levels for applicability may be different, however, because VOC's are the subject of the CTG's and the NSPS, and organic HAP's are the subject of the proposed HON.

F.3.4 <u>Comment</u>: Several commenters (IV-D-3, IV-D-4, IV-D-5, IV-D-6, IV-G-2, IV-G-3) recommended the incorporation of a TRE index as another option to the already suggested presumptive norm for RACT. Two commenters (IV-D-3, IV-G-2) suggested that using a TRE index would help to achieve a more cost-effective VOC control by using the least amount of energy, capital, and total resources. The commenters also suggested that incorporation of a TRE index furthers the application of pollution prevention principles by encouraging increased product recovery techniques and other process modifications that ultimately reduce VOC emissions, often by using more cost-effective techniques.

<u>Response</u>: To remain consistent with the other SOCMI regulations, the EPA has decided to incorporate the TRE index applicability approach to replace the flow and concentration limits that appeared in the draft CTG. This decision was reached after the draft CTG document was made available for public comment. The final copy of the CTG includes the TRE index.

The TRE index equation is a decision tool used to determine if the annual cost of controlling a given vent stream (as determined using the standard procedure described in Chapter 5) is acceptable when considering the emission reductions achieved. The TRE index is a measure of the total resource burden associated with emission control for a given vent stream. The TRE index equation is normalized so that the decision point has a defined value of 1.0. The variables in the TRE index equation are the stream characteristics (i.e., flow rate, heat content, VOC emission rate). This TRE index equation is developed from a multivariable linear regression of the cost algorithm. It is recommended that the owner or operator demonstrate that a TRE index is greater than 1.0 at the outlet of the final

recovery device in order to avoid having to control VOC emissions. If the TRE index is less than or equal to 1.0 at the point of measurement, the owner or operator could elect either to modify the process or, install an additional recovery device or a control device that results in a TRE index greater than 1.0.

The cost-effectiveness criteria built into the TRE index equation allow for greater emission reductions at the same cost compared to the flow and concentration limits alone. With the TRE equation, the CTG allows the flexibility to reduce VOC emission by whatever means the owner or operator prefers. Pollution prevention that increases product or raw material recovery may be the most cost-effective (and even the most beneficial) method to reduce VOC emissions and is encouraged.

F.3.5 Comment: Several commenters (IV-D-3, IV-D-5, IV-G-2, IV-G-3, IV-G-4) questioned the feasibility and stringency of the CTG combined vent criteria. Several commenters (IV-D-3, IV-D-5, IV-G-2, IV-G-3) argued that the concentration and flow cutoff should apply only to individual vent streams and not the combination of all vent streams in the process unit. Two commenters (IV-D-3, IV-G-2) also pointed out that the combined vent criteria appear to be more stringent than those in the NSPS because the CTG flow cutoff applies to multiple vents, regardless of whether a common recovery system into which the vents are discharged exists.

Several commenters (IV-D-3, IV-G-2, IV-G-3, IV-G-4) suggested that situations exist where it is not technically feasible, economical, or safe to combine vent streams. One commenter (IV-G-3) noted the following two examples that illustrate the safety concerns:

- Combining two streams where one stream is below the lower explosive limit and another stream is above the explosive limit, or

- Combining two streams that are chemically reactive.

Response: The combined stream criteria were included in this CTG because the practice of combining streams is often used in industry for similar process vent streams within the same process unit. The EPA recognizes that circumstances exist where it may not be technically feasible, economical, or safe to combine vent streams and, therefore, it should not be a control criterion. Because this approach cannot be generalized across the entire industry, the combined vent applicability

approach has been omitted from the CTG document. Furthermore, it should be noted that the applicability limits were written for individual streams and were not intended to determine applicability limitations on a combined stream basis. The applicability calculations continue to be conducted on an individual vent stream basis after the CTG was revised to incorporate the TRE.

F.3.6 <u>Comment</u>: One commenter (IV-D-1) noted that on page 2-7 of the draft CTG, the EPA refers to "176 high-volume chemicals" that "involve reactor processes." The commenter further noted that on page 2-33, the EPA refers to the scope of the reactor processes covered in the CTG as representing "one of the 173 reactor process chemicals." The commenter recommended that the EPA revise Appendix A of the CTG to indicate 173 chemicals (thus representing the similar list used in the NSPS), which the CTG intended to cover under reactor processes.

In addition, the commenter noted that the final NSPS for distillation operations lists the chemicals for its applicability. The commenter recommended that Appendix A of the draft CTG be shortened to include only those chemicals used for determining applicability of distillation operations. The commenter then suggested that the applicability statement in Section D.2.a on page D-1 of Appendix D in the draft CTG should be expanded to state that the process unit subject to this CTG should be one for which a chemical is listed in Appendix A.

<u>Response</u>: The reference on page 2-7 of the document is an industry characterization. There is no statement to suggest that the 176 high-volume chemicals listed there are the only chemicals within the scope of this CTG. These 176 chemicals are a subset of SOCMI chemicals that are produced in large quantities. Appendix A lists the 719 chemicals subject to this CTG. This list also identifies those chemicals that are also subject to the Distillation NSPS, Air Oxidation NSPS, the Reactor Process NSPS, the HON and other chemicals under the SOCMI source category. It is the intent of the EPA to make subject of this CTG, any distillation column or reactor operating as part of a process unit that makes one of the chemicals listed in Appendix A. The applicability statement in Appendix D has been expanded to state that the applicability of this CTG is based on the chemicals that are listed in Appendix A.

F.3.7 <u>Comment</u>: One commenter (IV-D-1) recommended that Table 2-5 on page 2-47 of the draft CTG be revised to address more clearly the minimal emissions occurring from atmospheric distillation operations. The commenter said that, as drafted, the table does not identify what type of operation corresponds to either the high or low emission rates. The commenter cited personal experience that atmospheric distillation columns used with low vapor pressure chemicals, such as adiponitrile or hexamethylene diamine, do not have any detectable emissions from the atmospheric vent.

The commenter also argued that condensers between the steam jets and sometimes on the final jet discharge are very effective in controlling emissions from distillation columns that process low-volatility chemicals, with control efficiencies exceeding 95 percent in situations as described above.

<u>Response</u>: Table 2-5 of the CTG document lists the average operating characteristics of the distillation emission profile, in addition to the range for these characteristics. The EPA realizes that the types of operations that correspond to the values listed are not identified and that processes may exist that are below those values.

With respect to the alternative VOC emissions reduction approach described by the commenter, the EPA would like to clarify that the RACT presumptive norm would not preclude the use of a condenser to reduce VOC emissions from affected vent streams. If use of such a condenser were to result in a TRE index value for the vent stream that is above the limit, then no additional control would be required.

F.4 RECOMMENDATION OF REASONABLE AVAILABLE CONTROL TECHNOLOGY

F.4.1 <u>Comment</u>: Several commenters (IV-D-2, IV-D-4, IV-D-6, IV-G-2, IV-G-4) expressed concern that the recommended control applicability cutoff is too stringent. Six commenters (IV-D-4, IV-D-5, IV-D-6, IV-G-2, IV-G-3, IV-G-4) pointed out that the proposed RACT <u>de minimus</u> flow rate is up to four times more stringent than the distillation operations NSPS requirements.

One commenter (IV-G-4) said that CTG cutoffs of 0.1 standard cubic feet per minute (scfm) and 0.05 weight-percent VOC would result in a calculated TRE of approximately 6,000 using the TRE equation from the proposed HON. The commenter also noted that the proposed cutoffs

correspond to a VOC emission rate of less than 5 pounds per year (lb/yr), and compared this emission rate to that of a single "nonleaking" valve in light liquid service, which has an emission rate of 6 lb/yr as calculated using the EPA emission factors.

Two commenters (IV-D-6, IV-G-2) suggested that the CTG adopt Option 3 (e.g., flow rate ≤ 0.5 scfm and VOC weight percent ≤ 1) in Table 6-1 as the RACT cutoff. One commenter (IV-D-6) emphasized that this option reduces nationwide emissions by over 73 percent, and reduces the nationwide cost of control by nearly 60 percent; yet still obtains almost 77 percent of the emissions reduction achieved by the RACT cutoff proposed by the EPA.

Response: The EPA has reevaluated the applicability cutoff, as mentioned in the response to comment number F.3.6, and the TRE index equation will replace the flow or concentration limits that appeared in the draft CTG. As pointed out by the commenters, use of the TRE equation will provide consistency with the distillation NSPS and HON requirements.

F.4.2 Comment: One commenter (IV-D-3) noted that it is not obvious whether the RACT cutoffs recommended by the CTG refer to instantaneous or average values. The commenter suggested that the EPA specifically state that the cut-off criteria for the concentration and flow are to be based on an annual weighted average.

Response: The inputs to the TRE index equation are stream flow rate, VOC emission rate, and heat content. These parameters should be average values over the period of the performance test. The performance test should be conducted under typical operating conditions, the specifics of which are defined in the example rule (Appendix D).

F.4.3 Comment: One commenter (IV-D-6) stated that by definition in the CAA, RACT requirements are less stringent than MACT requirements. Therefore, the proposed RACT for SOCMI should be less stringent than MACT for the same source categories.

Response: There is some confusion between MACT and RACT and the level of stringency for each requirement. One cannot compare the stringency levels of the two requirements because they are applicable to two different groups of pollutants; MACT is applied to HAP's listed in Section 112(b) of the CAA as amended in 1990, whereas RACT is applicable to various of the criteria pollutants, including VOC, a precursor to ozone. In some cases, the same vent stream may be subject to RACT criteria but not

MACT criteria. Regardless of the applicability criteria, the control requirement in all SOCMI regulations is 98 percent reduction of pollutants or pollutant reduction down to a concentration level of 20 parts per million by volume (ppmv) on a dry basis, corrected to 3 percent oxygen.

F.4.4 <u>Comment</u>: One commenter (IV-G-2) stated that the presumptive norm described in the CTG document for SOCMI does not accurately describe the types of emissions found to be emitted from reactor processes and distillation operations. Although the VOC concentration cutoff and flow rate cutoff help to ensure that insignificant vent streams do not require unnecessary cost controls, the cutoffs do not account for the variation that occurs from stream to stream due to chemical properties and associated heating values. The commenter argued that a low heating value stream would result in a much higher control cost than a high heating value stream, and may not be appropriate as a presumptive norm for RACT.

    <u>Response</u>: The EPA understands that in some cases low heating value streams could result in higher costs than high heating value streams to control, and has, therefore, incorporated the TRE index equation to the applicability section. The TRE index identifies only those streams that can be controlled in a cost-effective manner.

F.4.5 <u>Comment</u>: One commenter (IV-G-2) observed that the <u>de minimus</u> levels suggested in the CTG document are incompatible with the levels found in the NSPS. The commenter said that the establishment of such a low level will prove to be of little use to the regulated community and, furthermore, by setting a level that is inconsistent with current NSPS regulations, the EPA places facilities in the awkward position of trying to comply with two conflicting levels of control.

    <u>Response</u>: This comment is resolved by the incorporation of TRE. As indicated in the previous response, the parameters incorporated into the TRE equation will allow for control of only those streams that can be controlled on a cost-effective basis.

F.5 COST EFFECTIVENESS AND COST ESTIMATION

F.5.1 <u>Comment</u>: One commenter (IV-G-3) suggested that because a scrubber is needed to remove hydrogen chloride (HCl) from the incinerator flue gas, the discharge from this scrubber may significantly contaminate wastewater, which would require treatment prior to discharge. Another commenter (IV-D-5) questioned the EPA's judgment that costs associated with the

disposal of salty wastewater formed by the neutralization of acidic scrubber effluent were not significant. The commenter suggested that the opportunity to use on-site wells is significantly limited, not only by geographic considerations, but also regulatory concerns. Direct and indirect discharges could also be limited by aquatic toxicity limits of the National Pollutant Discharge Elimination Standards (NPDES) permit program.

   Response: It is the decision of the EPA not to include the costs associated with the disposal of salty wastewater in the cost equation for VOC control devices. This decision was based on earlier work done on the SOCMI reactor process NSPS. The effects from the discharge of wastewater from the scrubbers were presented in 1984 in the background information document (BID) for the Reactor Process NSPS. The water pollution impacts were studied in 1982, at which time it was determined that the costs associated with the disposal of the salty wastewater are not significant in comparison to the overall control costs and, therefore, were not included in the projected cost impacts. The specific reference in the Reactor Process NSPS docket that explains the methodology is EPA Docket No. A-83-29, Item No. II-B-25.

F.5.2 Comment: Several commenters (IV-D-4, IV-D-6 IV-G-2, IV-G-3) emphasized that the EPA underestimated the installed equipment costs, resulting in lower average cost-effectiveness numbers than industry is currently experiencing. Three commenters (IV-D-4, IV-G-2, IV-G-3) noted that the EPA indicated an installation factor of 1.61, which is much lower than installation factors of 3 to 10 commonly encountered in the chemical industry.

   Response: The installed equipment costs and the installation factor of 1.61 were determined using the EPA's Office of Air Quality Planning and Standards Control Cost Manual (OCCM). Each chapter of the OCCM underwent extensive industry review prior to finalization making this document the accepted source by the EPA. The EPA believes that this installation factor is consistent with what the majority of facilities from different industries that install incinerators would encounter.

F.5.3 Comment: Two commenters (IV-G-4, IV-D-6) suggested that the cost-effectiveness analysis is flawed and does not support the applicability criteria. One commenter (IV-G-4) noted that in Table 6-1 of the CTG, the average emission reduction per vent in the increment going

from Option 3 to Option 2 is 0.0035 megagrams per year (Mg/yr). However, vents of less than 0.003 Mg/yr would have to be controlled by the 0.1 scfm and 0.05 weight percent applicability criteria given in the draft CTG. Thus, the incremental cost effectiveness is calculated on a basis that misrepresents the recommended applicability criteria by more than four orders of magnitude. The commenter further noted that the cost effectiveness of controlling a 0.1 scfm and 0.05 weight percent vent stream is not addressed, and it should be in order to support its selection.

The commenter also felt that the cost data used to analyze regulatory options is very low and unrealistic and should be updated or corrected to reflect actual costs based on real plant experience. The commenter noted a cost of $5,274 was assumed for 400 feet of an 8-inch flare collection header, and suggested that the actual cost for this piping would exceed $34,000, even in a noncongested area where pipe supports already exist. The commenter also expressed concern that the flare cost estimate does not appear to include the cost of piping and pumps to manage liquid from the knockout drum, or the cost of piping and controls for the water supply to the water seal drum, or for the air, steam, or gas to the flare tip.

Two commenters (IV-D-4, IV-D-6) stated that under the recommended minimum emission levels, an emission flow rate of 0.11 scfm, with VOC concentration of 0.06 weight-percent (which corresponds to 2.6 lb/yr), would require incineration and control. The cost effectiveness for the low flow low heat case in Table 5-6 is $23,954 per megagram (Mg) for a 1.3 lb/hr VOC inlet flow. The de minimus flow rate mentioned above emits 400 times less. The commenter then said that by simple multiplication, the cost effectiveness balloons to $96,000,000 per megagram.

Response: The incremental cost effectiveness was calculated correctly in the draft CTG document. The data base used for this analysis contains many streams with high flow rates, but low concentrations. Therefore, some streams with relatively high VOC loadings are not included in the analysis until the most stringent options are imposed. Again, further discussion of this table and calculated cost effectiveness is no longer appropriate because the applicability format has been changed to incorporate a TRE index equation. The TRE equation takes into account these high cost considerations.

As stated in response F.5.2, all costing analyses are in accordance with the OCCM. The duct work cost assumptions are believed to represent industry averages. The flare costs do include water seals and steam piping to flare tip. Piping costs are accounted for by an installation factor.

F.5.4 Comment: Three commenters (IV-D-5, IV-G-2, IV-G-7) questioned whether the EPA accounted for full "costing" of controls. One commenter (IV-D-5) expressed concern that the EPA neither acknowledged nor adequately considered the upstream impact of the control equipment in their emissions analysis. The commenter suggested that there is a direct usage of fuel to run control devices, as well as indirect emission impacts of:
(1) producing the fuels consumed as energy to produce the controls;
(2) producing the raw materials, such as caustic, to operate the control devices; and (3) transporting these materials. The commenter asserted that the EPA should consider these upstream impacts by including a factor, such as an economic or cash flow multiplier, that would account for these indirect impacts in the decision process as to what levels of controls are actually environmentally beneficial.

Another consideration regarding full costing of controls was made by two commenters (IV-G-2, IV-G-7) who requested that the EPA give greater consideration to secondary air impacts due to the application of the suggested control technologies. One commenter (IV-G-2) noted that by the EPA's own admission, the recommended 98 percent control requirements generate additional oxides of nitrogen (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO) and particulate matter (PM). The commenter suggested that by reducing the required level of control efficiency, secondary air impacts will be reduced. One commenter (IV-G-7) argued that a significant issue with thermal incineration is the production of NO_x and CO as secondary pollutants when large amounts of fuel are combusted to sustain the high temperatures needed to operate these units. The commenter further cited several disadvantages of thermal incineration including:

- High operating temperatures usually mean additional fuel requirements and associated higher fuel costs;

- High generating temperatures require the use of special, more costly heat resistant materials;

- Longer residence times (greater than 1.5 seconds) than those cited in the draft CTG mean larger, heavier reactors, which generally must be installed at ground level rather than roof mounted, resulting in additional expenses.

The commenter recommended that these should be viewed as disadvantages for this control technology, and that Sections 3.1.2.1 and 3.1.2.2 of the CTG be expanded to include those disadvantages.

Response: With respect to "upstream" effects, it is beyond the scope of this CTG to include in the costing equation those indirect emission impacts listed by the commenter. However, the EPA generally includes secondary air impacts due to the application of the suggested control technologies in the analysis of RACT. These secondary air impacts are explained in the environmental impacts discussion in Section 4.1.2 of the draft CTG document rather than in the process description discussion. Local agencies should consider the NO_x and CO emissions associated with control devices and may allow lower levels of VOC control to mitigate secondary impacts if appropriate.

The disadvantages concerning thermal incineration cited in the comment are realized by the EPA; however, recommendations for control technologies assume average stream characteristics therefore, while thermal incineration may not be appropriate for some lines, it would be a cost effective means of control for others. The EPA need not consider the "worst case" in developing the CTG.

F.5.5 Comment: One commenter (IV-G-4) recommended that the costs of performance tests, monitoring, recordkeeping, and reporting also be included in the CTG cost analysis.

One commenter (IV-G-3) argued that as the level of control and monitoring continues to increase and as the regulatory guidelines for "Enhanced Monitoring" evolve, the costs associated with the required monitoring of new incineration devices are continuing to increase. The commenter recommended that the present instrumentation cost factor of 0.10A (e.g., instrument cost = 0.10 * [incinerator + auxiliary costs]) should be reevaluated in light of the increasing costs associated with regulatory monitoring requirements.

Response: The EPA's OCCM was used to determine the cost of combustion technologies for control of VOC emissions. The capital costs are presented in Table 5.2. As indicated in Table 5.2, performance test

costs are included in the indirect cost of the control. Also in Table 5.2, listed under the purchased equipment cost, is the instrumentation cost required for the control device. This instrumentation would be used for monitoring the control device. For example, temperature instrumentation can be used to monitor the control efficiency of the control device.

The "Enhanced Monitoring" rule requirements are under development, and that package will address the potential cost of the requirements of that regulation, including additional costs placed on sources that are already subject to some type of monitoring. The recordkeeping and reporting requirements will vary among the States and, therefore, are not included here.

F.5.6 Comment: One commenter (IV-G-4) thought that the annual operating cost for an incinerator seems to be reasonably accurate but on the low side.

Response: The EPA intends to investigate any documented numbers the public may have, and invites this commenter to submit any documented numbers to the EPA. Again, the annual operating costs were calculated from the EPA's OCCM (see the response to comment F.5.2).

F.6 MONITORING AND TESTING

F.6.1 Comment: Two commenters (IV-D-4, IV-D-6) stated that the requirements for scrubbing liquid temperature and specific gravity may not be pertinent compliance information for some scrubbers, such as a once-through water scrubber. They added that instrumentation should be required only if it provides information essential to emission compliance.

Response: The CTG document has been revised to address the issue of absorbers used as recovery devices versus absorbers used as scrubbers to scrub halogens from a vent stream following an incinerator. The EPA assumes that if an absorber is used in a recovery system, then the absorber recycles (or has the potential to recycle) a portion of its effluent and is not a once-though scrubber. Furthermore, the EPA assumes that the latter use of absorbers, that is, to scrub halogens from an incinerator's effluent, is the absorber the commenter refers to as a once-through scrubber. As such, there are two sets of monitoring and testing requirements in the model rule (Appendix D of the CTG) for the two absorber types just described. For absorbers used in recovery systems, a scrubbing liquid temperature monitor and a specific gravity monitor are required,

both with continuous recordkeeping. For absorbers used after an incinerator (a once-through scrubber), a pH monitoring device and flow meter to measure scrubber liquid influent and inlet gas flow rates are required, both with continuous recordkeeping.

F.6.2 Comment: One commenter (IV-D-6) suggested that as an alternative to monitoring low flow rate vents, engineering calculations, and/or mass balances information should be allowed to demonstrate an exemption from control requirements.

Response: In order to be consistent with the draft HON, the EPA has revised the section of the model rule [Section D.5(h)] addressing this issue. Engineering assessment is recommended in the model rule as an option to calculate process vent stream flow parameters for those streams with a TRE index of 4.0 or greater.

F.6.3 Comment

Two commenters (IV-D-4, IV-D-6) said that Section D-5 of the CTG document, "Performance Testing," should not be more restrictive than what was proposed in the Enhanced Monitoring Guidelines for existing sources. One commenter (IV-D-6) also suggested that an applicability paragraph be added that excludes small sources.

Response: The draft Enhanced Monitoring Guidelines for existing sources has not been proposed, making it difficult to comment on stringency comparison between its requirements and those within this CTG. With respect to the applicability paragraph, it was difficult to interpret if commenter IV-D-6 was requesting an applicability cutoff for performance testing or general facility applicability. However, it should be noted that facilities with a very low capacity (less than 1 gigagram of chemicals per year) were exempt from recommended RACT requirements. Additionally, the CTG has been revised to recommend exempting certain individual streams with low flow rates from TRE testing.

F.6.4 Comment: Two commenters (IV-D-3, IV-G-4) argued that requiring flow indicators on individual streams prior to a control device is an excessive cost that is not necessary in determining when a flow is diverted.

One commenter (IV-D-3) recommended that the current reference to flow indicators in D.6(a)(2), (b)(2), and (c)(1) be eliminated and replaced with language similar to the following:

(i) Install a flow indicator at the entrance to any bypass line that could divert the vent stream away from the control device to the atmosphere; or

(ii) Secure the bypass line valve in the closed position with car-seal, locked, or otherwise secured arrangement. A visual inspection of the secured arrangement shall be performed once a month to ensure that the valve is maintained in the closed position and that the vent stream is not diverted through the bypass line.

Response: The EPA considers it very important to ensure that vent streams are continuously vented to the flare (or other combustion device). The primary intent of the flow monitoring recommendation in this CTG was to provide a means for indicating when vent streams are bypassing the flare or other combustion device. The flow indicators envisioned by the EPA were intended to provide an indication of flow or no flow, and not to provide quantitative estimates of flow rates.

The EPA has reevaluated the use of flow indicators in process vent streams in light of the comments received for the SOCMI Reactor Process NSPS as proposed. Because flow indicators located on the vent stream between the emission source and the combustion device may be insufficient to meet the intent of the CTG, the EPA has decided to alter the flow indicator location. The CTG will be revised to indicate that the new flow indicator location will be at the entrance to any bypass line that could divert the vent stream before it reaches the combustion device. This location would indicate those periods of times when uncontrolled emissions are being diverted to the atmosphere. In those instances when the vent stream is rerouted to another combustion device, a performance test would need to be conducted on the second combustion to determine if it meets the control requirements.

In some situations, there may be no bypass lines that could divert the vent stream to the atmosphere. In these cases, there will be no flow indicator recommendation. Language similar to the commenter's suggested paragraph (ii) have been added to the CTG document. In addition, records that show an emission stream is hardpiped to a combustion source are

F-18

sufficient to demonstrate that the entire flow will be vented to the combustion device. Other piping arrangements can be used, but flow indicators located in any bypass line that could divert a portion of the flow to the atmosphere, either directly or indirectly, become necessary. If the piping arrangement for the process changes, then it is recommended that the facility revise and retain the information.

The CTG was revised to suggest a flow indicator be equipped to indicate and record whether or not flow exists at least once every 15 minutes. Because the monitor collects flow or no flow data on a continuous basis, this additional recording would not be an additional burden. If an owner or operator believes that an alternate recording frequency or placement of a flow indicator is equally appropriate, then the owner or operator can petition the State regulating agency.

F.6.5 Comment: One commenter (IV-D-1) said that the requirement that temperature monitors be equipped "with strip charts" is too narrowly drawn. The commenter pointed out that many instrument systems in the modern chemical plant are computer driven and the recordkeeping is not via the "old" strip chart method. The commenter suggested that the EPA require continuous temperature monitoring, without a reference to the recordkeeping mode selected by the source.

Response: The temperature monitoring recording requirements have been revised, omitting any specific reference to a strip chart.

F.6.6 Comment: One commenter (IV-D-1) noted that on page D-9 of the draft CTG, subparagraphs (a)(2), (b)(2) and (c)(1), require the installation of a "flow indicator" on the vent stream to the control device. The commenter emphasized that difficulties were encountered when attempting to comply with similar requirements promulgated in the NSPS for air oxidation unit processes and distillation operations. Specifically, the vent streams from the affected distillation systems were hardpiped to a common flare header with no means to automatically divert the vent stream to the atmosphere. Each system had a nitrogen purge on its vent stream to the flare header to control plugging caused by the polymerization of organics. The continuous nitrogen purge precludes accurate measurement of vent stream flow to the flare. The commenter suggested the problem may be widespread, noting that a number of organic compounds will polymerize under the right set of conditions. In addition to causing line pluggage, the commenter added that

F-19

polymerization can also plug flow measuring devices, negating any opportunity to select appropriate instrumentation. The commenter then recommended adding a provision to this CTG that allows an appropriate compliance alternative method for flow indication, with a reference to the means by which a source could seek approval.

Response: The paragraphs cited in the comment contain a discussion about the need to monitor the flow of streams before they are joined with similar streams to a common control device. As a result of public comments from this CTG and the distillation operations NSPS, these paragraphs have been deleted from the final CTG document for two reasons: (1) the EPA is no longer requiring that similar vent streams be combined due to technical and safety concerns that may exist at some facilities (see response to Comment F.3.5), and (2) the EPA has revised the purpose of flow indicators so that they now continuously monitor the presence, not the extent, of vent stream flow. Please refer to the response to comment number F.6.4 to determine how the flow indicator section is being revised in the CTG. The owner or operator can petition the State agency if it is felt that an alternate method for flow indication should be conducted.

F.6.7 Comment: One commenter (IV-D-1) cited a significant recordkeeping burden in complying with requirements promulgated in the NSPS for air oxidation processes and the NSPS for distillation operations, and that the CTG contains the same recordkeeping requirements. The commenter then recommended that the source be allowed to select an annual performance test as an alternative means of compliance.

Response: Conducting an annual performance test in lieu of the required reporting requirements is not an appropriate alternative to monitoring a process parameter. An annual performance test would not indicate compliance through the year. The reporting and recordkeeping requirements provide a means of documenting monitoring compliance on a continuous basis and allow the source to demonstrate its continuous ability to meet the standard.

F.6.8 Comment: One commenter (IV-D-3) noted that the reporting requirements for the control and recovery devices in Section D.7(b) of the CTG document require exceedance reports when temperatures or flows deviate by more than a set level. The commenter further noted that current interpretations of reporting requirements have identified situations where

"deviations" require reporting, even when the regulated vent stream has been shut down for maintenance and a vent is not actually flowing to the control or recovery device. The commenter requested that language be added to ensure that this reporting is required only during those periods when a vent stream is actually flowing to the control or recovery device.

Response: The exceedance reporting requirement section of the CTG is being revised. The final document will incorporate the language for these requirements from the draft Enhanced Monitoring Guideline.

F.7 CONTROL TECHNOLOGY

F.7.1 Comment: Several commenters (IV-D-5, IV-D-6, IV-G-6, IV-G-7, IV-G-8) argued that RACT should not be limited to combustion control devices. One commenter (IV-G-8) suggested that rather than choosing combustion devices or the most widely applicable control technique and critically analyzing the limitations of alternative methods, the CTG should point out applications or guidelines that indicate when use of each technique is appropriate. The commenter was also disappointed that the EPA had chosen to emphasize control devices that destroy rather than recover solvents, noting that this decision seemed to be a counterproductive solution to pollution prevention.

Three commenters (IV-D-5, IV-G-6, IV-G-7) recommended that catalytic oxidation be recognized as an acceptable control alternative. By excluding catalytic oxidation in the CTG, one commenter (IV-D-5) expressed concern that the EPA is unnecessarily limiting its use since the lengthy approval process required for alternative controls effectively precludes their use within the defined compliance time limit.

Two commenters (IV-G-6, IV-G-7) provided data to support the conclusions that modern catalytic oxidation systems perform well in almost all circumstances, require minimum maintenance, minimize the formation of secondary air pollutants, and commonly achieve values as high as 99.0 percent destruction for years without interruption. The commenters requested that the CTG reflect this information when it is issued in its final form.

One commenter (IV-G-7) cited personal experience that has shown that catalytic oxidizers operate very successfully on SOCMI exhaust streams and

recommended that the EPA delete the present statement in Section 3.1.4.3 and replace it with the following new language:

> Catalytic oxidation is very effective in controlling VOC emissions; it is an extremely flexible technology that can be applied to a variety of SOCMI processes. It is basically a chemical process which operates at much lower temperature than thermal incineration and thereby minimizes fuel and other costs. In addition, catalytic oxidation does not produce secondary air emissions such as NO_x and CO as occurs with thermal incineration. High destruction efficiency (>98 percent) is achieved through catalytic oxidation. Catalytic streams are successfully operating on SOCMI vent streams. The SOCMI exhausts are generally very clean and are therefore suitable for catalytic systems. The SOCMI industry has been accustomed to using a variety of process catalysts and are very skilled in understanding and maintaining catalytic systems at maximum performance. Sulfur resistant and halocarbon resistant catalysts are available when needed.

One commenter (IV-D-6) stated that recovery devices and other upstream process changes should be allowed to demonstrate RACT control. Furthermore, to enable the use of these alternative pollution prevention techniques, a suitable before control emission point must be defined. The commenter recommended the following definition for before control emissions:

> Emissions after the first reflux/product recovery condenser, or actual hourly average emission rate, after all control for the years 1987 to present, whichever is greater.

Response: It is not the intent of this CTG to limit the owner or operator to only one VOC control technology, many technologies are presented in the CTG. For the purpose of calculating national impacts, however, combustion via thermal incineration or flaring was chosen as the control technology. This decision was based on the wide applicability and ability of combustion devices to achieve 98 percent destruction efficiency for SOCMI reactor and distillation vents. Additionally, even though pollution prevention in the form of product or solvent recovery may be more economical, these control techniques require modifications within the process and are site specific, making it difficult to generalize these modifications across the entire industry. Appropriate applications for each control technology are given in Chapter 3.0 of the CTG. Catalytic

incinerators are, in fact, recognized as acceptable alternative controls as discussed in the CTG document.

The EPA appreciates the comment regarding Section 3.1.4.3 of the document and has revised that section to incorporate some of the language suggested.

F.7.2 Comment: One commenter (IV-D-3) said that the monitoring requirements for carbon adsorbers should be modified to accommodate the various types of regeneration systems currently in use. The commenter recommended the following:

- All references to the use of "steam" for carbon adsorbers be replaced with the term "regeneration stream." Changing to this recommended language allows the owner or operator to use either steam, a regeneration gas, heated nitrogen, or similar technologies in the absorber system without requiring specific waivers in a case-by-case basis.

- The recordkeeping and reporting requirements associated with carbon absorber units refer only to "mass" flow measurements. Rather than specifically referring to mass, we recommend that either a mass or volumetric flow rate is appropriate.

Response: The EPA realizes that steam is not the sole method of carbon adsorber regeneration. The CTG document has been revised to reflect the commenters recommendations to modify the monitoring requirements for carbon adsorbers.

F.7.3 Comment: One commenter (IV-G-5) expressed concern that two proposed controlled techniques may pose worker safety or health hazards. Specifically, the commenter named the combustion of VOC's in flares with high velocity steam injection nozzles, and combustion of VOC's in boilers or process heaters as potentially hazardous. The commenter noted that the safety concern of high velocity steam injection nozzles is the increased noise. Also, the variation in the flow rate and organic content of the vent stream could lead to explosive mixtures with a boiler furnace.

Response: The proposed control techniques discussed in the CTG document must be installed in compliance with Occupational Safety and Health Administration (OSHA) requirements. Specifically, the flares must be installed at such a height and location to minimize noise.

The venting of streams to boiler furnaces is listed as an alternative control technology because it is not appropriate for all vent streams for the exact reasons the commenter listed. As stated in the CTG, "variations

F-23

in vent stream flow rate and/or heating value could affect the heat output or flame stability...and should be considered when using these combustion devices."

F.7.4 <u>Comment</u>: One commenter (IV-G-8) recommended that the discussion in the CTG regarding condensation as an emission control technique needs clarification.

Regarding Section 3.2.3.1, the commenter noted that chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons can be used in single stage or cascade cycles to reach condensation temperatures below -73 °C (-100 °F), and liquid chillers using d-limonene are capable of reaching temperatures below -62 °C (-80 °F).

With reference to Section 3.2.3.2, the commenter stated that condenser efficiencies are frequently in excess of 95 percent, with recovery by condensation working particularly well for low flow rates (less than 2,000 cubic feet per minute [cfm]) and high VOC concentration (greater than 5,000 ppmv). The commenter said that it is below the 5,000 ppmv concentration level that the recovery efficiency of condensation drops below 95 percent, and, furthermore, since condensation is not recommended for use in applications involving concentration levels below 5,000 ppmv, it does not make sense for the CTG to state that "efficiencies of condensers usually vary from 50 to 95 percent."

Regarding Section 3.2.3.3, the commenter requested that the CTG document state that condensation is applicable in many cases where other control methods are not, including when lower explosion limits are too high, when flow rates are too low; and when recovery rather than destruction is required.

<u>Response</u>: The ranges listed in the CTG document (e.g., "below -34 °C") include the specific examples cited by the commenter.

In Section 3.2.3.2 of the draft CTG, it is stated that the condenser efficiency ranges depend on the flow parameters of the vent stream and the operating parameters of the condenser. A statement has been added to the CTG explaining that the higher efficiencies are expected for the low flow (less than 2,000 cubic feet per minute [cfm]), high VOC concentration (greater than 5,000 ppmv) streams. Finally, the CTG document has been revised to state those cases where condensation is applicable and other control methods are not.

F.8 EDITORIAL

F.8.1 <u>Comment</u>: Two commenters (IV-D-6) recommended that the introduction state clearly what sources are included and excluded by this CTG, preferably in the opening paragraph.

<u>Response</u>: Chapter 1.0 of the CTG document has been revised to incorporate a discussion of the applicable chemicals.

F.8.2 <u>Comment</u>. Four commenters (IV-D-3, IV-D-5, IV-D-6, IV-G-2) observed that the flow rate cutoffs do not appear to be consistent, and requested additional clarification. The commenters noted that the flow rate cutoff in D.2(b)(3) is 0.011 scm/min (0.4 scfm), but the RACT summary on page 6-7 refers to the presumptive norm for RACT by requiring controls on streams with a flow rate greater than 0.1 scfm.

<u>Response</u>: The units listed in D.2(b)(3) contained a typographical error in the draft CTG document; however, this comment is no longer of concern because the low flow cutoff for individual streams will be calculated by determining the flow rate which identifies those streams with a TRE index less than or equal to 1.0 when the stream characteristics from the data base are inserted into the TRE equation. Furthermore, the comparison of this number with the flow and concentration cutoff is no longer of concern because the latter is being replaced with the TRE index equation to determine applicability.

F.8.3 <u>Comment</u>: Several commenters (IV-D-3, IV-D-5, IV-D-6, IV-G-2) said that in Section D.6 of the CTG, paragraph (a)(1), the temperature monitoring requirements for incineration appear to be incomplete and additional language (e.g., ± 1 percent of temperature) is necessary.

<u>Response</u>: The CTG document has been revised to reflect this comment.

F.8.4 <u>Comment</u>: Two commenters (IV-D-4, IV-D-6) argued that the definition of "total organic compounds" should be changed to exclude all compounds accepted by the EPA as photochemically nonreactive.

<u>Response</u>: The EPA agrees with this comment. The current, updated list of compounds considered photochemically nonreactive by the Administrator has been incorporated into the document (see page D-5).

F.8.5 <u>Comment</u>: One commenter (IV-D-3) requested that the use of the term "recovery device" be clarified. The commenter noted that the current recovery device definition states that the equipment is capable of <u>and used</u> <u>for</u> the purpose of recovering chemicals for use, reuse, or sale. The

commenter emphasized that situations exist where the recovered material from an absorber or condenser does not technically meet the recovery device definition and it would not be subject to the monitoring and reporting standards of the rule. In addition, the commenter stated that if the concentration at the outlet vent of the condenser falls below the concentration and flow cutoff, and if it is the only vent for the process, then only minimum recordkeeping applies. The commenter asserted that this type of "recovery device" also meets the intent of the rule and that many compliance interpretation issues could be eliminated by revising the definition. The definition recommended by the commenter is "...an individual unit of equipment, used for the purposes of recovering chemicals for use, reuse, sale, or treatment."

Response: The EPA appreciates this comment and the CTG document has been revised to reflect this comment.

F.8.6 Comment: One commenter (IV-D-3) pointed out that the text that identifies the examples in Figures 2-6 and 2-7 does not currently match the diagrams.

Response: Figures 2-6 and 2-7 represent specific examples of a direct reactor process vent and a recovery vent applied to the vent stream from a liquid phase reactor, respectively. More specifically, Figure 2-6 presents a schematic of nitrobenzene production venting to the atmosphere, whereas Figure 2-7 depicts an alkylation unit process used to produce ethylbenzene. The EPA believes the figures do correspond to the text. The EPA invites the commenter to call the EPA for further clarification if this is still unclear.

F.8.7 Comment: Two commenters (IV-D-5, IV-G-2) suggested that the Chemical Abstracts Service (CAS) number of the individual chemicals listed in Appendix A should be provided.

Response: The EPA agrees with this comment and the CTG document has been revised to reflect this comment.

F.8.8 Comment: One commenter (IV-D-6) noted that in the K_s definition in the middle of page D-6, K_s should be K_2.

Response: The EPA agrees with this comment and the document has been revised to reflect this comment.

F.8.9 Comment: One commenter (IV-D-1) recommended that the definition of "product" would be clearer if the EPA would define it as "any compound or

chemical listed in Appendix A which is produced as that chemical for sale as a final product, by-product, co-product, or intermediate or for use in the production of other chemicals or compounds."

Response: The EPA agrees with this comment and the CTG document has been revised to reflect this comment.

F.8.10 Comment: One commenter (IV-D-1) said that the definition of "affected facility" would be easier to follow if it were changed as follows: "an affected facility is an individual reactor process or distillation operation with its own individual recovery system (if any) or the combination of two or more reactor processes or distillation operations and the common recovery system they share." The commenter noted that reactor processes and distillation columns are not single pieces of equipment, but embrace several other components which are considered part of the system. The commenter suggested that rewording this definition would help make this distinction more apparent to the reader.

Response: The EPA agrees with this comment and the CTG document has been revised to reflect this comment.

F.8.11 Comment: One commenter (IV-D-1) noted that the CTG states that of the three possible emission limitation formats, the regulatory agency should consider applying the "percent reduction format" since the EPA believes it "best represents performance capabilities of the control devices used to comply with the RACT regulation." The commenter suggested that there are other opportunities which would present themselves for using one of the other two formats. The commenter then recommended that the wording at the top of page 7-4 be changed in the second line by eliminating "...are not preferred because they...." The commenter noted that this does not change the general intent of the statements contained on the page, but does remove a direct inference that the other two formats should not be used.

Response: This comment is no longer applicable because the applicability format has been revised to incorporate the TRE index equation. The CTG now recommends reduction of VOC emissions until the TRE index is greater than one.

F.8.12 Comment: One commenter (IV-G-2) requested that any deviation from the list of chemicals established in the corresponding NSPS for reactor processes and distillation operations be explained in the CTG.

Response: The list of applicable chemicals for this CTG correspond to all appropriate chemicals addressed by previous NSPS plus chemicals in the SOCMI source category. Any deviations in the list of chemicals in this CTG from the list presented in previous NSPS result from the inclusion of SOCMI chemicals.

F.8.13 Comment: One commenter (IV-G-7) recommended the following language changes in Section 3.1.4.1:

- Paragraph 1, sentence 5, change to read: "Combustion catalysts include palladium and platinum group metals, manganese oxide, copper oxide, chromium and cobalt."

- Paragraph 3, sentence 1, charge to read: "The operating temperatures of combustion catalysts usually range from 500 °F to 800 °F."

- Paragraph 3, sentence 3, change to read: "Temperatures greater than 1,350 °F may result in shortened catalyst life." Delete the rest of the original sentence because it is not true that the catalyst or substrate will evaporate or melt at higher temperatures (>1,200 °F). In order for a metal substrate to melt the temperature must exceed 2,600 °F."

- Paragraph 3, add the following after the last sentence: "Materials accumulated on the catalyst can be removed by physical or chemical means, thus restoring the catalyst activity to its original (fresh) level. Condensed organics accumulated on the catalyst can be removed with thermal treatment.

The commenter also stated that not all of the poisons listed in paragraph 3 of Section 3.1.4.1 are detrimental to VOC catalysts. The commenter suggested that masking of the catalyst by particulate or carbon-based materials is reversible, and catalysts are commercially available to handle many of the poisons listed, including sulfur, halocarbons, and phosphorous.

Response: The EPA agrees with all these comments and will revise the CTG document to reflect them.

F.8.14 Comment: One commenter (IV-G-7) said that the example cited in Section 3.1.4.2 is an oversimplification and is not VOC species specific. The commenter stated that at 840 °F and a space velocity of 30,000/seconds (the example shown), many VOC's can be reduced by 99 percent or more with catalytic oxidation technology.

<u>Response</u>: The EPA believes that the commenter cited an example that verifies the referenced numbers in the document. The CTG document stated that "catalytic oxidizers have been reported to achieve efficiencies of 98 percent or greater," and the 99 percent reduction reported by the commenter does fall within the 98 percent or greater range.

F.8.15 <u>Comment</u>. One commenter (IV-G-7) recommended that sentence 2 of paragraph 2 in Section 3.3 be deleted. The commenter stated that there are not technical obstacles preventing catalytic oxidation from achieving at least 98 percent destruction efficiency, and that this level of control is becoming the rule rather than the exception.

<u>Response</u>: The sentence the commenter is referring to states that, with the exception of catalytic oxidizers, the other combustion devices listed are applicable to a wide range of vent streams. The EPA agrees with this comment and has revised the CTG document to reflect this comment.

F.8.16 <u>Comment</u>: One commenter (IV-G-7) requested that several statements in Section 6.2 of the draft CTG be modified to present a more neutral treatment of catalytic oxidation and to ensure that this technology is not excluded from consideration as an available control technology.

<u>Response</u>: The EPA has revised the CTG document to reflect this request.