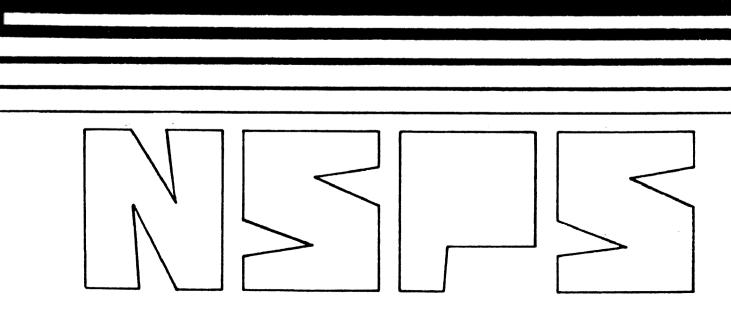
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VOC Emissions
From Petroleum
Refinery
Wastewater
Systems—
Background
Information for
Proposed Standards

Preliminary Draft

Draft EIS



NOTICE

This document has not been formally released by EPA and should not now be construed to represent agency policy. It is being circulated for comment on its technical accuracy and policy implications.

VOC Emissions from Petroleum Refinery Wastewater Systems— Background Information for Proposed Standards

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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SUMMARY

Standards of performance for new stationary sources are established under Section 111 of the Clean Air Act (42 U.S.C. 7411), as amended in 1977. Section 111 directs the Administrator to establish standards of performance for any category of new stationary source of air pollution which "causes or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare."

1.1 REGULATORY ALTERNATIVES

The analysis of environmental, economic, and energy impacts were based on consideration of three regulatory alternatives for each emission source. The regulatory alternatives are given below:

Process Drain Systems:

Regulatory Alternative I: No additional control.

Regulatory Alternative II: Require water seals on process drains and

junction boxes.

Regulatory Alternative III: Require completely closed drain systems

with vapors vented to a control device.

Oil-Water Separators:

Regulatory Alternative I: No additional control.

Regulatory Alternative II: Require gasketed and sealed fixed or

floating roofs.

Regulatory Alternative III: Require gasketed and sealed fixed roof with

vapors vented to a control device.

Air Flotation Systems:

Regulatory Alternative I. No additional control.

Regulatory Alternative II. Require gasketed and sealed fixed roofs and

access doors.

Regulatory Alternative III. Require gasketed and sealed fixed roofs and

access doors with vapors vented to a

control device.

Regulatory Alternative I requires no action. Under this alternative, emissions would be controlled to levels established by existing State regulations. Of the sources included in this NSPS, only oil-water separators are regulated by existing regulations.

Requiring water seals on process drains and junction boxes will result in emission reductions of 50 percent or more when compared to Regulatory Alternative I. A fixed or floating roof on an oil-water separator will result in emission reduction of 85 percent. A fixed roof on a dissolved air flotation system will result in emission reductions of 77 percent. Gasketing and sealing an induced air flotation system will result in a 23 percent reduction. Again, these emission reductions are those achieved in comparison to Regulatory Alternative I.

The more stringent requirements of Regulatory Alternative III result in a 98 percent reduction in emissions from process drain systems. A fixed roof on an oil-water separator or dissolved air flotation system with captured VOC vented to a control device will result in emission reductions of 94 to 97 percent, depending on the efficiency of the control device. Gasketing and sealing an IAF system and venting the captured VOC to a control device will result in emission reductions of 70 to 85 percent, again depending on the efficiency of the control device. All emission reductions are those achieved in comparison to Regulatory Alternative I.

1.2 ENVIRONMENTAL IMPACT

Implementation of either Alternative II or Alternative III for all three emission sources will result in a beneficial impact on air quality. Implementation of Alternative II will reduce VOC emissions by approximately 1630 Mg/yr in 1989. This represents a 50 percent reduction below Regulatory Alternative I. Implementation of Alternative III will reduce VOC emissions by approximately 3055 Mg/yr in 1989. This represents a 95% percent reduction below Alternative I. It should be noted that the regulatory alternatives can be independently applied to each of the three emission sources. Therefore, depending upon the specific regulatory alternative

picked for each source, the actual emission reduction achieved by the NSPS can range from 1630 Mg/yr to 3055 Mg/yr. These reductions in VOC emissions can be accomplished without causing any adverse environmental impacts.

No water pollution impact will result from implementation of any of the regulatory alternatives. Small quantities of water will be required if regenerative carbon adsorbers are used to control VOC vented from oil-water separators and air flotation systems. However, the quantity of water needed will be insignificant.

Solid waste will be generated by carbon adsorption systems if they are used for VOC control. Again, the amount of solid waste generated will be minimal. Energy impacts will result only by implementing Regulatory Alternative III. These impacts are also expected to be minimal.

Table 1-1 summarizes the environmental and energy impacts of the regulatory alternatives. A more detailed analysis of these impacts is presented in Chapter 7.

1.3 ECONOMIC IMPACT

The preliminary economic analysis indicates that the fifth-year annualized costs of the most stringent regulatory alternatives for each emission source are \$6.3 million dollars. This is well below the \$100 million level that Executive Order 12291 identifies as the threshold for major regulatory actions. Additionally, the price increase and output reduction due to the most costly alternatives are 0.1 percent and 0.03 percent, respectively.

TABLE 1-1. ASSESSMENT OF ENVIRONMENTAL, ENERGY, AND ECONOMIC IMPACTS FOR EACH REGULATORY ALTERNATIVE CONSIDERED FOR PETROLEUM REFINERY WASTEWATER SYSTEMS

Administrative alternative	Air impact	Water impact	Solid waste impact	Energy impact	Economic impact
Regulatory Alternative I	0	0	0	0	0
Regulatory Alternative II	+2	0	0	0	0
Regulatory Alternative III	+3	0	0	0	-1

aKEY: + Beneficial impact - Adverse impact 0 No impact 1 Negligible impact

² Small impact3 Moderate impact4 Large impact5 Very large impact

2. INTRODUCTION

2.1 BACKGROUND AND AUTHORITY FOR STANDARDS

Before standards of performance are proposed as a Federal regulation, air pollution control methods available to the affected industry and the associated costs of installing and maintaining the control equipment are examined in detail. Various levels of control based on different technologies and degrees of efficiency are examined. Each potential level of control is studied by EPA as a prospective basis for a standard. The alternatives are investigated in terms of their impacts on the economics and well-being of the industry, the impacts on the national economy, and the impacts on the environment. This document summarizes the information obtained through these studies so that interested persons will be able to see the information considered by EPA in the development of the proposed standard.

Standards of performance for new stationary sources are established under Section 111 of the Clean Air Act (42 U.S.C. 7411) as amended, hereinafter referred to as the Act. Section 111 directs the Administrator to establish standards of performance for any category of new stationary source of air pollution which ". . . causes, or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare."

The Act requires that standards of performance for stationary sources reflect "... the degree of emission reduction achievable which (taking into consideration the cost of achieving such emission reduction, and any nonair quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated for that category of sources." The standards apply only to stationary sources, the construction or modification of which commences after regulations are proposed by publication in the Federal Register.

The 1977 amendments to the Act altered or added numerous provisions that apply to the process of establishing standards of performance.

- 1. EPA is required to list the categories of major stationary sources that have not already been listed and regulated under standards of performance. Regulations must be promulgated for these new categories on the following schedule:
 - a. 25 percent of the listed categories by August 7, 1980.
 - b. 75 percent of the listed categories by August 7, 1981.
- c. 100 percent of the listed categories by August 7, 1982. A governor of a State may apply to the Administrator to add a category not on the list or may apply to the Administrator to have a standard of performance revised.
- 2. EPA is required to review the standards of performance every four years and, if appropriate, revise them.
- 3. EPA is authorized to promulgate a standard based on design, equipment, work practice, or operational procedures when a standard based on emission levels is not feasible.
- 4. The term "standards of performance" is redefined, and a new term "technological system of continuous emission reduction" is defined. The new definitions clarify that the control system must be continuous and may include a low- or non-polluting process or operation.
- 5. The time between the proposal and promulgation of a standard under Section 111 of the Act may be extended to six months.

Standards of performance, by themselves, do not guarantee protection of health or welfare because they are not designed to achieve any specific air quality levels. Rather, they are designed to reflect the degree of emission limitation achievable through application of the best adequately demonstrated technological system of continuous emission reduction, taking into consideration the cost of achieving such emission reduction, any non-air-quality health and environmental impacts, and energy requirements.

Congress had several reasons for including these requirements. First, standards with a degree of uniformity are needed to avoid situations where some States may attract industries by relaxing standards relative to other

States. Second, stringent standards enhance the potential for long-term growth. Third, stringent standards may help achieve long-term cost savings by avoiding the need for more expensive retrofitting when pollution ceilings may be reduced in the future. Fourth, certain types of standards for coalburning sources can adversely affect the coal market by driving up the price of low-sulfur coal or effectively excluding certain coals from the reserve base because their untreated pollution potentials are high. Congress does not intend that new source performance standards contribute to these problems. Fifth, the standard-setting process should create incentives for improved technology.

Promulgation of standards of performance does not prevent State or local agencies from adopting more stringent emission limitations for the same sources. States are free under Section 116 of the Act to establish even more stringent emission limits than those established under Section 111 or those necessary to attain or maintain the National Ambient Air Quality Standards (NAAQS) under Section 110. Thus, new sources may in some cases be subject to limitations more stringent than standards of performance under Section 111, and prospective owners and operators of new sources should be aware of this possibility in planning for such facilities.

A similar situation may arise when a major emitting facility is to be constructed in a geographic area that falls under the prevention of significant deterioration of air quality provisions of Part C of the Act. These provisions require, among other things, that major emitting facilities to be constructed in such areas are to be subject to best available control technology. The term Best Available Control Technology (BACT), as defined in the Act, means

. . . an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from, or which results from, any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such facility through application of production processes and available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of each such

pollutant. In no event shall application of "best available control technology" result in emissions of any pollutants which will exceed the emissions allowed by any applicable standard established pursuant to Section 111 or 112 of this Act. (Section 169(3))

Although standards of performance are normally structured in terms of numerical emission limits where feasible, alternative approaches are sometimes necessary. In some cases physical measurement of emissions from a new source may be impractical or exorbitantly expensive. Section 111(h) provides that the Administrator may promulgate a design or equipment standard in those cases where it is not feasible to prescribe or enforce a standard of performance. For example, emissions of hydrocarbons from storage vessels for petroleum liquids are greatest during tank filling. The nature of the emissions, high concentrations for short periods during filling and low concentrations for longer periods during storage, and the configuration of storage tanks make direct emission measurement impractical. Therefore, a more practical approach to standards of performance for storage vessels has been equipment specification.

In addition, Section 111(i) authorizes the Administrator to grant waivers of compliance to permit a source to use innovative continuous emission control technology. In order to grant the waiver, the Administrator must find: (1) a substantial likelihood that the technology will produce greater emission reductions than the standards require or an equivalent reduction at lower economic, energy, or environmental cost; (2) the proposed system has not been adequately demonstrated; (3) the technology will not cause or contribute to an unreasonable risk to the public health, welfare, or safety; (4) the governor of the State where the source is located consents; and (5) the waiver will not prevent the attainment or maintenance of any ambient standard. A waiver may have conditions attached to assure the source will not prevent attainment of any NAAQS. Any such condition will have the force of a performance standard. Finally, waivers have definite end dates and may be terminated earlier if the conditions are not met or if the system fails to perform as expected. In such a case, the source may be given up to 3 years to meet the standards with a mandatory progress schedule.

2.2 SELECTION OF CATEGORIES OF STATIONARY SOURCES

Section 111 of the Act directs the Administrator to list categories of stationary sources. The Administrator "... shall include a category of sources in such list if in his judgment it causes, or contributes significantly to, air pollution which may reasonably be anticipated to endanger public health or welfare." Proposal and promulgation of standards of performance are to follow.

Since passage of the Clean Air Amendments of 1970, considerable attention has been given to the development of a system for assigning priorities to various source categories. The approach specifies areas of interest by considering the broad strategy of the Agency for implementing the Clean Air Act. Often, these "areas" are actually pollutants emitted by stationary sources. Source categories that emit these pollutants are evaluated and ranked by a process involving such factors as (1) the level of emission control (if any) already required by State regulations, (2) estimated levels of control that might be required from standards of performance for the source category, (3) projections of growth and replacement of existing facilities for the source category, and (4) the estimated incremental amount of air pollution that could be prevented in a preselected future year by standards of performance for the source category. Sources for which new source performance standards were promulgated or under development during 1977, or earlier, were selected on these criteria.

The Act amendments of August 1977 establish specific criteria to be used in determining priorities for all major source categories not yet listed by EPA. These are (1) the quantity of air pollutant emissions that each such category will emit, or will be designed to emit; (2) the extent to which each such pollutant may reasonably be anticipated to endanger public health or welfare; and (3) the mobility and competitive nature of each such category of sources and the consequent need for nationally applicable new source standards of performance.

The Administrator is to promulgate standards for these categories according to the schedule referred to earlier.

In some cases it may not be feasible immediately to develop a standard for a source category with a high priority. This might happen when a program of research is needed to develop control techniques or because techniques for sampling and measuring emissions may require refinement. In the developing of standards, differences in the time required to complete the necessary investigation for different source categories must also be considered. For example, substantially more time may be necessary if numerous pollutants must be investigated from a single source category. Further, even late in the development process the schedule for completion of a standard may change. For example, inability to obtain emission data from well-controlled sources in time to pursue the development process in a systematic fashion may force a change in scheduling. Nevertheless, priority ranking is, and will continue to be, used to establish the order in which projects are initiated and resources assigned.

After the source category has been chosen, the types of facilities within the source category to which the standard will apply must be determined. A source category may have several facilities that cause air pollution, and emissions from some of these facilities may vary from insignificant to very expensive to control. Economic studies of the source category and of applicable control technology may show that air pollution control is better served by applying standards to the more severe pollution sources. For this reason, and because there is no adequately demonstrated system for controlling emissions from certain facilities, standards often do not apply to all facilities at a source. For the same reasons, the standards may not apply to all air pollutants emitted. Thus, although a source category may be selected to be covered by a standard of performance, not all pollutants or facilities within that source category may be covered by the standards.

2.3 PROCEDURE FOR DEVELOPMENT OF STANDARDS OF PERFORMANCE

Standards of performance must (1) realistically reflect best demonstrated control practice; (2) adequately consider the cost, the non-air-quality health and environmental impacts, and the energy requirements of such control; (3) be applicable to existing sources that are modified or

reconstructed as well as new installations; and (4) meet these conditions for all variations of operating conditions being considered anywhere in the country.

The objective of a program for developing standards is to identify the best technological system of continuous emission reduction that has been adequately demonstrated. The standard-setting process involves three principal phases of activity: (1) information gathering, (2) analysis of the information, and (3) development of the standard of performance.

During the information-gathering phase, industries are queried through a telephone survey, letters of inquiry, and plant visits by EPA representatives. Information is also gathered from many other sources, and a literature search is conducted. From the knowledge acquired about the industry, EPA selects certain plants at which emission tests are conducted to provide reliable data that characterize the pollutant emissions from well-controlled existing facilities.

In the second phase of a project, the information about the industry and the pollutants emitted is used in analytical studies. Hypothetical "model plants" are defined to provide a common basis for analysis. The model plant definitions, national pollutant emission data, and existing State regulations governing emissions from the source category are then used in establishing "regulatory alternatives." (For the refinery wastewater standard, there are a few deviations from this model plant and regulatory analysis approach, as described in Chapters 6 through 8.) These regulatory alternatives are essentially different levels of emission control.

EPA conducts studies to determine the impact of each regulatory alternative on the economics of the industry and on the national economy, on the environment, and on energy consumption. From several possibly applicable alternatives, EPA selects the single most plausible regulatory alternative as the basis for a standard of performance for the source category under study.

In the third phase of a project, the selected regulatory alternative is translated into a standard of performance, which, in turn, is written in the form of a Federal regulation. The Federal regulation, when applied to newly

constructed plants, will limit emissions to the levels indicated in the selected regulatory alternative.

As early as is practical in each standard-setting project, EPA representatives discuss the possibilities of a standard and the form it might take with members of the National Air Pollution Control Techniques Advisory Committee. Industry representatives and other interested parties also participate in these meetings.

The information acquired in the project is summarized in the Background Information Document (BID). The BID, the standard, and a preamble explaining the standard are widely circulated to the industry being considered for control, environmental groups, other government agencies, and offices within EPA. Through this extensive review process, the points of view of expert reviewers are taken into consideration as changes are made to the documentation.

A "proposal package" is assembled and sent through the offices of EPA Assistant Administrators for concurrence before the proposed standard is officially endorsed by the EPA Administrator. After being approved by the EPA Administrator, the preamble and the proposed regulation are published in the <u>Federal Register</u>.

As a part of the <u>Federal Register</u> announcement of the proposed regulation, the public is invited to participate in the standard-setting process. EPA invites written comments on the proposal and also holds a public hearing to discuss the proposed standard with interested parties. All public comments are summarized and incorporated into a second volume of the BID. All information reviewed and generated in studies in support of the standard of performance is available to the public in a "docket" on file in Washington, D.C.

Comments from the public are evaluated, and the standard of performance may be altered in response to the comments.

The significant comments and EPA's position on the issues raised are included in the "preamble" of a promulgation package, which also contains the draft of the final regulation. The regulation is then subjected to another round of review and refinement until it is approved by the EPA

Administrator. After the Administrator signs the regulation, it is published as a "final rule" in the <u>Federal Register</u>.

2.4 CONSIDERATION OF COSTS

Section 317 of the Act requires an economic impact assessment with respect to any standard of performance established under Section 111 of the Act. The assessment is required to contain an analysis of: (1) the costs of compliance with the regulation, including the extent to which the cost of compliance varies depending on the effective date of the regulation and the development of less expensive or more efficient methods of compliance;

- (2) the potential inflationary or recessionary effects of the regulation;
- (3) the effects the regulation might have on small business with respect to competition; (4) the effects of the regulation on consumer costs; and
- (5) the effects of the regulation on energy use. Section 317 also requires that the economic impact assessment be as extensive as practicable.

The economic impact of a proposed standard upon an industry is usually addressed both in absolute terms and in terms of the control costs that would be incurred as a result of compliance with typical, existing State control regulations. An incremental approach is necessary because both new and existing plants would be required to comply with State regulations in the absence of a Federal standard of performance. This approach requires a detailed analysis of the economic impact from the cost differential that would exist between a proposed standard of performance and the typical State standard.

Air pollutant emissions may cause water pollution problems, and captured potential air pollutants may pose a solid waste disposal problem. The total environmental impact of an emission source must, therefore, be analyzed and the costs determined whenever possible.

A thorough study of the profitability and price-setting mechanisms of the industry is essential to the analysis so that an accurate estimate of potential adverse economic impacts can be made for proposed standards. It is also essential to know the capital requirements for pollution control systems already placed on plants so that the additional capital requirements

necessitated by these Federal standards can be placed in proper perspective. Finally, it is necessary to assess the availability of capital to provide the additional control equipment needed to meet the standards of performance.

2.5 CONSIDERATION OF ENVIRONMENTAL IMPACTS

Section 102(2)(C) of the National Environmental Policy Act (NEPA) of 1969 requires Federal agencies to prepare detailed environmental impact statements on proposals for legislation and other major Federal actions significantly affecting the quality of the human environment. The objective of NEPA is to build into the decisionmaking process of Federal agencies a careful consideration of all environmental aspects of proposed actions.

In a number of legal challenges to standards of performance for various industries, the United States Court of Appeals for the District of Columbia Circuit has held that environmental impact statements need not be prepared by the Agency for proposed actions under Section 111 of the Clean Air Act. Essentially, the Court of Appeals has determined that the best system of emission reduction requires the Administrator to take into account counterproductive environmental effects of a proposed standard, as well as economic costs to the industry. On this basis, therefore, the Court established a narrow exemption from NEPA for EPA determination under Section 111.

In addition to these judicial determinations, the Energy Supply and Environmental Coordination Act (ESECA) of 1974 (PL-93-319) specifically exempted proposed actions under the Clean Air Act from NEPA requirements. According to Section 7(c)(1), "No action taken under the Clean Air Act shall be deemed a major Federal action significantly affecting the quality of the human environment within the meaning of the National Environmental Policy Act of 1969." (15 U.S.C. 793(c)(1)).

Nevertheless, the Agency has concluded that the preparation of environmental impact statements could have beneficial effects on certain regulatory actions. Consequently, although not legally required to do so by Section 102(2)(C) of NEPA, EPA has adopted a policy requiring that environmental impact statements be prepared for various regulatory actions,

including standards of performance developed under Section 111 of the Act. This voluntary preparation of environmental impact statements, however, in no way legally subjects the Agency to NEPA requirements.

To implement this policy, a separate section in this document is devoted solely to an analysis of the potential environmental impacts associated with the proposed standards. Both adverse and beneficial impacts in such areas as air and water pollution, increased solid waste disposal, and increased energy consumption are discussed.

2.6 IMPACT ON EXISTING SOURCES

Section 111 of the Act defines a new source as "... any stationary source, the construction or modification of which is commenced ... " after the proposed standards are published. An existing source is redefined as a new source if "modified" or "reconstructed" as defined in amendments to the general provisions of Subpart A of 40 CFR Part 60, which were promulgated in the <u>Federal Register</u> on December 16, 1975 (40 FR 58416).

Promulgation of a standard of performance requires States to establish standards of performance for existing sources in the same industry under Section 111(d) of the Act if the standard for new sources limits emissions of a designated pollutant (i.e., a pollutant for which air quality criteria have not been issued under Section 108 or which has not been listed as a hazardous pollutant under Section 112). If a State does not act, EPA must establish such standards. General provisions outlining procedures for control of existing sources under Section 111(d) were promulgated on November 17, 1975, as Subpart B of 40 CFR Part 60 (40 FR 53340).

2.7 REVISION OF STANDARDS OF PERFORMANCE

Congress was aware that the level of air pollution control achievable by any industry may improve with technological advances. Accordingly, Section 111 of the Act provides that the Administrator "...shall, at least every four years, review and, if appropriate, revise ..." the standards. Revisions are made to assure that the standards continue to reflect the best systems that become available in the future. Such revisions will not be retroactive, but will apply to stationary sources constructed or modified after the proposal of the revised standards.

3. DESCRIPTION OF PETROLEUM REFINERY WASTEWATER SYSTEMS AND VOC EMISSIONS

This chapter presents a description of petroleum refinery wastewater systems. Section 3.1 provides general information about the petroleum refining industry and also presents an overview of petroleum refinery wastewater systems. Section 3.2 describes the processes used in the wastewater system and emissions from these processes. Section 3.3 presents growth estimates for the source category while Section 3.4 presents baseline emissions from petroleum refinery wastewater treatment systems.

3.1 INTRODUCTION AND GENERAL INFORMATION

Wastewater is generated by many of the refining processes used by the petroleum refining industry. This wastewater is collected by a plant wide sewer system, which carries the flow to a treatment system. An introduction to petroleum refining processes and the related wastewater collection and treatment systems is presented in the following sections. Section 3.1.1 presents a general discussion of the petroleum refining industry, while Section 3.1.2 covers sources of wastewater from petroleum refining.

3.1.1 Petroleum Refining Industry

The petroleum refining industry is defined by Standard Industrial Classification (SIC) Code 2911 of the U.S. Department of Commerce. SIC Code 2911 includes facilities primarily engaged in producing hydrocarbon materials through the distillation of crude petroleum and its fractionation products. As of January 1, 1984, there were 220 operating refineries in the United States. They are distributed among 34 states with 44 percent of the refineries located in Texas, California, and Louisiana. This represents 18, 17, and 9 percent of the total number of refineries, respectively, in these three states. Approximately 28 percent of the total crude refining capacity

is located in Texas. California contains 15 percent of the total crude capacity while Louisiana holds 14 percent. The geographic distribution of U.S. refineries is shown in Figure 3-1.

The refining industry in the United States has experienced a reversal in growth trends as a result of the reduction in consumption of petroleum products that has occurred since 1978. U.S. crude oil runs peaked at 14.7 million barrels per day in that year. Crude oil runs have decreased each year since then reaching 12.5 million barrels per day for 1981 and 11.5 million barrels per day in early 1982. Since January 1, 1981, more than 75 refineries have discontinued operations. It is expected that refinery activity will recover somewhat and projections for 1985 and 1990 estimate crude oil runs of 14.4 million barrels per day and 13.4 million barrels per day, respectively.

Based on the above forecasts, very few, if any, new refining facilities will be built at undeveloped sites over the next 10 years. However, it will be necessary for refineries to modernize and expand downstream processes at existing refinery sites to allow increasingly heavier and higher sulfur crude oils to be processed. This will allow for the production of lighter and higher quality products that will be demanded by the marketplace. In 1980, approximately 15 percent of the crude processed in the United States was heavy, with a sulfur content over 1 percent. This quantity will have to increase as 85 percent of foreign crude reserves and 58 percent of U.S. crude reserves have a high sulfur content.

3.1.2 Overview of Petroleum Refinery Wastewater Systems

Most petroleum refineries use some type of wastewater collection and treatment system as part of their operations. These systems are designed to collect wastewater generated during the refining process as well as storm water run-off from the facility grounds. Wastewater is treated by various means to remove contaminants such as hydrocarbons and phenols. The specific design of such a system will depend on the quantity of wastewater generated, the contaminant concentration, and the necessary level of treatment. Generally a wastewater collection and treatment system will consist of the following:



Figure 3-1. Geographical Distribution of Petroleum Refineries in the United States as of January 1, 1984.

- o A drainage and collection system;
- o Gravity oil-water separators;
- o Air flotation systems for further oil removal from the separator effluent, if necessary; and
- o Secondary treatment, if needed, following oil removal.

Figure 3-2 illustrates the components of an example petroleum refinery wastewater system. As shown, wastewater is collected by individual drains located throughout each process unit area. The drains feed into a series of lateral sewers which converge into junction boxes. Wastewater from the junction boxes is led to the oil-water separators by gravity flow or pumping. These separators can either be small units which handle the flow from one process unit or a group of process units, or they can be large separators which handle the wastewater from the whole refinery. Air flotation may also be used after the oil-water separators if secondary oil removal is necessary. Following oil removal, secondary and tertiary treatment processes can be used to further improve wastewater quality before discharge. Refineries which dispose of wastewater by direct discharge into surface waters must meet effluent guidelines established under the authority of the Clean Water Act (40 CFR 419). Refineries which direct their wastewater to a Publicly Owned Treatment Works (POTW) must meet pretreatment standards which have also been established under the authority of the Clean Water Act. 6 Refineries may also dispose of some or all of their wastewater in disposal wells, surface ponds located on site, or through contractors. 7,8 Others not discharge any wastewater. Table 3-1 lists the various processes which can be used by a refinery and the objectives of each treatment stage.

A facility's wastewater system can consist of separate collection and treatment systems each designed to handle wastewater streams containing similar levels of contamination. ^{10,11} A simplified flow diagram of a segregated system handling four basic types of wastewater is shown in Figure 3-3. The non-oily sewer system collects wastewater that does not contain significant quantities of oil. This water can be directed through

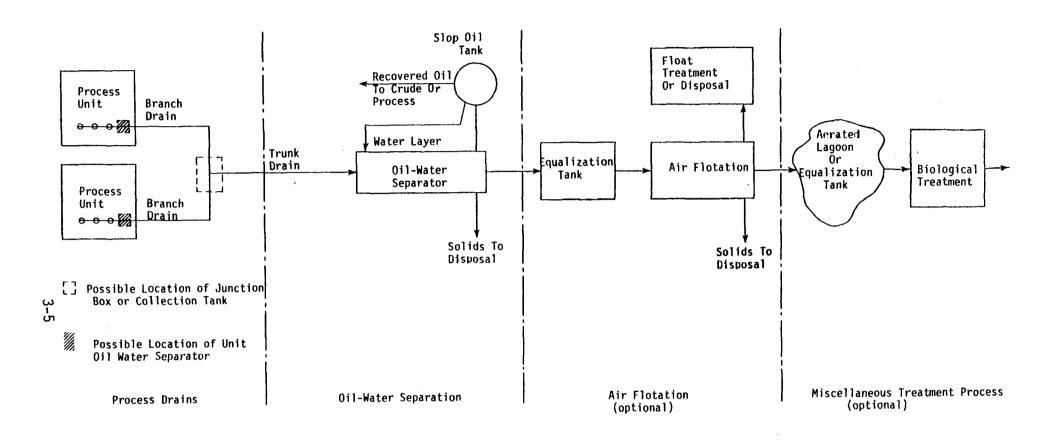


Figure 3-2. Block Diagram of a Petroleum Refinery Wastewater System.

TABLE 3-1. CLASSIFICATION OF REFINERY WASTEWATER TREATMENT PROCESSES

Treatment	Objectives 0	Example Processes
Primary Treatment	Free Oil and Suspended Solids Removal	API Separators Parallel Plate Separators CPI Separators
Intermediate Treatment	Emulsified Oil, Free Oil, Suspended Solids, and Colloidal Solids Removal	Dissolved Air Flotation Induced Air Flotation Coagulation-Flotation Coagulation-Precipitation Filtration
Secondary Treatment	Dissolved Organics Removal, Reduction in BOD and COD	Activated Sludge Trickling Filters Aerated Lagoons Oxidation Ponds Rotating Biological Contact
Tertiary Treatment	Final Polishing	Carbon Adsorption Filtration

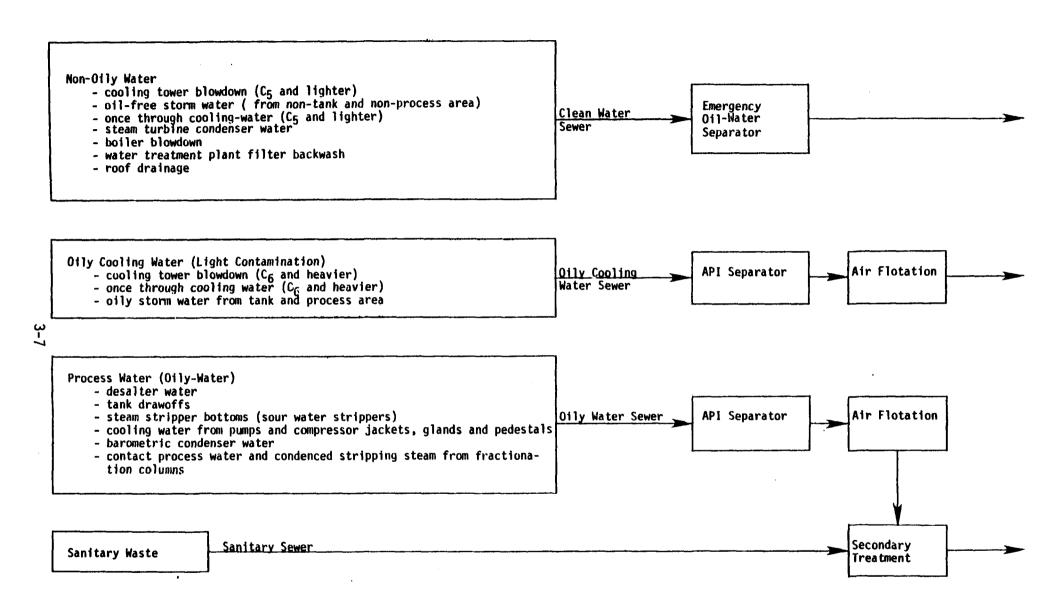


Figure 3-3. Example of a Segregated Wastewater Collection and Treatment System 12,13

oil-water separators which can remove oil from leaks or spills. ¹⁴ The oily cooling water sewer handles wastewater which has been lightly contaminated with hydrocarbons from leaks in the heat exchanger equipment and from stormwater runoff. This water can also be treated by oil separation before it undergoes secondary treatment or is discharged. ¹⁴ Process water originates from a variety of processes which use water or steam, and may contain oil, emulsified oil and various chemicals. This wastewater is usually treated by oil separation and may require further secondary treatment. ¹² Sanitary wastewater from lavatories and locker rooms must be treated by an inplant sewage treatment facility or it can be discharged to a local POTW. ¹²

3.1.2.1 <u>Sources of Refinery Wastewater</u>. A petroleum refinery is a complex operation consisting of a number of interdependent processes. Over 150 separate processes were identified in a 1977 EPA survey of the petroleum refining industry. Each refining process consists of a series of unit operations which cause chemical and physical changes in the feedstock or products. Each unit operation may have different water usages associated with it. The wastewater is generated by a variety of sources including cooling water, condensed stripping steam, tank draw offs, and contact process water.

The total wastewater flow generated by a refinery varies from one refinery to another. Some of the factors which influence the quality of wastewater produced are:

- o the process configuration of the refinery;
- o age of refinery and degree of good "housekeeping' practiced within the refinery;
- o the degree of air-cooling and of wastewater reuse to minimize the overall water demand of the refinery;
- o type of cooling water system;
- o whether or not the refinery handles tanker ballast water; and
- o annual rainfall at the refinery. 16

Some of the major sources of wastewater within a refinery are shown in Table 3-2. This table provides a brief description of the specific wastewater sources from each of these processes, the U.S. production capacity for the process, and the estimated wastewater generation rates. As can be seen from this table, the wastewater may not be directly discharged to the sewer system. It may first undergo some type of treatment, such as steam stripping for the removal of sulfides, mercaptans and phenolics. Additionally, the discharge of cooling water blowdown from the cooling water system can be considered an indirect discharge to the sewer system. There are also general sources of wastewater not specific to any one process which are not listed in the table. These sources include pump and compressor cooling water, pump and compressor seal water, stormwater runoff, equipment washing, steam traps, and leaks or spills.

Based on the information presented in Table 3-2, the processes which generate the largest volume of wastewater are catalytic cracking, vacuum distillation, crude desalting and crude/product storage. Additionally, the wastewater streams from these processes contain high concentrations of oil, emulsified oil and COD as shown in Table 3-3. Thus, these streams may be the major sources of VOC compounds in the wastewater.

The specific source of wastewater within each process, as shown in Table 3-2, will vary depending on the process design and operating characteristics. A general evaluation can be made of some of the major sources of wastewater, as follows:

<u>Crude Oil and Product Storage</u>. During storage, a water layer accumulates below the oil and is drained off at intervals. The water layer is likely saturated with VOC which is often carried along as a water emulsion when the water layer is drawn off to the sewer.

Water associated with crude may come from the production unit or from the ballast water used by tankers and product vessels. Tankers used to ship crude and products generally use water as ballast. The crude is loaded on top of the ballast water, most of which is displaced during loading. However, large quantities of water may remain as emulsion. This emulsion

Table 3-2. Wastewater Sources and Generation Rates. 17,18,19,20

			u.s.	Waste Water Generation Factors (Gal/bbl)						
Process	Process Description	Waste Water Sources	Process Capacity MMB/SD		Indirect Via Cooling-Tower	Direct Via Sour Water Treatment	Direct Via Chemical Treatment			
Crude Separation										
Crude Storage	Store crude oil in tanks	Residual water in crude	>6.9	2.0				2.0		
Desalting	Removal of salt, water and water soluble compounds from crude	Water washing	>6.9	0.002		2.1		2.1		
Atmospheric Distillation	Separates light hydro- carbons from crude in a distillation column under atmospheric pressure	Condensed stripping steam from overhead accumulator	>6.9	0.3		0.04	** ~	0.3		
Gas Processing	Separates gases, such as LPG; fuel gas; isobutane; butylene and light naphtha, from the light ends of the atmospheric distillation unit	Caustic and water wash	N/A	0.08	0.07		3.2	3.3		
Vacuum Distillation	Separates heavy gas oil from the bottoms of the atmospheric distillation unit, under a vacuum	Jet ejectors, barometric condensers	6.9	0.8	1.3	5.2		7.3		
Hydrogen Production	Produces hydrogen from either light hydrocarbons (steam-hydrocarbon process) or heavy oils (partial oxidation process). Used for hydrotreating processes	Partial oxidation: water quench/wash Steam-hydrocarbon: caustic and water wash	1900.0 (MMcfd)	65.0 (MMcfd)	46.0 (MMcfd)			111.0 (MMcfd		
Light Hydrocarbon Processing Naphtha Hydro- desulfurization	Removes sulfur and nitro- gen from naphtha stream from atmospheric distil- lation through catalytic treatment with hydrogen	Condensed stripping steam from overhead accumulator	6.6ª	0.06	0.4	1.4		1.9		

Table 3-2. (Continued)

			U.S.	Waste Water Generation Factors (Gal/bbl)							
Process	Process Description	Waste Water Sources	Process Capacity MMB/SD	Direct to Sewer	Indirect Via Cooling-Tower	Direct Via Sour Water Treatment	Direct Via Chemical Treatment	_			
Catalytic Reforming	Converts low octane naphthas into high octane gasoline blending compounds by contacting feedstock with hydrogen over a catalyst	Condensed stripping steam from overhead accumulator	3.9	0.22	1.0	0.004	·	1.2			
Isomerization	ation Converts n-butane, Caustic washer n-pentane and n-hexane into their respective isoparaffins		N/A	0.24	1.0	• •		1.2			
Alkylation	lation Catalytically combines Overhead acc an olefin with an fractionation isoparaffin to form high caustic wash octane gasoline blending acid alkylaticompounds		0.92	0.41	5.7		0.40	6.5			
Middle and Heavy Distillate Processing											
Chemical Sweeting	Chemically removes mercaptans, hydrogen sulfide and sulfur	Water washers, caustic washer, spent caustic	N/A	N/A	N/A	N/A	N/A	N/A			
Hydrodesulfuri- zation	Removes sulfur, nitrogen and metallic compounds	Overhead accumulator on fractionator (steam	1.9	0.088	0.95	5.2		0.2 erosene)			
	through catalytic treatment with hydrogen	strippers), sour water stripper bottoms		0.12	0.58	3.4	`	4.1 (light pas/oil)			
Catalytic Cracker	Converts heavy petroleum fractions to lighter products using a high-temperature catalytic process	Overhead accumulators and steam strippers on the fractionator, catalyst regeneration	6.0	1.1	3.0	5.4	~ ~	9.5			

Table 3-2. (continued)

			U.S	Waste Water Generation Factors (Gal/bbl)							
Process Hydrocracking	Process Description	Waste Water Sources	Process Capacity MMB/SD	Direct to Sewer	Indirect Via Cooling-Tower	Direct Via Sour Water Treatment	Direct Via Chemical Treatment				
	Converts heavy petroleum fractions to lighter products using a cata- lytic cracking in the presence of hydrogen	High and low pressure separators, accumulator on fractionator	0.94	0.64	0.81	3.0		4.5			
Lube Oil Processing solvent refining	Removal of aromatics, unsaturates, naphthenes and asphalts from lubri- cating-oil base stocks using solvents such as furfural or phenol	Bottom from fractionation towers, contact process water	0.23 (est)	11.0	1.6	- -		13.0			
Dewaxing	Removal of wax from lubricating-oil base stocks using solvents, such as MEK or propane, under reduced temperature conditions.	Compressor cooling	0.23(est)	5.8	6.7			12.5			
Lubricating-oil finishing (hydrotreating)	Removes sulfur, nitrogen and metallic compounds through catalytic treat- ment with hydrogen	Overhead accumulator on fractionator	0.23	N/A	N/A	N/A		N/A			
Residual Hydro- Carbon Processing Visbreaking	Reducing the viscosity of residual feed materials through mild thermal cracking	Accumulator on the fractionator	N/A	₩/A	N/A	N/A	N/A	N/A			
Coking	Converts crude oil residue and tar pitch products into gas, oil, and petroleum coke by a thermal cracking process	Contact process water and steam overhead accumulators	N/A (56 T/D)	31	2.6	0.70		6.4			

Table 3-2. (Continued)

Process			U.S.	Waste Water Generation Factors (Gal/bbl)						
	Process Description	Waste Water Sources	Process Capacity MMB/SD	Direct to Sewer	Indirect Via Cooling-Tower	Sour Water	Direct Via Chemical Treatment	Total		
Deasphalting	Removes asphaltic materials from heavy oil and residual fractions using solvent extraction	Steam jet ejectors, condensors	N/A	N/A	N/A	N/A	N/A	N/A		

^aIncludes: Pretreating catalytic reformer feeds; naphtha desulfurizing; naphtha, olefin or aromatics saturation; straight run distillate; other distillate; lube-oil polishing.

Notes:

N/A: Not Available

MMB/SD: Million Barrels per Stream Day

Table 3-3. Qualitative Evaluation of Wastewater Characteristics by Fundamental Refinery Processes (21)

						Emulsifie	d						Susp.
Fundamental Processes	800	COD	Pheno1	Sulfide	0i1	011	ph	Temp.	Ammonia	Chlorides	Acidity	Alkalinity	Solids
Crude Oil and Product Storage	1	3			3	2	0	0	0	-	0	-	2
Crude Oil Desalting	2	2	1	3	ì	3	1	3	2	3	0	1	3
Crude Oil Distillation	1	1	2	3	2	3	1	2	3	1	0	1	1
Thermal Cracking	1	1	1	1	1		2	2	2	2	0	2	1
Catalytic Cracking	2	2	3	3	1	1	3	2	3	1	0	3	1
Hydrocracking				2				2				un 100	
Reforming	0	0	1	1	1	0	0	1	1	0	0	0	0
Polymerization	1	1	0	1	1	0	1	1	1	1	1	0	1
Alkylation	1	1	0	2	1	0	2	1	1	2	2	0	2
Isomerization						v							
Solvent Refining		1	1	0		1	1	0		4- %	0	1	
Dewaxing	3	3	1	0	1	0						~-	
Hydrotreating	1	1		2		0	2		0	0	0	1	0
Drying and Sweetening	3	1	2	0	0	1	2	0	1	0	1	1	2

^{3 -} Major Contribution

^{2 -} Moderate Contribution

^{1 -} Minor Contribution

^{0 -} Insignificant Contribution

^{-- -} No data

often does not break and the water cannot be removed by the tanker crew. A significant quantity often remains and is pumped along with the crude to the refinery. ²²

Crude Desalting. Desalters are a major source of oil and oil-water emulsion loss to the refinery sewer system. An oil-water emulsion is purposely formed in the desalter to allow salt removal. Most emulsions are likely to pass through oil-water separators and are, therefore, potential sources of VOC emulsions throughout the refinery wastewater system.

When the emulsion is not completely resolved into two components, an interface of emulsion forms and builds up to the point where it is periodically discharged to the oily sewer system through the water outlet. Such an emulsion interface is usually stabilized with solids from the reprocessing of slop oil and the use of stripped foul water. Additionally, wastewater containing various removed impurities is discharged from the desalter to the wastewater system. Some of these desalting processes require holding the crude at high temperatures. The temperature of the desalting wastewater often exceeds 95°C. Such high temperatures may cause VOC to volatilize from the wastewater system.

Overhead Accumulator Fractionation Column. Overhead vapors from fractionation columns are condensed and collected in an accumulator, as shown in Figure 3-4. The water originates from condensed stripping steam and residual water in the feed. The water is separated from the product in the accumulator and discharged to the wastewater treatment system. Since this water has been in direct contact with the product it can contain soluble hydrocarbons. This type of wastewater source can be found in many processes which use distillation for product separation. These processes include atmospheric distillation, catalytic reforming, hydrodesulfurization, and cracking operations.

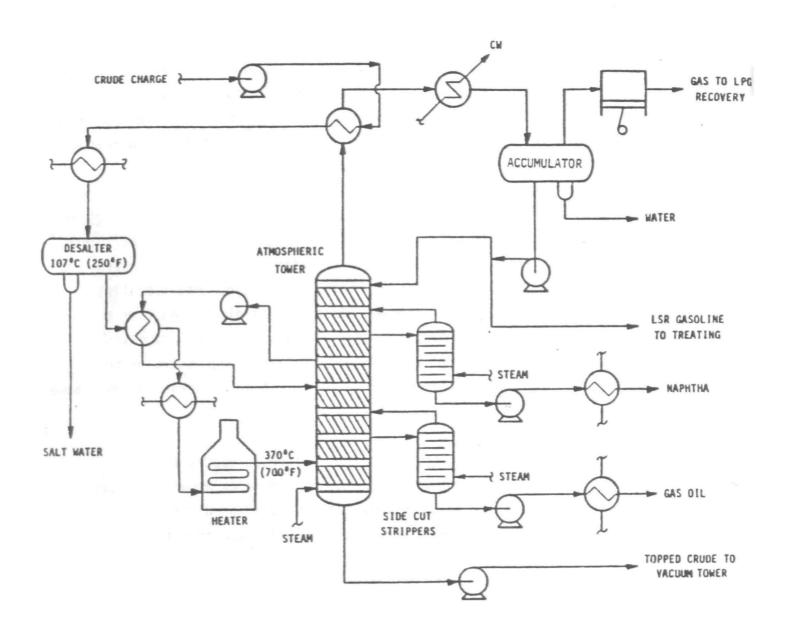


Figure 3-4. Atmospheric distillation system.²⁴

Steam Jet Ejectors/Condensers. A steam jet ejector is a device which uses one fluid to pump another. It is usually used as a vacuum pump for distillation columns. In this device, high velocity steam is discharged across a suction chamber that is connected to the equipment being evacuated. Figure 3-5 shows an example of a steam jet ejector.

After the ejector, a condenser can be used to condense the vapors. 26 This can either be a direct contact (barometric) or surface type (shell and tube) condenser. Of the two types, barometric condensers generate the largest quantity of wastewater, as the vapors from the column are condensed by direct contact with a water spray. Since the water directly contacts the vapors, it can contain soluble and emulsified oil. 26

 $\frac{\text{Cooling Tower Blowdown.}}{\text{water must be regularly discharged in order to control the build up of dissolved solids in the system.}}$ This water may contain VOC from leaks in the heat exchanger equipment. 14

3.1.2.2 Future Trends in Refinery Wastewater Generation. The future trends in petroleum refinery wastewater production depend on many variables. These variables include future environmental regulations, new refinery technology, new refinery feedstocks, and water reuse and conservation practices. Environmental regulations relating to both water and air pollution control will affect wastewater generation. More stringent water regulations may result in further water conservation practices or addition of wastewater treatment facilities. Regulations controlling air pollutants from refinery boilers and process heaters may require flue gas scrubbers which would result in additional wastewater generation. 27

New refinery technology is constantly being developed. Although it is difficult to predict technology development, it can be predicted with some certainty that refineries will become increasingly complex. Increased complexity in a refinery has been shown to result in increased wastewater generation. This has been demonstrated in one study which compared wastewater production of a topping and integrated refinery.

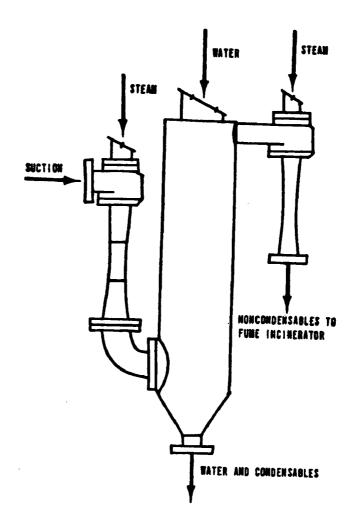


Figure 3-5. Two stage steam actuated vacuum jet system. 28

As mentioned in Section 3.1.1., future crude supplies will be higher in sulfur content. Processing higher sulfur crude oils will require more hydrogen synthesis units. Hydrogen synthesis units require large amounts of steam which will lead to increases in wastewater production. Some of the increases in wastewater production will be offset by the trend towards water conservation. Water conservation in a refinery will include practices such as:

- o replacement of once through cooling water systems with circulatory systems using evaporative cooling towers;
- o raising the level of concentration cycles within existing circulatory cooling water systems by reducing the amount of blowdown;
- o more usage of air-cooling rather than water-cooling, and
- o more intensive efforts to reduce water-cooling and steam heating needs by using more process heat recovery.

3.2 PETROLEUM REFINERY WASTEWATER PROCESSES AND VOC EMISSIONS

As discussed in Section 3.1.2, a basic petroleum refinery wastewater treatment system consists of a drain system connected to a series of treatment steps. This section will discuss each of the major components in this system. The sources and factors affecting emissions, and emission estimates from major sources will be presented. The components examined include process drain systems, oil-water separators, air flotation systems and miscellaneous treatment processes.

3.2.1 Process Drain Systems

Although the number of process drains may vary widely among refineries and individual process units, the general layouts of process drain systems are similar. The process drain system, the types of process drains, and the emissions from process drains and junction boxes are described below.

3.2.1.1 <u>Description of Process Drain System</u>. In petroleum refineries, oily water from various sources enters the oily water collection system

through numerous, generally small, individual process drains. Many of these drains are open to the atmosphere. The numbers of these drains in refineries have been estimated to be more than 1000 in some medium-sized refineries and in excess of 3000 for some large refineries. 29,30

The general principles of refinery drain systems are well defined. 5,31,32 Details of the individual drain systems do vary, however, depending on the needs of a specific facility and on the design choices made by individual refiners. Variations can include pipe size, type of traps, processes handled, and type of junction boxes.

A generalized refinery drain system is conceptually illustrated in Figure 3-6. Liquid is collected in individual small drains distributed throughout each process unit. Some drains may be dedicated to a single piece of equipment (e.g., a single pump), while others might serve several sources. In some cases, these drains may be completely closed instead of open to atmosphere. The individual drains are connected directly to lateral sewer lines. There may be several lateral lines in a process unit. The lateral sewers from the process drains flow into junction boxes, which provide effective vapor seals. The vapor seals prevent hydrocarbons from backing up into other lateral lines and confine any fire or explosion to a small area.

The wastewater leaves the junction boxes through branch lines. Branch lines from refinery units and processing areas generally flow through a gas-trap manhole before entering the trunk line system. The gas-trap manhole is often located at the boundaries of the process unit and prevents vapor from the trunk system from backing up into the sewer lines. Manholes also serve to isolate the individual branch lines. Because the function and structure of junction boxes and gas-trap manholes are similar, both will be referred to collectively as junction boxes in this document.

The trunk sewer system carries wastewater from the branch sewers to the wastewater treatment system. The number and configuration of lateral, branch, and trunk lines vary considerably among refineries.

Current design practice normally provides for segregated wastewater sewers. Storm drainage systems are separated from oily water drains and

Figure 3-6. General Refinery Drain System.

sewers. Clean process water and condensate may also be drained into the storm drains. In some cases, additional wastewater streams, such as foul water, may have separate drain and sewer systems³³. Separate systems, such as storm drains, may also be configured with lateral, branch, and trunk sewers. Storm water runoff is generally collected by open troughs or sumps covered with iron or steel grating and located below grade.

In general, the refinery sewer system is designed for gravity flow of the liquid. Pumping of wastewater is minimized because of the tendency to form oil-water emulsions. In cases where pumping cannot be avoided, special pumps are used to reduce the formation of emulsions.

3.2.1.2 Process Drain Types. Several types of individual drains are used in petroleum refineries. These types of drains are shown in Figure 3-7. A configuration common in older refineries is shown in Configuration A. A straight section of pipe, usually four to six inches in diameter, extends vertically to a height of 4-6 inches above grade. The pipe is connected directly to a lateral sewer line with the pipe directed either straight down or at an offset. There is no liquid seal to prevent vapors from rising from the lateral line, which is normally connected to several other drains. Drain lines/piping from the various sources within the process unit generally terminate just within, at, or slightly above the mouth of the process drain. There is often more than one drain line directed to a single drain opening.

Another drain type used in refineries is shown in Configuration B in Figure 3-7. The straight section of the drain inlet is connected below grade to a "P"-bend which provides a liquid seal in the individual drain. Vapors from the downstream drainage system are prevented from escaping by the liquid seal.

An external liquid seal arrangement is shown in Configuration C. A cap covers the drain opening, and the bottom edge of the cap extends below the level of the drain entrance. Liquid from the various drain pipes falls into the drain area outside of the cap and then flows under the edge of the cap and into the drain line. Thus, the liquid seal prevents emissions of those

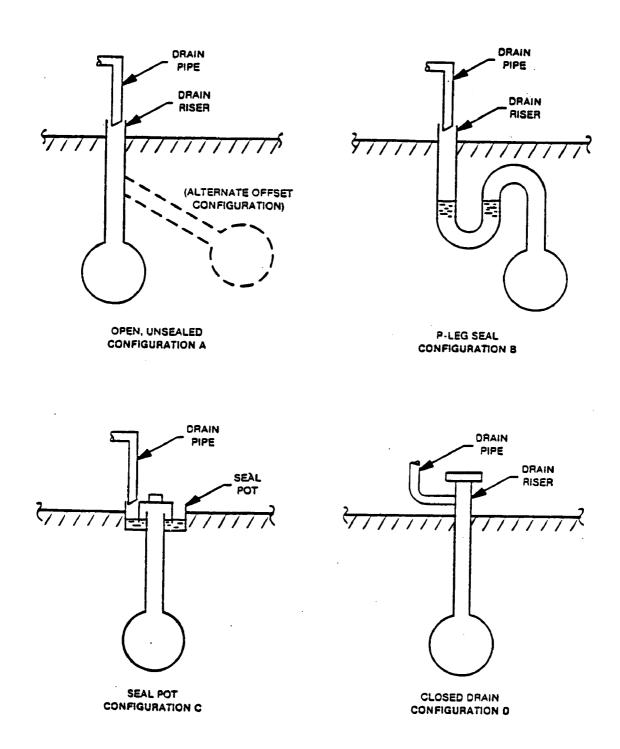


Figure 3-7 Types of Individual Refinery Drains for Oily Wastewater

vapors which may be present in the downstream drainage system. A "P"-seal is not needed in this configuration. The drain cap can be easily removed to clean the drain entrance and drain line, if necessary.

A completely closed drain system was observed in one refinery process unit. This type of drain is illustrated in Configuration D of Figure 3-7. The drain riser extends about 12-18" above grade. The top of this riser is completely sealed with a flange. Drain pipes are welded directly to the riser at points between grade and the flange seal. In some cases, an "extra" drain nozzle is also welded to the riser. This line is normally closed with a valve, but provides access to the closed drain system for intermittent and infrequent needs such as pump drainage. Hoses or flexible lines can be connected to the riser valve from the liquid source.

All the drains in this system are connected through lateral and branch drain lines to an underground collection tank. To avoid the danger of explosion, the entire system is purged with some type of gas which does not contain oxygen (such as refinery fuel gas or nitrogen). The underground tank is vented to the flare system. This closed drain system prevents any VOC emissions to the atmosphere. The complete system is shown schematically in Figure 3-8.

3.2.1.3 Junction Box Types. Lateral and branch sewers generally flow through trapped junction boxes before entering the trunk (and/or branch) sewers. The purpose of the junction boxes is to permit ready access to the sewer lines to facilitate cleaning and inspection, as well as to isolate the branch or lateral sewers from one another. This isolation prevents the travel of hydrocarbon vapors from one line to another and thus reduces the area in which a fire or explosion could occur. A typical vented junction box is shown in Figure 3-9. The junction boxes are normally vented to prevent siphoning and vapor locks. A junction box equipped with a vent seal pot is shown in Figure 3-9. A small amount of water flows continually down the vent pipe and into the seal pot, assuring a continuous seal. A third type of junction box is shown in Figure 3-10. This type of junction box is often referred to as a gas trap manhole.

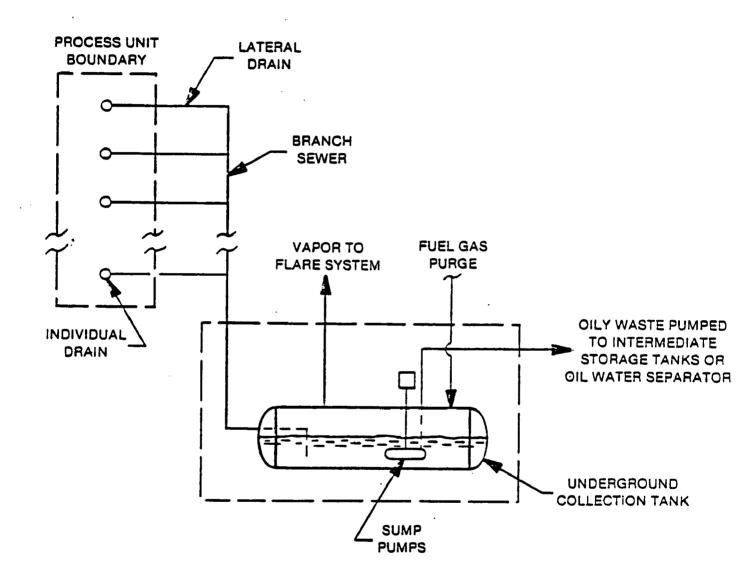
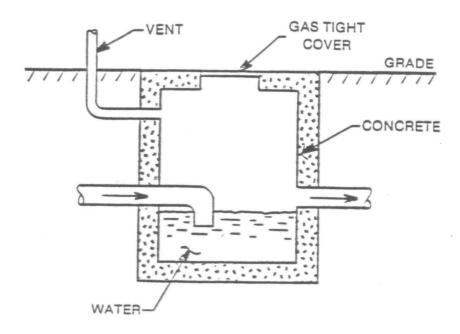
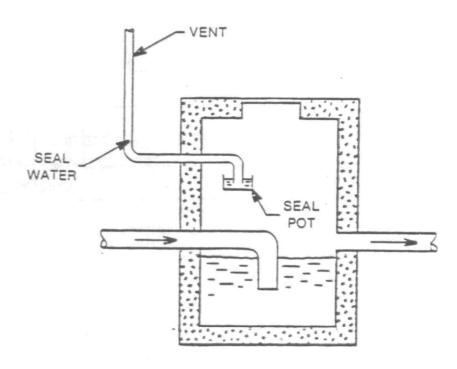


Figure 3-8. Closed Drain and Collection System.



(a) TYPICAL JUNCTION BOX



(b) JUNCTION BOX WITH WATER-SEAL POT

Figure 3-9 Refinery Drain System Junction Boxes

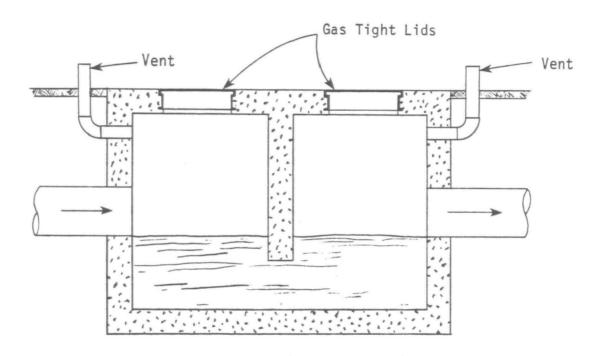


Figure 3-10. Gas Trap Manhole. 32

Most vents on junction boxes are at least 4 inches in diameter. 23 Smaller vents can develop problems such as freezing during low temperatures or clogging from gradual deposition of scale and sediment. The vent usually drains to the junction box and is free of excessive bends and other obstructions which might cause blockages.

- 3.2.1.4 <u>Factors Affecting Emissions From Process Drains and Junction Boxes</u>. VOC are known to be emitted from refinery process drains. The factors influencing emissions are the composition of wastewater entering the drain system, drain design characteristics, and climatic factors. Specifically, these factors include:
 - o Rate of molecular diffision of compounds through air and water;
 - o Rate of convection;
 - o Solubility and vapor pressure of the compounds found in the wastewater stream;
 - o Frequency and composition of wastewater discharge through the drain;
 - o Wastewater temperature;
 - o Ambient temperature;
 - o Wind speed;
 - o Length of drain or vent pipe;
 - o Length of water seal; and
 - o Concentration of compounds in the sewer vapor space and in the waste water

No predictive theoretical or even semi-theoretical models for process drain emissions have been published. However, some factors affecting emissions can be evaluated by theoretical means. These factors include diffusion and convection.

The rate at which molecular diffusion can transport volatile compounds through air can be calculated by using the following formula: 37

$$N_{A} = \frac{AD_{V} p_{m}}{B_{T}} \ln \frac{1-Y}{1-Y_{i}}$$

Where:

NA = Flux (mole/sec)
A = Exposed surface area (cm²)
p_m = Molar Density (mole/cm³)
B_T = Diffusion path length (cm)
Y_i = Initial concentration (atm)
Y = Final concentration (atm)
D_V = Diffusion coefficient (cm²/sec)

The density and diffusion coefficient are both controlled by the temperature of the vapor in the drain pipe. Thus, the factors which control molecular diffusion through air are temperature, drain design, solution density, and the concentration gradient. Since the coefficient is inversely proportional to the diffusion path length, the greater the drain length, the lower the flux rate. Another controlling factor is the media through which the compound is diffusing. For example, the diffusion coefficient for benzene through air is $0.085 \text{ cm}^2/\text{sec}$ while the diffusion coefficient for benzene through water is $1.02 \times 10^{-5} \text{ cm}^2/\text{sec}$.

The rate of molecular diffusion is very small and can be overshadowed by the effects of convection. This effect was demonstrated by one study which showed that the rate of diffusion of hexane through different size openings was 1.0 to 31.7 times the calculated diffusion rate. This study was based on the results of laboratory evaluations of the emission rates from different size and shaped fittings placed into covered drums containing hexane. These fittings ranged from circular open pipes to complex shaped steel support structures. The rate was found to depend on the design of the opening. A small covered opening had less convective flux than a complex shaped large opening.

Another factor which may influence the convective flux is wind speed. 39 One study showed that the mass transfer coefficient for a spilled compound is proportional to $\mathbf{u}^{0.78}$, where \mathbf{u} is equal to the wind speed. Convective flux can therefore increase the total flux through an

uncontrolled drain pipe. For a water sealed drain (with no VOC contamination in the water), the molecular diffusion through the water layer will control the mass flux and convection cannot increase this rate. Thus, water seals can reduce VOC emissions by eliminating the effects of convection.

The rate at which compounds can transfer across the wastewater/air interface and the resulting equilibrium concentration will also control the emission rate. The faster the mass transfer rate, the greater the potential for high vapor concentrations. The state of the compounds (i.e., whether the compound is dissolved in the wastewater or in a separate phase) will also affect this rate. The effects of film transport can be assumed to be negligible. To estimate the maximum potential vapor concentration, Henry's law can then be used to estimate vapor concentrations over solutions while the vapor pressure can be used to estimate the vapor concentration over an immiscible phase.

The final controlling factor is the rate and composition of the wastewater stream entering a water sealed drain. If the wastewater stream is highly contaminated, the water seal may become saturated with the compounds in the stream. Additionally, if the compounds are immiscible with water, they may float on top of the water seal. In either of these cases, the effectiveness of the water seal will be negated, and the drain will act as if no seal were present until the VOC are weathered off or drain is flushed with fresh water. Fresh water flowing into such a drain can flush out any residual compounds, restoring the effectiveness of the water seal.

3.2.1.5 <u>VOC Emissions From Process Drains</u>. A study sponsored by the EPA is the only study in which the emission rate from drains has been measured. A 1958 study of refinery emissions in Los Angeles County provided an overall emission rate estimate for the combined process drain and wastewater treatment system. However, this estimate was based primarily on qualitative observations. Little, if any, quantitative emission data were obtained. Additionally, the VOC emissions from drains alone cannot be estimated from this information.

The EPA-sponsored study of atmospheric VOC emissions in petroleum refineries was published in $1980.^{36}$ The results of this study were used to develop emission factors for fugitive sources, including drains, in petroleum refineries. These factors have since been included in EPA's AP-42. The emission factor for refinery drains is 0.032~(0.010,~0.091) kg/hr-drain. The numbers in parentheses are the lower and upper limits of the 95% confidence interval about the average value of 0.032~kg/hr-drain.

The VOC emission measurements were made on a total of 49 process drains. The ratio of trapped (liquid-sealed) to untrapped drains in the sampled population was not determined. These drains were sampled in 13 different refineries, and the sampled population was intended to be reasonably representative of refinery practices in the 1976-1979 time period. It seems probable that the majority of the drains were unsealed, since it was not common practice to install individually sealed drains. This is borne out in responses to inquiries of refineries by the California Air Resources Board in 1978. The responses indicated that the majority of the refinery drains were not equipped with liquid seals. It is assumed in this document that the emission factor represents emissions from untrapped drains.

3.2.1.6 <u>VOC Emissions from Junction Boxes</u>. There are no studies of VOC emissions from junction boxes. For the purposes of this document, it is assumed that all junction boxes are sealed and vented to atmosphere. Since the diameters of the vent lines are in the same size range as those of drains, the mechanism for VOC emissions was assumed to be the same as that for open, untrapped drains. Under these conditions, the emission rate from junction box vents was estimated to be the same as the emission rate from open drains. Thus, the junction box vent emission factor is estimated to be 0.032 kg/hr-junction box.

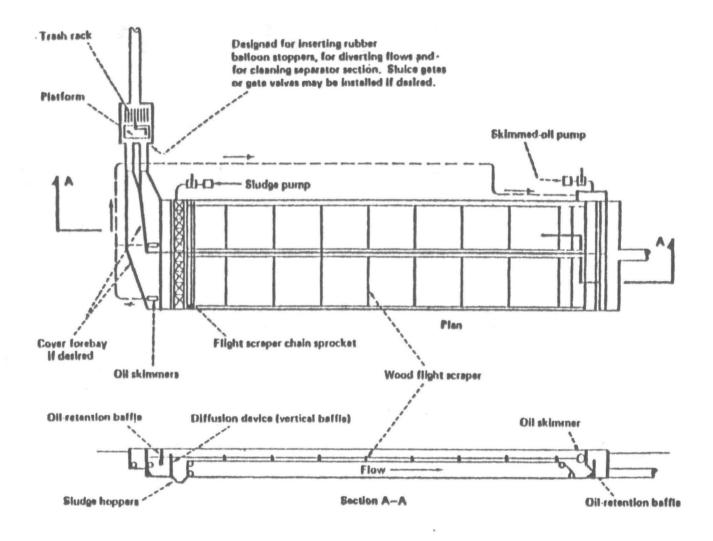
3.2.2 <u>Oil-Water Separators</u>

Oil-water separators are commonly used by most refineries as the primary method of separating and removing oil from oily process water. Since these separators remove much of the VOC with the skimmed oil, the units following this process will have lower VOC emissions. 42

Oil-water separators are the first step in the treatment of refinery wastewaters. Most refinery layouts provide sufficient difference in elevation between the oil-water separator and the various areas being drained to cause the oily process waters to flow by gravity to and through the oil-water separator. Some refineries have installed small oil-water separators close to the source of the oily-water. This minimizes the formation of emulsions which cannot be removed by a separator and provides overall improvements in efficiency of VOC recovery. 10,43 The operation of oil-water separators and the emissions from this system will be discussed in more detail in the following sections of this chapter.

3.2.2.1 Types of Oil-Water Separators. All oil-water separators rely on the different densities of oil, water, and solids for successful operation. Within the separator, the wastewater stream is led to a quiescent zone where the various phases separate. Oils and solids with specific gravities less than that of water float to the top of the aqueous phase, while heavy sludges and solids sink to the bottom of the vessel. As mentioned earlier, oil-water separators will not break emulsions nor will they separate substances in solution.

The most commonly used type of oil-water separator is the American Petroleum Institute (API) type separator. A typical API separator is shown in Figure 3-11. In API separators, the influent wastewater passes through trash bars and a skimmer (the forebay) before entering the quiescent zone of the separator (main bay). In this quiescent zone, the wastewater velocity is kept very low to prevent any turbulent mixing. Here, free oil droplets rise to the surface where they coalesce. The resulting oil layer is then skimmed from the water surface at the downstream end of the tank.



Note: This diagram is not to scale. A typical API separator is about 15 feet wide by 60 feet long.

Figure 3-11. Oil-Water Separator. 45

Several types of skimmers are currently used including rotary drums, slotted pipes, and floating oil skimmers. These can be used in both the main bay and forebay. In the main bay, slowly moving paddles or a water spray can be used to direct the oil layer to the end of the tank where it can be skimmed. API separators have been, for many years, constructed with reinforced concrete. However, at least one supplier offers fiberglass packaged units.

Other separator designs have been developed that enhance the coalescing of oil droplets and therefore improve the oil removal efficiency of the unit. Collectively, these separators can be referred to as enhanced oil-water separators. The most commonly used enhanced oil-water separator is the corrugated plate interceptor (CPI).

A corrugated plate interceptor, shown in Figure 3-12, consists of a number of parallel corrugated plates mounted from 2 to 4 cm apart at a 45° to 50° angle to the horizontal. Between 12 and 48 plates are typically used. Wastewater flows downward between the plates, with the lighter oil droplets floating upward into the tops of the corrugation, where they coalesce. The oil droplets move up the plates to form a floating layer that is skimmed from the surface of the treatment tank. These systems do not use moving paddles to collect the oil on the surface nor are sludge rakes used.

By using these plates the effective coalescing surface area in a CPI is increased. Thus, for the same wastewater treatment capacity a CPI will have a smaller surface area than a corresponding API separator. This smaller surface area enables the systems to be supplied as prefabricated units, usually including a cover. Manufacturers offer prefabricated systems which can handle flow rates from 2 gpm to 2,000 gpm.

3.2.2.2 <u>Major Factors Affecting VOC Emissions</u> Volatilization of organic compounds from the oily surface of an oil-water separator is a complex mass transfer phenomenon. The force behind the volatilization process is the drive to reach equilibrium between the oil layer and the atmosphere. This driving force can be considered to be the difference in

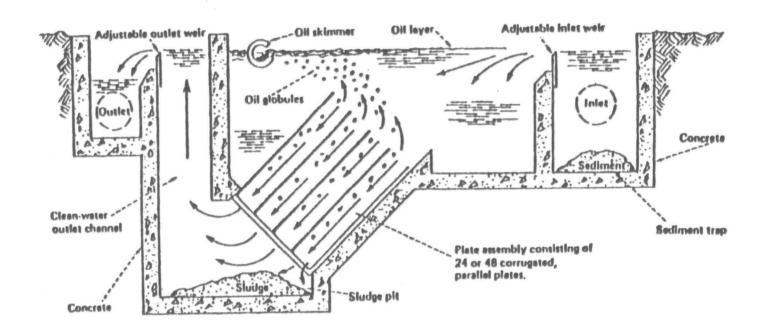


Figure 3-12. Corrugated Plate Separator. 50

partial pressure of a compound between the two phases.⁵¹ The rate at which volatilization will occur per unit surface area can be assumed to be proportional to the difference between the vapor pressure of a compound in the liquid phase and its partial pressure in the gas phase.

Four studies have examined the physical and chemical factors which control this transfer process. One study, conducted by Litchfield⁵², used a small hot water bath to simulate the operating conditions of a API separator. Tests were conducted by placing weighed pans of actual API separator influent oil in the hot water bath. After 24 hours the pans were reweighed and the losses calculated.⁵² The results of this study related the percent volume loss of oil in a separator to the ambient temperature, influent wastewater temperature, and the 10 percent true boiling point of the influent oil. The 10 percent point is an indication of the oil's vapor pressure. The lower the 10 percent true boiling point, the higher the vapor pressure.

The relationship developed by Litchfield is as follows: 52

 $V = -6.6339 + 0.0319 \times -0.0286 Y + 0.2145 Z$

where:

V = Percent volume loss after 24 hours

X = Ambient temperature (°F)

Y = 10% point (°F)

Z = Influent temperature (°F)

This equation predicts losses within 2.58 percent with a confidence limit of 95 percent. These three independent variables accounted for 82 percent of the total losses. The factors not taken into account during this study include the thickness of the oil layer, the average wind velocity, and the surface area of the separator, all of which can affect the emission rate.

The results of the study showed that ambient temperature had the least effect on the percent volume of oil lost. For each 10°F increase in ambient temperature, a 0.3 percent increase in losses was experienced, shown in

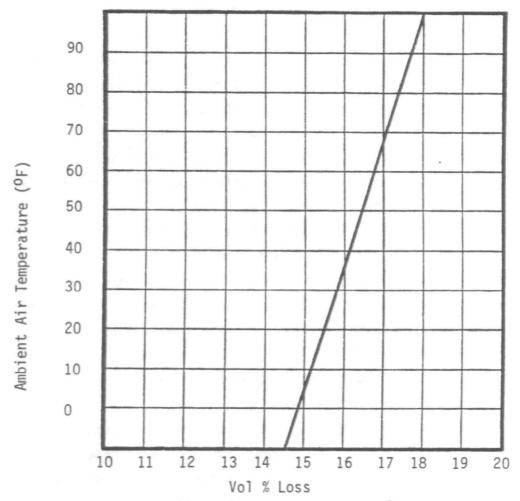
Figure 3-13. As shown in Figure 3-14, a 20°F decrease in the 10 percent point of the influent oil will increase losses by 0.6 percent. Influent temperature had the greatest effect on the loss rate amounting to a 2.2 percent increase in losses for every 10°F increase in temperature, as shown in Figure 3-15.

The second study, by Jones and Viles 53 , concluded that the variables controlling air emissions from API separators were the vapor pressure of the influent oil and the wind speed over the basin. Figure 3-16 shows the results of this study. As can be seen, an increase in either the wind velocity or the vapor pressure will increase the emission rate.

Several other factors can also affect the VOC emission rate including surface area of separator, time of exposure (frequency of oil skimming) and oil layer thickness. 54 These factors are interrelated, as the size of the separator and frequency of oil removal will control the oil layer thickness. This oil layer may suppress VOC emissions because the volatilization of VOC from the oil layer will change its composition as more volatile compounds are lost. 55 If no fresh oil is mixed with the surface oil layer and the rate at which VOC can diffuse into this layer is small, the emission rate could decrease with time. The weathered oil layer could then act as a blanket and suppress vapor emissions.

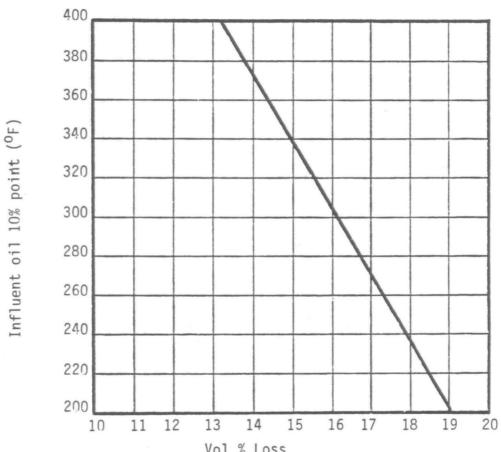
Two theoretical models for predicting VOC emissions from separators were developed by the Shell Oil Company. The first model predicts the mass transfer of VOC from an open flat oil surface into a well developed wind profile. The air is assumed to flow over flat terrain before encountering an oil surface that is level with the terrain. Mass transfer is assumed to be gas phase controlling. The mass transfer coefficient is calculated based on an eddy diffusion model that includes a logarithmic distribution of wind speed with height. 56

The second model developed by Shell is based on the Sherwood-Pigford correlation and the Colburn j factor. This correlation is based on a boundary layer solution of momentum transfer for flow over flat plates. The Sherwood-Pigford correlation is used to caluclate the average mass transfer coefficient which is then used to estimte the average mass flux of VOC. ⁵⁶



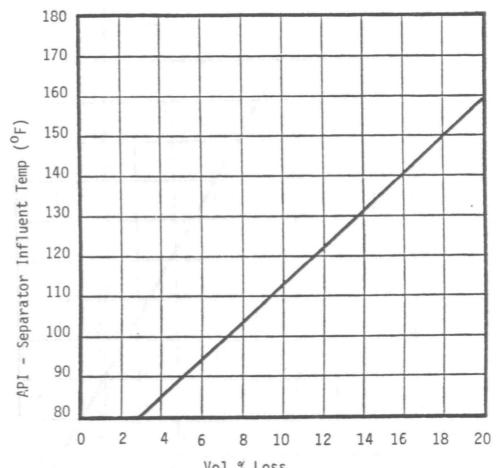
Note: Constant 10% point of 300°F

Figure 3-13. Effect of ambient air temperature on Evaporation. (52)



Vol % Loss Note: Ambient Temperature of $40^{\rm OF}$ and influent temperature of $140^{\rm OF}$

Figure 3-14 · Effect of 10% point on evaporation. 52



Vol % Loss Note: 10% point of 300°F and ambient air temperature of 40°F

Figure 3-15. Effect of influent temperature on evaporation. 52

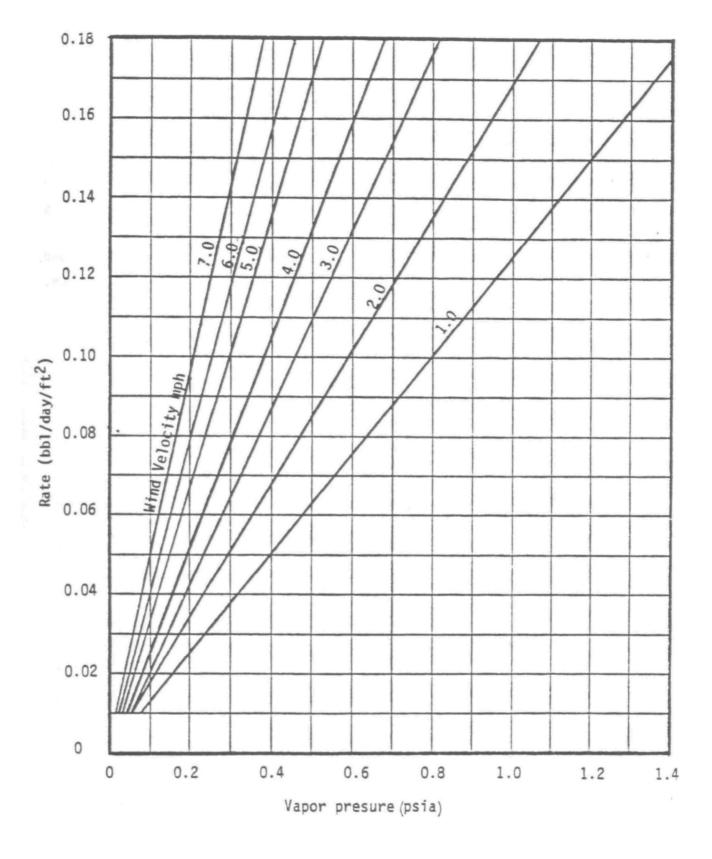


Figure 3-16. Relationship between vapor pressure, wind speed, and loss rate. (53)

A method for applying the second model to predicting emissions from site specific separators was also developed by Shell. This method is based on measuring the evaporation rate of a specific liquid hydrocarbon from open pans placed in the oil-water separator. The measured volatilization rate is then adjusted by a series of correction factors to estimate the volatilization rate of the separator oil. Correction factors were developed for the boiling point of the test liquid, temperature of the liquid surface, wind speed, height of the measurement of wind speed, and length of the liquid surface. ⁵⁶

3.2.2.3 <u>VOC Emissions From Oil-Water Separators</u>. The earliest detailed study of VOC emissions from oil-water separators was performed in 1958 in Los Angeles County. 57 This study estimated the emissions from sumps, drains and API separators to range from 30 kg/1000 m 3 of crude to 600 kg/1000 m 3 of crude with an average refinery emission rate of 2700 kg/day. Based on this average rate and a reported wastewater flow of 31.9 million gallon per day, the emission factor was 85 kg/MM gallons of wastewater flow. The emission factor listed in AP-42 is based on the 600 kg/1000 m 3 of crude value reported by the Los Angeles County study. 41

There have been many changes since 1958 in the quantity and quality of wastewater generated in refineries and the associated emissions. In addition to decreasing wastewater flow, industry has reduced the amount of oil lost to the wastewater streams. These two trends would indicate that the emission factors determined in 1958 are higher than today's or at least that the lower end of the range is more representative of today's operations.

Due to the large surface area size of oil-water separators and the physical/chemical characteristics of oil, it is difficult to make direct measurements of VOC emissions. ⁵⁹ Recent estimations of VOC emissions have been based on the study done by Litchfield. A discussion of these emission estimates follows:

American Petroleum Institute⁶⁰; The API estimated an annual emission rate for an API separator based on the factors shown in Table 3-4. The results, based on Litchfield's study, showed an estimated 12 percent volume loss. This results in an emission factor of 570 kg/MM gallons of wastewater using an influent oil concentration of 1500 mg/L.

State of California 61; The State of California, in 1979, estimated the annual emission rates for the API separators located in their state. The bases for these calculations are shown in Table 3-4. California estimated that about half the separators at refineries in the state were completely covered. From these, VOC emissions were thought to be minimal. Most of the oil-water separator systems at the remainder of the refineries were partially covered. Often a covered primary separator was followed by an uncovered seperator. For the oil-water separator systems that were partially covered, 950 cubic meters (6000 bbls) per day of oil entered oil water separators in the state. The State assumed that 80 percent of the 950 cubic meters per day of oil was recovered in the covered part of separators. That is, 760 cubic meters per day of oil were recovered and 190 cubic meters per day entered the uncovered part of the separator. Litchfield's method was used to estimate a volume loss rate of 10 percent which equals an emission factor of 526 kg per MM gallons of wastewater for the uncovered portion of the separators. The inlet VOC concentration was assumed to be 2000 mg/L.

TABLE 3-4. FACTORS FOR CALCULATING EMISSION LOSSES USING THE LITCHFIELD METHOD FOR THE LITCHFIELD METHOD

Study	Ambient Temperature (°F)	Influent Temperature (°F)	10% Point (°F)	Influent Conc. (mg/L)	Flow (gpm)	Refinery Capacity (m³/day)	Emission Rate (kg/1000 m ³ of cude)	Volume Percent Loss (%)
API	50	120	300	1,500	5,000	16,000	256	12
California	65	110	300	2,000	17,500 ^a	192,000 ^b	68	10

^aFlow of wastewater in all of California to uncovered separators.

 $^{^{\}rm b}$ Total State refining capacity.

The emission factors developed by API and the State of California using the Litchfield study cannot be used to calculate the current emissions from API separators for several reasons. Both of these studies use higher influent oil concentrations than recent industrial contacts and a review of current data have indicated. As refineries are trying to reduce both the quantities of wastewater generated and the amount of oil contamination, a value of 1000 mg/L (0.1%) is a more accurate current estimate. The high emission factor calculated by the API study was based on wastewater generation rates which have been significantly reduced since that study was conducted. On the other hand, the California study assumed that the first basin of the API separator was covered and estimated the emission factor only for the second basin.

The models developed by Shell are more complex than the method developed by Litchfield. However, these models are more applicable to site specific applications. Additionally, neither model has been adequately field tested. Therefore, because the Litchfield method is based on measured test data, this method is judged to be the best available method for estimating VOC emissions from oil-water separators.

The Litchfield equation can be used to estimate the percent volume loss from an API separator under a set of conditions more representative of present day refineries. The influent temperature was selected based on actual values found at several refineries. These temperatures ranged from 90°F to 150°F. An average temperature of 120°F was selected based on this range. The 10 percent point of the influent oil was assumed to be 300°F. This is the value used in the Litchfield study which has been verified by recent information. The ambient temperature is assumed to be 65°F. Based on the variables listed in Table 3-5, a percent volume loss rate of 12.6 percent was calculated. Assuming an influent VOC concentration of 1000 mg/L (0.1%), an emission factor of 420 kg/MM gallons of wastewater was calculated.

A recent study by the State of California estimated a wastewater to crude throughput ratio of 0.5. 59 Using this estimate, the VOC emission factor of 420 kg/MM gallon of wastewater is equivalent to 56 kg/1000 m 3 crude.

TABLE 3-5. DATA USED TO CALCULATE EMISSION FACTOR

Ambient Temperature:	65°F
Influent Temperature:	120°F
10% True Boiling Point:	300°F
Influent Oil Concentration:	1000 mg/L
Specific Gravity:	0.85

3.2.3 Air Flotation Systems

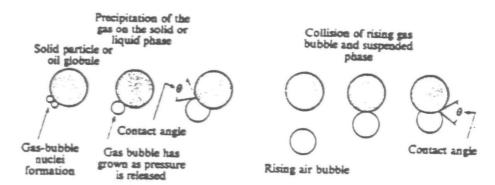
Air flotation is commonly used in refinery wastewater treatment systems to remove free oil, colloidal solids, emulsified oil and suspended solids. Air flotation usually follows the oil-water separator and precedes biological treatment. The air flotation process, types of air flotation systems, and emissions from air flotation systems are described below.

3.2.3.1 <u>Description of Air Flotation Systems</u>. In air flotation systems, bubbles are formed by introducing gas or air directly into the wastewater by mechanical means. These bubbles become attached or entrained with free and emulsified oil, suspended solids, and colloidal solids, causing the combined density of these substances to be less than the density of the

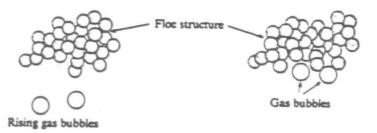
liquid phase. The bubbles, therefore, create a buoyancy which allows these substances to rise to the surface of the flotation chamber where they are removed. The basic mechanisms by which air or gas bubbles intereact with suspended substances are shown in Figure 3-17.65,66

Two types of air flotation systems are used in petroleum refinery wastewater treatment. These are the dissolved air flotation system (DAF) and the induced air flotation system (IAF). Both systems rely on basic flotation principles for removing free and emulsified oil, colloidal and suspended solids. However, the two systems have a number of mechanical and structural differences. Each system will be described separately followed by a general comparison of the two.

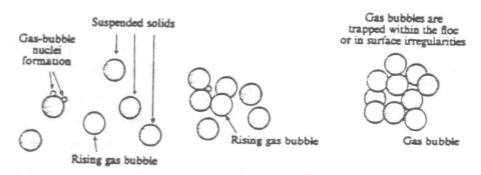
Dissolved Air Flotation. In a DAF system, wastewater is saturated with air or gas under pressure and passed into a flotation chamber at atmospheric pressure. The reduction in pressure results in the formation of small bubbles which interact with colloidal and suspended solids and free and emulsified oil, and carry these to the surface of the flotation chamber. Here, the floated material is removed by mechanical flight scrapers. A DAF system is shown in Figure 3-18.



A) Adhesion of a bubble to a solid or liquid surface



B) Trapping of gas bubble in a floc structure



C) Incorporation of gas bubbles into floc structure

Figure 3-17. Interaction of gas bubbles with suspended solids or liquid phases. (65)

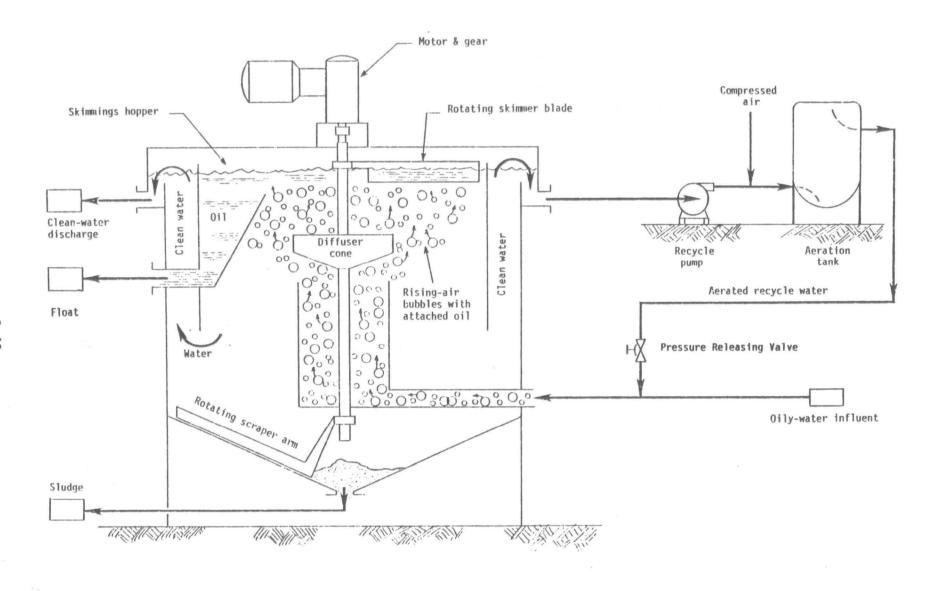


Figure 3-18. Dissolved Air Flotation System (DAF). 67

The DAF can be divided into a number of sub-processes: 1) pretreatment of the waste stream, 2) solution of the gas, 3) dissolution of the gas, 4) mixing of the gas bubbles and wastestream; 5) flotation of the colloidal and suspended solids and free and emulsified oils, and 6) removal and disposal of the floated material. The overall design of the system varies from site to site and depends on the needs of the refinery. Pretreatment of the waste stream can consist of pH adjustment and/or the addition of chemical coagulants followed by flocculation. The coagulation/flocculation process assists flotation by breaking the colloidal suspensions and oily emulsions in the wastewater and by forming a floc which can easily interact with bubbles in the flotation chamber. Commonly used coagulants include lime, ferric chloride, alum, and various-cationic polyelectrolytes. 68,69

Air is most commonly used as the flotation gas in a DAF system. However, nitrogen and natural gas have also been used in refinery applications. ^{70,71} The choice of the gas is dependent on cost, availability, and safety considerations. Nitrogen and fuel gas can reduce the likelihood of an explosion in the flotation system.

Three principal modes are used for pressurizing and mixing gas with the wastewater stream. In full stream pressurization, the entire influent is pressurized, aerated, and then released to the flotation tank. In split stream pressurization, a portion of the influent is pressurized, aerated, and then mixed with the remainder of the influent after reduction in pressure. And finally, recycle pressurization involves recycling a portion of the effluent which is then pressurized and mixed with the influent after reduction of the pressure.

DAF flotation tanks can be rectangular or circular. Retention times and quantity of recycle water are variable. Skimming mechanisms also vary from system to system.

Induced Air Flotation. Induced air flotation has been used extensively in the mining industry for ore beneficiation. Only recently has the IAF been introduced as a treatment process for refinery wastewater. In induced air flotation, bubbles can be produced by the following techniques:

(1) mechanical shear or propellers; (2) diffusion of gas through a porous medium, or (3) mixing of a gas and liquid stream. The bubbles formed interact with suspended solids and oils and carry these substances to the surface of the IAF where they are removed by a surface skimmer. Two types of IAF systems are commonly used for treating refinery wastewater. These are the impeller type, which use mechanical shear, and nozzle type systems, which mix gas and a liquid stream.

The impeller IAF is the older of the two systems. It consists of a rotating impeller suspended between a cylindrical stand-pipe and draft tube. Rotation of the impeller generates a liquid vortex flow pattern with a gas liquid interface. The interface extends from the midpoint of the inner wall of the standpipe through the interior of the impeller section down to the upper portion of the tube axis. The gas cavity formed within the vortex will be at sub-atmospheric pressure. As a result, gas from the vapor space of the flotation cell is induced through gas inlet ducts into the interior of the rotor. Impeller rotation causes liquid to circulate upward from the bottom of the cell. The liquid and gas phases are mixed by the impeller and gas bubbles are formed. Further gas liquid mixing occurs when the wastewater passes through a disperser which surrounds the impeller. After escaping the mixing region, gas bubbles enter a quiescent region of the cell. Here, the gas bubbles attach to suspended materials and rise to the surface of the cell where they are removed. 73 The mechanisms of an impeller IAF are shown in Figure 3-19.

The nozzle IAF is mechanically simpler than the impeller type. In the nozzle IAF, treated effluent is recycled to the flotation cells. Air or gas is drawn into the liquid by means of the venturi effect and bubbles are formed through agitation of the liquid-gas mixture. The gas bubbles formed in the nozzle type are distributed throughout the flotation cell as opposed to the concentration of bubbles in the upper portion of the impeller type. A nozzle type IAF is shown in Figure 3-20.

Both the nozzle and impeller IAF systems are multi-staged units usually consisting of four flotation cells in series. Contaminant removal efficiency increases as wastewater moves from cell to cell. Chemical conditioning can also increase the efficiency of both IAF systems.

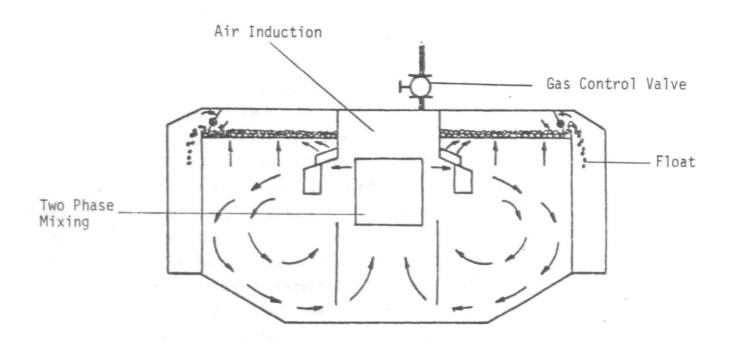


Figure 3-19. Mechanism of an Impeller Type IAF. '3

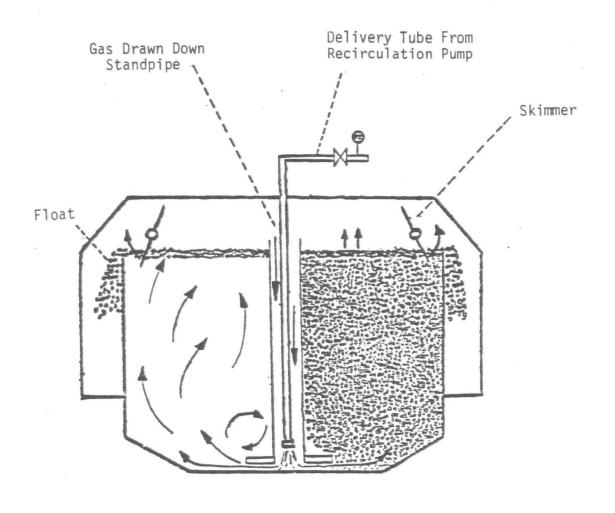


Figure 3-20. Mechanism of a Nozzle Type IAF.

Comparison of DAF and IAF Systems. The DAF and IAF systems have been shown to be equally effective in removing oil and suspended solids from refinery wastewater when operated properly. 74 For both systems, the factors affecting flotation performance include influent characteristics, hydraulic loading, chemical conditioning, and the operation of the skimmer. Additionally, DAF performance can be influenced by the recycle rate and gas pressure while the performance of an impeller IAF is influenced by impeller speed and impeller submergence level. A DAF is characterized by relatively quiescent flotation, high retention times, and usage of small quantities of (dissolved) gas. An IAF is a more turbulent system, has lower retention times, and uses large quantities of recirculated (ambient) gas. Both systems can be improved by chemical conditioning. A DAF, because of the quiescent flotation, may be more suitable for use with a wide range of chemical coagulants. An impeller IAF has a tendency to inhibit floc formation because of the sheering action of the impellers. However, the nozzle type IAF does not subject the floc formed to high sheering and is therefore better suited for chemical conditioning. 68,73

- 3.2.3.2 <u>Factors Affecting Emissions</u>. The factors affecting VOC emissions from air flotation systems are much the same as those affecting emissions from API separators. Five factors which are the same include:
 - o quantity of VOC in wastewater entering the air flotation system;
 - o exposed surface area of the system;
 - o temperature of the wastewater;
 - o ambient temperature; and
 - o wind flow across the surface of the flotation chamber.

The above factors were discussed in detail in Section 3.2.2.2. The quantity of VOC in wastewater entering the air flotation system is dependent on the processes preceding air flotation. Most of the light end VOC would be expected to be removed from the wastewater in preceding processes. An increase in the concentration of volatile compounds in the influent oil, however, will increase the emission rate. $^{52}, ^{53}$

Factors affecting emissions which are unique to air flotation include:

- o use of air or gas used for flotation; and
- o physical design characteristics of the flotation system.

Use of Gas for Flotation

A factor which is unique to air flotation systems is the introduction of a gas into the wastewater. This gas could act to strip out volatile hydrocarbons. The factors which control the stripping rate include the surface area available for transfer (interfacial area), air flow rate, temperature, and residence time of stripping. This relationship can be expressed as follows:

 $C_t - S = (C_0 - S)^{-(k)(A)(t)/(V)}$

where:

 C_{t} = Final concentration (mg/L)

 C_0 = Initial concentration (mg/L)

S = Concentration of unstrippable compounds (mg/L)

A = Area available for transfer

V = Volume of liquid (L)

T = Residence time (min)

K = Constant

This equation assumes that the volatilization rate will follow first order kinetics. Although first order kinetics may not be applicable to all the compounds in the wastewater stream, it has been shown to be true for some compounds and waste streams from petroleum refining and petrochemical manufacturing. 75,76 This equation can be simplified by assuming that the compounds in the wastewater are completely soluble and that an overall mass-transfer coefficient, K, can be used in place of the term (k)(A)/(V). This coefficient is a function of many factors including air flow rate, water temperature, and tank configuration.

The relative amount of emissions due to air stripping and evaporation was estimated by examining the properties of an example VOC, benzene. Theoretical calculations were performed to estimate the emissions of benzene due to air stripping as well as evaporation from a DAF system. The operational and design characteristics of the DAF system were assumed to be the same as an actual refinery DAF system tested by the EPA. The characteristics are given in Table 3-6.

The emissions due to air stripping can be estimated by using the above equation. The overall mass transfer coefficient was not readily available in the literature. Experimental studies of another compound, acetone, indicate a value of 0.006/hr for K at the low air flow used in DAF systems. Based on this value, the mass-transfer coefficient for benzene can be related to that for acetone by the following equation: 79

$$K_{A} = \frac{(N_{PR})_{B}^{2/3} (N_{SC})_{B}^{-2/3}}{(N_{PR})_{A}^{2/3} (N_{SC})_{A}^{-2/3}}$$

where:

 K_B = mass-transfer coefficient for benzene K_A = mass-transfer coefficient for acetone $(N_{PR})_B$ = Prandtl number for benzene = 4.37

(N)

 $(N_{PR})_{A}$ = Prandtl number for acetone = 22.3

 $(N_{SC})_B$ = Schmidt number for benzene = 0.299

 $(N_{SC})_A$ = Schmidt number for acetone = 0.32

Based on this equation, the mass-transfer coefficient for benzene is 0.0096/hr. Using this coefficient and the DAF parameters shown in Table 3-6, the benzene losses due to air stripping are estimated to be 0.3 kg/MM gallons of wastewater.

TABLE 3-6. TYPICAL DAF DESIGN CHARACTERISTICS 78,81

Volume of DAF System: 174,000 gallons

Influent Flow: 1,800 gallons/minute

Recycle 520 gallons/minute

Air Temperature 70°F

Wind Speed 16,000 meters/hr

Diameter of DAF 15.8 meters

Area 197 meters²

Residence Time: 1.25 hr

Initial Concentration: 700 mg/L

Concentration of Unstrippable Compounds: 0 mg/L

Air Flow Rate: 1.5 cfm

The emissions due to evaporation of benzene from the DAF system can be estimated by using relationships developed for calculating emissions from oil spills. One method based on mass transfer theory and laboratory experiments closely agrees with field data. 80 This equation, based on first order kinetics, is as follows:

$$C = C_0 e^{-(k_g)(A)(P)(t)/(n_t)}$$

where:

C = Mass of compound remaining (mg)

C = Initial mass of compound (mg)

 k_q = Mass transfer coefficient (/atm hr)

A = Surface area (m²)

P = Vapor pressure of compound (atm)

t = Time (hr)

 n_{+} = Total number of moles of liquid in float

and:

$$k_g = \frac{0.0292 \ \mu^{0.78} \ d^{-0.11}Sc^{-0.67}}{RT}$$

where:

 μ = Wind speed (m/hr)

d = Tank diameter (m)

 S_c = Gas-phase Schmidt number = 1.76 R = Gas constant = 8.206 x 10^{-5} atm $m^3/(mole K)$

T = Temperature(K)

Based on these equations and the input variables given in Table 3-6, the emission rate of benzene due to evaporation is estimated to be 2.6 Kg/MM gallons. This shows that emissions due to air stripping are small (less than 10% of total emissions) compared to the losses due to evaporation. It

should be noted that the total benzene emissions of 2.9 kg/MM gallons estimated by the theoretical calculations compares with measured emissions of 3.1 kg/MM gallons during EPA tests. The details of these tests are presented in Appendix C.

Design Characteristics

The physical design characteristics of air flotation systems are also important factors influencing emissions. The flotation chamber in a DAF is usually open to the atmosphere where ambient conditions such as wind speed can increase volatility of the VOC. Therefore, the flotation chamber will be the major emission point for a DAF.

IAF systems, on the other hand, are usually supplied with a cover. This consists of a roof and two access doors on each of the four flotation chambers. These doors can be gasketed and sealed to reduce emissions. Further, IAF's are usually equipped with a pressure/vacuum relief valve so that the system can be operated gas tight. One study showed that the access doors and pressure/vacuum relief valves are the major point of emissions from IAF systems. 82

The action of the skimmer mechanisms in both DAF and IAF systems can also affect emissions. If a skimmer is not in operation, a film of oil will form on the surface of the flotation tank and inhibit the release of VOC. Constant skimming of the oil allows for greater mass transfer of VOC to the atmosphere. The effect of skimmer operation on VOC emissions was observed during emissions testing of a DAF. 63

3.2.3.3 <u>VOC Emissions From Air Flotation Systems</u>. Emissions from air flotation systems were estimated from the results of EPA tests on five air flotation systems. These tests were performed on one DAF and four IAF systems. The details of the tests are included in Appendix C of this document.

Three of the IAF systems and the DAF system treated oily process wastewater while one IAF system treated only non-oily wastewater. The influent wastewater characteristics of the DAF and three IAF's treating oily process wastewater were similar. As expected, the influent wastewater

characteristics of the IAF treating non-oily wastewater differed greatly from the other four systems. Therefore, only emissions results from the tests of the four systems treating oily wastewater were used to estimate an emission factor.

The results of the four tests used to estimate the emission factor are given in Table 3-7. It should be noted that air purging was used to test all four systems. Therefore, the emission results represent the emission potential of the systems rather than the actual emissions resulting from a system operating under normal conditions. The discussion and calculations given in the preceding sections have shown that air stripping is not a major cause of VOC emissions from a DAF system. Since evaporation losses are the major cause of VOC emissions, the emission potential of IAF and DAF systems would be equal if both are considered to have flotation chambers open to the atmosphere. The air purging of the systems during the tests created conditions similar to those that would exist if both types of systems were open to the atmosphere.

As shown in Table 3-7, the VOC emissions measured at these systems varied over a wide range. This variation could be due to design and operational differences between the systems, differences in the concentration of hydrocarbons in the wastewater, or differences in the purge rate used during the tests. Therefore, to account for these variations and due to the fact that the emission tests represent emission potential, an average uncontrolled emission factor was calculated. This uncontrolled emission factor for air flotation systems is 15.2 kg/MM gallons of wastewater. However, as discussed previously, an IAF does not normally operate in a completely uncontrolled state because a cover 1s usually provided. The emission factor for an IAF under normal operating conditions is estimated to be 3.0 kg/MM gallons of wastewater. The derivation of this emission factor is presented in Section 4.1.3.2.

3.2.4 Miscellaneous Wastewater Treatment Processes

Following oil-water separation and air flotation, wastewater streams can be further treated by a number of processes as shown in Table 3-1 and

TABLE 3-7. SUMMARY OF RESULTS OF EPA TESTS ON AIR FLOTATION SYSTEMS 78,83,84

Refinery	Air Flotation Type	Emission Factor (kg VOC/MM gal Wastewater)		
Chevron	DAF	30.0		
Golden West	IAF	21.2		
Phillips	IAF	5.0		
Phillips	IAF	4.5		
		15.2		

Figure 3-2. The majority of the oil and VOC in the wastewater is removed in primary and intermediate treatment. Hence, the potential for VOC emissions from the treatment processes which follow is greatly reduced. There may be situations, however, where a processs such as equalization precedes air flotation. In these situations, the emission potential may be higher. A brief description of the miscellaneous treatment processes is given below.

3.2.4.1 <u>Intermediate Treatment Processes</u>. The intermediate treatment processes discussed in this section include coagulation-precipitation, filtration, and equalization. Air flotation, which represents about 75 percent of the intermediate treatment processes, has been discussed in detail in Section 3.2.3. Coagulation-precipitation and filtration remove emulsified oil and suspended solids which have not been removed in the primary treatment processes. Equalization is used to balance the quantity and quality of the wastewater before entering downstream treatment.

Coagulation-Precipitation. Coagulation-precipitation begins with the addition of chemical coagulants to the wastewater. Chemicals used for coagulation include lime, ferric chloride, alum, and various cationic polymers. The wastewater and coagulant are then rapidly mixed in a tank which is followed by slow agitation of the mixture in a flocculation chamber. The coagulant breaks the oily emulsion by reducing charge repulsion between particles and allowing the particles to combine and form a floc structure. The floc particles are then allowed to settle or float by gravity in a precipitation or sedimentation tank.

<u>Filtration.</u> Filtration can be used as both an intermediate treatment process and as a polishing step. Several types of filtration devices have been developed for removing free and emulsified oil from refining wastewaters. These filters range from units using a simple sand medium to those containing media which exhibit specific affinities for oil. 86

The filtering medium is usually contained within a basin or tank and is supported by an underdrain system. The underdrain system allows the

filtered water to be drawn off while retaining the filter medium in place. The filter must be frequently backwashed to prevent a buildup of solids in the medium which would reduce the filtration rate. The spent backwash water contains the suspended solids removed from the water and must be treated. 87

Equalization. Flow equalization is used to balance the quantity and quality of wastewater before further treatment. Equalization has been found to greatly improve treatment results. Biological processes as well as physical-chemical systems operate more efficiently if the composition and flow of the wastewater feed is relatively constant. Periodic and unpredictable large discharges can occur in any refinery. Equalization basins act to minimize the effects of these increased loadings on downstream treatment processes.

The size of an equalization system is dependent on the storage capacity required. Tanks or basins may be used. Equalization basins can consume large land areas. They are often aerated to maintain aerobic conditions in the wastewater and to alleviate odor problems.

3.2.4.2 <u>Secondary Treatment Processes</u>. The secondary treatment processes which will be discussed include activated sludge, trickling filters, aerated lagoons, oxidation ponds, and rotating biological contactors. Secondary treatment processes are used to remove dissolved organics through oxidative decomposition by microorganisms. The processes used in each refinery are determined by the flow and contaminant characteristics of the wastewater to be treated.⁸⁸

Activated Sludge. Activated sludge is a continuous flow, biological treatment process which uses microorganisms to remove organic materials by biochemical synthesis and oxidative reaction. The microorganisms convert the organics to carbon dioxide, water, and new cell material. The process is carried out in a reaction tank where the wastewater is mixed with the microorganisms in the presence of oxygen. Oxygen is supplied to the tank either by mechanical aerators or a diffused air system. A clarification

tank follows the reaction tank to allow for liquid-solids separation. A portion of the microorganisms settled out in the clarifiers is recycled to the reaction tank while the excess is sent to sludge handling facilities. 88,89

Trickling Filters. Trickling filters can be used as complete secondary treatment processes or as pretreatment devices to reduce the organic load on subsequent activated sludge units. A trickling filter consists of a large, open topped vessel containing a packed medium that provides a growth site for microorganisms. Wastewater is usually applied to the medium by a rotary distributor and the treated wastewater is collected in an underdrain system. Soluble organics are consumed by the microorganisms and converted to carbon dioxide, water, and new protoplasm. 90

Aerated Lagoons. Aerated lagoons are medium depth basins (about 10 feet) designed for the biological treatment of wastewater on a continuous basis. Oxygen is supplied to the lagoon by mechanical devices such as surface aerators and submerged turbine aerators. Microorganisms convert dissolved or suspended organics in the wastewater to stable organics, carbon dioxide, and water. Aerated lagoons are often used as a polishing step following removal of organics.

Oxidation Ponds. The depth of an oxidation pond is normally limited to three to four feet to assure an adequate supply of oxygen so that aerobic conditions are maintained without mechanical mixing. Aeration is achieved by oxygen transfer at the surface and by the photosynthetic action of algae present in the pond. Microorganisms then cause aerobic degradation of organic contaminants in the wastewater. 91

Oxidation ponds have been used in the past as the only treatment of refinery waste and also as a polishing step for the effluent from physical-chemical or other biological waste treatment processes. Multicellular ponds are used in some instances, especially if the oxidation pond is used as a basic treatment unit rather than polishing unit. 92

Rotating Biological Contactor. A rotating biological contactor (RBC) is a mechanical process that brings wastewater, air, and microorganisms together for biological oxidation. This process consists of a series of closely spaced discs (10-12 feet in diameter) which are mounted on a horizontal shaft and rotated with about one-third of the surface immersed in the wastewater. The discs are typically constructed of light-weight plastic. When the process is placed in operation, the microbes in the wastewater begin to adhere to the rotating surfaces and grow there until the entire surface area is covered with a 1/16-1/8 inch layer of biological growth. As the discs rotate, they carry a film of wastewater into the air where it trickles down the surface of the discs, absorbing oxygen. Upon completion of a rotation, the aerated and partially treated wastewater is mixed with the balance of the wastewater. This adds to the dissolved oxygen content and reduces the concentration of organic matter in the tank. BOD removal and oxidation of ammonia nitrogen is inversely proportional to the hydraulic loading on the disc units. 90

3.2.4.3 Additional Treatment Processes. Following secondary treatment, a number of processes are used to remove dissolved organics and suspended solids that remain in the wastewater. These processes include clarification, polishing ponds, and carbon adsorption. Filtration, which has been described under intermediate treatment, may also be used in this stage of treatment.

Clarification is used to remove suspended solids by gravity separation and always follows biological treatment systems. Clarification tanks can be circular or rectangular in shape and have a depth of up to 15 feet. The settled solids are transported along the bottom of the tank by a scraper mechanism. When following an activated sludge system, clarification helps to produce a concentrated return sludge flow which helps to sustain biological treatment. 93 Polishing ponds also remove suspended solids by gravity separation. The depth of a polishing pond is usually 3 to 5 feet.

Carbon adsorption can be used to remove non-biodegradable and toxic organics which may be present in the wastewater after biological treatment.

Activated carbon systems have functioned both as polishing units following a biological system and as the major treatment process in a physical/chemical treatment system. However, the use of activated carbon adsorption processes has not been widespread for refinery wastewater treatment. 94,95

3.2.4.4 <u>VOC Emissions for Miscellaneous Wastewater Treatment</u> <u>Processes.</u> The majority of the oil in a refinery wastewater is removed by the oil-water separator. The effluent leaving the oil-water separator usually contains oil and grease concentrations less than 200 mg/l. ⁹⁶ Concentrations may be higher or lower at some plants depending on the design of the system and the retention time of the wastewater in the oil water separator. In general, separators can remove 50 to 99 percent of the separable oil in a refinery wastewater.

Because the concentrations of oil and other pollutants are highest when entering the separator, the greatest potential for VOC emissions from treatment processes would be from that source. Air flotation systems often follow oil-water separators. Due to their location in the treatment scheme air flotation is the next largest potential source of VOC emissions. As wastewater continues to move through the treatment scheme, additional quantities of pollutants are removed and the quality of the wastewater improves. Secondary treatment processes also remove organic material by biological means which further reduces the potential for air emissions.

A limited amount of emissions data are available for the treatment processes discussed in this section. One study estimated VOC emissions from an activated sludge system while a second study described a theoretical method for estimating emissions from oxidation ponds.

In estimating VOC emissions from an activated sludge system, the air stripping rate for organics in a typical refinery wastewater was calculated. The wastewater flowing to the activated sludge system was assumed to have a chemical oxygen demand (COD) of 600 mg/l. Using these two parameters, mass VOC emissions were calculated for a 90,000 barrel per day refinery. The calculated emission factor was 0.006 pounds per barrel of crude throughput (17 kg per thousand cubic meters). This emission factor is based on

wastewater flow of 50 gallons per barrel of crude. Using the estimated wastewater flow to crude ratio of 0.5, the emission factor would 0.0025 pounds per barrel of crude. Due to the aeration mechanism and retention time common in activated sludge systems, this factor can be assumed to represent the maximum emissions which would result from all of the treatment processes following oil removal. Very little, if any, VOC would remain in the wastewater following activated sludge treatment.

One study indicated that VOC emissions from oxidation ponds can be estimated by determining the surface area of the pond, the concentration of the various organic compounds in the wastewater, the molecular weight of the compounds, and by calculating the overall mass transfer coefficient of each compound. Actual examples of emissions from oxidation ponds used to treat refinery wastewaters were not given.

3.3 GROWTH OF SOURCE CATEGORY

This section present growth estimates for each emission source in the source category. Section 3.3.1 will discuss growth estimates for process drains and junction boxes. Section 3.3.2 and 3.3.3 will discuss growth estimates for oil-water separators and air flotation systems, respectively.

3.3.1 Process Drains and Junction Boxes

Estimates of new process drains and junction boxes can be made by evaluating projected refinery construction. Available sources indicate that approximately 102 new process units will be built in the five year period from 1985 to 1989. 98,99,100 These new process units will include approximately 4,900 new drains and 1,000 new junction boxes. In addition to new units, it is also expected that a number of process units will be expanded and/or modified. Approximately 180 process units will be expanded and/or modified by 1989. It is estimated that 10 percent of the drain systems of these process units will be affected by the modification/reconstruction provisions of the NSPS. Therefore, approximately 5,800 drains and 1,200 junction boxes will be affected by the NSPS in the five year period from 1985 to 1989.

3.3.2 <u>Oil-Water Separators</u>

An estimate of new oil-water separators to be built from 1985 to 1989 can be made by evaluating new construction and expansion of existing refineries. New process units and expansion of existing process units will result in additional wastewater generation. Using 1983 construction projections, it is estimated that approximately 136,000 barrels per day (5.7 MMgpd) of wastewater will be produced by new process units and expansion of existing process units. 101,99 Table 3-8 lists these expected increases for some of the major refinery process units. These units will account for approximately 124,000 barrels per day of new wastewater. It is estimated that additional new process units and auxillary refinery operations will produce an additional 10 percent increase in wastewater. Therefore, the total estimated annual increase in wastewater production is 136,000 barrels per day. It is assumed, based on projected construction rates, that similar wastewater production increases can be expected each year from 1985 to 1989.

Closer analysis of construction projections shows that a large portion of the new process units will not significantly increase wastewater generation at a specific refinery. Unused capacity of existing separators should handle any small increases in wastewater. However, there are a number of major construction projects planned which may warrant additional oil-water separators. These projects include greenfield refineries and expansion of existing refineries to handle heavy, sour crudes. Large separators may be needed to treat wastewater produced by these projects. Further, some refineries use unit oil-water separators to recover oil at the source of generation. Addition of new process units will therefore call for the addition of some smaller separators.

Based on projected refinery construction and subsequent wastewater increases, it is estimated that 30 new oil-water separators can be expected over the five-year period from 1985-1989. The majority of these separators are expected to be small in size because most of the constructions projects are minor. A few large separators will be required by major projects. Additionally, it was assumed that another 10 percent (3 oil-water separators) may become modified affected facilities during this time period.

TABLE 3-8. PROJECTED ANNUAL INCREASE IN REFINERY WASTEWATER FROM 1985 TO 1989

Process	Increased Capacity From New Units (Mbb1/d)	Increased Capacity From Expansion (Mbbl/d)	Wastewater Generation Factor (gal/bbl)	Increase In Wastewater (thousand gal/day)
Hydrotreating	146	-	4.0	584
Hydrorefining	136	-		-
Light Ends	-	-	2.5	-
Cat Reform/Platformer	75	23.7	1.2	118
Vacuum Distillation	-	142.0	7.3	1,037
Hydrogen (MM cfd)	243.7	95.0	111.1 (MM	cfd) 37.6
Lube 0il	-	-	12.1	-
Alkylation	7.7	20.1	6.5	180.7
Cat Polymerization	11.0	-	-	-
Thermal Cracking/Coking	61.2	101.7	6.4	1,042
Hydrocracking	13.0	99.8	4.4	496
Crude Distillation	80.0	83	3.4	554
FCC	101.0	19.5	9.5	1,144 5,194 M gal/day (124,000 bbl/day)

3.3.3. Air Flotation

Although addition of a new oil-water separator may not necessarily warrant a new air flotation system, increases in wastewater generation may result in some refineries adding air flotation. Further, air flotation alone may be added in an effort to upgrade existing wastewater treatment facilities. Estimates of new air flotation systems can be derived using the growth estimates for oil-water separators. Available information indicates that approximately 75 percent of the operating refineries use air flotation in their wastewater treatment systems.

Assuming that the number of new air flotation systems will be about 75 percent of the new oil-water separators, it is estimated that 25 new air flotation systems will be built over the five-year period from 1985-1989. Modified air flotation systems are assumed to equal approximately 10 percent of the new air flotation systems (i.e. 3 air flotation systems).

3.4 BASELINE EMISSIONS

The baseline emission level is the level of control that is achieved by industry in the absence of NSPS. Baseline reflects the emission controls currently required by state regulations. Section 3.4.1 will discuss baseline control for process drains and junction boxes. Sections 3.4.2 and 3.4.3 will discuss baseline control for oil-water separators and air flotation systems, respectively.

3.4.1 Process Drains and Junction Boxes

There are presently no specific state regulations controlling VOC emissions from process drains and junction boxes. A few refineries do exist that apply various levels of control to process drains for emission offset purposes. These control measures include water sealed or capped drains. However, due to absence of state regulations, new drain systems may or may not use any control measures. Therefore, baseline control for process drains and junction boxes is assumed to be no control.

Current nationwide VOC emissions from process drains can be estimated by applying the emission factor given in Section 3.2.1.5 to an estimate of

the national drain population. The nationwide drain population can be estimated by extrapolating data from the EPA study 36 and the California study. The uncontrolled emission rate of VOC from an estimated 145,940 drains is 40.6 gigagrams per year (Gg/yr), with an approximate 95 percent confidence interval range of 6.6 to 174.2 Gg/yr. This estimate does not include the uncertainty in the estimate of total drain population.

Current nationwide VOC emissions from junction boxes can be estimated by applying the emission factor given in Section 3.2.1.6 to the nationwide junction box population. Based on information collected in the California study 30 , it is estimated that one junction box is needed for every six drains. Therefore, the number of junction boxes nationwide is one sixth the number of drains, or approximately 24,300. The estimated VOC emission rate from junction boxes is therefore 6.8 Gg/yr.

Based on the emission factors presented in Sections 3.2.1.5 and 3.2.1.6 and the growth projections presented in Section 3.3.1, the baseline emissions from process drains and junction boxes in the 120 new, modified, and reconstructed process units will be 1920 Mg per year in 1989.

3.4.2 Oil-Water Separators

Nearly all states where petroleum refineries are presently located have some regulations controlling VOC emissions from oil-water separators. These regulations vary considerably due to provisions for various exemptions in many states. Table 3-9 provides an overview of existing state regulations applicable to oil-water separators. As shown in the table, some states have designated minimum separators capacity, emission level, or vapor pressure as criteria for coverage by regulations.

As a result of state regulations, separators can generally be divided into three classes. State regulations may require separators to be fully covered, partially covered, or they may not be regulated. In order to determine the proportion of each type of separator, state agencies in major oil refining states were contacted. In addition, information on individual refineries in a number of states was compliled. Table 3-10 summarizes the information obtained.

Table 3-9. Existing State Regulations Applicable To Oil-Water Separators
In Petroleum Refineries

	ATTAINMENT AREA	NO Sources	NO REGULATION	COVER SEPARATORS	COVER FOREBAYS	OTHER	MINIMUM SIZE Cutoff	NOTES
Alabama				Х			sources with potential to emit < 100 TPY	
Alaska	x							
Arizona		X					sources with potential to emit < 100 TPY	
Arkansas		X						a
California				X	X			þ
Colorado						X		С
Connecticut		X						
Delaware				X			emits ≤ 10 lb/day	
Florida				X			emits < 15 lb/day and < 3 lb/hr	
Georgia				X			sources with potential to emit < 100 TPY	
Hawaii	X							
Idaho	X							
Illinois						X	•	đ
Indiana				X				
Iowa	X							
Kansas				X			sources with potential to emit < 100 TPY	
Kentucky					X		recovers < 200 gal/day	е
Louisiana X				f				
Maine		X					sources with potential to emit < 100 TPY	
Maryland		X						
Massachusetts		X						
Michigan				X			receive <u>></u> 200 gal/day VOC	
Minnesota	X							
Mississippi	X							
Missouri				X				g
Montana	X							
Nebraska			χ,					
Nevada		X						
New Hampshire				X			source with potential to emit < 100 TPY	
New Jersey				X			•	
New Mexico			X					h
New York				X	X		> 200 gal/day recovered	i
North Carolina				X				
North Dakota	X							
Ohio				X			200 gal/day recovered	

Table 3-9. Continued

	ATTAINMENT AREA	NO SOURCES	NO REGULATION	COVER SEPARATORS	COVER FOREBAYS	OTHER	MINIMUM SIZE CUTOFF	NOTES
)klahoma				Х		 		
O reg on				X				
Pennsylvania				X			receive > 200 gal/day VOC	
Rhode Island		X						
South Carolina		X						a
South Dakota	X							
Tennessee				X	X			
Texas				X			receive ≥ 200 gal/day VOC	e,k
Utah				X				1
Vermont		X						
Virginia				X			emissions > 7.3 tons/yr, 40 lb/day, and 8 lb/hr	m
Washington				X			emissions < 25 TPY	
West Virginia				X				
Wisconsin				X				
Wyoming	X							
District of Columbia		X						
TOTALS	10	10	2	25	4	2		

NOTES

No 100 TPY sources exist.

Colorado regulation No. 7 provides for VOC emission control for oil separation equipment. Covers listed as an option for vapor loss control.

Must install air pollution control equipment with 85 percent efficiency or more.

Exempts separators used exclusively in conjunction with crude oil production.

Requires sealed openings, floating roofs with closure seals, vapor disposal systems, or other approved equipment.

In actual applications only the forebay on PRWS OWS is required to be covered although regulation states all components unless exempted.

This reflects the Kansas City area; there are no refineries in the St. Louis area.

No regulations have been established because emissions from refinery sources are considered insignificant.

New York City Metropolitan Area and upstate New York.

Nashville/Davidson county has no sources. In nonattainment areas, VOC must have a true vapor pressure of ≥ 0.5 psia; in certain other counties VOC must have a true vapor pressure of > 1.5 psia.

All VOC contaminated wastewater must be directed to the separator. 1.

Vapor control system must be at least 95 percent efficient.

California's regulations vary by Air Quality Management Districts (AQMD). Bay Area AQMD exempts separators processing < 200 gal/day organic liquids or organic liquids with Reid vapor pressure ≤ 0.5 psi. San Diego County has no sources. South Coast AQMD exempts units which handle only coal tar products and gravity separators used exclusively for the production of crude oil if the water fraction entering contains less than 5 ppm hydrogen sulfide plus organic sulfides and less than 100 ppm ammonia. The Kern County AQMD exempts separators based on the surface area of the separator, the oil recovery rate, and the estimated fractional volume loss of oil.

The information given in Table 3-10 was used to estimate the level of control required for new separators. The percentage of covered, partially covered, and uncovered separators in each state was applied to the crude throughput in that state. For example, if it is known that 100 percent of the separators in a state are required to be covered, 100 percent of the crude throughput is assumed to be processed at refineries with covered separators. Crude throughputs were calculated using 1983 refining capacity figures and assuming 60 percent capacity utilization (1982 estimate 104). Applying the percentages to crude throughput in each state provided an estimate of nationwide crude processed at refineries with the different levels of control. These estimates are shown in Table 3-11.

According to Table 3-11, the nationwide crude throughput in 1983 was 1540 thousand cubic meters of crude per calendar day $(10^3 \text{m}^3/\text{cd})$. Of this, 1348 x $10^3 \text{m}^3/\text{cd}$, or approximately 85 percent, was processed at refineries which are located in states requiring separators to be covered. Further, $42 \times 10^3 \text{m}^3/\text{cd}$, or approximately 5 percent was processed at refineries required to have partially covered separators. And the remaining 10 percent was processed at refineries in states with no regulations. Assuming that new refinery construction will be proportional to the current breakdown of refining capacity by state, it is estimated that 85 percent of the new oilwater separators will be required to be covered, 5 percent will be required to be partially covered, and 10 percent will not be covered at all.

Current nationwide VOC emissions from oil-water separators can be estimated by applying the emission factor given in Section 3.2.2.4 to the estimates of crude throughput given in Table 3-11. Consideration must be given to the emission reduction achieved by the various methods of control. Control efficiencies of the various control techniques are discussed in Chapter 4. Using this information, current nationwide VOC emissions can be estimated. Current nationwide VOC emissions from oil-water separators are estimated to be 7.5 gigagrams per year (Gg/year).

Baseline emissions from the 33 new and modified oil-water separators are estimated to be 1211 Mg per year in 1989. This estimate is based on the emission factor presented in Section 3.2.2.4 and on the assumption that

TABLE 3-10. SUMMARY OF BASELINE CONTROL FOR OIL-WATER SEPARATORS

State	% Separators Fully Covered	% Separators Partially Covered	% Separators Uncovered	Comments
California				
- Bay Area	100			
- Kern County	40		60	Only large refineries covered by regulation
- South Coast	90		10	Some small refineries may be exemp
Delaware	100			
Illinois	50		50	Some separators exempted by regulation
Indiana	90		10	Smaller refineries may be exempt
Louisiana	80	20		Covering forebay only can meet regulations under exemption
New Jersey	100			provisions
Ohio	100			
Oklahoma	100			
Pennsylvania	85		.15	
Texas	100		·	
Other States	85		15	85 refineries in these states, 33% of which are located in attainment areas

References: 102,103,104,105,106,107,108,109,110,111

TABLE 3-11. ESTIMATE OF CRUDE THROUGHPUT AT REFINERIES HAVING VARYING EMISSION CONTROLS

State	Total Crude ₃ Capacity (10 m /cd)	Crude Throughput ¹ At Refineries With Covered Separators	Crude Throughput ¹ At Refineries With Partially Covered Separators	Crude Throughput At Refineries With Uncovered Separators
California	397	-	-	
- Bay Area	128	77 ²	-	-
- Kern County	52	13 ³	-	19
- South Coast	217	1174	••	13
Delaware	22	13 ²	-	-
Illinois	159	48	-	48
Indiana	74	42	-	2
Louisiana	349	167	42	-
New Jersey	80	48 ²	-	-
Ohio	82	49 ²	-	-
Oklahoma	75	45 ²	-	-
Pennsylvania	114	58	-	10
Texas	721	433 ²	-	-
Other States	495	238 ⁵	<u>-</u>	_60
	2,568	1,348	42	152

¹Capacity utilization of 60% used to estimate crude throughput (Reference 112)

²State regulations require all separators to be covered.

 $^{^{3}}$ Only three large refineries covered by regulation requiring covers. This accounts for 40% of crude throughput.

⁴Assumes 90% of crude throughput designated to covered separators. Some small refineries assumed to be exempt.

 $^{^{5}\}mbox{Assumes}$ 85% of crude throughput designated to covered separators.

85 percent of the separators will be located in states requiring covered separators, 5 percent in states requiring partially covered separators, and 10 percent in states with no regulations.

3.4.3 Air Flotation Systems

There are currently no state regulations that apply directly to controlling VOC emissions from air flotation systems. However, some states may apply regulations applying to oil recovery facilities to air flotation. Further, new source reviews of refinery sites may call for control of emissions from air flotation. California is one state where new source reviews have been applied to these systems. Two refineries have been located that control emissions from air flotation for odor control purposes. Both of these refineries are located in California. 70,71

Control of emissions from air flotation would be on a site specific basis. Because of this, it is difficult to determine how may, if any, new air flotation systems would be controlled. Therefore, baseline control for air flotation systems is assumed to be no control.

Current nationwide VOC emissions from air flotation systems can be estimated by using the emission factor given in Section 3.2.3.3. It is assumed that 75 percent of the refineries in the U.S. use air flotation. Using this information, current baseline VOC emissions are estimated to be $0.64 \, \text{Gg/year}$.

Baseline emissions from new and modified air flotation systems are estimated to be 84 Mg per year in 1989. This estimate is based on the emission factors presented in Section 3.2.3.3 and the assumption that 50 percent of the new air flotation systems will be DAF systems and 50 percent will be IAF systems. Current information indicates that approximately 30 percent of existing air flotation system are IAF systems. However, the number of IAF systems is expected to increase since this technology is a relatively new application for petroleum refinery wastewater systems. There is no distinct preference for either type of system and therefore, new air flotation systems can be expected to be equally distributed between the two types of systems.

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4. EMISSION CONTROL TECHNIQUES

Petroleum refinery wastewater systems contain several sources of volatile organic compound (VOC) emissions. These emissions result from the evaporation of VOC from oily wastewater at points, or sources, where the wastewater is exposed to the atmosphere. Three sources of emissions are process drain systems, oil-water separators, and air flotation systems. These sources and their uncontrolled emissions have been described in Chapter 3.

There are only a limited number of methods available to reduce VOC emission from refinery wastewater systems. These methods depend upon one or more of the following basic principles:

- o reduction of VOC entering the wastewater system;
- o reducing the surface area of wastewater exposed to the atmosphere; and
- o enclosing the system to isolate it from the atmosphere.

The reduction of VOC entering the wastewater system is very desirable from both an economic and environmental standpoint. Many, if not most, refineries are actively pursuing this approach, and have found it to be cost effective. The reduction can be achieved by reducing either the total quantity of oily water sent to the wastewater system or by reducing the quantity of VOC in the oily water. One plant reported reductions of 50-55 percent in the quantity of fresh water used for cooling towers and boilers. Another refinery reported a reduction of 90 percent in the volume of wastewater.

It must be recognized, however, that there is diversity among refineries in terms of the design and arrangement of their wastewater systems, as well as the volume and composition of wastewaters. Thus, it is difficult to quantitatively define either the general effectiveness of such programs in reducing VOC entering the wastewater system or the resultant reduction in VOC emissions.

Other methods are available for reducing VOC emissions by reducing the surface area of wastewater exposed to the atmosphere and/or enclosing all or part of the emission sources. In a few cases, the effectiveness of some of these methods has been measured or estimated. These methods are discussed in detail in Section 4.1.

There are a number of technologies that are available to either destroy, collect or recover and/or process VOC from gaseous streams which have been captured by a control system. Typical VOC control devices which may be applicable include:

- o flares;
- o carbon adsorption;
- o incineration;
- o condensation;
- o industrial boilers and heaters, and
- o catalytic oxidation.

These control technologies are reviewed and discussed in Section 4.2.

4.1 METHODS FOR REDUCTION OF VOC EMISSIONS

Methods which can be used to reduce and/or capture VOC emissions from sources in the wastewater system are described in the following sections.

4.1.1. Process Drains and Junction Boxes

Process drains and junction boxes, as described in Section 3.2.1, make up the wastewater collection system within a refinery. The VOC emissions result from vaporization from the open surfaces of drains and vents on the junction boxes. The technologies for reducing these emissions are discussed below.

4.1.1.1 <u>Methods for Controlling VOC Emissions</u>. The alternatives for reducing emissions from oily water process drains and junction boxes involve some type of closure or seal. A common method involves the use of a P-leg

in the drain line with a water seal. A less common, but more effective method, is a completely closed drain system. Junction box emissions can be reduced with a water-filled seal pot.

As described in Section 3.2.1, many refinery drains are connected directly to lateral sewer lines, which in turn are generally connected to several other drains. There is no seal or other means for preventing VOC vapors present in the sewer line from escaping to the atmosphere through the open drains. A water seal in the drain can result in a reduction in the emissions from open drains.

A P-leg water seal was discussed in Section 3.2.1.2. Such a seal could prevent a substantial portion of the VOC in the drain system from entering the atmosphere. It is possible that some emissions will occur from the surface of the liquid seal in the leg of the trap which is open to the atmosphere. Emissions will be less than those from an open drain unless the drain is allowed to dry out and the water seal is lost.

The vent lines from sealed junction boxes may be equipped with water-filled seal pots, as discussed and illustrated in Section 3.2.1.3. As long as the seal pot is filled with liquid, it will provide an effective barrier for emissions. The only means whereby VOC emissions can occur are by diffusion through the water seal, a breach of the water seal, or from leakage around the cover of the junction box. A small, continuous flow of water can be directed into the seal pot to keep it filled to the desired level. Leaks around the cover can be eliminated or minimized by proper seals or caulking. Pressure/vacuum valves could also be used to prevent emissions from junction box vents. However, use of this control technique has not been found in an operating refinery.

There are several factors which affect the performance of water-sealed drains and junction boxes in reducing VOC emissions. Some of these factors are the drainage rate, composition of the liquid entering the drain, temperature of the liquid entering the drain, and

ambient atmospheric conditions. The most important factor in the performance of the junction box seal pot is the pressure within the junction box. If a significant pressure buildup occurs, the water seal will be breached and VOC will be emitted from the vent.

As discussed previously in Section 3.2.1, a completely closed drain system was observed in a BTX unit at one refinery. This system prevents exposure of any oily wastewater to the atmosphere within the process unit. Thus, VOC emissions to the air are completely eliminated within the process unit. This is assuming that the system does not leak.

In this type of control system the mouth of the vertical drain riser is closed with a flange. Equipment drain lines are piped into the flange or directly into the perimeter of the drain risers depending on the number of connecting lines required per drain. The waste liquid flows into the drains which are connected to lateral sewer lines. Drainage flows through the underground lateral drains to a buried collection tank. The collected liquid is pumped to an oil-water separator. A fuel gas purge removes VOC to a control device. The entire system is purged by the fuel gas and is maintained at a very slight positive pressure ($\sim 0.5 - 1.0$ " H₂0).

Since the system is completely closed, there are very few factors which would seriously affect its performance with the exception of equipment failures and equipment leaks. Parameters such as wastewater flow rates, wastewater composition, and system temperature may affect the amount of material being directed to the control device, but emissions within the unit will be unaffected.

4.1.1.2 <u>Effectiveness of VOC Emission Controls</u>. The effectiveness of water seal drain in reducing VOC emissions has been evaluated using two methods. First, process drains at three petroleum refineries were screened for VOC concentration with a portable hydrocarbon analyzer. And second, a theoretical analysis of the effectiveness of water seals was conducted. These two methods are discussed below.

A portable organic vapor analyzer (OVA) was used to screen drains at three refineries. The drains at one refinery were uncontrolled.⁵ The

drains at the second refinery were equipped with water seals.⁶ And the drains at the third refinery were equipped with seal pots having caps which could be manually removed.⁷ The drains having seal pots were screened with the cap in place and after the cap had been removed. Removing the cap broke the water seal on the drain and left the drain in an uncontrolled state.

The results of the screening study were analyzed using two approaches. In the first approach, all screening values from uncontrolled drains were averaged and compared with the average of all screening values from controlled drains. A total of 200 screening values for controlled drains were included in the analysis and 169 screening values for uncontrolled drains. The averaged screening values were converted to leak rates using the correlation established in an EPA study of atmosphere emissions from petroleum refineries. This correlation is as follows:

 Log_{10} (Non Methane Leak Rate, ppmv) = -4.9 + 1.10 Log_{10} (Max. Screening Value)

The leak rate for controlled drains was 0.00353 lbs/hr. The leak rate for uncontrolled drains was 0.00592 lbs/hr. Based on the leak rates derived from averaging screened values, the emission reduction achieved by water seals is approximately 40 percent.

The second approach used to evaluate the screening results was to evaluate the drains at the refinery having capped drains both before and after the cap was removed. Seventy-six drains were evaluated using this method. The number of drains evaluated is smaller than the total number of drains screening because some drains were already uncapped, the caps could not be removed, or the data taken were for various reasons unusable (e.g. cap was not sealed, cap could not be put in place, or another VOC source was near drain). If multiple readings were taken on one drain, the last reading was used in the analysis if it was the lowest of a

consistently declining set of readings. If multiple readings varied substantially for the same drain, an average value was used. The results of this approach are shown in Table 4-1. The results indicate an emission reduction of approximately 50 percent.

A further analysis grouped drains into two categories to see if the uncontrolled leak rate had any effect on the emission reduction that could be achieved. Those with uncontrolled screening values less than 100 ppm were placed in one group while those with values greater than 100 ppm were placed in a second group. Of the 76 uncontrolled drains that were screened, 18 had values greater than 100 ppm. The screening value, estimated leak rate, and the emission reduction factor for each of these drains is shown in Table 4-2.

As shown in the table, the average emission reduction was approximately 50 percent. In most cases, the percentage reduction for individual drains was greater than 50 percent. One drain had a negative percentage reduction. If this value is removed, the emission reduction would be 74 percent.

Based on the analyses of drains screening data, emission reductions of 40 percent to 50 percent are achievable by water seal drains. Values for a specific drain can vary from 0 percent to 99 percent.

A theoretical analysis of the effectiveness of water seal drains was also conducted. As discussed in Chapter 3, emissions from drains are primarily influenced by the forces of convection and diffusion. Three types of drains were evaluated using benzene as an example compound: an uncontrolled drain, a P-trap water sealed drain with no contaminated water and a P-trap water sealed drain saturated with benzene from a contaminated stream.

The benzene emissions due to molecular diffusion through the water seal were estimated based on the equation presented in Section 3.2.1.3. The assumptions used to estimate emissions are presented in Table 4-3. The emissions due to convection were estimated based on a study which showed that the total emissions due to convection and molecular diffusion were 1.0 to 31.7 (average of 25) times molecular diffusion. ¹⁴ This value was then adjusted to account for windspeed by by making three assumptions. First, it

TABLE 4-1. SUMMARY OF SCREENING VALUES FOR INDIVIDUAL DRAINS

# of Drains Screened	Type of Drain	Leak Rate (1bs/hr)	
76	Controlled	0.10184	
76	Uncontrolled	0.20484	

TABLE 4-2. SUMMARY OF EMISSION RATES AND EMISSION REDUCTION FOR DRAINS WITH A LEAK RATE >100 PPM

	Drain	Screening Values		Estimated Emission Rate, LB/HR		Est. Emission Reduction	
Unit	No.	Cap On	Cap Off*	Cap On	Cap Off*	LB/HR	<u>%</u>
27.1	6 7	12	1,000	0.00019	0.02512	0.02493	99.
	7	10	100	0.00016	0.00200	0.00184	91.
	17	10	120	0.00016	0.00244	0.00228	93.
26.2	3	4	100	0.00005	0.00200	0.00195	97.
27.2	1	40	110	0.00073	0.00222	0.00149	66.
	1 2 3	2,000	1,750	0.05384	0.04649	-0.00735	-15.
	3	7	300	0.00011	0.00668	0.00657	98.
	11	50	300	0.00083	0.00792	0.00709	89.
		40	400	0.0000	0,00,52	***************************************	
	12	10	178	0.00016	0.00376	0.00360	97.
25	11	8	300	0.00012	0.00668	0.00656	98.
	19	120	400	0.00244	0.00917	0.00673	73.
	23	20	120	0.00034	0.00244	0.00210	86.
	69	12	150	0.00019	0.00312	0.00293	93.
	. 83	7	200	0.00011	0.00428	0.00417	97.
	84	70	100	0.00135	0.00200	0.00065	32.
	85	70	300	0.00135	0.00668	0.00533	79.
	86	1,000	1,500	0.02512	0.03924	0.01412	36.
	94	8	150	0.00012 0.08737	0.00312 0.17536	0.00300 0.08800	<u>96.</u> 50.

^{*}Reading(s) taken after cap had been removed for a while.

TABLE 4-3. ASSUMPTIONS FOR ESTIMATING BENZENE EMISSIONS FROM EXAMPLE DRAINS

Uncontrolled Drain

- Benzene concentration in vapor phase = 0.125 atm Wastewater temperature = 150°F Ambient temperature = 70°F

- Drain diameter = 4 in
- Length of drain = 4.25 ft
- Average temperature in drain = 110°F
- Diffusion coefficient in air = 0.097 cm²/sec
- Total mass transport 150 times molecular diffusion
- Benzene concentration at top of drain = 0 mg/L
- Wind speed = 10 ft/sec

P-Trap Water Sealed Drain with Clean Wastewater

- Length of water seal = 1.6 ft
- Temperature of water seal = 68° F
- Drain diameter = 4 in
- Length of drain above water seal = 2.25 ftDiffusion coefficient in water = $1.02 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 68°F
- Henry's Law applies
- Henry's Law coefficient = 5.49×10^{-3} atm/m² mole
- Concentration at bottom of water seal in equilibrium with vapor phase
- Concentration of benzene at top of water seal = 0 moles/L
- No convection (i.e., diffusion through water seal controls mass transfer)

P-Trap Water Sealed Drain with Contaminated Wastewater

- Water seal saturated with benzene
- Temperature of water seal = 68° F
- Length of drain above water seal = 2.25 ft
- Diameter of drain = 4 in
- Benzene concentration at top of drain = 0 mg/L
- Solubility of benzene in water = 1780 mg/l
- Total mass transport 150 times molecular diffusion
- Continuous wastewater flow into drain
- Wind speed = 10 ft/sec
- Diffusion coefficient of benzene in air = 0.085 cm²/sec

References: 10,11,12,13,14,15

was assumed that the mass transfer coefficient for benzene is proportional to $\mu^{0.78}$, where μ is the windspeed. 14 Second, it was assumed that the windspeed at which the convection data was collected was not greater than one ft/second. And finally, windspeed used for the example calculations was 10 ft/second. Based on the above, the mass flux of benzene was calculated to be 150 times molecular diffusion.

The benzene emissions due to diffusion through the water seal were calculated based on the following equation: 12

$$N_A = D_V A C_{AV} (X_{A1} - X_{A2})$$

$$B_T \frac{(X_{B1} - X_{B2})}{\ln (X_{R2}/X_{R1})}$$

Where:

 D_V = Diffusion coefficient

 B_T = Length of water seal

 C_{AV} = Average benzene concentration

 X_{A1} = Initial mole fraction of benzene

 X_{A2} = Final mole fraction of benzene

 X_{B1} = Initial mole fraction of water

 X_{B2} = Final mole fraction of water

A = Cross sectional area of drain

Based on the above discussion along with the assumptions presented in Table 4-3, the benzene emissions from each drain configuration were calculated. The results are presented in Table 4-4.

As shown in the table, the clean water seal is estimated to reduce emissions by about 99.9 percent over the uncontrolled drain. This reduction is due to the elimination of the effects of convection. The water seal also acts as a barrier to molecular diffusion, greatly slowing down the movement of benzene through the drain.

The estimate of emissions from a water seal saturated with benzene show how the seal could lose its effectiveness. The emissions from a water seal contaminated with benzene was calculated to be 555 gm/day. This is over 1.7 times the rate of an uncontrolled drain and over 2 x 10^5 times the emission rate from an uncontaminated water seal. The increase in emissions over an uncontaminated water seal is due to the fact that benzene does not have to diffuse through a water seal. The length of the diffusion path is greatly reduced and the convection effects are not eliminated.

In an actual refinery sewer system, there will be both contaminated and uncontaminated water seals. The larger percentage will be uncontaminated water seals as shown by the drain screening data. Of the 76 drains with caps properly placed, only three had a screening value of 100 ppm or greater in the controlled states (caps on). The low screening values of the other 73 drains indicate very little or no contamination. Additionally, the vapor space in the sewer pipe may not be saturated with hydrocarbon as assumed in the example calculations. Only 19 drains at the refinery having capped drains were found to have a screening value of 100 ppm or greater with the cap off, and only six drains had values between 50 and 100 ppm.

Using both the screening analysis and theoretical analysis as bases, it is estimated that water seal drains reduce VOC emissions by 50 percent. The screening study indicates emission reductions of 40 to 50 percent are achievable. The theoretical analysis indicates that emission reduction may be much greater, particularly with a well maintained water seal. Water seals can be maintained by periodic inspection of the drains to ensure the seal is in place.

TABLE 4-4. BENZENE EMISSIONS FROM EACH DRAIN CONFIGURATION

CONFIGURATION	EMISSIONS DUE TO MOLECULAR DIFFUSION(gm/day)	EMISSIONS DUE TO CONVECTION (gm/day)	TOTAL EMISSIONS (gm/day)	
Uncontrolled Drain	2.1	312	315	
Uncontaminated Controlled Drain	0.0026		0.0026	
Contaminated Controlled Drain	3.7	551	555	

A completely closed drain system can capture virtually 100% of the VOC emissions. The overall reduction in VOC emissions will depend on the efficiency of the control device. For example, a smokeless flare can achieve about a 98 percent destruction efficiency.

4.1.2 Oil-Water Separators

Oil-water separators, as described in Section 3.2.2, rely on gravity separation to remove the oil fraction of the wastewater stream. The VOC emissions occur as a result of vaporization from the open surfaces of uncontrolled separators. The technologies for reducing these emissions are described below.

- 4.1.2.1 <u>Methods for Controlling VOC Emissions</u>. The most effective method for controlling VOC emissions from oil-water separators is to use either floating or fixed covers. ⁹ This will reduce VOC emissions by:
 - o Reducing the oil surface exposed to the atmosphere,
 - o Reducing the effects of wind velocity,
 - o Insulating the oil layer from solar radiation.

A fixed cover can be installed on most separators without interfering with the oil-skimming system. The cover may be constructed of various materials including truncated case aluminum segments, steel plates, or concrete. 18,19,20,21 The roof can be mounted on the sides of the separator or supported by horizontal steel beams set into the sides of the tank. 18,22 The covers usually have gas tight access doors which are used for inspection and maintenance. 21,22 The space between the cover and the edge of the separator can be sealed using a urethane or neoprene gasket. 18,22

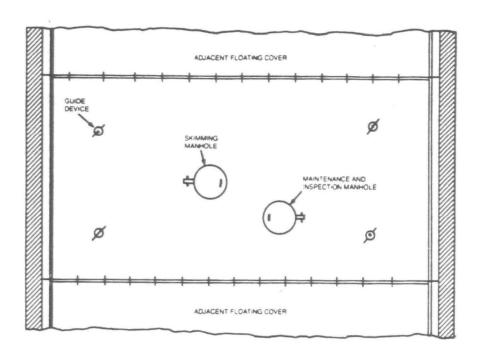
The vapor space present under fixed covers may constitute an explosion or fire hazard. In order to eliminate this problem the vapor space can be blanketed with either plant gas or an inert gas, such as nitrogen. ¹⁹ Additionally, the vapor space can be purged with air, steam, inert gas or product gas, and the vapors sent to a recovery or destruction device. Such a system can greatly reduce VOC emissions. The technologies used to control VOC gases are discussed in Section 4.2.

In contrast to fixed roofs, which are always above the oil layer, floating roofs actually float on the oil surface. This eliminates most of the vapor space above the liquid, thus greatly reducing the potential for volatilization from the oil layer. To prevent the roof from interfering with the operation of the flight scraper, the water level can be raised in the separator so that the top of the oil surface is above the flight scraper blades. An example of a floating cover on an API separator is shown in Figure 4-1.

The cover can be constructed of plastic or glass foam blocks, aluminum pontoons or fiberglass. ^{18,24,25} Gas tight doors can be installed in the roof for inspection and maintenance. ¹⁸ To prevent VOC from leaking around the edges of the cover, seals are used between the cover and the walls of the separator. These seals are usually resilient foam wrapped with a coated fabric. The seal is placed in direct contact with the edge of the cover and the separator wall. One manufacturer of floating roof covers uses a polyurethane foam wrapped with a nylon-polyurethane fabric. ²⁶ This seal is shown in Figure 4-2.

There are several factors which can affect the overall performance of the two types of covers in reducing VOC emissions. The most obvious is the degree of maintenance. The seals must be kept in good condition to minimize leakage around joints and seals. With the exception of leakage, the control effectiveness of closed systems which are vented to recovery or destruction devices is relatively insensitive to variations in system parameters. The efficiency of those covered units which are vented to the atmosphere depends on system variables such as VOC content of the incoming water, the temperature of the liquid phase, the ambient temperature, amount of solar insulation, extent of surface area, and thickness of the oil layer. All of these factors were discussed in detail in Section 3.2.2.2.

4.1.2.2 <u>Effectiveness of VOC Emission Controls</u> Very little data are available regarding the reduction of VOC emissions which can be achieved by installing a cover over an oil-water separator. The only published study, done by Litchfield, found that by using 2 inch thick Foamglas slabs as a



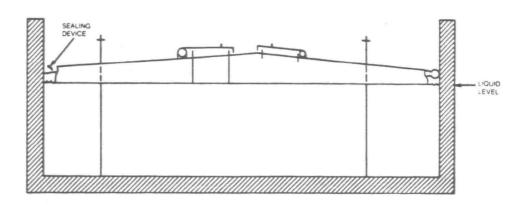


Figure 4-1. Floating Cover on an API Separator. 23

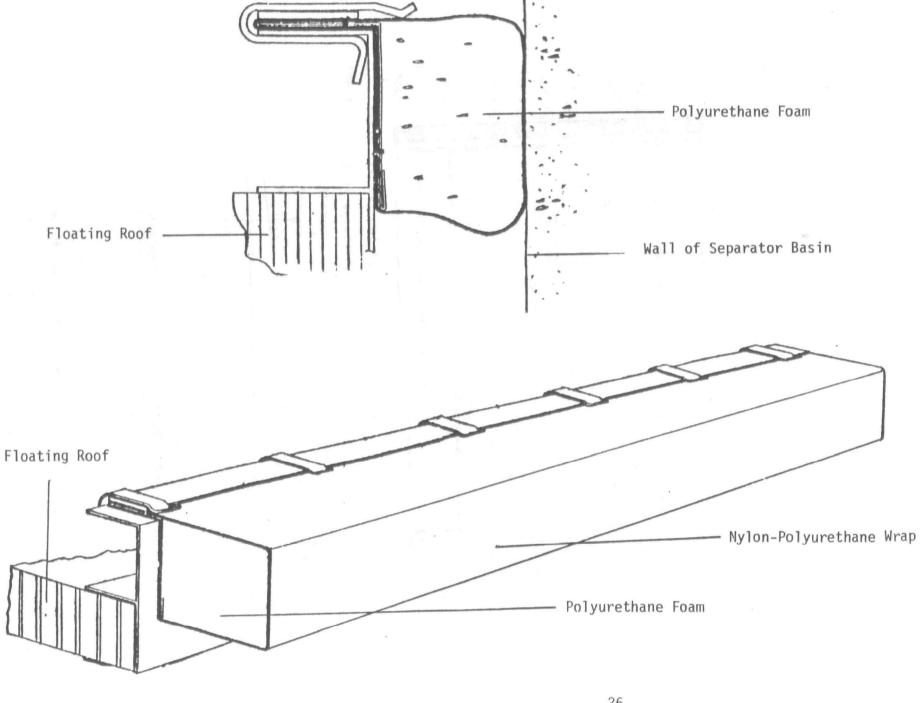


Figure 4-2. Polyurethane Foam Seal on a Floating Cover. 26

floating cover, the evaporation losses could be reduced by 85 percent. 23 Other sources report varying levels of emission reduction but give no supporting documentation. The American Petroleum Institute stated that a floating or fixed cover would reduce emissions by 90 percent to 98 percent. 27 In AP-42, an emission reduction value of 96 percent was reported. Eurther, in a recent study the State of California estimated that a 90 percent reduction in emission could be achieved by using covers. 29

The reduction in VOC emissions which can be obtained using a cover was assumed to be 85 percent. This factor is based on the only documented study, done by Litchfield. 23 It is assumed that a fixed roof and a floating roof provide equivalent control efficiency.

The addition of a fixed roof vapor collection system, and direction of the collected vapor to a control device, will result in a greater overall control of captured VOC emissions. Due to some possible leakage, the capture efficiency of the roof in this type of control system would be approximately 99 percent. The actual efficiency of the system will depend on the efficiency of the control device. For example, the efficiency of a flare is estimated to be 98 percent. Therefore, the overall efficiency of a fixed roof with vapors vented to a flare would be 97 percent $(0.99 \times 0.98 = 97\%)$. The efficiencies of various control devices are discussed in Section 4.2.

4.1.3 Air Flotation Systems

Air flotation systems are used to remove free and emulsified oil, suspended solids, and colloidal solids from refinery wastewater. Their operation has been described in Chapter 3.2.3. VOC emissions occur as a result of volatilization from the exposed surface of the air flotation system. The methods for controlling these emissions are described below.

4.1.3.1 <u>Methods for Controlling Emissions</u> Methods for controlling VOC emissions from air flotation systems differ depending upon the type of air flotation system. Induced air flotation systems (IAF) usually are equipped with a cover while dissolved air flotation systems (DAF) are open to the

atmosphere. Gas or air used for flotation in an IAF is usually recirculated in the vapor space while the gas or air used for flotation in a DAF is introduced into the system from an outside source.

Control of VOC emissions from an IAF can be accomplished by operating the IAF under gas tight conditions. IAF systems usually are equipped with a cover on top and eight access doors on the sides. The access doors can be gasketed and tightly sealed during operation of the system. A slight negative pressure is created in the vapor space of the IAF due to the action of the impellers or recycled wastewater. The impellers or recycled wastewater create a vortex which draws gas or air into the wastewater. The only emissions resulting from a gas tight IAF would be from breathing losses. The breathing losses would result in VOC being emitted through an atompheric vent or pressure/vacuum valve located on the roof of the cover. The pressure/vacuum valve is needed to safely operate the system.

VOC emissions from DAF systems can be controlled by placing a fixed cover on the flotation chamber. Because of the slight positive pressure created by the flotation gas or air, the cover must be provided with an atmosphere vent or vent equipped with a pressure/vacuum valve. Only fixed covers can be used for DAF systems due to the design of the systems. Floating covers would interfere with the skimming devices and inhibit the formation of floating oil and suspended solids. Fixed covers would be of the same type and design as covers discussed for oil-water separators. At least two refineries presently use fixed covers with atmospheric vents on DAF systems. 30,31

A more stringent level of control for both IAF and DAF systems would be to completely seal the flotation chamber with a fixed cover and vent the captured VOC to a control device Incinerators, flares, process heaters, or carbon absorbers are some of the devices used to control the collected vapor. VOC emissions captured by a fixed cover are diverted to the control device using air, inert gas (such as nitrogen), or plant gas to purge the vapor space. ^{18,20,32,33,6}

Four refineries have been identified as using emission control systems with captured VOC vented to a control device. In one refinery, the two DAF

systems used in the wastewater treatment system are covered and the vapors are collected. The collected vapors are directed to an incinerator. Nitrogen is used as the DAF flotation gas and fuel gas from the plant fuel gas system is used as the source of fuel for the incinerator. The control system shown in Figure 4-3 was installed by the refinery to control odors arising from the wastewater system.³⁴

A second refinery uses a segregated wastewater system. The bulk of the oily wastewater is treated by two DAF's operating in parallel to treat the effluent from the one oil-water separator. The flotation chambers are covered, and the vapors are collected and directed to an activated carbon bed. An IAF unit is also used to treat effluent from a second oil-water separator. The IAF is also covered, and its vapors are collected and directed to two 55-gallon drums filled with activated carbon. The system was installed to eliminate odor problems, ³² and is shown in Figure 4-4.

The third refinery uses fuel gas in the DAF systems. The flotation chambers are covered and the vapors are recycled to the refinery fuel gas system. 33 Another refinery uses purge air to direct emissions from the IAF unit to a process heater. 6

4.1.3.2 Effectiveness of VOC Emission Controls The effectiveness of emission control techniques differs between the IAF and DAF systems. An IAF is usually provided with a cover and some emission reduction results due to this cover. Operating the IAF with the access doors in a closed state achieves additional reduction in emissions. The DAF system usually is not equipped with a cover and is therefore in a totally uncontrolled state.

Emission reduction achieved by covering a DAF will be less than that for a gas-tight IAF or a covered oil-water separator. This is due to the slight positive displacement of gas caused by the flotation mechanism. Theoretical analyses presented in Section 3.2.3.2 examined the effects of evaporation and air stripping on emissions from a DAF. Example design specifications for the DAF were chosen and input parameters based on the test results were used in calculating emissions. These input parameters included the influent oil concentration and influent benzene

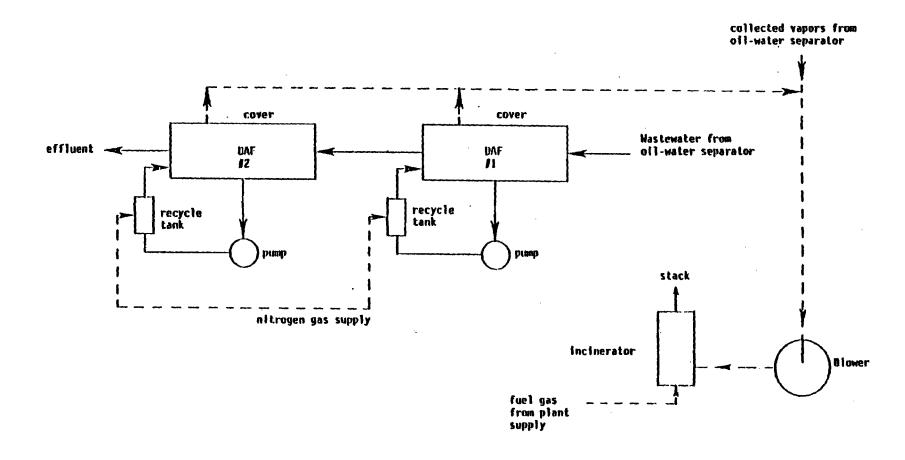
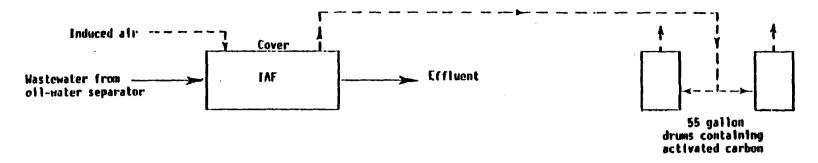


Figure 4-3. Example of DAF Emission Control System.



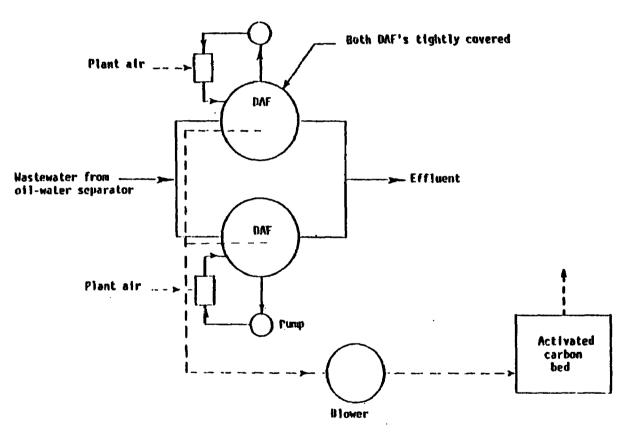


Figure 4-4. Examples of DAF and IAF Control Systems.

conconcentration. Appropriate calculations were then used to estimate benzene losses due to evaporation and air stripping. The analyses indicate that the major cause of emissions is evaporative losses. Evaporative losses have been estimated to account for 90 percent of the total losses. It is assumed that covering a DAF will reduce the evaporative losses by 85 percent, as determined by Litchfield. The air stripping losses would continue to be emitted through the atmospheric vent. Therefore, the overall emission reduction achieved by a fixed roof will be (0.9)(0.85) = 77 percent. 35,36

An estimate of the emission reduction achieved by a completely gasketed and sealed IAF can be made using test data, a laboratory study, and engineering judgment. Consideration must first be given to the emission reduction achieved by an IAF operating under "normal" conditions. A typical IAF is expected to be operated with the doors closed but not gasketed and sealed. The emission reduction achieved by a gasketed and sealed IAF can be estimated by calculating an emission factor for an IAF operating under four conditions: completely uncovered; covered with the doors open; covered with the doors closed but not gasketed; and covered with the doors gasketed and sealed.

As mentioned in Section 3.2.3.3, the emission potential of an uncovered IAF is approximately 15.2 kg/MM gallons of wastewater. This emission factor is based on test data. An emission factor for a covered IAF with all the access doors open can be estimated using engineering judgment. In Section 4.1.2.2, it is estimated that a tightly sealed cover on an oil-water separator will reduce emissions by 85 percent. This estimate is based on the Litchfield Study. It is assumed that a cover on an IAF would reduce the emissions from the top of the IAF by 85 percent. An IAF system with all the access doors open would have 50 percent of the surface area exposed. This estimate is based on design specifications of an IAF provided by a vendor. Therefore, 50 percent of the emissions from the IAF (through access doors) are completely uncontrolled while the other 50 percent (through the top) are controlled by 85 percent. Thus the emissions from an IAF operating under this condition are 15.2-(15.2) (0.5) (0.85) = 8.7 Kg/MM gal.

The emission reduction achieved by an IAF with the doors closed can be estimated using data from a study conducted by the Chicago Bridge and Iron Company. In this study, emissions were measured from drums filled with hexane. Different levels of control were placed on the drums. One level of control included a cover having 1/8" gaps between the tank wall and the cover. The second level of control included a cover with an 8 inch diameter opening. Extropolation of the emission results from this experiment can be used to estimate emissions from an IAF with the doors closed (but not gasketed) and an IAF with the doors open.

In the CBI study, the 8-inch opening in the drum represents 12.6% of the total surface area of the cover. As discussed above, if all the access doors in an IAF are open, 50% of the surface area of the IAF is exposed. Assuming a proportional relationship between exposed surface area and emissions, the emissions from the drum (with 50 percent of the surface area exposed) can be estimated as follows:

$$\frac{12.6 \%}{0.02 \text{ lb/hr}} = \frac{50 \%}{X}$$

$$X = 0.079 \text{ lbs/hr}$$

The emission rate from the drum having a cover with a 1/8" gap between the cover and drum walls was measured to be 0.02 lbs/hr. This represents a 75 percent reduction over the drum with 50 percent of the surface area exposed. Extrapolating these data to an IAF systen, it can be estimated that a 75 percent reduction will occur if the doors are closed (over the case where the doors are left open). This results in an emission factor of 15 - (15) (0.5)(0.25) - (15) (0.5) (0.75) = 3.0 Kg/MM gallon for an IAF with the doors closed but not gasketed and sealed.

As mentioned above the emission reduction achieved by an oil-water separator equipped with a tightly sealed cover is 85 percent. Therefore, it is assumed that the emission reduction for a tightly sealed IAF would also be 85 percent. An 85 percent emission reduction over the uncontrolled state

would result in an emission factor of 2.3 kg/MM gallon for the IAF. Therefore, the emission reduction achieved by gasketing and sealing an IAF is 3.0 - 2.3 = 0.7 kg/MM gallons, a 23 percent reduction from the typical operating condition.

The emission reduction achieved by tightly covering a DAF or IAF and venting the captured emissions to a control device will be dependent on the efficiency of the control device. Venting the emissions to a control device will require some type of purging system. As discussed in Section 3.2.3.3, the emission potential of the DAF and IAF is equal when both systems are purged. However, the percentage emission reduction achieved by the vent system will be less for the IAF because some control is achieved by the cover normally found on the system. For example, tightly covering a DAF and venting the emissions to a flare will reduce emissions by approximately 97 percent. This assumes a 99 percent capture efficiency for the roof and a 98 percent destruction efficiency for the flare. The destruction efficiency of a flare has been established by a number of studies which are discussed in the following section. Tightly covering an IAF and venting the emissions to a flare will reduce emissions by 85 percent. Although the amount of VOC captured and destroyed is equivalent to that for the DAF, the percentage reduction from the uncontrolled state is less since some control is achieved by the cover normally found on the "uncontrolled" IAF.

4.2 CONTROL OF CAPTURED VOC

There are several methods that may be used to control VOC emissions, either by recovery of VOC from gas streams or by destruction of the VOC by means of combustion. These methods include the following:

- o flare systems;
- o carbon adsorption;
- o incineration:
- o condensation;
- o industrial boilers and process heaters; and
- o catalytic oxidation.

Some of these control methods, such as flare systems, incineration, carbon adsorption, and process heaters have been applied to the VOC emissions from refinery wastewater sources. Others have the potential for application to these sources. All of the above listed control methods are described in the section which follow. In addition, factors which affect their performance are discussed and control efficiencies are defined.

4.2.1 Flare Systems

Flares are a method of controlling VOC emissions by thermal destruction. This is a proven technology that is used for controlling a wide range of gaseous emissions. A brief description of the technology, factors affecting its performance, and the potential as a VOC control method for refinery wastewater sources are discussed in this section.

4.2.1.1 <u>Operating Principles</u>. For safety and environmental reasons, refinery discharges of flammable and/or toxic vapors (and liquids) must be either recovered or removed to an appropriate location and destroyed. The vapors are collected and transported through a header or blowdown system. The most widely accepted method of disposing of these vapors is to burn a flare.

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.

There are two types of flares: ground level flares and elevated flares. Kalcevic presents a detailed discussion of different types of flares, flare design and operating considerations, and a method for estimating capital and operating costs for flares. The basic elements of an elevated flare system are shown in Figure 4-5. Process off-gases are sent to the flare through the collection header (1). The off-gases entering the header can vary widely in volumetric flow rate, moisture content, VOC

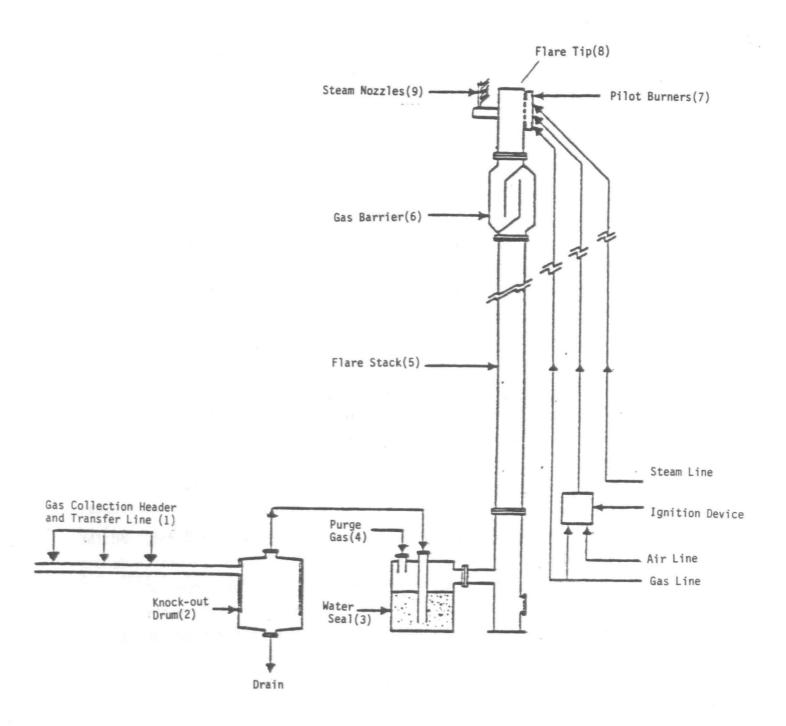


Figure 4-5. Steam-Assisted Elevated Flare System.

concentration, and heat value. The knock-out drum (2) removes water or hydrocarbon droplets that could extinguish the flame or cause irregular combustion. Off-gases are usually passed through a water seal (3) before going to the flare. This prevents possible flame flashbacks, caused when the off-gas flow to the flare is too low and the flame front pulls down into the stack.

Purge gas $(N_2, CO_2, or natural gas)$ (4) also helps to prevent flashback in the flare stack (5) caused by low off-gas flow. The total volumetric flow to the flame must be carefully controlled to prevent low flow flashback problems and to avoid a detached flame (a space between the stack and flame with incomplete combustion) 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). If the gas has sufficient oxygen and 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 fuel flow in a flare requires more combustion air at a faster rate than simple gas diffusion can supply so flare designers add steam injection nozzles (9) to increase gas turbulence in the flame boundary zones, drawing in more combustion air and improving combustion efficiency. This steam injection promotes smokeless flare operation by minimizing the cracking reactions that form carbon. Significant disadvantages of steam usage are the 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 0.15 to 0.5 kg of steam per kg of flare gas is required. Gases with heating values of below about 18 MJ/scm (500 Btu/scf) may be flared smokelessly with steam or air assist.

Steam injection is usually controlled manually with the operator observing the flare (either directly or on a television monitor) and adding steam as required to maintain smokeless operation. Several flare

manufacturers offer devices such as infrared sensors which sense flare 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 expensive steam is not required. Air assist is rarely used on large flares because air flow is difficult to control when the gas flow is intermittent. About 0.8 hp of blower capacity is required for each 100 lb/hr of gas flared.

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 flared gas itself (because of the high nozzle pressure drop) is usually adequate to provide the mixing necessary for smokeless operation and air or steam assist 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. ⁴⁰

4.2.1.2 <u>Factors affecting efficiency</u>. The flammability limits of the gases flared influence ignition stability and flame extinction. (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, H₂ and acetylene) are therefore usually easier to burn. However, in spite of wide flammability limits, CO is difficult to burn because it has a low heating value and slow combustion kinetics.

The auto-ignition temperature of a fuel affects combustion because gas mixtures must be at high enough temperature to burn. A gas with low

auto-ignition temperature will ignite and burn more easily than a gas with a high auto-ignition temperature. Hydrogen and acetylene have low auto-ignition temperatures while CO has a high one.

The heating value of the fuel also affects the flame stability, emissions, and flame structure. A lower heating value fuel produces a cooler flame which does not favor combustion kinetics and also is more easily extinguished. The lower flame temperature will also reduce buoyant forces, which reduces mixing (especially for large flares on the verge of smoking). For these reasons, VOC emissions from flares burning gases with low Btu content may be higher than those from flares which burn high Btu gases.

The density of the gas flared also affects the structure and stability of the flame through the effect on buoyancy and mixing. The velocity in many flares is very low, therefore, most of the flame structure is developed through buoyant forces as a result of the burning gas. Lighter gases therefore tend to burn better. The density of the fuel also affects the minimum purge gas required to prevent flashback and the design of the burner tip.

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 recover hydrocarbons from the flare header system for reuse. Recovered hydrocarbons may be used as a feedstock in other processes or as a 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 which the baseload system is not designed to recover and unrecoverable hydrocarbons. In some cases, the operation of a baseload gas recovery system may offer an economic advantage over operation of a flare alone since sufficient quantity of useable hydrocarbons can be recovered.

4.2.1.3 <u>Control Efficiency</u>. This section presents a review of the flares and operating conditions used in five studies of flare combustion efficiency. Each study summarized in Table 4-1.

Palmer experimented with a 1.3 cm (1/2-inch) ID flare head, the tip of which was located 1.2 m (4 feet) from the ground. Ethylene was flared at 15 to 76 m/s (50 to 250 ft/sec) at the exit, 0.1 to 0.6 MW (0.4×10^6 to 2.1×10^6 Btu/hr). Helium was added to the ethylene as a tracer at 1 to 3 volume percent and the effect of steam injection was investigated in some experiments. Destruction efficiency (the percent ethylene converted to some other compound) was 97.8 percent. 41

Siegel made the first comprehensive study of a commercial flare system. He studied burning of refinery gas on a commercial flare head manufactured by Flaregas Company. The flare gases used consisted primarily of hydrogen (45.4 to 69.3 percent by volume) and light paraffins (methane to butane). Traces of $\rm H_2S$ were also present in some runs. The flare was operated from 30 to 2900 kilograms of fuel/hr (287 to 6,393 lb/hr), and the maximum heat release rate was approximately 68.96 MW (235 x 10^6 Btu/hr). Combustion efficiencies (the percent VOC converted to $\rm CO_2$) averaged over 99 percent. 42

Lee and Whipple studied a bench-scale propane flare. The flare head was 5.1 cm (2 inches) in diameter with one 13/16-inch center hole surrounded by two rings of 16 1/8-inch holes, and two rings of 16 3/16-inch holes. This configuration had an open area of 57.1 percent. The velocity through the head was approximately 0.9 m/s (3 ft/sec) and the heating rate was 0.1 MW (0.3 x 10^6 Btu/hr). The effects of steam and crosswind were not investigated in this study. Destruction efficiencies were 99.9 percent or greater. 43

Howes, et al. studied two commercial flare heads at John Zink's flare test facility. The primary purpose of this test (which was sponsored by the EPA) was to develop a flare testing procedure. The commercial flare heads were an LH air assisted head and an LRGO (Linear Relief Gas Oxidizer) head manufactured by John Zink Company. The LH flare burned 1,043 kg/hr (2,300 lb/hr) of commercial propane. The exit gas velocity based on the pipe diameter was 8.2 m/s (27 ft/sec) and the firing rate was 13 MW

(44 x 10^6 Btu/hr). The LRGO flare consisted of 3 burner heads located 0.9 m (3 feet) apart. The 3 burners combined fired 1,905 kg/hr (4,200 lbs/hr) of natural gas. This corresponds to a firing rate of 24.5 MW (83.7 x 10^6 Btu/hr). Steam was not used for either flare, but the LH flare head was in some trials assisted by a forced draft fan. Combustion efficiencies for both flares during normal operation were greater than 99 percent. 44

A detailed review of all four studies was done by Joseph, et al. in January 1982. 40 A fifth study 45 determined the influence on flare performance of mixing, Btu content, and gas flow velocity. A steam-assisted flare was tested at the John Zink facility using the procedures developed by Howes. The test was sponsored by the Chemical Manufacturers Associated (CMA) with the cooperation and support of the EPA. All of the tests were with an 80 percent propylene, 20 percent propane mixture diluted as required with nitrogen to give different heat content values. This was the first work which determined flare efficiencies at a variety of "nonideal" conditions where lower efficiencies had been predicted. All previous tests were of flares which burned gases which were very easily combustible and did not tend to soot (i.e., they tended to burn smokelessly). This was also the first test which used the sampling and chemical analysis methods developed for the EPA by Howes. The steam-assisted flare was tested with exit flow velocities ranging up to about 19 m/s (63 ft/sec), with heat contents from 11 to 84 MJ/scm (300 to 2,200 Btu/scf) and with steam to gas (weight) ratios varying from 0 (no steam) to 6.86. Air-assisted flares were tested with fuel gas heat contents as low as 3 MJ/scm (83 Btu/scf). Flares without assist were tested down to 8 MJ/scm (200 Btu/scf). All of these tests, except for those with very high steam to gas ratios, showed combustion efficiencies of over 98 percent. Flares with high steam to gas ratios (about 10 times more steam than that required for smokeless operation) had lower efficiencies (69 to 82 percent) when combusting 84 MJ/scm (2,200 Btu/scf) gas.

After considering the results of these five studies, the EPA has concluded that 98 percent combustion efficiency can be achieved by steam-

assisted flares with exit flow velocities less than 19 m/s (63 ft/sec) and combustion gases with heat contents over 11 MJ/scm (300 Btu/scf) and by flares operated without assist with exit flow velocities less than 18 m/s (60 ft/sec) and burning gases with heat contents over 8 MJ/scm (200 Btu/scf). Flares are not normally operated at the very high steam to gas ratios that resulted in low efficiency in some tests because steam is expensive and operators make every effort to keep steam consumption low. Flares with high steam rates are also noisy and may be a neighborhood nuisance.

The EPA has a program under way to determine more exactly the efficiencies of flares used in the petroleum refining industry/SOCMI and a flare test facility has been constructed. The combustion efficiency of four flares (1 1/2 inches to 12 inches ID) will be determined and the effect on efficiency of flare operating parameters, weather factors, and fuel composition will be established. The efficiency of larger flares will be estimated by scaling.

4.2.1.4 Applicability. Flares are commonly used at refineries as emission control devices. They can be used for almost any VOC stream and can handle fluctuations in VOC concentration, flow rate, and inerts content. Flares should be applicable to the control of VOC emissions from oil-water separators, air flotation systems, and closed drains systems. Flares would be particularly attractive for these processes if existing flares are accessible at a given refinery. Small ground flares dedicated to the wastewater treating units might be considered as an alternative to directing the captured VOC emissions into the refinery flare system.

4.2.2 <u>Carbon Adsorption</u>

Carbon adsorption is a method of controlling VOC emissions by fixation of the organic compounds to the surface of activated carbon. When the capacity of the carbon to adsorb VOC is exhausted, the spent carbon is replaced or regenerated. Carbon adsorption is a proven technology for the control of numerous organic compounds from a wide variety of industrial

sources, including refinery wastewater sources.⁴⁶ The theory and operating principles of carbon adsorption have been extensively reviewed in the literature. A brief description of the technology, factors affecting its performance, and its potential as a VOC control method for refinery wastewater sources are discussed in this section.

4.2.2.1 Operating Principles. Two basic configurations of carbon adsorption systems are typically used for VOC control--regenerative and non-regenerative systems.

In regenerative systems, multiple and separate carbon beds are typically used to remove and concentrate organic compounds from a gas stream. The beds alternate adsorption/regeneration duty in a cyclical manner. Regeneration of spent carbon is normally accomplished by <u>in situ</u> thermal desorption of the organics, usually by stripping with low pressure steam. The desorbed organics and steam are condensed and separated. The water phase is reused, further processed, or discarded without further treatment. The recovered organic phase is typically reused. In a refinery application, the recovered organics would be reprocessed or used as fuel.

In non-regenerative systems, the basic absorption mechanism is identical. However, when activated carbon in a non-regenerative system becomes spent, it is simply replaced with a fresh charge. The spent carbon is discarded or reactivated off-site for eventual reuse. Equipment requirements are much less complex, but periodic carbon replacement is necessary.

The feasibility of using regenerative or non-regenerative carbon adsorption for a particular VOC control application is determined primarily by operating economics, with the cost difference largely dependent on the required frequency of regeneration or carbon replacement. VOC sources within refinery wastewater systems are expected to emit varying concentrations and types of organics, but at relatively low total mass rates. Therefore, the activated carbon charge in a VOC control system would probably become spent only at infrequent intervals. For this reason and other described in the following discussion, the less complex

non-regenerative configuration appears to be more applicable to the control of VOC emissions from refinery wastewater sources.

A typical non-regenerative system is shown in Figure 4-6. The effluent gas streams are ducted to one or multiple parallel vessels containing activated carbon particles held in fixed beds. The VOC are adsorbed onto the surface of the carbon, and the treated gas exits at a very low VOC concentration. As the capacity of the carbon bed to adsorb additional VOC is exceeded, the outlet VOC concentration begins to increase. This increase in concentration is referred to as VOC breakthrough and signals the need for carbon replacement.

- 4.2.2.2 <u>Factors Affecting Performance and Applicability</u>. Factors that affect the adsorption capacity of activated carbon in non-regenerative systems include:
 - o VOC type and inlet mass loading;
 - o moisture content of the inlet gas;
 - o temperature of the inlet gas; and
 - o carbon type, amount, and condition.

Similarly, these factors determine the performance and applicability of carbon adsorption as a VOC control method for refinery wastewater sources.

The types of VOC vented to a carbon adsorption system from wastewater sources are variable. The majority of the compounds are low boiling compounds since wastewater system normally operate at temperatures below 140°F. Typical compounds emitted during emissions testing of air flotation systems included paraffins and aromatics such as benzene, toluene, and xylene. The nature of the organics emitted would not result in any significant carbon fouling problems. However, if severe carbon fouling did occur, off-site carbon reactivation (non-regenerative systems) would be the most practical choice, since high boiling compounds are difficult to remove by steam stripping. Furthermore, if the carbon would need regeneration/replacement only infrequently, the organics on the carbon may become even more irreversibly adsorbed due to chemical or polymerization reactions that may occur because of the long residence time on the carbon. While the light

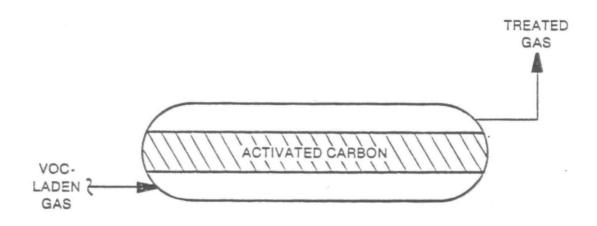


Figure 4-6. Schematic of Non-Regenerative Carbon Adsorption for VOC Control.

molecular weight of the emitted organics may preclude severe carbon fouling, the full potential adsorption capacity of the carbon might not be realized. Activated carbon has a greater affinity for larger nonpolar molecules; very light organics can pass through carbon virtually uncontrolled. 46

The VOC mass rate is determined by the inlet gas flow rate and the VOC concentration. The VOC mass rate is of significance in determining the service life of the carbon. The inlet gas flow rate affects the gas-phase residence time in the bed and therefore the VOC control efficiency. If VOCs are conveyed in an oxygen-containing gas stream, the inlet VOC concentration is of significance for safety reasons—the concentration should be outside of the explosive range of the mixture. In a refinery wastewater control application, the source(s) might be purged with nitrogen or refinery fuel gas to reduce the possibility of oxygen contamination. Nitrogen may be the preferred purge gas; fuel gas would not only increase the chance of an explosive situation but would also represent an additional VOC loading for the carbon adsorption control system.

Moisture content of the inlet gas stream affects the adsorption capacity of the carbon for VOCs. Water vapor competes with organic compounds for adsorption sites, particularly at moisture levels corresponding to relative humidities greater than 50 percent. Therefore, saturation or near-saturation levels of moisture in VOC-laden gas streams from wastewater sources may significantly inhibit the ability of carbon adsorption systems to control VOCs. Demister pads are used by one refinery to remove excess moisture from the VOC gas stream. ⁴⁷

VOC adsorption capacity is inversely related to inlet gas temperature. Most carbon adsorption systems are designed to treat gas streams having temperature lower than 120°F. The temperatures of VOC-laden gas streams from refinery wastewater sources should be within the acceptable range.

Finally, the properties of the carbon within the beds significantly affect the VOC control efficiency. Many types and grades of carbon are available. Selection of the appropriate carbon types and amount will determine its adsorption capability and service life. The ease of

replacement is important to the overall design, whether the carbon is removed from containment vessels (e.g., by vacuum) or whether the containment vessels themselves are removable (e.g., 55-gallon drums). 48

4.2.2.3 <u>Control Efficiency</u>. Well-designed and operated state-of-the-art carbon adsorption systems can reliably remove 95 percent of many types of VOCs from contaminated gas streams. Some systems are capable of achieving VOC control efficiencies exceeding 99 percent. A non-regenerative system tested at one refinery was operating at 90 percent efficiency. This system was controlling VOC emissions from an equalization tank of the wastewater treatment system.

A non-regenerative carbon adsorption system must be designed and operated conservatively and/or be monitored continuously to ensure that it is controlling VOC emissions efficiently. Frequent replacement of carbon and continuous monitoring of the treated exhaust gas for VOC content are two methods whereby maximum VOC control efficiency can be maintained.

4.2.3 Incineration

Incineration, or thermal oxidation, is a method for controlling VOC emissions by high-temperature oxidation of the organic compounds to carbon dioxide and water. Incineration is recognized as the most universally applicable of available VOC control methods because it can be used to destroy essentially all types of organic compounds from a variety of sources, including refinery wastewater sources. 51,52,53 The technology is described briefly in this section, with emphasis placed upon its potential as a VOC control device for wastewater sources.

4.2.3.1 Operating Principles Design specifications for incinerators used for VOC control devices may vary considerably, but the basic design and operating principles are represented by the schematic system shown in Figure 4-7. In this system, the VOC-laden gas stream is ducted from the emission sources to a burner zone. A flame is established in the burner zone by combustion of auxiliary fuel (e.g., refinery fuel gas) and air. The

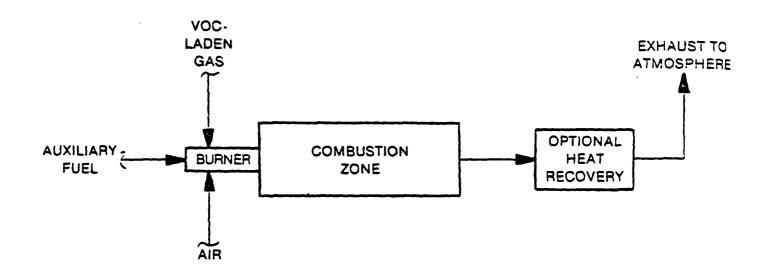


Figure 4-7. Schematic of Incineration System for VOC Control.

high-temperature gases are expanded into a combustion chamber maintained at a constant temperature, typically in the range of 1000°F to 1600°F. The gases remain in the combustion zone for a residence time sufficient to oxidize the VOC, typically 1 second or less. The combustion products are then exhausted to the atmosphere. Heat recovery (e.g., inlet air preheat) can be employed to minimize fuel consumption.

- 4.2.3.2 <u>Factors Affecting Performance and Applicability</u>. A number of factors determine the effectiveness of incineration as a VOC control method. These include:
 - o inlet waste stream characteristics;
 - o temperature;
 - o residence time;
 - o auxiliary fuel/air requirements; and
 - o other design parameters.

The effect of these factors on incineration systems is discussed below.

Incineration represents a flexible control method in terms of inlet VOC type and concentration. Factors relevant to induction of the inlet waste stream from refinery wastewater to an incinerator are similar to those described for carbon adsorption in Section 4.2.2. In summary, oxygen-free purge gases would be preferred. One possible handicap inherent with an incineration system might be the necessity of a relatively constant inlet flow rate. VOC-laden gases can be allowed to "breathe" through a carbon adsorber, but an incinerator may require a steadier inlet flow rate of waste gases from wastewater sources in order to sustain stable flame conditions. An incinerator can handle minor flow fluctuations, but more severe flow fluctuations might require the use of a flare for VOC control. ⁵⁴

Combustion zone temperature can have a pronounced effect on VOC destruction efficiency and auxiliary fuel consumption. The required temperature, which is controlled by the auxiliary fuel flow rate, would be determined by the VOC type and the required level of control. Figure 4-8 represents an example case showing the effect of combustion zone temperature on VOC destruction efficiency.

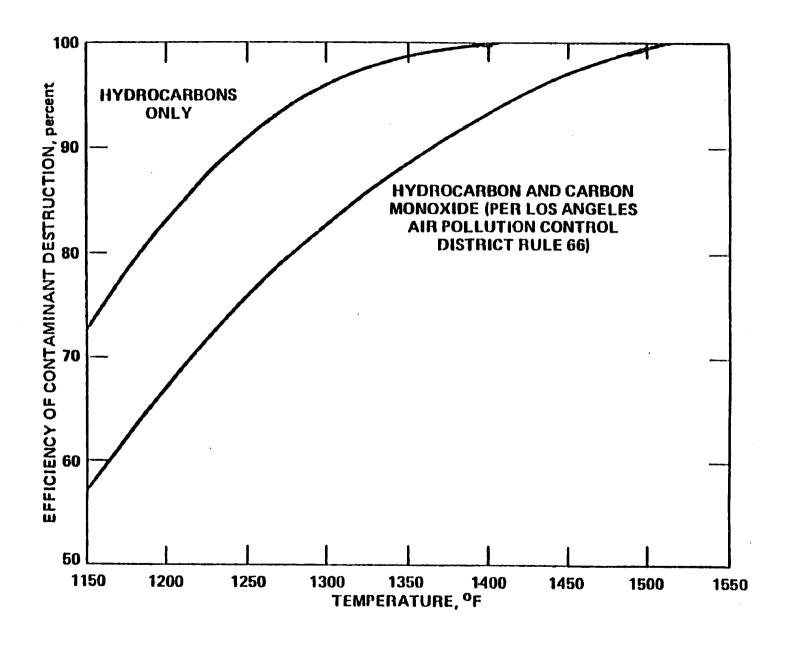


Figure 4-8. Typical Effect of Combustion Zone Temperature on Hydrocarbon and Carbon Monoxide Destruction Efficiency. 55

In addition to combustion zone temperature, gas-phase residence time in the combustion zone also contributes to the degree of completion of the oxidation reaction. Residence times on the order of 0.3 seconds to 1.5 seconds are typical for VOC control applications. 54,55,56,57,58,59

Auxiliary fuel and air requirements also affect the operation of an incinerator. Fuel type affects the design of an incinerator and fuel rate determines its operating costs. Some excess air is required for proper fuel/air mixing and completion of the combustion reaction. However, too much excess air can have a negative impact on auxiliary fuel requirements (heat losses) and design size.

Other factors affect the performance and applicability of incineration as a VOC control method for refinery wastewater sources. A major consideration is heat recovery. Primary or secondary heat recovery is often utilized to minimized operating costs. Primary heat recovery refers to heat exchange between the hot combustion gases and the cool inlet VOC-laden gas or auxiliary air stream. Secondary heat recovery refers to heat transfer between an incinerator gas stream and an adjacent, yet separate, process stream. Use of secondary heat would be limited to those situations in which such a process stream was adjacent and available to serve as a heat sink.

Incineration represents a simple and reliable method of VOC control, but several problems can limit its performance. Fouling can occur, particularly on heat exchange surfaces, although the probability of significant fouling may be low for a refinery wastewater control application. Incinerator internals may be subject to corrosion in the presence of sulfur- or halogen-containing compounds. The existence of the former would be expected in refinery wastewater effluent gases, but its potential for causing corrosion problems in an incinerator is unknown. Also, operation of an incinerator can be expected to result in secondary emissions of oxides of nitrogen, carbon monoxide, and possibly combustion-created organic reaction products. However, proper design and operation of the incinerator should result in negligible secondary emission problems.

4.2.3.3 <u>Control Efficiency</u> Incineration of VOCs from refinery wastewater would be expected to achieve destruction efficiencies equivalent to those achieved in other applications (i.e., 90 percent to 99+ percent at temperatures between 1,000°F and 1,600°F). 54,56,59,60,61 The performance of incineration with regard to VOC destruction efficiency would not be expected to degrade over a period of time, as is typically the case for carbon adsorption and catalytic oxidation systems.

4.2.4 <u>Catalytic Oxidation</u>

Catalytic oxidation is a method of controlling VOC emissions by oxidation to carbon dioxide and water in the presence of a catalyst. Many factors important to the design and operation of a catalytic oxidation VOC control system parallel those of an incineration system, which were described above. Therefore, the discussion in this section will be limited to those aspects of catalytic oxidation that cause it to differ significantly from incineration with regard to VOC control.

4.2.4.1 Operating Principles. Catalytic oxidation featues the use of a metal- or metallic-alloy based catalyst to promote higher rates of VOC/oxygen reactions at lower energy (temperature) levels. Thus, temperature and auxiliary fuel requirements are lowered. A schematic diagram of a typical catalytic oxidation system is shown in Figure 4-9. It is generally similar to the incineration system described previously, except for the presence of a catalyst chamber downstream of the burner zone.

In operation, the VOC-laden gas is typically heated to 500°F to 900°F by contact with hot combustion products of an auxiliary fuel/air burner. The heated gas then enters the catalyst chamber. The catalyst chamber contains the catalyst material fixed on a substrate structure of large surface area (e.g., pellets or a honeycomb configuration). The catalyst consists of platinum-, palladium-, copper-, chromium-, nickel-, cobalt-, managanese-, or rhodium-based material layered onto the substrate. 56,60 VOC oxidation occurs in the catalyst bed, with subsequent release of heat and an increase in temperature. The treated gas, at 700°F to 1200°F, exits the

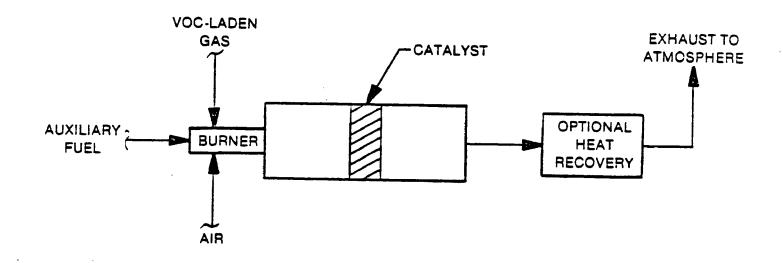


Figure 4-9. Schematic of Catalytic Oxidation System for VOC Control.

reaction chamber and is exhausted to the atmosphere. Temperature is controlled by auxiliary fuel flow rate; the controlling temperature can be measured at the catalyst inlet or outlet or as the average of the inlet and outlet. 52,53,56

4.2.4.2 <u>Factors Affecting Performance and Applicability</u>. Catalytic oxidation present potential advantages over incineration, but its use is limited because of its sensitivity to inlet waste stream characteristics.

If inlet VOCs are relatively heavy in molecular weight, they may collect or polymerize on the catalyst surface, thus reducing the available surface area of the catalyst. Also, the presence of sulfur-, halogen-, or heavy metal-containing compound in the inlet gas can poison the catalyst or suppress its activity. ^{56,60} The presence of the former could be expected in waste gas streams from refinery wastewater. When the catalyst is poisoned or deactivated, a portion of the inlet VOCs can either pass through the system uncontrolled or be converted to aldehydes, ketones, or organic acids. ⁵⁸ Also, typical catalytic oxdiation systems are unable to handle excursions of high inlet VOC concentrations. Excessive VOC loading can increase the heat release in the catalyst bed such that temperatures become high enough to sinter (deactivate) or volatilize the catalyst.

The gradual loss of catalyst activity due to any of the reasons described above introduces additional maintenance requirements for catalyst cleaning and/or replacement.

4.2.4.3 <u>Control Efficiency</u>. Catalytic oxidation systems can achieve VOC destruction efficiencies approaching 99 percent. 60,62 However, certain data indicate that, to achieve destruction efficiencies approaching or exceeding 95 percent, operating temperatures have to increase to levels that threaten to sinter or deactivate the catalyst. Recent test data for catalytic oxidation systems used in other industrial for VOC control indicate that half of the tested units achieved greater than 90 percent VOC destruction. The remaining tested units were capable of achieving 80 or 90 percent VOC destruction. 57

4.2.5 Condensation

In a vapor containing two components, one of which is essentially non-condensible at system conditions, condensation of the condensible component occurs when its partial pressure exceeds its vapor pressure. Any component in a vapor mixture can ultimately be condensed if the temperature is lowered far enough. The point where condensation first occurs is called the dew point. As the vapor is cooled below the dew point, condensation will continue until the partial pressure in the vapor phase is once again equal to the vapor pressure of the liquid phase at the lower temperature.

In the cases where the hydrocarbon concentration in the gas phase is high, condensation is relatively easy. When concentrations are low, condensation at reasonably achieved temperatures can be difficult. Table 4-5 contains some examples of the temperatures required to achieve 90-95 percent condensation of some organic solvents. It can be seen that relatively low temperatures are needed, even for compounds such as xylene, toluene, benzene and hexane. These compounds are commonly found in gaseous emissions from wastewater systems.

There are two ways to obtain condensation. First, at a given temperature, the system pressure may be increased until the partial pressure of the condensible component exceeds its vapor pressure. Alternately, at a fixed pressure, the temperature of the gaseous mixture may be reduced until the partial pressure of the condensible component exceeds its liquid-phase vapor pressure. In practice, condensation is achieved mainly through removal of heat from the vapor. Also in practice, some components in multicomponent condensation may dissolve in the condensate even though their boiling points are below the exit temperature of the condenser.

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

Most surface condensers are common shell-and-tube heat exchangers. The coolant usually flows through the tubes and the vapors condenses on the

Table 4-5. Physical Constants and Condensation Properties of Some Organic Solvents. 63

Compound	Normal Boiling Point, °F	LEL.	25% of LEL Concentration		90% Condensation From 25% of LEL		95% Condensation From 25% of LEL		90% Condensation From 200 ppm	
			Partial Pressure, mm of Hg	Dew Point, °F	Partial Pressure, mm of Hg	Temp,	Partial Pressure, mm of Hg	Temp, °F	Partial Pressure, mm of Hg	Temp,
Dodecane	421	0.6	1.1	120	0.11	61	0.55	54.4	0.15	19
Pinene C ₁₀ H ₁₆ (Terpentine)	3 00	0.7	1.3	53	0.13	116	0.065	-31.4	0.015	-60
0-xylene C ₈ H ₁₀	280	1.0	1.9	26	0.19	-31	0.095	-36.5	0.015	-72
Toluene C ₇ 11 ₈	211	1.4	2.7	5	0.27	-51	0.135	-54.3	0.015	-103
Benzene	175	1.3	2.5	-15	0.25	-69	0.125	-96.4	0.015	-114
Methanol C ₂ H ₆ O	147	6.0	11.4	2	1.14	-41	0.57	-68.7	0.015	-126
llexane C ₆ ll ₁ ,	155	1.2	2.3	-39	0.23	-93	0.115	-108	0.015	-129

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

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

Contact condensers are, in general, less expensive, more flexible and more efficient in removing organic vapors than surface condensers. On the other hand, surface condensers may recover marketable condesate and minimize waste disposal problems. Often condensate from contact condensers cannot be reused and may require significant wastewater treatment prior to disposal.

The coolant used in surface condensers depends on the saturation temperature (dew point) of the VOC. Chilled water can be used to bring temperatures as low as 7° C, brines down to -34° C, and freens below -34° C.

The major pieces of equipment in a condenser system consist of the condenser, refrigeration system, storage tanks, and pumps. A typical arrangement is shown in Figure 4-10.

4.2.5.1 <u>Factors Affecting Performance and Applicability</u>. Condensers are not well suited to treatment of gas streams containing VOC with low boiling points or streams containing large quantities of inert and/or noncondensible gases such as air, nitrogen, or fuel gas (methane).

Condensers used for VOC control must often operate at temperatures below the freezing point of water. Thus, moist vent streams (such as would be present in gas streams from wastewater sources) must be dehumidified before treatment to prevent the formation of ice in the condenser.

Particulate matter should be removed because it may deposit on the tube surfaces and interfere with gas flows and heat transfer. Gas flow rates in

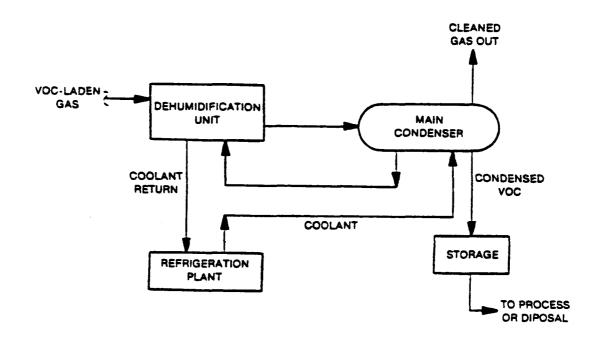


Figure 4-10. Condensation System.⁵⁴

the range of 100-200 cfm are typical of the capacities of condensers used as emission control devices.

Vent streams containing less than 0.5 percent VOC are generally not considered for control by condensation. $^{64}\,$

Oil-water separators and air flotation systems usually operate at temperatures below 140°F. The vapor streams from these sources will generally be saturated with water and will probably contain a large number of compounds with a broad range of boiling points. It is doubtful whether a condenser system can be effective as a primary VOC control device. There could conceivably be applications in which the gas stream from the emission sources is first passed through a condenser to recover some of the "higher boiling" compounds.

4.2.5.2 <u>Control Efficiency</u>. The VOC removal efficiency of a condenser is highly dependent upon the type of vapor stream entering the condenser, and on the condenser operating parameters. Efficiencies of condensers usually vary from 50 to 95 percent. ⁶⁵

4.2.6 Industrial Boilers and Process Heaters

Industrial boilers and heaters are widely used for the thermal destruction of captured VOC emissions. A brief description of the technology, factors affecting its performance and its potential as a VOC control method for refinery wastewater sources are discussed below.

4.2.6.1 Operating Principles. Boilers and process heaters are used extensively in petroleum refineries. They represent a potential emissions control system for combusting captured VOC emissions from sources in refinery wastewater systems.

Industrial Boilers. Most refineries use boilers to provide steam for direct use of various processes (e.g., light end strippers), for heating and for the production of electrical power (via steam turbines). Boilers in refineries are fired with the most available (and economical) fuel, such as

purchased natural gas, refinery fuel gas (mostly methane), residual oil, and and combinations of these various fuel types. Surveys of industrial boilers used in the chemical industry have shown that the majority are of watertube design, and it seems reasonable to assume that similar situation prevails in the petroleum industry. ⁵⁴

A watertube boiler is designed such that hot combustion gases are present outside of heat transfer tubes. Water flows inside the tubes and is vaporized by the heat that is transmitted through the tube walls. The tubes are interconnected to stream drums in which the steam and hot water are collected, separated, and stored. The water tubes are relatively small in diameter (2.0 inch being a typical diameter) to produce high liquid velocities, good heat transfer, rapid response to steam demands, and relatively high thermal efficiency. The thermal efficiency of the tubes and drum system can be as high as 85 percent. The efficiency can be increased by recovering heat from the flue gas by exchange with combustion air or feedwater.

When firing natural gas, forced or natural draft burners are used to thoroughly mix the incoming fuel and combustion air. If a waste gas stream, such as that from an oil-water separator vent, is combusted in a boiler, it can either be mixed with the incoming fuel or fed directly to the furnace through a separate burner. A particular burner design commonly known as a high intensity or vortex burner can be effective for waste gas streams with low heating values (i.e., streams where a conventional burner may not be applicable). Effective combustion of streams with low heating values 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 for industrial boilers vary as a function of the furnace and burner configuration, fuel type, heat input, and excess air level. 67 This model predicts mean furnace residence times of from 0.25 to 0.83 seconds for natural gas-fired water tube boilers in the size range from 4.4 to 44 MW (15 to 150 x 10^6 Btu/hr). Furnace exit temperatures for this range of boiler sizes are at or above 1475° K (2810° F). Residence times for oil-fired boilers are similar to those of the natural gas-fired boilers. 54

<u>Process Heaters</u>. Process heaters are used in petroleum refineries as reboilers for distillation columns and to provide heat for reaction (naptha reforming, thermal cracking, coking) and for preheating feed stocks. Natural gas, refinery fuel gas, and various grades of fuel oil are all used to fire process heaters.

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 to be heated. Most heaters also contain a convective heat transfer to the process fluid.

Process heater applications in the petroleum refining industry can be broadly classified with respect to firebox temperature: (1) low firebox temperature applications such as steam superheaters, and (3) high firebox temperature applications such as thermal cracking furnaces and catalytic reformers. Firebox temperatures within the refining industry can be expected to range from about 750°F for preheaters and reboilers to more than 2000°F for coking process furnaces.

function of boilers and heaters in refineries is to generate steam and provide process heat, respectively. Their successful operation is critical for the successful operation of refinery process units. Thus, it is extremely important that any injection of waste gases be done in a manner that precludes any reduction in the efficiency, operability, and/or reliability of the affected heater or boiler. Variability in the flow rate or composition of gas streams from wastewater sources could have an effect on the combustion characteristics and heat output if the stream represents a significant source of fuel relative to the normal fuel rate.

Waste streams containing relatively high concentration of chlorinated or sulfur-containing compound could cause corrosion problems in heater/boilers that are not designed to handle either the compounds or their combustion products. When such VOC compounds are burned, the flue gas temperature must be maintained above the acid dew point to prevent acid

condensation and subsequent corrosion. However, the VOC being emitted from refinery wastewater sources is expected to contain minimal amounts of sulfur- or halogen-containing compounds.

If the volume of the waste gas stream is significant when compared to that of the heater/boiler fuel, its injection could affect the heat transfer characteristics of the furnace. Heat transfer characteristics are dependent on the flow rate, heating value, and elemental composition of the waste gas 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 water gas stream can, in some cases, lead to some reduction in the amount of fuel required to achieved the desired heat production. Wastewater streams are expected to be relatively small compared to the total amount of fuel provided to most heaters and boilers in refineries.

If the waste stream volume is significant, and the heat content relatively low, the change in heat transfer characteristics after injecting the waste stream could have an adverse effect on the heater/boiler performance. Even equipment damage could result. In addition to these reliability problems, there are also potential safety problems associated with ducting wastewater emission vent to a boiler or process heater. Variation in the flow rate and organic content of the vent stream could cause extensive damage. Another related problem is flame fluttering which could result from these variations. Potential flashback is another possibility that must be considered. Presently, there is only one refinery known to be venting emissions from an air flotation system to a process heater. No safety problems have been reported by the refinery.

4.2.6.3 <u>Control Efficiency</u>. Some testing has been performed to evaluate the performance of boilers and heaters in destroying hydrocarbon gases injected into the flame zones of the combustion devices. The EPA sponsored a test to determine the capability of an industrial boiler for destroying polychlorinated biphenyls (PCB). A relatively small quantity of PCB is added to the fuel oil which is then burned in the boiler. The test results indicated that more than 99.9 percent of the PCB was destroyed in the boiler.

Other tests conducted by EPA measured the efficiency of five processes heaters for destroying a mixture of benzene off-gas and natural gas. 70,71,72 The heaters were representative of those with both low- and medium-temperature fireboxes. In both types of heaters, more than 99 percent of the total C_1 to C_6 hydrocarbons in the gas injected into the flame zone was destroyed.

Thus, when boilers or process heaters are available, it appears that they are acceptable control devices for waste gas streams. In general, they appear to be at least 98 percent efficient for destroying VOC in the vapor phase. The collected VOC gas streams from refinery wastewater sources may, in some cases, be suitable for control with this technology.

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5. MODIFICATION AND RECONSTRUCTION

In accordance with Title 40 of the Code of Federal Regulations (CFR), Sections 60.14 and 60.15, an existing facility can become an affected facility and, consequently, subject to applicable standards of performance if it is modified or reconstructed. An "existing facility," defined in 40 CFR 60.2, is a facility of the type for which a standard of performance is promulgated and the construction or modification of which was commenced prior to the proposal date of the applicable standards. The following discussion examines the modification and reconstruction provisions and their applicability to petroleum refinery wastewater systems, specifically, to process drain systems, oil-water separators, and air flotation systems.

5.1 GENERAL DISCUSSION OF MODIFICATION AND RECONSTRUCTION PROVISIONS

5.1.1 Modification

Modification is defined in Section 60.14 as any physical or operational change to an existing facility which results in an increase in the emission rate of the pollutant(s) to which the standard applies. Paragraph (e) of Section 60.14 lists exceptions to this definition which will not be considered modifications, irrespective of any changes in the emission rate. These changes include:

- 1. Routine maintenance, repair, and replacement;
- 2. An increase in the production rate not requiring a capital expenditure as defined in Section 60.2;
 - 3. An increase in the hours of operation;
- 4. Use of an alternative fuel or raw material if, prior to the standard, the existing facility was designed to accommodate that alternative fuel or raw material;

- 5. The addition or use of any system or device whose primary function is the reduction of air pollutants, except when an emission control system is removed or replaced by a system considered to be less environmentally beneficial.
 - 6. The relocation or change in ownership of an existing facility.

As stated in paragraph (b), emission factors, material balances, continuous monitoring systems, and manual emission tests are to be used to determine emission rates expressed as kg/hr of pollutant. Paragraph (c) affirms that the addition of an affected facility to a stationary source through any mechanism -- new construction, modification, or reconstruction -- does not make any other facility within the stationary source subject to standards of performance. Paragraph (f) allows provisions of the applicable subpart to supersede any conflicting provisions of 40 CFR 60.14. Paragraph (g) stipulates that compliance be achieved within 180 days of the completion of any modification.

5.1.2 Reconstruction

Under the provisions of Section 60.15, an existing facility becomes an affected facility upon reconstruction, irrespective of any change in emission rate. A source is identified for consideration as a reconstructed source when: (1) the fixed capital costs of the new components exceed 50 percent of the fixed capital costs that would be required to construct a comparable entirely new facility, and (2) it is technologically and economically feasible to meet the applicable standards set forth in this part. The final judgment on whether a replacement constitutes reconstruction will be made by the Administrator of the EPA. As stated in Section 60.15(f), the Administrator's determination of reconstruction will be based on:

- 1. The fixed capital cost of the replacement in comparison to the fixed capital cost of constructing an entirely new facility;
- 2. The estimated life of the facility after replacements compared to the life of a comparable entirely new facility;
- 3. The extent to which the components being replaced cause or contribute to the emissions from the facility; and

4. Any economic or technical limitations in compliance with applicable standards of performance which are inherent in the proposed replacements.

The purpose of the reconstruction provision is to ensure that an owner or operator does not perpetuate an existing facility by replacing all but minor components, support structures, frames, housing, etc., rather than totally replacing it in order to avoid being subject to applicable performance standards. In accordance with Section 60.5, the EPA will, upon request, determine if an action taken constitutes construction (including reconstruction). As with modification, individual standards may include specific provisions which refine and limit the concept of reconstruction in 40 CFR 60.15.

5.2 APPLICABILITY OF MODIFICATION AND RECONSTRUCTION PROVISIONS TO VOC FMISSIONS FROM PETROLEUM REFINERY WASTEWATER SYSTEMS

Changes in refinery product demand and in available refinery feedstocks are expected to result in a number of modernization and alteration projects at existing refineries over the next several years. Some of these projects could result in existing process drain systems, oil-water separators, and air flotation systems becoming subject to regulation under provisions of Sections 60.14 and 60.15. Examples in which this could occur are presented below.

5.2.1 Modification

Refinery modernization and alteration projects will result in new process units being built and older units being modified. These changes will allow refineries to process heavier and higher sulfur crude. New and modified process units could result in increased wastewater production. New drains will be added along with new or expanded wastewater treatment facilities.

Modification is defined as any physical or operational change to an existing facility which results in increased emissions. There are two general events that would cause an increase in emissions from process drain systems, oil-water separators, and/or air flotation systems. These events

are an increase in organic loading of process wastewater and an increase in the volume of wastewater without necessarily a change in organic loading. Either or both of these events would be caused by the following:

- 1. Addition of a process unit to be serviced by the wastewater system.
- 2. Modification of an existing process unit already serviced by the wastewater system.
 - 3. Changes in product slates.
 - 4. Changes in the type of crude oil processed.

Increased emissions from affected facilities could result in these facilities being subject to the NSPS under the modification provisions. Determination of modification will be made on a case by case basis.

5.2.2 Reconstruction

Expansion of existing process units and renovation of wastewater treatment facilities could result in affected facilities being subject to the NSPS under the reconstruction provisions. Reconstruction is determined by the criteria given in Section 5.1.2. Determination of reconstruction will be made on a case by case basis.

6. MODEL UNITS AND REGULATORY ALTERNATIVES

The purpose of this chapter is to define model units and identify regulatory alternatives. Model units are parametric descriptions of a representative cross-section of the units that, in the judgment of EPA are likely to be constructed, modified or reconstructed. The model unit parameters are used as a basis for estimating the environmental, energy, and economic impacts associated with the application of the regulatory alternatives to the model units.

6.1 MODEL UNITS

Petroleum refinery wastewater systems differ considerably from site to site. Because wastewater characteristics such as flow rate and oil content may be unique to each refinery, various treatment schemes and techniques may be employed by each refinery. For this reason, it is difficult to define a model petroleum refinery wastewater system and more reasonable to define model units for specific emission sources in petroleum refinery wastewater systems. Section 6.1.1. discusses model units for process drains and junction boxes. Sections 6.1.2 and 6.1.3 discuss model units for oil-water separators and air flotation systems, respectively.

6.1.1 Process Drains and Junction Boxes

An EPA study of emissions in petroleum refineries provided information on the population of fugitive emission sources. ¹ Included in the sources counted were drains and pumps. Thus, drain populations as well as the ratios of drains to pumps, were obtained for several refinery process units of varying complexities. Further, information gathered by California Air Resources Board has allowed estimates of junction box population, and ratio of drains to junction boxes to be developed. ² These relationships were used in developing model units. The number of process drains and junction boxes

in a process unit was found to be dependent on the complexity of the unit and independent of unit capacity or size. Therefore, model units are developed on the basis of drain population.

Model units for process drains and junction boxes are presented in Table 6-1. Refinery process units have been grouped into three model units based on the complexity of the process unit. Model Unit A represents process units of high complexity. It should be noted that within the high complexity model unit category, process units can be of varying capacity. Using information acquired in the EPA and California studies, the number of pumps in these process units is estimated to be ten. Applying a ratio of 2.75 drains per pump, an estimate of 94 drains is derived. Further, using the ratio of six drains per junction box, it is estimated that sixteen junction boxes are located in these units.

The number of drains and junction boxes in Model Units B and C are estimated using the same method. Model Unit B represents process units of medium complexity while Model Unit C represents units of low complexity.

6.1.2 Oil-Water Separators

Model Units for oil-water separators are presented in Table 6-2. As discussed in Chapter 3, the major factors affecting emissions are wastewater flow rate and VOC concentration. The cost of regulatory alternatives discussed in Section 6.2 depend on the surface area of the oil-water separator that is open to the atmosphere. Therefore, model units are characterized according to these three parameters.

In choosing wastewater flow rates for the oil-water separator model units, consideration was given to crude oil production capacities at individual refineries, flow rates observed during plant visits, and design information from vendors. The largest flow rate (1500 gpm) is based on an actual installation at a large refinery. If a refinery generates a larger flow rate than 1500 gpm, it is very likely that multiple units will be installed. The smallest flow rate (50 gpm) is based on information provided by vendors on the smallest size oil-water separators used in petroleum refinery applications. A mid-point flow rate (750 gpm) was chosen for the medium sized model unit.

TABLE 6-1. PROCESS DRAINS MODEL UNIT PARAMETERS

Model	Representative	Model	Jnit Capacities	Nu	umber of sou in Model Ur		
Unit	Process Unit Types	Range	Capacity Mbpd	Pumps	Drains	Junction Boxes	Uncontrolled Emissions (Mg/yr)
Α	Crude Distillation Fluid Catalytic Cracking	Small ^a	20				
	Trusta catalycic cracking	Average	47	34	94	16	30.8
		Large ^b	113				
В	Treating Processes Lube Oil Processing	Small ^a	3				
	Alkylation	Average	17	16	44	8	14.6
	Catalytic Polymerization Isomerization Thermal Cracking/Coking Solvent Extraction Hydrocracking	Large ^b	36				
С	Hydrotreating	Small ^a	5				
	Hydrorefining Light Ends/LPG	Average	28	10	28	5	9.3
	Catalytic Reforming Vacuum Distillation Hydrogen Manufacture	Large ^b	67				

^aAverage of smallest 10 percent of representative unit types.

^bAverage of largest 10 percent of representative unit types.

^CEstimated using factor of 2.75 drains/pump. (Reference 1).

 $^{^{}m d}$ Estimated using factor of 6.0 drains/junction box. (Reference 2).

TABLE 6-2. OIL-WATER SEPARATORS MODEL UNIT PARAMETERS

Model plant	Wastewate thousand E	er flow BPD (gpm)	Surface ^a <u>Area</u> m	Uncontro emiss kg/hr	lled _b VOC <u>ions</u> Mg/yr
Α	50	(1500)	107	37.8	331.0
В	25	(750)	58	18.9	165.6
С	2	(50)	58	1.3	11.0

aRefers to the surface area of the separator that will be open to the atmosphere. Surface areas were calculated using American Petroleum Institute (API) design specifications (Reference 3).

^bCalculated using Litchfield Method assuming conditions listed in Table 3-5.

VOC concentration levels were found to range quite widely between refineries. As discussed in Section 3.2.2.4, a typical level of 1000 mg/liter of VOC at the inlet to the oil-water separator was chosen for emission calculations.

Surface area is the area of the separator that is open to the atmosphere. Surface area is dependent on the wastewater flow and was calculated using API design specifications. However, a broad range of flow rate conditions can be handled by a given surface area. Model Units B and C, therefore, have the same surface areas because API design surface area of 58 m³ includes the 50 to 750 gpm range.

6.1.3. <u>Air Flotation Systems</u>

Model units for air flotation systems are presented in Table 6-3. As in the case of oil-water separators, air flotation model units were characterized according to wastewater flow rates and surface areas. However, instead of calculations based on VOC concentration, uncontrolled emission estimates are based on actual test data.

The smallest flow rate used in the model units, 50 gpm, approaches the size of the smallest IAF system available. Conversations with vendors and industry indicate that DAF systems also approach this size in actual applications. The flow rates of 1500 gpm and 750 gpm shown in Table 6-3 are representative of a large number of actual IAF and DAF systems. Larger flow rates than 1500 gpm are possible. However, flow rates greater than 1500 gpm would most likely be handled in multiple units to allow for operating flexibility.

Surface areas for air flotation systems were calculated using an empirical formula provided by a vendor. The surface areas are only applicable to DAF systems. Most IAF systems used in refinery applications come equipped with covers. Surface area represents the area of the DAF system open to atmosphere. The uncontrolled emission levels for air flotation systems are based on emissions testing conducted by EPA at three petroleum refineries.

TABLE 6-3. AIR FLOTATION MODEL UNIT PARAMETERS

Model Unit	Wastewate thousand B		Surface ^a Arga m	Uncontro emission kg/hr	olled VOC ns - DAF Mg/yr	Uncontr emissio kg/hr	olled VOC ns - IAF Mg/yr
A	50	(1500)	70.0	1.37	12.0	0.27	2.4
В	25	(750)	35.0	0.68	6.0	0.14	1.2
С	2	(50)	2.3	0.05	0.4	0.01	0.1

^aRefers to the surface area of the dissolved air flotation system only. Surface areas calculated using formula that assumes 1 square foot of surface area is required for 2 gpm of wastewater flow (Reference 1). The surface area is given only for a DAF since this area will determine the cost of control. IAF systems come equipped with covers.

bUncontrolled emissions for a DAF are based on the emission factor determined by testing. This emission factor is 15.2 kg per MM gallons of wastewater flow.

CUncontrolled emissions for an IAF are based on the emission factor determined by testing. The emission factor has been modified to account for the cover supplied with the IAF system as explained in Chapter 4, section 4.1.3.2.

6.2 REGULATORY ALTERNATIVES

This section presents regulatory alternatives for controlling VOC emissions from process drains, oil-water separators, and air flotation systems. These regulatory alternatives are summarized in Table 6-4.

Regulatory Alternative I

Regulatory Alternative I represents no additional control over baseline. Baseline control is defined as the level of control currently achieved by industry. This usually reflects the degree of control required by state and local regulations. Regulatory Alternative I provides the basis for determining the impacts of other regulatory alternatives.

Regulatory Alternative II

Regulatory Alternative II provides a higher level of control than required by Regulatory Alternative I. For process drains, this alternative requires all drains and junction boxes to be water sealed. Oil-water separators are to be completely covered with either a fixed or floating roof. Dissolved air flotation systems are also required to be covered with a fixed roof. For induced air flotation systems, work practices are required to operate the IAF under gas tight conditions. These control techniques have been discussed in Chapter 4.

Regulatory Alternative III

Regulatory Alternative III requires the highest level of emission reduction. For process drains, a completely closed drain system is required with vapors vented to a control device. Under Regulatory Alternative III, oil-water separators are also required to be completely covered with a gasketed and sealed fixed roof with vapors to be vented to a control device. Air flotation systems, both DAF and IAF, are also required to be completely covered with a fixed roof with vapors vented to a control device. The control techniques for Regulatory Alternative III have been discussed in Chapter 4.

TABLE 6-4. REGULATORY ALTERNATIVES

Regulatory Alternative	I.	II.	III.
Process Drains	No Additional Control	Water-sealed process drains and junction boxes.	Completely closed drain system with vapors led to a control device.
Oil-Water Separators	No Additional Control	Gasketed and sealed fixed or floating roof.	Gasketed and seal fixed roof with vapors vented to a control device.
Air Flotation Systems	No Additional Control	DAF systems provided with a gasketed and sealed fixed roof, vented to atmosphere. IAF systems maintained gas tight by gasketing and sealing access doors.	Gasketed and sealed fixed roof with vapors vented to a control device.

6.3 REFERENCES

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- 6. Telecon. Mitsch, B. F., Radian Corporation, with Chuck Bassett, Huntway Refining Company, Benicia, California. June 29, 1983. Conversation concerning the wastewater treatment system at Huntway.
- 7. Komline Sanderson. Dissolved Air Flotation. Bulletin No. KSB 123-8106.

7. ENVIRONMENTAL IMPACTS

7.1 INTRODUCTION

The purpose of this chapter is to present the environmental impacts of the regulatory alternatives specified in Chapter 6. The primary emphasis is on VOC emissions which would result from implementation of each of the alternatives presented. The impacts of the regulatory alternatives on water quality, solid waste, and energy are also addressed in this chapter.

7.2 AIR POLLUTION IMPACTS

Implementation of Regulatory Alternatives II and III for each of the three emission sources will reduce VOC emissions from refinery wastewater systems. Emission reductions achieved by implementing these alternatives are estimated for the three emission sources in the source category. These emission reductions are presented for individual model units on an annual basis. Additionally, nationwide emission levels resulting from new and modified/reconstructed process drains and junction boxes, oil-water separators, and air flotation systems are estimated on a five-year basis.

7.2.1 Estimated Emissions and Percent Emission Reduction for Model Units

Table 7-1 lists the estimated emissions and percent emission reduction for each model unit and regulatory alternative in the source category. Regulatory alternatives were described in Chapter 6. Emission factors used to estimate emissions from each model unit have been given in Chapter 3. The control efficiencies of the various regulatory alternatives have been described in Chapter 4. The percent reductions achievable by the regulatory alternatives for each model unit are given in parenthesis in Table 7-1.

TABLE 7-1. ESTIMATED EMISSIONS AND EMISSION REDUCTIONS FOR EACH MODEL UNIT AND REGULATORY ALTERNATIVE

Model Units ^a	Estimated	Emission	Regulato s, Mg/yr	ory Alter (% Reduc	natives tion From Reg. Alt. I)
Process Drains and Junction Boxes	Ip			<u> </u>	III
A	30.8			(50)	0.6 (98) ^c
В	14.6	(0)	7.3	(50)	0.3 (98) ^C
С	9.3	(0)	4.7	(50)	0.2 (98) ^c
Dil-Water Separators					
A	331.0	(0)	49.7	(85)	9.9 (97) ^C
В	165.6	(0)	24.8	(85)	5.0 (97) ^c
С	11.0	(0)	1.7	(85)	0.3 (97) ^c
Air Flotation Systems (DAF)					
A	12.0	(0)	2.8	(77)	0.4 (97) ^C
В	6.0	(0)	1.4	(77)	0.2 (97) ^c
С	0.4	(0)	0.1	(77)	0.01 (97) ^c
Air Flotation Systems (IAF)					
A	2.36	5	1.81	(23)	0.4 (85) ^c
В	1.18	3	0.91	(23)	0.2 (85) ^c
С	0.07	7	0.06	5 (23)	0.01 (85) ^C

^aModel Units are described in Chapter 6.

^bRegulatory Alternative I represents no control.

CCaptured VOC emissions vented to an existing flare.

7.2.2 <u>Projected VOC Emissions for Petroleum Refinery Wastewater System</u> Source Category

Tables 7-2, 7-3, and 7-4 provide estimates of projected VOC emissions from new and modified/reconstructed model units during the period 1985 to 1989. Table 7-2 lists projections for new and modified/reconstructed process drain systems. Tables 7-3 and 7-4 list projections for new and modified/reconstructed oil-water separators and air flotation systems, respectively.

Growth projections for each emission source were presented in Chapter 3. Over the next five years, 102 new process units are estimated to be built with 30 new oil-water separators and 25 new air flotation systems. Additional estimates of modified/reconstructed models units have been determined in order to estimate projected VOC emissions from these units. The number of modified/reconstructed process drain model units was determined by evaluating the current construction projects at existing petroleum refineries. It was assumed that the current construction level would continue over the next five years and that approximately 10 percent of the drain systems in existing units with ongoing construction projects will be impacted by the NSPS under the modification/reconstruction provisions.

Estimates of the number of modified/reconstructed oil-water separators and air flotation systems were determined by assuming that these units will equal 10 percent of the new units. Therefore, it is estimated that approximately three oil-water separators and three air flotation systems will be impacted by the NSPS under the modification/reconstruction provisions during the five-year period.

In Tables 7-2, 7-3, and 7-4, baseline reflects the level of control currently required by State regulations. Baseline for the three emission sources were presented in Section 3.4. Only oil-water separators are currently controlled by State regulations. As a result of the State regulations, about 85 percent of the new separators will be covered, 5 percent partially covered, and 10 percent uncovered.

TABLE 7-2. PROJECTED VOC EMISSIONS FROM NEW AND MODIFIED/RECONSTRUCTED PROCESS DRAIN SYSTEMS FOR REGULATORY ALTERNATIVES IN PERIOD FROM 1985 - 1989

Year	Number o	f Affected	Model Units	Each Regulatory Alternative (Mg/yr)			
	<u>A</u>	<u>B</u>	<u>c</u>	<u>Baseline^a</u>	<u>II</u>	111	
1985	6	6	12	384	192	8	
1986	12	12	24	768	384	15	
1987	18	18	36	1152	576	23	
1988	24	24	48	1536	768	31	
1989	30	30	60	1920	960	38	

^aBaseline reflects current level of control required by State regulations. For process drains and junction boxes, there is no control required by State regulations.

TABLE 7-3. PROJECTED VOC EMISSIONS FROM NEW AND MODIFIED/RECONSTRUCTED OIL-WATER SEPARATORS FOR REGULATORY ALTERNATIVES IN PERIOD FROM 1985 - 1989

Year	Number of Affected Model Units			Total Annual VOC Emissions Projected Each Regulatory Alternative (Mg/yr)		
	<u>A</u>	<u>B</u>	<u>C</u>	Baseline ^a	<u>II</u>	<u> 111</u>
1985	1	2	3	527	104	21
1986	2	4	6	828	208	42
1987	3	6	9	926	312	62
1988	4	8	12	1030	416	83
1989	6	11	16	1211	597	119

^aBaseline reflects the current level of control required by State regulations. The State regulations for oil-water separators are presented in Section 3.4.

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TABLE 7-4. PROJECTED VOC EMISSIONS FROM NEW AND MODIFIED/RECONSTRUCTED AIR FLOTATION SYSTEMS FOR REGULATORY ALTERNATIVES IN PERIOD FROM 1985 - 1989

Year	Number of Affected Model Units			<pre>lotal Annual VOC Emissions Projected f Each Regulatory Alternative (Mg/yr)</pre>		
	<u>A</u>	<u>B</u>	<u>c</u>	<u>Baseline^a</u>	<u>II</u>	<u> 111</u>
1985	1	2	2	14.8	4.7	0.7
1986	2	4	4	29.7	9.5	1.5
1987	3	6	6	44.5	14.2	2.2
1988	4	8	8	59.3	18.9	3.0
1989	6	11	11	85.1	27.1	4.3

^aBaseline reflects the current level of control required by State regulations. For air flotation systems, there is no control required by State regulations.

The projected emissions for process drain systems were estimated using emission factors determined for drains and junction boxes and the projected growth estimate discussed above. For oil-water separators, similar information was used along with information regarding current State regulations. The projected emissions reflect the current percentage of separators estimated to be fully covered, partially covered, and uncovered.

Projected emissions from air flotation systems are based on the emission factors and projected growth estimates. Further, as discussed in Chapter 3, it is estimated that 50 percent of the new units will be IAF systems and 50 percent will be DAF systems.

7.2.3 Secondary Air Pollution Impacts

Secondary air pollution impacts are those impacts generated by the emission control techniques. Control techniques required by Regulatory Alternative II include water seals for drains and junction boxes, covers for oil-water separators and DAF systems, and gas-tight operation for IAF systems. These controls would not create any secondary air pollution impacts.

Regulatory Alternative III for all three emission sources require VOC destruction devices. Carbon adsorption systems require steam to be used for regeneration of the carbon beds. Fuel combustion to produce steam may result in emissions of some air pollutants. However, the quantity of air pollutants produced is expected to be minimal. For example, if all new separators and air flotation systems required a designated carbon adsorber, the amount of natural gas needed to produce steam to regenerate these units is estimated to be 1.82 million cubic feet per year. The amount of secondary pollutants generated by burning this amount of natural gas would be approximately 1.1 pounds of SO_{X} and 255 pounds of NO_{X} .

Other VOC destruction devices such as flares, boilers, and incinerators would produce some secondary air pollutants. The quantity of these pollutants directly attributable to VOC control for refinery wastewater systems would also be negligible.

7.2.4 Summary of Air Pollution Impacts

Table 7-5 summarizes the air pollution impacts of the regulatory alternatives for the source category. Implementation of Regulatory Alternative II for all emissions sources and Regulatory Alternative III for process drains and junction boxes and oil-water separators would result in positive air pollution impacts. The percent reduction from baseline and incremental emission reduction are also shown in the table.

7.3 WATER POLLUTION IMPACTS

Implementation of any of the regulatory alternatives would not have an adverse impact on water quality. The control techniques proposed would not interfere with the basic water treatment functions of oil-water separators and air flotation systems. Further, as explained below, suppression of VOC in the wastewater by covering separators and air flotation systems will not result in a significant increase in organic loading to subsequent treatment processes.

Data collected in an EPA study² showed that VOC have a greater affinity for the oil phase of wastewater than for the water phase. The concentration of VOC in the oil phase was about one thousand times that in the water phase. To the extent that control techniques suppress emissions of VOC, these VOC will mostly be captured in the oil and removed to recovery processes. Suppression into the oil phase would not be expected to be as great if the vapor space of a separator or air flotation system is purged (as required by Regulatory Alternative III for separators and air flotation). However, when the vapor space is purged, the VOC removed would be directed to a control device. Again, no adverse impact on water quality would occur.

7.4 SOLID WASTE IMPACTS

There will not be a significant amount of solid waste produced as a result of implementing the regulatory alternatives. The only possible source of solid waste will be from carbon adsorption systems. If activated carbon is disposed rather than regenerated, small quantities of solid waste will be produced.

TABLE 7-5. SUMMARY OF ANNUAL EMISSIONS AND EMISSION REDUCTION BY 1989 FOR SOURCE CATEGORY (NEW AND MODIFIED/RECONSTRUCTED UNITS)

Emission Source	Regulatory Alternative	Annual Emissions by 1989 (Mg/yr)	% Reduction From Baseline
Process Drains and Junction Boxes	I	1920	-
	II	960	50
	111	38	98
Oil-Water Separators	I	1211	-
	II	597	54
	III	119	91
Air Flotation Systems	I	84	•
	II	27	69
	III	4	95

7.5 ENERGY IMPACTS AND WATER USAGE

Implementation of Regulatory Alternative II for all three emission sources would not require high usage of water or energy. Implementation of Regulatory Alternative III for these sources and Regulatory Alternative II for air flotation systems would result in consumption of small quantities of steam, water, electricity and fuel gas. As explained in Chapter 6, these alternatives require that VOC be captured and vented to a control device. In some cases, refineries will have existing control devices accessible to these emission sources. Only blowers would be required to transport the VOC to the existing control device. Electricity would be required to power the blowers. If designated control devices are needed, utilities would be required to operate the control device. In the case of carbon absorbers, water, steam, and electricity would be needed.

Table 7-6 is a summary of utility requirements which would result from implementing Regulatory Alternative III for process drain systems, oil-water separators, and air flotation systems.

7.6 OTHER ENVIRONMENTAL CONCERNS

Implementation of the regulatory alternatives is not expected to result in a large commitment of energy or other non-renewable resources. As discussed above, implementation of the regulatory alternatives would not impact water quality or solid waste generation. However, a delay in the regulatory action would adversely affect air quality at the rate shown in Table 7-5.

TABLE 7-6. ENERGY REQUIREMENTS AND WATER DEMAND - REGULATORY ALTERNATIVE III FOR PROCESS DRAINS AND JUNCTION BOXES, OIL-WATER SEPARATORS, AND REGULATORY ALTERNATIVE II FOR AIR FLOTATION SYSTEMS.

Emission Source	# Affected Units by 1989	Fuel Gas ^a (MM scf/yr)	Electricity (kWh/yr)	Water (m³/yr)	Steam (Mg/yr)
Process Drains	120	13	352,350	-	_
Oil-Water Separators ^b	33	~	161,730	-	-
Oil-Water Separators ^C	33	-	330,000	12,400	354
Air Flotation Systems ^b	28	-	137,230	-	_
Air Flotation Systems ^C	28	-	280,000	10,528	300

^aFuel gas assumed to be used to purge closed drain system.

Assumes existing control device available. Electricity requirements for blowers to transport VOC to control device. Cost sharing possible between separators and air flotation systems but has not been considered in this analysis.

^CElectricity, steam, water, needed for blower, carbon adsorption system. Cost sharing possible between separators and air flotation systems but has not been considered in the analysis.

7.7 REFERENCES

- 1. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Third Edition. AP-42, Supplement 13. August 1982. p. 1.4-1.
- Wetherold, R. G., L. P. Provost, and C. D. Smith. (Radian Corporation.) Assessment of Atmospheric Emissions from Petroleum Refining. Volume 3: Appendix B. Prepared for U.S. Environmental Protection Agency. Publication No. EPA 600/2-80-075C. April 1980.

8. COSTS

This chapter presents the methods used to estimate costs for controlling volatile organic compounds (VOC) from petroleum refinery wastewater systems. Cost estimates are given for each regulatory alternative and model unit described in Chapter 6. In Chapter 9, the results of this cost analysis are used to determine the economic impact of the regulatory alternatives.

8.1 COST ANALYSIS OF REGULATORY ALTERNATIVES

The costs of major equipment (covers for oil-water separators and air flotation systems) needed for the regulatory alternatives were acquired from actual installations in the refining industry. The costs of additional equipment such as piping, blowers, and vapor control devices were estimated using engineering references. 1,2,3,4,5 Standard costing procedures devised by Uhl^{1,2} were then used to estimate capital and annual costs for each model unit and regulatory alternative. Tables 8-1 and 8-2 present the cost algorithms used in the analysis. All costs were updated to third quarter 1983 dollars using Chemical Engineering Plant Cost Indices. 8

Section 8.1.1 presents the costs associated with implementing the regulatory alternatives for process drains and junction boxes. Sections 8.1.2 and 8.1.3 present the costs associated with implementing the regulatory alternatives for oil-water separators and air flotation systems, respectively. For all three emission sources, costs for both new and retrofitted control systems are discussed.

8.1.1 Process Drains and Junction Boxes

Regulatory alternatives for process drains and junction boxes have been discussed in Section 6.2. Regulatory Alternative I requires no additional control and, therefore, does not result in any costs. The costs for implementing Regulatory Alternatives II and III are discussed below.

Direct Costs

Purchased equipment costs Installation costs includes:

Piping
Structural Steel
Concrete
Electrical
Instrumentation
Other (paint, insulation, etc.)
Installation labor

Total Direct Capital Cost (TDC)

Indirect Cost

Engineering and supervision 10% of TDC Miscellaneous field expenses 5% of TDC

Cumulative Subtotal A

Contractors' fees 10% of subtotal A Contingencies 15% of subtotal A

Cumulative Subtotal B

Interest during construction 12% of subtotal B Startup 5% of subtotal B

Total Depreciable Investment (TDI)

Subtotal B + interest + startup

^aReferences 1 and 2.

Basis: 24 hour/day, 365 d/yr. Direct Annual Operation and Maintenance	Expenses (O&M)
Labor - Operating - Maintenance - Supervisory - Other	hr/yr x \$14.00/hr ^b 2.5% of TDC 10% of O&M labor -0-
Materials - Operating - Maintenance	-0- 2.5% of TDC
Fuel gas	annual usage x \$3.50/1000 scf ^C
Electricity	annual usage x \$.05/kWh ^C
Other (list as required)	
Total Direct O&M (DOM)	Sum of the above
Indirect Annual O&M Expenses	
Overhead General and administration Insurance and Property Taxes	70% of all labor 2% of TDI 2% of TDI
Total Indirect O&M (IOM)	Sum of the above
Total Annual O&M Expenses (TAOE)	DOM + IOM
Capital Recovery (CR) (Capital recovery factor for 10% over 10 years x TDI)	0.163 x TDI
Total Annual Cost	TAOE + CR

aReferences 1 and 2. bReference 6. cReference 7.

8.1.1.1 Regulatory Alternative II - Water Sealed Drains and Junction Boxes.

New Process Drains and Junction Boxes

A P-trap water sealed drain was used as the basis for estimating the costs for Regulatory Alternative II. A P-trap drain has been illustrated in Figure 3-7. The materials needed to construct uncontrolled, P-trap, and closed drains are given in Table 8-3. The materials needed for these drain types were derived from actual installations and from engineering judgement. The cost associated with implementing Regulatory Alternative II is the additional cost of a P-trap drain over an uncontrolled drain. The difference in total depreciable investment (TDI) between an uncontrolled drain and a P-trap is approximately 172 dollars. The difference in cost is due primarily to additional materials and labor needed for the P-trap. Therefore, 172 dollars represents the cost per drain of implementing Regulatory Alternative II.

A water seal pot with a water line was used as the VOC reduction technique for junction boxes. The water seal pot has been illustrated in Figure 3-9. The materials used to construct a water seal pot and the associated costs are given in Table 8-3. Using these cost estimates and the costing algorithms given in Table 8-1, total cost for controlling VOC from junction boxes was estimated to be \$362 dollars per junction box.

The costs for implementing Regulatory Alternative II for new process drain model units are shown in Table 8-4. These costs were derived by applying the costs of P-traps drains and controlled junction boxes to the number of drains and junction boxes in each model unit. Additionally, the cost effectiveness of controlling VOC emissions from each model unit is provided in the table. Cost effectiveness estimates for Regulatory Alternative II are approximately \$350 per Mg.

Retrofit Process Drains and Junction Boxes

The cost for retrofitting an existing process unit with P-trap drains and controlled junction boxes was also estimated. The additional cost required to retrofit a P-trap drain over installing a new P-trap drain is

TABLE 8-3. TOTAL DIRECT CAPITAL COST OF MAJOR EQUIPMENT FOR VOC CONTROL ON PROCESS DRAINS

	Uncontrolled Drain System	Tota	al Installed ^a Cost (\$)
1. 2.	Straight Pipe (4" diameter, 4.25 ft) Wye (cast iron, no hub)	•	20 58
		Total	78
P-Tr	Water Sealed Drain Systems ap Drain		
1.	Straight Pipe (4" diameter, 4.25 ft) Wye (cast iron, no hub)		20 58
2.	P-trap (4" cast iron, 1/4 bend-3)		77 25
4.	El bend (4" cast iron)	Total	180
Wate	er Seal Pot on Junction Box		
1. 2. 3. 4. 5. 6.	Straight Pipe (4" diameter, 1 ft) 1/4 bend (4" cast iron) Cup (6" welded) Water refill line (20 ft 1/2 steel pipe) Globe value (bronze) 1/4 bends (2) (1/2" steel) Tee (1/2" cast iron)		5 25 65 28 30 20 42
		Total	215
Clo 1. 2. 3.	Closed Drain System sed Drain Straight Pipe (4" diameter, 4.25 ft) Wye (cast iron, no hub) Flange (4" carbon steel #150) Union (3/4" carbon steel)	Tatal	20 58 113 13 204
		Total	204
Und	erground Tank and Purge Gas System	ሱ	44 200 OO
1.	Fabricated tank ^C		14,298.00
2.	Purge Gas System ^C	<u> </u>	2,585.00

aCost includes materials and labor, 3rd quarter 1983 dollars.

bReference 3.

^CBreakdown of materials given in Table 8-6.

TABLE 8-4. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR NEW PROCESS DRAIN AND JUNCTION BOX SYSTEM

Regulatory Alternative ^a	Model Unit	Drains	Junction Boxes	Total Depreciable Investment (\$1,000)		al Cost (1 Indirect Expense	Capital	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectiveness (\$/Mg)
I	A B C	9 4 44 28	16 8 5	NO CONTROL	COSTS					
11	A	94	16	22.00	0.65	1.11	3.58	5.34	15.4	350
	B	44	8	10.50	0.31	0.53	1.71	2.54	7.3	350
	C	28	5	6.60	0.19	0.34	1.08	1.61	4.6	350
111	A ^C	94	16	150.00	11.31	11.70	24.61	47.62	30.2	1580
	B ^C	44	8	90.60	8.93	8.60	14.77	32.30	14.3	2260
	C	28	5	63.40	8.00	7.40	10.81	26.16	9.1	2880

a. Regulatory Alternative I - No action
Regulatory Alternative II - Require P-traps on all drains and seal pots on junction boxes.
Regulatory Alternative III - Require a sealed drain system vented to a control device.

- b. Costs are based on the factors and computational algorithms of Table 8.1 and 8.2. All costs are in 3rd quarter 1983 dollars.
- c. The capital cost of an underground collection tank was calculated assuming 42 drains. Costs for other size drain systems were estimated by the following equation (Reference 9): Cost = (Cost of tank for a 42 drain system) # of drains

Total depreciable investment for piping equal for all systems.

the cost of materials as well as labor and equipment necessary to remove the existing drains. Costs were based on a three man crew using a backhoe with a pneumatic jackhammer to remove concrete around the drain. Using engineering judgement, it was estimated that each drain would take one-half hour to excavate. Table 8-5 presents the costs for retrofitting water sealed drains in each model unit. The cost is \$486 per drain. The cost of retrofitting a junction box with a water seal is considered minimal because no excavation is necessary.

It is expected that most units which would be affected by the modification/reconstruction provisions would be down for reasons other than drain retrofitting. Therefore, no cost due to production losses would result from implementing the NSPS.

8.1.1.2 <u>Regulatory Alternative III - Closed Drain System.</u> New Process Drains and Junction Boxes

A completely closed drain system similar to that installed at one refinery 10 was used as the basis for the cost evaluation. The closed drain system uses sealed drains and an underground collection tank. The collection tank is purged with fuel gas to reduce the risk of explosions. The purge gas is then vented to an existing control device, such as a flare. The closed drain system has been illustrated in Figure 3-8.

The materials needed to install closed drains are given in Table 8-3. As with P-trap drains, the difference in cost between installing a closed drain and an uncontrolled drain is used for all cost calculations. The difference in cost is approximately \$210 per drain.

The materials and methods used to estimate the cost of constructing the underground collection tank and purge system are shown in Table 8-6. The tank was sized to handle wastewater from a process unit having 42 drains. The annual cost for operating the underground tank and purge system includes the electricity to operate the sump pump and fuel gas for the purge system. The costs for these utility requirements are shown in Table 8-7. The cost effectiveness for implementing Regulatory Alternative III for each model unit is also shown in Table 8-4. The cost effectiveness estimates range from \$1580 per Mg for Model Unit A to \$2880 per Mg for Model Unit C.

TABLE 8-5. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR RETROFITTING A PROCESS DRAIN AND JUNCTION BOX EMISSION REDUCTION SYSTEM

Regulatory Alternative ^a	Model Unit	Drains	Junction Boxes	Total Depreciable Investment (\$1,000)	Ann Direct Expense	ual Cost (Indirect Expense	Capital	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectiveness (\$/Mg)
I	A B C	94 44 28	16 8 5	NO CONTROL C	OSTS					
11	A	94	16	51.5	1.61	2.65	8.39	12.65	15.4	820
	B	44	8	24.3	0.76	1.25	3.96	5.97	7.3	820
	C	28	5	15.4	0.48	0.79	2.51	3.78	4.6	820
III	A ^C	94	16	182.6	12.29	13.33	29.76	55,38	30.2	1,830
	B ^C	44	8	105.4	9.40	9.36	17.18	35,94	14.3	2,510
	C ^C	28	5	75.8	8.29	7.83	12.35	28,47	9.1	3,130

- a. Regulatory Alternative I No action
 Regulatory Alternative II Require P-traps on all drains
 Regulatory Alternative III Require a sealed drain system vented to a control device.
- b. Cost assume 1.5 manhour to remove each old drain. Costs are based on the factors and computational algorithms of Table 8.1 and 8.2. All costs are in 3rd quarter 1983 Dollars
- c. The capital cost of an underground collection tank was calculated assuming 42 drains.

 Costs for other size drain system were estimated by the fallowing equation (Reference 9): '

 Cost = (Cost of Tank for a 42 drain system) # of drains

Total depreciable investment for piping equal for all systems.

TABLE 8-6. BASIS FOR BURIED TANK SUBSYSTEM COST ESTIMATE FOR REGULATORY ALTERNATIVE III

Direct capital cost based on vessel estimate using methods of Richardson².

Vessel specifications: 7 feet, i.d., 10.75 feet tangent-to-tangent length, ellipsoidal head, 5/16 inch thick carbon steel, welds spot checked. Vessel volume is approximately 400 ft (3000 gal). In practice an externally coated steel is likely to be used and costs of such coating are implicitly assumed to be within the overall estimate contingency allowance.

Vessel buried in excavation 11 feet deep by 14.75 feet long by 11 feet wide. Vessel rests directly on sand or gravel within excavation, and backfilled with original overburden.

Vessel contains two manways: 36" diameter and 24" diameter extending to ground surface. First manway is welded to exterior wall of vessel to provide access from above ground to piping nozzles attached to vessel wall. Second manway penetrates wall of vessel to provide access to vessel interior. Manways are covered with a bolt-on cover.

Two sump pumps each rated at 40 gpm, 25 psig discharge pressure, and requiring 1 hp motors are used to pump vessel liquid to wastewater treatment. Motors are located on ground level cover of 36" manway. Piping and shafts extend through manway, and then through nozzles in vessel wall.

Piping from plant fuel gas system to tank, installed. Piping between tank and facility flare system, installed.

Installation costs were estimated based on factors in Guthrie⁴ for horizontal process vessels and pumps.

Vessel capacity is directly proportional to the number of drains in the system. Therefore, the number of drains was used as the sizing factor.

Total Direct Capital Cost of Tank: \$44,298, Total Direct Capital Cost of piping: \$2585

TABLE 8-7. ANNUAL UTILITY COSTS FOR REGULATORY ALTERNATIVES

Process	Regulatory	Mode1		Ut11	ity Cost (\$1000)	
	Alternative	Unit	Water	Steam	Electricity	Fuel Gas
Process Drain System - New and	111	Ag			0.087	0.217
Retrofit	•••	a a a b b b c c c b b b c c c c b b b c c c c	_	-	0.136	0.342
		C <mark>a</mark>	-	-	0.278	0.696
)il-Water Separator-New and	III	A_{L}^{D}	-	-	0.245	-
letrofit		B ^D	-	-	0.245	-
		$C_{\mathbf{D}}^{\mathbf{D}}$	•	-	0.245	•
		A ^C	0.010	0.574	0.500	•
		B ^C	0.010	0.574	0.500	-
		C,C	0.010	0.574	0.500	~
CPI System	111	Ä,D	-	-	0.245	-
		B,D	-	•	0.245	-
		ÇD.	-	-	0.245	-
		Ā ^C	0.010	0.574	0.500	-
		RC	0.010	0.574	0.500	-
		Čc	0.010	0.574	0.500	-
OAF System	111	ŘĎ	-	-	0.245	-
J. 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5		Bb		_	0.245	_
		<u>c</u> p	-	-	0.245	-
		Ă ^C	0.010	0.574	0.500	-
		RC	0.010	0.574	0.500	-
		č.c	0.010	0.574	0.500	•
IAF System	111	ĂĎ	-	-	0.245	-
	•••	R D	_	-	0.245	_
		čp	_	-	0.245	-
		ÃC	0.010	0.574	0.500	_
		RC	0.010	0.574	0.500	_
		င်င	0.010	0.574	0.500	_

^aThe electrical requirements are based on a pumping rate of one-half the pumps design capacity for 2,920 hours per year. The fuel gas usage is based on a complete turn over of the collecton tank's vapor space every 24 hours, based on a tank sized for 42 drains. The utility costs were also adjusted for the different tank sizes using the following equation:

Utility Cost = U_{42} (D)

Where: U_{A2} = Utility cost for a tank serving 42 drains

D = Number of drains in Model Unit.

 $^{^{\}mathrm{b}}\mathrm{Captured}$ VOC emissions vented to an existing control device.

^CCaptured VOC emissions vented to a dedicated device (carbon adsorber).

Retrofit Process Drains and Junction Boxes

The cost for retrofitting an existing process unit with a closed drain system was also estimated. The additional cost of retrofitting a closed drain system over installing a new drain system is the labor and equipment needed to excavate the existing uncontrolled drains and weld on the necessary piping. Additional materials are also needed which add to the cost of a closed drain system. Costs were based on a three man crew using a backhoe with a pneumatic jackhammer to remove concrete around the drain. Field welding was also necessary to attach the piping to the existing drain. It was estimated that each drain would take one-half hour to excavate and 7 manhours to prepare and weld the necessary piping. The cost would be \$546 per drain. The cost for installing an underground tank is the same as that given in Table 8-6. Utility requirements for the purge system are shown in Table 8-7.

It is expected that most units which would be affected by the modification/reconstruction provisions would be down for reasons other than drain retrofitting. Therefore, no costs due to production losses would result from implementing the NSPS.

Table 8-5 presents the costs of retrofitting closed drain system for each model unit. Additionally, cost effectiveness estimates for implementing Regulatory Alternative III for each model unit are given. Cost effectiveness values range from \$1830 per Mg for Model Unit A to \$3130 per Mg for Model Unit C.

8.1.2 <u>Oil-Water Separators</u>

Regulatory Alternatives for oil-water separators have been discussed in Section 6.2. Regulatory Alternative I requires no additional control and therefore does not result in any costs. The costs for implementing Regulatory Alternatives II and III are discussed below.

The costs of covers for separators were provided by industry and represent retrofit costs. The costs for providing a cover on a newly installed separator were derived from the retrofit costs. For this reason, retrofit costs are presented first.

8.1.2.1 Regulatory Alternative II - Covered Separators. Information was provided by the refining industry regarding costs of actual installations of fixed and floating roofs on existing oil-water separators. These costs ranged from \$11/ft² to \$45/ft² for fixed roofs and from \$46/ft² to \$93/ft² for floating roofs. The wide range in costs is due to differences in material of construction, size of the roof, type of roof, and problems encountered during installation. To account for all of these factors, an average cost for installing a fixed or floating roof was developed using all available information. The average cost for installing a fixed or floating roof on an existing oil-water separator is \$56/ft². The total depreciable investment for Regulatory Alternative II was calculated by applying this unit cost to the size roof required by each model unit. Annual costs were then derived using the cost algorithms given in Table 8-2. Table 8-8 presents these costs as well as cost effectiveness estimates for each model unit.

A roof which is part of a newly installed oil-water separator would be expected to cost less than a roof retrofitted on an existing separator. A detailed cost breakdown of a retrofitted roof was provided by one refinery. It was determined that 33 percent of the costs for retrofitting would not have been required for a roof on a newly installed separator. This figure is supported by standard engineering estimations that consider retrofit construction to be 25 to 40 percent higher than new construction 1. Applying this reasoning, it was estimated that the total cost assignable to a roof on a new separator would be \$37/ft².

Table 8-9 presents the costs for Regulatory Alternative II for new oil-water separators. Cost effectiveness estimates for each model unit are also presented. These estimates range from \$40 per Mg for Model Unit A to \$610 per Mg for Model Unit C.

8.1.2.2 Regulatory Alternative III - Covered Separators with Vapor Control Systems. Two situations have been considered in estimating costs for Regulatory Alternative III. It is expected that an existing control device will be accessible to the separator. Therefore, costs have been

TABLE 8-8. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR A RETROFIT CONTROL SYSTEM ON AN API OIL-WATER SEPARATOR

Regulatory Alternative ^a	Model Unit	Total Depreciable Investment (\$1,000)	Annu Direct Expense	ual Cost (Indirect Expense	\$1000) ^b Capital Recovery	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectiveness (\$/Mg)
I	A B C	NO CONTROL CO	OST					
II	A	64.50	2.01	3.31	10.51	15.83	281.3	60
	B	34.90	1.09	1.80	5.70	8.59	140.8	60
	C	34.90	1.09	1.80	5.70	8.59	9.3	920
III	A ^C	70.50	10.87	9.52	11.49	31.88	321.1	100
	B ^C	40.50	9.95	8.01	6.78	24.74	160.6	150
	C	40.50	9.95	8.01	6.78	24.74	10.7	2,310
	Ad	134.70	13.94	12.81	21.96	48.56	311.4	160
	Bd	105.10	12.92	11.31	17.15	41.38	155.7	270
	Cd	105.10	12.92	11.31	17.15	41.38	10.3	4020

Regulatory Alternative I - No action
 Regulatory Alternative II - Require all oil-water separators to be covered with a fixed or floating roof.
 Regulatory Alternative III - As alternative II plus a vapor collection and control system

- b. Costs based on the factors and computational algorithms of Table 8-1 and Table 8-2. All costs are 3rd quarter 1983 dollars.
- c. VOC emissions vented to an existing control device.
- d. VOC emissions vented to a dedicated control device (carbon adsorber system).

TABLE 8-9. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR NEW API OIL-WATER SEPARATORS

Regulatory Alternative ^a	Model Unit	Total Depreciable Investment (\$1,000)	Direct	ual Cost (Indirect Expense	Capital	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectivenes (\$/Mg)
I	A B C		NO CONT	ROL COSTS				
II	A	42.6	1.32	2.20	6.94	10.47	281.3	40
	B	23.1	0.72	1.19	3.76	5.67	140.8	40
	C	23.1	0.72	1.19	3.76	5.67	9.3	610
III	A ^C	48.6	10.19	8.41	7.92	26.52	321.1	80
	BC	29.1	9.58	7.40	4.74	21.72	160.6	140
	C	29.1	9.58	7.40	4.74	21.72	10.7	2,030
	Ad	112.8	13.16	11.71	18.39	43.26	311.4	140
	Bd	93.3	12.55	10.70	15.21	38.46	155.7	250
	C	93.3	12.55	10.70	15.21	38.46	10.3	3,730

a. Regulatory Alternative I - No action Regulatory Alternative II - Require all oil-water separators to be covered with a fixed or floating roof Regulatory Alternative III - As alternative II plus a vapor collection and control system

- c. VOC emissions vented to an existing control device.
- d. VOC emissions vented to a dedicated control device (carbon adsorber system).

b. Total Depreciable Investment costs assumed to be 66% of the retrofit total depreciable investment cost. Costs are based on the factors and computational algoroithms of Table 8-1 and Table 8-2. All costs are 3rd quarter 1983 dollars.

calculated for this situation. However, cases may be found where an accessible control device is not available. For this reason, costs have also been calculated to include the cost of a dedicated control device. In the cost calculation, the dedicated control device is assumed to be a carbon adsorber.

The equipment needed to vent the captured VOC to an existing control device and the associated costs are given in Table 8-10. The materials and installation costs associated with a control system using a carbon adsorber are presented in Table 8-11. These costs are based on the design and operating parameters also given in the table. Utility requirements for these systems and associated costs have been shown in Table 8-7.

The costs for implementing Regulatory Alternative III for oil-water separators are presented in Tables 8-8 and 8-9. Table 8-8 presents the costs for separators retrofitted with covers. Table 8-9 presents costs for covers installed on new separators.

8.1.3 Air Flotation Systems

Three regulatory alternatives for air flotation systems have been discussed in Section 6.2. Regulatory Alternative I requires no additional control and therefore results in no costs. Regulatory Alternative II for DAF systems requires the flotation chamber to be covered with a fixed roof. For IAF systems, this alternative requires the system to be operated gas-tight. Regulatory Alternative III requires the flotation chamber of both types of systems to be tightly covered with captured VOC vented to a control device.

For purposes of the cost analysis, DAF and IAF systems are considered separately. IAF system are constructed with covers and, therefore, do not incur the cost for adding a cover. DAF systems have open flotation tanks and must have a cover installed. For this reason, control costs for DAF systems are higher than IAF systems.

The major equipment costs for controlling VOC from air flotation systems are listed in Table 8-10. The cost for a fiberglass roof was acquired from information provided by industry and equipment vendors. 13 , 14 The unit cost for installing a roof on a DAF system is 20 /ft. This cost can be applied to both new and retrofitted units due to the minimal modifications which would be required for a retrofitted roof.

TABLE 8-10. COST BREAKDOWN OF MAJOR EQUIPMENT FOR VOC CONTROL FOR OIL-WATER SEPARATORS AND AIR FLOTATION SYSTEMS

Oil-Water Separators	Unit Cost (\$/ft ²) ^b
 Cover - New (Fixed or Floating) Cover - Retrofit (Fixed or Floating) 	37 56
Dissolved Air Flotation Systems	
1. Cover - Fiberglass fixed	20
Induced Air Flotation Systems 1. Pressure/Vacuum Valve 2. Latches	<u>Unit Cost (\$)</u> 290 100
Fittings for Vapor Collection System (Oil-Water Separators and Air Flotation) 1. Carbon Steel pipe (200'x 2" 40 std) 2. Tees (4) (2" carbon steel 40 std) 3. Flame arrester (2" aluminum) 4. Flanges (2" carbon steel) 5. Blower and Motor (3/4 Hp)	Total Installed Cost ^{a,b} (\$) 725 278 370 62 2130

^aReference 3. ^b3rd quarter 1983 dollars.

1. Operating Parameters

a) VOC concentration = 1000 ppm
b) Operating capacity = 7 lb/1000 lb carbon
c) VOC content = 0.25 lb VOC/1000 scf
d) Carbon requirement = 0.5 lb carbon/1000 scf
e) Flow rate of gas = 300 scfm
f) Temperature = 100°F
g) Gas velocity = 100 fpm
h) Bed depth = 3 ft.
i) Pressure drop = 26.5 in. H₂0/ft. of carbon
j) Bed area = 3 ft
k) Carbon = 270 lbs
i) Steam = 0.3 lbs/lb carbon (93% efficiency)

= 23652 lbs/yr

2. Costs

a)	Total Depreciable Investment	\$70,213.00
b)	Annual Cost	
•	 carbon replacement 	\$ 126.36
	- steam	\$ 573.56
	- electricity	\$ 500.15
	- cooling water	\$ 9.90
	- labor (0.5 mhr/shift)	\$ 7,665.00

^aReference 5.

IAF systems can be made gas tight by gasketing the access doors which serve to cover the system. For Regulatory Alternative II, costs are added for the pressure/vacuum valve, latches, and gasketing. Additional costs for the piping and blower are included for Regulatory Alternative III.

Two situations have been considered in estimating costs for Regulatory Alternative III. As with oil-water separators, it is expected that an existing control device may be accessible to the air flotation system. However, some cases may exist where a dedicated control device is needed. Therefore, costs have been calculated for both situations. Again, the dedicated control device is assumed to be a carbon adsorber.

Tables of 8-12 and 8-13 present the annual costs and cost effectiveness estimates for DAF and IAF systems, respectively. Costs for utility requirements for the control system are shown in Table 8-7.

8.1.4 Incremental Cost Effectiveness

The incremental cost effectiveness between Regulatory Alternative II and III was calculated for new and retrofit process drain systems, new and retrofit oil-water separators and both types of air flotation system. The results of these calculations are presented in Table 8-14.

8.2 OTHER COST CONSIDERATIONS

Environmental, safety, and health statutes that may cause an expenditure of funds by the petroleum refining industry are listed in Table 8-15. Specific costs to the industry to comply with the provisions, requirements, and regulations of the statutes are unavailable. However, some references are listed which provide cost estimates for complying with specific regulations. 15,16,17

Few refineries are expected to close solely due to the cost of compliance with the total regulatory burden. The costs incurred by the petroleum refining industry to comply with all health, safety, and environmental regulations are not expected to prevent compliance with the proposed NSPS for refinery wastewater systems.

TABLE 8-12. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR DAF SYSTEMS

Regulatory Alternative ^a	Model Unit	Total Depreciable Investment (\$1,000)	Direct	Jal Cost (Indirect Expense	\$1000) ^b Capital Recovery	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectiveness (\$/Mg)
I	A B C	NO CONTROL CO	OSTS					
II	A	15.0	0.47	0.77	2.44	3.69	9.2	400
	B	7.5	0.24	0.39	1.22	1.85	4.6	400
	C	0.5	0.02	0.03	0.08	0.12	0.3	400
III	AC	21.1	9.43	6.98	3.45	19.86	11.6	1,710
	BC	13.5	9.20	6.60	2.21	18.01	5.8	3,110
	C	6.5	8.98	6.24	1.06	16.28	0.39	41,740
	Ad	85.3	12.30	10.29	13.89	36.48	11.3	3,230
	Bd	77.8	12.07	9.90	12.67	34.64	5.6	6,190
	C	70.7	11.85	9.54	11.52	32.91	0.38	86,600

- Regulatory Alternative I No action
 Regulatory Alternative II Requires a fixed cover
 Regulatory Alternative III Requires a fixed cover and vapor collection and control system on all DAF systems
- b. Costs are based on the factors and computational algorithms of Table 8-1 and Table 8-2. All costs are in 3rd quarter 1983 dollars
- c. VOC emissions vented to an existing control device
- d. VOC emissions vented to a dedicated control devices (carbon adsorber system).

TABLE 8-13. ANNUALIZED COST AND COST EFFECTIVENESS OF REGULATORY ALTERNATIVES FOR IAF SYSTEMS

Regulatory Alternative ^b	Model Unit	Total Depreciable Investment (\$1,000)	Direct	ual Cost (Indirect Expense	\$1000) ^C Capital Recovery	Total Annual Cost (\$1,000)	Emission Reduction (Mg/yr)	Cost Effectiveness (\$/Mg)
1	A B C	NO CONTROL						
11	A	0.4	0.01	0.02	0.06	0.10	0.55	180
	B	0.4	0.01	0.02	0.06	0.10	0.27	370
	C	0.4	0.01	0.02	0.06	0.10	0.02	5560
III	Ad	6.0	8.96	6.21	0.98	16.15	1.96	8,240
	Bd	6.0	8.96	6.21	0.98	16.15	0.98	16,480
	C	6.0	8.96	6.21	0.98	16.15	0.06	269,170
	A ^e	70.2	11.83	9.51	11.44	32.78	1.66	19,750
	B ^e	70.2	11.83	9.51	11.44	32.78	0.83	39,350
	C	70.2	11.83	9.51	11.44	32.78	0.05	655,600

a. Cost for vapor control device only, system assumed to be covered.

- c. Costs are based on the factors and computational algorithms of Table 8-1 and 8-2. All costs are 3rd quarter 1983 dollars.
- d. VOC emissions vented to an existing control device.
- e. VOC emissions vented to a dedicated control device (carbon adsorber system).

Regulatory Alternative I - No action
 Regulatory Alternative II - Gas tight system
 Regulatory Alternative III - Vapor collection and control system

TABLE 8-14. INCREMENTAL COST EFFECTIVENESS OF REGULATORY ALTERNATIVES

	Model Unit	Regulatory Annual Cost (\$1,000)	Alternative II Emission Reduction (Mg/yr)		y Alternative III Emission Reduction (Mg/yr)	Incremental Cost (\$/Mg)
Drain System - New	A	5.34	15.4	47.62	30.2	2,860
	B	2.54	7.3	32.30	14.3	4,250
	C	1.61	4.6	26.21	9.1	5,470
Orain System - Retrofit	A	12.65	15.4	55.38	30.2	2,890
	B	5.97	7.3	35.94	14.3	4,280
	C	3.78	4.6	28.47	9.1	5,490
Dil-Water Separator - New	Aa	10.47	281.3	26.52	321.1	400
	Ba	5.67	140.8	21.72	160.6	810
	Ca	5.67	9.3	21.72	10.7	11,460
	Ab	10.47	281.3	43.26	311.4	1,090
	Bb	5.67	140.8	38.46	155.7	2,200
	C	5.67	9.3	38.46	10.3	32,790
Oil-Water Separator-Retrofit	t A ^a	15.83	281.3	31.88	321.1	400
	B ^a	8.59	140.8	24.74	160.6	810
	C ^a	8.59	9.3	24.74	10.7	11,460
	Ab	15.83	281.3	48.56	311.4	1,090
	Bb	8.59	140.8	41.38	155.7	2,200
	C	8.59	9.3	41.38	10.3	32,790
Dissolved Air Flotation	A ^a	3.7	9.2	19.9	11.6	6,750
	B ^a	1.8	4.6	18.0	5.8	13,500
	C ^a	0.1	0.3	16.3	0.4	162,000
	Ab	3.7	9.2	36.5	11.3	15,620
	Bb	1.8	4.6	34.6	5.6	32,800
	C	0.1	0.3	32.9	0.4	328,000
Induced Air Flotation	A ^a	0.1	0.55	16.2	1.96	11,420
	Ba	0.1	0.27	16.2	0.98	22,680
	C ^a	0.1	0.01	16.2	0.06	322,000
	Ab	0.1	0.55	32.8	1.66	29,460
	Bb	0.1	0.27	32.8	0.83	58,390
	Cb	0.1	0.01	32.8	0.06	654,000

Regulatory Alternative II: Cover; Regulatory Alternative III: Captured VOC emissions vented to an existing control device.
 Regulatory Alternative II; Cover; Regulatory Alternative III: Captured VOC emissions vented to a dedicated control device (carbon adsorber).

Table 8-15 STATUTES THAT MAY BE APPLICABLE TO THE PETROLEUM REFINING INDUSTRY

Statute	Applicable provision, regulation or requirement of statute	Statute	Applicable provision, regulation or requirement of statute
Clean Air Act and Amendments	o State Implementation plans	Occupational Safety & Health Act	o Malking-working surface standard
	e Matiene) emission standards for hazardous air pollutants		e Moons of egress standards
	Benzene fugitive emissions		 Occupational health and environmental control standards
	e New source performance standards		o Hazardous material standards
	Air exidation		 Personal protective equipment standards
	Volatile organic liquid storage		• General environmental control standards
	e PSD construction permits		o Modical and first ald standards
•	e Non-attainment construction permits		e fire protection standards
lean Mater Act (federal Mater follution Act)	o Discharge permits	•	e Compressed gas and compressed air equipment
	e Effluent limitations guidelims		o Welding, brozing, and cutting standards
	e Hen source performence standards		
	e Control of oil spills and discharges	Coasto) Zono Monogement Act	e States may veto federal permits for plants to be sited in constal zoon
	o Pretrostment requirements		Constant form
	e Monitoring and reporting		
	 Permitting of industrial projects that impinge on wetlands or public waters 		
	o Environmental impact statements		
lescurce Conservation and Recovery Act	 Permits for treatment, storage, and disposal of hazardous wastes 	Mational Environmental Policy Act	o Requires anvironmental impact statements
	e Establishes system to track hazardous wastes	Safe Drinking Water Act	e Requires underground injection control permits
	 Establishes recordkeeping, reporting, labeling and monitoring system for hazardous wastes 	Marine Sanctuary Act	o Ocean dumping permits o Recordkooping and reporting
	Superfund		
loxic Substances Control	e Premanufacture natification		
Act	• Labeling, recordkeeping		
	• Reporting requirements		
	e Texicity testing		

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9.0 ECONOMIC IMPACT

9.1 INDUSTRY CHARACTERIZATION

9.1.1 General Profile

9.1.1.1 Refinery Capacity. On January 1, 1984, there were 220 petroleum refineries operating in the United States with a total crude capacity of 2,653,000 $\rm m^3$ per stream day. With respect to location, refining capacity is fairly well-concentrated, with 57 percent of domestic crude throughput capacity located in three states: Texas (28%), California (15%), and Louisiana (14%).

Although refining capacity grew steadily through the 1970s, a similar trend in capacity growth has not continued into the 1980s, as noted by Table 9-1. The decrease in the rate of capacity expansion can be traced to reduced consumption resulting from rising prices, the slowdown of economic growth, the availability of substitutes in some applications, and the increasing fuel efficiency of newer automobiles and industrial facilities. Those additions to capacity that have been made in the recent past and which will be made in the future will occur at existing refineries to allow the processing of lower-quality high-sulfur crudes, and increase the output of unleaded gasoline.²

While the number of refineries operating has declined dramatically in recent years (i.e. 1981 to 1984) the average capacity of existing refineries has increased. These trends indicate that many of the closing refineries are of relatively small capacity. Small refinery closures have been due largely to the elimination of Federal subsidies, such as the "small refiner bias" built into the Department of Energy's crude oil entitlements program. This program, as well as all Federal price controls on domestic crude oil and refined petroleum products, was eliminated in 1981 through Executive Order 12287.

Table 9-1. TOTAL AND AVERAGE CRUDE DISTILLATION CAPACITY BY YEAR^a
UNITED STATES REFINERIES, 1973-1983

Year (January 1)	Number of Refineries	Total Capacity (m ³ /sd)b,c	Average Refinery Capacity (m ³ /sd) ^D
1974	247	2,365,000	9,600
1975	259	2,459,000	9,500
1976	256	2,494,000	9,700
1977	266	2,689,000	10,100
1978	285	2,801,000	9,800
1979	289	2,870,000	9,900
1980	297	2,975,000	10,000
1981	303	3,080,000	10,200
1982	273	2,957,000	10,800
1983	225	2,704,000	12,000
1984	220	2,653,000	12,000

aReferences 1 and 3 through 12.

bNote: Capacity in stream days.

 $c_{1 m}^3 = 6.29 \text{ barrels.}$

It should be noted that in the production and capacity tables that follow, a distinction is often made between stream days (i.e., sd) and calendar days (i.e., cd). The basic difference between the two terms is that "stream day" refers to the maximum capacity of a refinery or unit on a given operating day, while "calendar day" production represents the average daily production over a one-year period. Since most refineries do not operate 365 days each year, stream day numbers are always slightly larger than those for calendar days.

9.1.1.2 <u>Refinery Production</u>. In terms of total national output, the percentage yields of most refined petroleum products have remained constant over recent years, although several exceptions are noted below. The percentage yields of refined petroleum products from crude oil for the years 1974 through 1981 are summarized in Table 9-2, while Table 9-3 lists the average daily output of the major products.

The diversity of refinery product output varies with refinery capacity. Large integrated refineries operate a wide variety of processing units, thus enabling the production of many or all of the products noted in Table 9-2. Other refineries are relatively small, have only a few processing units, and produce selected products such as distillate oil and asphalt.

9.1.1.3 Refinery Ownership, Vertical Integration and Diversification. A large portion of domestic refining capacity is owned and operated by large, vertically integrated oil companies, both domestic and international. The remainder is controlled by independent refiners such as Ashland, Charter, Crown Central Petroleum, Holly, Quaker State, Tesoro Petroleum and Tosco.

Table 9-4 lists twenty companies with the greatest capacity to process crude oil. Based upon the capacities noted, and a total domestic capacity of 2,704,000 $\rm m^3$ per stream day, the 4- and 8-firm concentration ratios are 27 and 47 percent, respectively. These ratios indicate a relatively high degree of ownership concentration of refinery capacity.

Refinery ownership is but one aspect of the vertical integration of the major oil companies. Such companies are integrated "backward" in that they own or lease crude oil production facilities, both domestic and international, as well as the means to transport crude by way of pipeline and tankers. On the international level, access to Saudi Arabian crude is maintained through Aramco which is owned by four international companies: Exxon, Standard Oil of California, Texaco, and Mobil.

Table 9-2. PERCENT VOLUME YIELDS OF PETROLEUM PRODUCTS BY YEAR^a
UNITED STATES REFINERIES, 1974-1981
(Percent)

Product	1974	1975	1976	1977	1978	1979	1980	1981
Motor Gasoline	45.9	46.5	45.5	43.4	44.1	43.0	44.5	44.8
Jet Fuel	6.8	7.0	6.8	6.6	6.6	6.9	7.4	7.6
Ethane	0.1	0.1	0.1	0.1	0.1	0.1		0.1
Liquefied Gases	2.6	2.4	2.4	2.3	2.3	2.3	2.4	2.4
Kerosene	1.3	1.2	1.1	1.2	1.2	1.3	1.0	0.9
Distillate Fuel Oil	21.8	21.3	21.8	22.4	22.4	21.5	19.7	20.5
Residual Fuel Oil	8.7	9.9	10.3	12.0	12.0	11.5	11.7	10.4
Petrochem. Feedstocks	3.0	2.7	3.3	3.6	3.6	4.7	5.1	4.7
Special Naphthas	0.8	0.6	0.7	0.6	0.6	0.6	0.7	0.6
Lubricants	1.6	1.2	1.3	1.2	1.2	1.3	1.3	1.3
Wax	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Coke	2.8	2.8	2.6	2.5	2.5	2.6	2.7	3.1
Asphalt	3.7	3.2	2.8	2.9	2.9	3.1	2.9	2.7
Road Oil	0.2	0.1	0.0	0.1	0.1		0.1	
Still Gas	3.9	3.9	3.7	3.6	3.6	3.8	4.0	4.3
Miscellaneous	0.5	0.7	1.0	1.0	1.0	0.8	0.8	0.7
Processing Gain ^b	3.9	3.7	3.5	3.6	3.6	3.6	4.4	4.2
Total ^C	103.9	103.7	103.5	103.6	103.6	103.6	104.4	104.2

aReference 13. Section VIII, Tables 4-4a.

bProcessing Gain = Product Yield - Process Feed (Input)

cTotals exceed 100 percent because product yields are greater than process feeds by an amount equal to the processing gain. In the catalytic reforming process, for example, straight-chain hydrocarbons are converted to branched configurations with hydrogen as a by-product, resulting in an overall net increase in volume.

Table 9-3. PRODUCTION OF PETROLEUM PRODUCTS BY YEARa,b
UNITED STATES REFINERIES, 1972-1981
(1,000 m³/cd)^c

Year	Motor Gasoline	Distillate Fuel Oil	Residual Fuel Oil	Jet Fuel	Kerosene	NGL and LRGd
1972	1,000	419	127	135	35	57
1973	1,039	449	154	137	35	60
1974	1,011	424	170	133	25	54
1975	1,037	422	197	138	24	49
1976	1,088	465	219	146	24	54
1977	1,118	521	279	155	27	56
1978	1,140	501	266	155	24	N.A.
1979	1,132	503	270	161	29	54
1980	1,083	440	262	159	22	N.A.
1981	1,019	416	209	154	19	N.A.

^aReference 13. Section VII. Tables 5, 6, 6a, 7, 7a, 14, 15, 16, 16a, 17, and 17a.

bTotal and product output reports may vary slightly by data source.

 $c_{1m}^3 = 6.29$ barrels.

dNGL = Natural Gas Liquids; LRG = Liquefied Refinery Gases.

Table 9-4. NUMBER AND CAPACITY OF REFINERIES OWNED AND OPERATED

BY MAJOR COMPANIES^a,^b

UNITED STATES REFINERIES, 1983

Company	Number of Refineries	Crude Capacity (1,000 m ³ /cd)
Chevron	12	212
Exxon	5	191
Shell	7	176
Amoco	7	161
Texaco	9	149
Gulf	5	140
Mobil	6	135
ARCO	5	113
Marathon	4	93
Union Oil	4	78
Sohio/BP	3	72
Conoco	5	61
As h1 and	5	59
Sun	3	57
Cities Service	1	51
Phillips	3	47
Champlin	3	46
Getty	3	45
Tosco	3	41
Koch	2	38

aReference 14.

bRecent mergers have combined Chevron with Gulf, and Texaco with Getty.

With regard to transportation by pipeline, the major oil companies have been the main source of capital for the construction and operation of these facilities, due largely to the huge investments required. On the other hand, tanker ownership is split among the major oil companies and independent operators who charter tankers to oil companies and traders. The presence of independent tanker operators is a result of the relatively small financial requirements, compared to pipeline ownership. However, the profitability of such operations has declined along with the volume of crude refined.

While many of the low-volume refinery products are marketed directly by the refiners themselves, the sale of gasoline on the retail level is handled primarily by franchised dealers and independent operators. The major refiners do, however, have a high degree of control over the distribution of their products with regard to market area. This is so because the major refiners select sites for the construction of service stations before the facilities are leased to independent operators under franchise agreements. The major refiners do maintain the direct operation of some service stations for purpose of measuring the strength of the retail market. However, no more than 5 percent of all facilities in operation are managed in this fashion. 16

Many of the firms that operate refineries, notably the larger oil companies, are diversified as well as vertically integrated. Several refiners are vertically integrated through the manufacture of petrochemicals and resins. Among the firms that have interests in these areas are Getty Oil, Occidental Petroleum, and Phillips Petroleum. Ashland Oil's construction division operates the nation's largest highway paving company.

Several instances of diversification can be observed. Exxon Enterprises develops and manufactures various high-technology products. The Kerr-McGee Corporation is the largest supplier of commercial grade uranium for electricity generation and also manufactures agricultural and industrial chemicals. Mobil Oil Corp. is owned by Mobil Corp. which owns both Montgomery Ward and Co. and The Container Corporation of America. The Charter Co., the largest of the independent refiners, is also engaged in broadcasting, insurance, publishing, and commercial printing.

9.1.1.4 <u>Refinery Employment and Wages</u>. Total employment at domestic petroleum refineries has grown steadily since the mid-1960's, with minor disruptions during periods of economic contractions. As Table 9-5 demonstrates,

Table 9-5. EMPLOYMENT IN PETROLEUM AND NATURAL GAS EXTRACTION

AND PETROLEUM REFINING BY YEAR^a

UNITED STATES, 1972-1981

(1,000 Workers)

Year	Petroleum and Natural Gas Extraction	Petroleum Refining
1972	268.2	152.3
1973	277.7	149.9
1974	304.5	155.4
1975	335.7	154.2
1976	360.3	157.1
1977	404.5	160.3
1978	417.1	163.0
1979	476.3	168.5
1980	547.4	154.2
1981	657.2	169.6

aReference 13. Section V. Table 2.

there were 170 thousand workers employed at refineries in 1981.17 With 303 refineries operating that year, 11 average employment at each refinery is approximately 560 persons.

The average hourly earnings of petroleum refinery workers have consistently exceeded average wage rates for both the mining and manufacturing industries. 18 Petroleum refinery hourly earnings have also exceeded those for other sectors of the oil industry as noted in Table 9-6.

9.1.2 Refining Processes

Refineries process crude oil through a series of physical and chemical processes into many individual products. The four major product areas are as follows:

- o Transportation fuels -- motor gasoline, aviation fuel;
- o Residential/commercial fuels -- middle distillates;
- o Industrial/utility fuels -- residual fuel oils; and
- Other products -- liquified gases and chemical process feeds. As noted in Table 9-2, motor gasoline is by far the largest volume product of U.S. refineries. Motor gasoline is produced through blending the products of various refinery units such as those described below. Estimated 1981 gasoline pool composition is presented in Table 9-7. 19
- 9.1.2.1 <u>Crude Distillation</u>. The initial step in refining crude oil is to physically separate the oil into distinct components or fractions through distillation at atmospheric pressure. There are several possible combinations of fractions and quantities available from crude distillation dependent upon the type of crude being processed and the products desired. High boiling point components are often further separated by vacuum flashing or vacuum distillation. The crude oil still provides feedstock for downstream processing and some final products. 21
- 9.1.2.2 Thermal Operations. Thermal cracking operations include regular coking as well as visbreaking. In each of these operations, heavy oil fractions are broken down into lighter fractions by the action of heat and pressure while heavy fuels and coke are produced from the uncracked residue. 22 Visbreaking is a mild form of thermal cracking that causes very little reduction in boiling point but significantly lowers the viscosity of the feed. The furnace effluent is quenched with light gas oil and flashed in the bottom of a fractionator while gas, gasoline, and heavier fractions are recycled.

Table 9-6. AVERAGE HOURLY EARNINGS OF SELECTED INDUSTRIES BY YEAR^a
UNITED STATES, 1972-1981^a
(\$/Hour)^b

Year	Petroleum Refining	Petroleum and Natural Gas Extraction	Total Manufacturing	Total Mining
1972	5.25	4.00	3.81	4.41
1973	5.54	4.29	4.08	4.73
1974	5.96	4.82	4.41	5.21
1975	6.90	5.34	4.81	5.90
1976	7.75	5.76	5.19	6.42
1977	8.44	6.23	5.63	6.88
1978	9.32	7.01	6.17	7.67
1979	10.08	7.73	6.69	8.48
1980	10.94	8.55	7 . 27	9.18
1981	12.17	9.49	7.98	10.06

aReference 13. Section V. Table 2.

bCurrent dollars.

Table 9-7. ESTIMATED GASOLINE POOL COMPOSITION BY REFINERY STREAM^a
UNITED STATES REFINERIES, 1981

Stream	Amount (m ³ /cd)	% of Total
Reformate	355,000	29.9
FCC Gasoline	408,000	34.4
Alkylate	162,000	13.7
Raffinate	17,000	1.4
Butanes	75,000	6.3
Coker Gasoline	15,000	1.3
Natural Gasoline	30,000	2.5
Light Hydrocrackate	22,000	1.9
Isomerate	16,000	1.3
Straight Run Naphtha	86,000	7.3
Total	1,186,000	100.0

aReference 19.

Coking is a severe form of thermal cracking in which the feed is held at a high cracking temperature long enough for coke to form and settle out. The cracked products are separated and drawn off and heavier materials are recycled to the coking operations. 20

- 9.1.2.3 <u>Catalytic Cracking</u>. Catalytic cracking is used to increase the yield and quality of gasoline blending stocks and produce furnace oils and other useful middle distillates.²² By this process the large hydrocarbon molecules of the heavy distillate feedstocks are selectively fractured into smaller olefinic molecules. The use of a catalyst permits operations at lower temperatures and pressures than those required in thermal cracking. In the fluidized catalytic cracking processes, a finely-powdered catalyst is handled as a fluid as opposed to the beaded or pelleted catalysts employed in fixed and moving bed processes.²⁰
- 9.1.2.4 <u>Reforming</u>. Reforming is a molecular rearrangement process to convert low-octane feedstocks to high octane gasoline blending stocks or to produce aromatics for petrochemical uses.²⁰ Hydrogen is a significant co-product of reforming, and is in turn, the major source of hydrogen for processes such as hydrotreating and isomerization.
- 9.1.2.5 <u>Isomerizaton</u>. Isomerization, like reforming, is a molecular rearrangement process used to obtain higher octane blending stocks. In this process, light gasoline materials (primarily butane, pentane, and hexane), are converted to their higher octane isomers.
- 9.1.2.6 Alkylation. Alkylation involves the reaction of an isoparaffin (usually isobutane) and an olefin (propylene or butylenes) in the presence of a catalyst to produce a high octane alkylate, an important gasoline blending stock. 20,22
- 9.1.2.7 <u>Hydrotreating</u>. Hydrotreating is used to saturate olefins and improve hydrocarbon streams by removing unwanted materials such as nitrogen, sulfur, and metals. The process uses a selected catalyst in a hydrogen environment.²⁰ Hydrofining and hydrodesulfurization are two subprocesses used primarily for the removal of sulfur from feedstock and finished products. Sulfur removal is typically referred to as "sweetening".
- 9.1.2.8 <u>Lubes</u>. In addition to or in place of drying and sweetening of hydrotreating units, petroleum fractions in the lubricating oil range are further processed through solvent, acid, or clay treatment in the production

of motor oils and other lubricants. These subprocesses can be used to finish waxes and for other functions. 20

- 9.1.2.9 <u>Hydrogen Manufacture</u>. The manufacture of hydrogen has become increasingly necessary to maintain growing hydrotreating operations. Natural gas and by-products from reforming and other processes may serve as charge stocks. The gases are purified of sulfur (a catalyst poison) and processed to yield moderate to high purity hydrogen. A small amount of hydrocarbon impurity is usually not detrimental to processes where hydrogen will be used.²⁰
- 9.1.2.10 <u>Solvent Extraction</u>. Solvent extraction processes separate petroleum fractions or remove impurities through the use of differential solubilities in particular solvents. Desalting is an example whereby water is used to wash water soluble salts from crude.²¹ Several complex refining processes employ solvent extraction during the production of benzene-related compounds.
- 9.1.2.11 <u>Asphalt</u>. Asphalt is a residual product of crude distillation. It is also generated from deasphalting and solvent decarbonizing -- two specialized steps that increase the quantity of cracking feedstock.²¹
 9.1.3 Market Factors
- 9.1.3.1 <u>Demand Determinants</u>. Most projections of refined product demand conclude that in terms of total refinery output, existing capacity is capable of satisfying demand over the foreseeable future.²³,²⁴ However, expansions and modifications will be undertaken at existing refineries in order to allow the processing of greater proportions of high-sulfur crudes, and to permit the production of increasing levels of high-octane unleaded gasoline. It is also possible that shifts in demand on the regional level may allow the construction of a few new small refineries, and several of these projects are currently known to be planned or under construction.

In Table 9-8 DOE estimates of daily demand levels for the four major refinery products are presented under several assumptions regarding the world price of oil. Reduced driving and greater vehicle efficiency have combined to reduce the future demand for motor gasoline. As Table 9-8 indicates, it is unlikely that gasoline demand will, within the forecast period, reach those levels observed during 1983. This conclusion holds true for all assumptions regarding the future of world oil prices with the exception of the low price scenario for 1985.

Table 9-8. REFINED PRODUCT DEMAND PROJECTIONS FOR U.S. REFINERIES UNDER THREE WORLD OIL PRICE SCENARIOS^a
1983-1986-1989

	World Crude		Demand (1,000 m ³ /cd)						
Year	0il Pr \$/BBL.	fice b,c	Motor Gasoline	Distillate Oil	Residual Oil	Jet Fuel	Tota1 ^d		
1983	30.00	188.70	988.7	425.8	209.1	160.5	2,320.79		
1986 Low Mid High	21.00 28.00 38.00	132.09 176.12 239.02	1,015.7 941.7 869.7	609.3 539.0 482.4	422.0 388.8 329.2	184.6 180.0 173.4	2,880.53 2,657.94 2,419.68		
1989 Low Mid High	26.00 36.00 45.00	163.54 226.44 283.05	883.8 814.3 764.9	625.5 534.3 485.2	425.9 361.0 276.1	196.9 189.5 183.6	2,796.68 2,514.29 2,287.66		

aReference 23, pp. 68, 103, 138.

bReference 23, p. 17.

c₁₉₈₂ dollars.

dTotal includes the four products listed plus all other refined products.

Reduced total gasoline demand does not, however, imply that existing gasoline production facilities are currently capable of meeting future gasoline requirements. In particular, the continued phase-out of leaded gasoline and demand for higher octane ratings will require some additions to refinery capacity. Consequently, refiners can be expected to increase cracking, catalytic reforming, and alkylation capacities in order to maintain octane requirements. 25

Distillate fuel oils are used in home heating, utility and industrial boilers, and as diesel fuel. Unlike the other three major petroleum product categories noted in Table 9-8, demand for distillate fuel oil is projected to increase under all price scenarios. The expected increase can be traced to two major factors namely, the growing popularity of diesel-powered automobiles and light trucks and the phased deregulation of natural gas prices. The shift from gasoline toward diesel fuel, along with a projected increase in vehicle miles traveled by heavy diesel-powered trucks, accounts for the expected increase in distillate fuel demand in the transportation sector. In the residential sector it is expected that the continued deregulation of natural gas prices will reduce the price advantage previously held by natural gas in space heating applications.

Residual fuel oil is used as a bunker fuel in large ships, large utility and industrial boilers, and in the heating of some buildings. Residual fuel oil competes with coal for use as a fuel in the applications noted above. Table 9-8 shows that the most recent recession depressed residual fuel demand in 1982, and that little growth in demand is expected in the near future. This lack of growth is attributable to the increasing ability of refiners to crack residual fuel into more valuable lighter products as well as a general decline in demand from industrial and utility consumers. Among the factors that are adversely affecting the demand for residual fuel oil are: a slowdown in the generation of electricity and conversions to coal and nuclear energy by major utilities, and increased fuel efficiency and closing of obsolete plants in the industrial sector. 26

Finally, the demand for some products not shown on Table 9-8 remains promising for the foreseeable future. Such products include solvents, lubes, and petrochemical feedstocks. 27

The elasticity of demand is a measure of the relative change in quantity demanded of a product, in response to a relative change in its

price. With regard to the elasticity of demand for various petroleum products, most analysts agree that in the short-term, quantity demanded is not very sensitive to price changes due to the inability of consumers to easily shift to other technologies. However, as the focus shifts to the longer term, the elasticity of demand increases as consumers have increased ability to shift to other fuels or more fuel-efficient products. DOE estimates of longer term (i.e. to 1990) demand elasticities are summarized in Table 9-9.

9.1.3.2 <u>Supply Determinants</u>. As noted in the previous section, it is unlikely that the supply of refined petroleum products will be restricted for reason of inadequate domestic refining capacity. It is, however, possible that disruptions in the flow of imported oil could result from international developments, in particular, political instability in the Middle East.

Attempts to reduce dependence upon imported oil have focused upon four major areas: reduced consumption through conservation, increased domestic production through the decontrol of domestic oil prices, domestic stockpiling of imported oil, and the development of a synthetic fuels industry. While price decontrol and synthetic fuels development may have a significant impact in terms of import reductions, these measures are essentially mid- to long-term solutions. Conservation, on the other hand, has offered more immediate results.

The effects of higher prices and recent conservation efforts, including decreased gasoline consumption, and conversion of facilities to coal and natural gas, can be observed in Table 9-10. In particular, imports of crude oil have declined significantly after reaching a historic high of 384 million m³ in 1977, and the reduction of imports has continued into the 1980's. Domestic consumption has also fallen considerably since the peak levels observed during 1978. However, it should be noted that some portion of the decline in both imports and domestic consumption may be attributed to the recession of 1981-82.

Price controls on domestic crude oil and refined petroleum products were revoked by Executive Order 12287 (January 28, 1981). This Order essentially rescinded the price and allocation authority granted to the Department of Energy under the Emergency Petroleum Allocation Act of 1973. The progressive decontrol of domestic crude oil prices has been accompanied by increased exploration, and is expected to increase stocks of already proven reserves.

Table 9-9. PRICE ELASTICITY ESTIMATES FOR MAJOR REFINERY PRODUCTS

BY DEMAND SECTOR^a

UNITED STATES, 1990

Demand Sector	Refinery Product	Price Elasticity ^b
Residential	Distillate Oil	-0.46
Commerical	Distillate Oil	-0.45
Industrial	Distillate Oil	-0.64
	Residual Oil	-0.45
Transportation	Gasoline	-0.45
	Distillate Oil	-0.89
	Residual Oil	-0.09
	Jet Fuel	-0.52

^aReference 28. p. 333.

^bPercent change in quantity demanded in response to a one percent increase in price.

Table 9-10. CRUDE OIL PRODUCTION AND CONSUMPTION BY YEAR^a
UNITED STATES, 1970-1982
(1,000,000 m³/year)^b

Year	Domestic Production ^C	Imports ^C	Domestic Consumption ^e	Exports ^e	Year-End Stocks ^e	Stocks as Percent of Consumption
1970	559	77	633	0.8	44	6.94
1971	549	98	649	0.1	41	6.36
1972	549	129	680	0.1	39	5.76
1973	534	188	723	0.1	39	5.33
1974	486	202	688	0.2	42	6.13
1975	465	238	703	0.3	43	6.14
1976	452	308	760	0.5	45	5.97
1977	457	384	841	2.9	55	6.57
1978	485	369	854	9.2	60	7.01
1979	474	376	850	13.6	68	8.05
1980	500	303	802	16.7	27	3.37
1981	497	240	753	13.2	34	4.51
1982	503 ^d	201 ^d	703	13.7	37	5.26

^aReference 2. p. 073 (1970-1979 data).

 $b_{1m}^3 = 6.29 \text{ barrels.}$

^cReference 13. (1980-1981 data).

dReference 29. Table 2.

eReference 29. Table 22, (1980-1982 data).

Finally, evidence of changing supply conditions in the industry can be seen in the fate of the synthetic fuels industry. The development of such an industry was a priority during the energy short years of the mid to late 1970's. However, the incentive to develop technologies capable of converting oil shale, gas, and coal to liquid fuels has been reduced due largely to abundant oil supplies, reduced Federal funds, and high interest rates. Consequently, it is not expected that the availablity of synthetic fuels will affect the oil supply situation in this decade.

9.1.3.3 Prices. Table 9-11 indicates historic wholesale price levels for gasoline, distillate fuel oil, and residual fuel oil. For each product, a pattern of stable prices, followed by rapid price increases in 1974 and 1979 through 1981, can be observed. The increases observed during both periods can be attributed to the pass-through of increases in the price of crude oil supplied by the OPEC nations.

Future prices of refined products will continue to rise in response to increases in the price of both imported and domestic crude. The Department of Energy expects that average worldwide crude oil prices should increase at an annual rate of about 3.1 percent up to 1989 (see Table 9-19).

9.1.3.4 Imports. Imports of both crude oil and refined products are expected to continue to decline through the 1980's. In the case of crude oil, the fall in import levels can be attributed to increases in the price of OPEC oil, and the increased production of domestic crude prompted by its price decontrol.

Low sulfur (sweet) crudes are generally more desirable than high sulfur (sour) crudes because the refining of the latter requires a larger investment in desulfurization capacity to meet process as well as environmental needs. While more than half of the current crude imports are sweet, only 15 percent of OPEC's total oil reserve is sweet crude. Occupantly, it is most likely that future imports will contain higher proportions of sour crudes and thus make sour crude processing a more profitable investment for many refineries.

With regard to refined petroleum products, the importation of most of these products is expected to decline as it has since the mid-1970's. Table 9-12 shows that for the major refined products, imports peaked during 1973-1974. In general, imports of refined products have been relatively small compared with production at domestic refineries. One notable exception is residual fuel oil. The relatively high ratio of imports to domestic

Table 9-11. AVERAGE WHOLESALE PRICES: GASOLINE, DISTILLATE FUEL
OIL, AND RESIDUAL FUEL OIL BY YEAR^a
UNITED STATES, 1968-1982
(¢/liter)

Year	Gasoline ^{b,C}	Distillate Fuel Oilb,c	Residual Fuel Oilb,c
1968	4.4	2.7	1.5
1969	4.5	2.7	1.5
1970	4.7	2.9	1.9
1971	4.8	3.1	2.6
1972	4.7	3.1	3.0
1973	5.2	3.6	3.4
1974	8.1	5.6	6.8
1975	9.5	8.2	6.8
1976	10.3	8.7	6.6
1977	11.2	9.8	7.9
1978	11.8	9.9	7.4
1979	16.4	14.3	10.2
1980	24.0	21.3	14.6
1981	26.9	26.0	18.2
1982	24.7	24.4	16.7

aCurrent dollars

^bReference 12, P. 079 (1968-1979)

^cReference 29. Table 42 (1980-1982)

Table 9-12. IMPORTS OF SELECTED PETROLEUM PRODUCTS BY YEAR^a
UNITED STATES, 1969-1981
(1,000 m³/cd)

	Motor Gasoline	Distillate Fuel Oil	Residual Fuel Oil	lot Fuel	V	NGL and LRG
<u>Year</u>		ruel oil	ruel Ull	Jet Fuel	Kerosene	
1969	10	22	201	20	0.5	6
1970	11	24	243	23	0.6	8
1971	9	24	252	29	0.2	17
1972	11	29	277	31	0.2	28
1973	21	62	295	34	0.3	38
1974	32	46	252	26	8.0	34
1975	29	25	194	21	0.5	29
1976	21	23	225	12	1.4	31
1977	34	40	216	12	3.0	32
1978	31	27	214	14	1.7	22
1979	29	31	182	14	1.4	37
1980	22	22	146	13	1.5	NA
1981	24	27	127	6	1.1	NA NA

aReference 13. Section VII, Table 5, 6, 6a, 7, 7a, 14, 15, 16, 16a, 17, 17a

NA - not available.

production of this product is attributed to the orientation of U.S. refineries toward the production of higher levels of more valuable lighter products, such as motor gasoline, through the "cracking" of residual oil. The importation of greater amounts of residual oil is therefore required to satisfy the requirements of utilities and large industrial boilers in this country.

9.1.3.5 Exports. Exports of crude oil and refined petroleum products are a small portion of total U.S. production, and amount to less than eight percent of the volume imported.³¹ All exports are controlled by a strict licensing policy administered by the U.S. Department of Commerce. Recently, crude oil exports have increased in response to the Canada-United States Crude Oil Exchange Program. The program is mutually beneficial in that acquisition costs are minimized through improved efficiency of transportation.

Table 9-13 summarizes recent trends in major refined product exports. The decline in exports through the 1970s can be attributed to both increased domestic demand and the expansion of foreign refining capacity.

9.1.4 Financial Profile

The financial status of the oil industry is generally regarded as strong, although recent supply/demand imbalances have affected profitability. Recent below average performance has been attributed to a number of factors including, reduced demand due to conservation, oversupply due to new discoveries, and major recessions in Western Europe and the United States. 32

Profit margins and returns on investment for both major oil companies and independent refiners are summarized in Tables 9-14 and 9-15. In those tables, profit margin refers to net (after-tax) income as a percentage of sales, while return on investment expresses net (after-tax) income as a percentage of total investment or total assets.

Table 9-13. EXPORTS OF SELECTED PETROLEUM PRODUCTS BY YEAR^a
UNITED STATES, 1969-1981
(1,000 m³/cd)

Year	Motor Gasoline	Distillate Fuel Oil	Residual Fuel Oil	Jet Fuel	Kerosene	NGL and LRG
1969	0.3	0.5	7.3	0.8	0.2	5.6
1970	0.2	0.5	8.6	1.0	-	4.3
1971	0.2	1.3	5.7	0.6	0.2	4.1
1972	0.2	0.5	5.2	0.3	-	4.9
1973	0.6	1.4	3.7	0.8		4.3
1974	0.3	0.3	2.2	0.3	-	4.0
1975	0.3	0.2	2.4	0.3	-	4.1
1976	0.5	0.2	1.9	0.3	-	4.0
1977	0.3	0.2	1.0	0.3	-	2.9
1978	0.2	0.5	2.1	0.2	-	3.2
1979	0.0	0.5	1.4	0.2	-	NA
1980	0.2	0.5	5.2	0.2	-	NA
1981	0.3	0.8	18.8	0.3	<u></u>	NA

aReference 13. Section VII, Tables 5, 6, 6a, 7, 7a, 14, 15, 16, 16a, 17 and 17a. NA - not available.

Table 9-14. PROFIT MARGINS FOR MAJOR CORPORATIONS WITH

PETROLEUM REFINERY CAPACITY, 1977-1981a

(Percent)

Company	1977	1978	1979	1980	1981
Integrated-International	2.0	3.1	8.9	6.9	4.2
British Petroleum	3.0		5.4	5.5	5.2
Exxon Corp.	4.5	4.6		5.3	4.4
Gulf Oil	4.2	4.4	5.5	4.7	3.8
Mobil Corp.	3.1	3.2	4.5	6.3	4.7
Royal Dutch Petroleum	6.0	5.0	11.1		5.4
Standard Oil of California	4.9	4.8	6.0	5.9	4.0
Texaco, Inc.	3.3	3.0	4.6	4.4	4.0
Integrated-Domestic					
Amerada Hess	3.9	3.0	7.5	6.9	2.3
American Petrofina	3.6	2.8	5.2	4.9	2.9
Atlantic Richfield	6.4	6.5	7.2	7.0	6.0
Diamond Shamrock	10.6	7.8	7.6	6.4	6.8
Getty 0il	9.9	9.3	12.5	8.6	6.6
Kerr-McGee	5.5	5.7	6.0	5.2	5.5
Murphy 0il	4.2	3.9	6.6	7.7	6.7
Occidental Petroleum	3.6	0.1	5.9	5.7	4.9
Phillips Petroleum	8.2	10.2	9.4	8.0	5.5
Shell Oil	7.3	7.4	7.8	7.8	7.9
Standard Oil (Indiana)	7.8	7.2	8.1	7.3	6.4
Standard Oil (Ohio)	5.2	8.7	15.0	16.4	14.5
Sun Co.	5.6	4.9	6.6	5.6	7.2
Union Oil of California	5.9	6.4	6.6	6.5	7.4
Refiners					
Ashland Oil	3.4	4.7	8.1	2.5	1.0
Charter Co.	1.3	1.2	8.7	1.1	1.1
Crown Central Petroleum	2.0	2.8	6.8	1.5	0.2
Holly Corp.	3.8	3.5	2.6	2.2	1.4
Quaker State	6.0	4.9	4.9	3.1	3.0
Tesoro Petroleum	0.1	2.4	2.5	2.9	2.6
	1.2	1.6	4.1	1.9	0.7
Tosco Corp.	1 ° L				

^aReference 14, p. 088.

Table 9-15. RETURN ON INVESTMENT OF MAJOR CORPORATIONS
WITH PETROLEUM REFINERY CAPACITY 1977-1981a

(Percent)

			 		
Company	1977	1978	1979	1980	1981
Integrated-International					
British Petroleum	4.3	4.1	11.8	8.8	4.4
Exxon Corp.	6.5	6.9	9.5	10.7	9.4
Gulf Oil	5.4	5.4	8.2	7.8	6.5
Mobil Corp.	5.1	5.2	8.0	9.3	7.2
Royal Dutch Petroleum	8.0	6.0	13.5	7.7	5.5
Standard Oil of California	7.1	7.0	10.2	11.9	10.4
Texaco, Inc.	5.0	4.4	8.1	9.1	8.7
Integrated-Domestic					
Amerada Hess	6.0	4.2	11.3	9.6	3.5
American Petrofina	4.6	3.5	8.0	9.2	6.4
Atlantic Richfield	6.8	6.7	8.9	10.7	9.1
Diamond Shamrock	9.4	6.7	7.0	7.5	7.5
Getty Oil	0.8	7.4	11.2	12.2	9.6
Kerr-McGee	6.9	6.1	7.3	7.1	6.8
Murphy 0il	3.7	3.2	6.1	7.2	6.4
Occidental Petroleum	5.0	0.2	10.9	11.1	9.0
Phillips Petroleum	9.5	11.1	11.5	11.7	8.3
Shell Oil	8.3	8.4	9.1	N/A	9.0
Standard Oil (Indiana)	8.4	8.0	9.6	10.4	8.9
Standard Oil (Ohio)	2.3	5.0	13.4	17.0	14.0
Sun Co.	6.6	6.8	10.2	7.8	9.5
Union Oil of California	7.0	7.3	8.7	10.1	11.0
Refiners				5.0.	0.4
Ashland Oil	6.7	8.8	20.2	6.8	2.4
Charter Co.	3.2	3.4	29.1	2.8	3.4
Crown Central Petroleum	5.1	6.4	16.8	3.6	0.6
Holly Corp.	10.6	9.9	8.0	8.0	3.8
Quaker State	7.3	6.3	7.6	5.3	5.4
Tesoro Petroleum	0.7	5.3	9.9	1.7	10.5
Tosco Corp.	2.8	4.2	14.2	6.2	2.3

^aReference 14, p. 087.

9.2 ECONOMIC IMPACT ANALYSIS

9.2.1 <u>Introduction and Summary</u>

In the following sections the economic impacts of the regulatory alternatives noted in Chapter 6 are discussed. Also presented is a summary of the method used to estimate such impacts. In general, economic impacts are described in terms of the price increases that may be prompted by the various regulatory alternatives, and the potential reductions in petroleum product output that could result as consumers respond to increased prices. The socioeconomic impacts of the proposed NSPS including inflationary, employment, balance of trade, and small business impacts are addressed in Section 9.3. As noted in that section, the fifth-year annualized costs of the most costly regulatory alternatives are \$6.3 million, well below the \$100 million level that Executive Order 12291 identifies as the threshold for major regulatory actions.

With regard to the price increases and industry-wide output reductions that could result from the costs of this NSPS, all price and output changes are very small. If Regulatory Alternative II is required for the three sources described in the previous section, price increases would be less than \$0.03 per m³ (\$0.005/Bb1) and industry-wide output reductions would be about 110 m³ per day (about 710 Bb1/day). These changes represent a 0.01 percent increase in price and a 0.004 percent decrease in quantity demanded. With the higher costs of Regulatory Alternative III for the three sources, price increases would be less than \$0.34 per m³ (\$0.05/Bb1) and output reductions would be about 1,200 m³ per day (about 7,560 Bb1/day). In this case the price increase is about 0.13 percent, and the quantity demanded is reduced 0.05 percent.

9.2.2 Method

As explained in Chapter 3, the petroleum refinery wastewater system collects wastewater from numerous points throughout the refinery, and treats it by way of the separation and flotation processes previously described. Such wastewater is generated through the operation of various process units and may also be the result of storm water runoff at the refinery site. For these reasons, the costs of operating a specific wastewater system cannot be attributed to the production of an individual refined petroleum

product, or group of products, but should be allocated over all products produced at the refinery. Likewise, the total annualized costs incurred by the refinery in the control of VOC emissions from the wastewater system should also be evaluated from the perspective of total refinery output, rather than the output of an individual product, or group of products.

The method used to evaluate potential price and output impacts has three basic parts:

- o the estimation of the annualized control cost per unit of output produced at a new refinery (i.e. required price increase),
- o the estimation of the price per unit of refinery output and total output demanded in 1989, as well as the demand curve for petroleum products in that year, and
- o the estimation of product prices and demand from domestic refineries in 1989 both with and without the costs related to the wastewater NSPS.

Each of these tasks is discussed in greater detail below.

For purposes of this analysis it is assumed that the market for refined petroleum products is basically competitive, and that there is little competition from imports of refined products. It is also assumed that, as projected by the U.S. Department of Energy (DOE), continued economic growth will result in 1989 prices and production levels that are higher than those currently observed. Under such conditions, 1989 prices and output will be influenced by changes in the cost structure of the few totally new refineries expected to be constructed over the next five years. This is true because these refineries will have higher average total costs relative to existing refineries, and as such, will determine the point of intersection between the industry supply and demand curves. Consequently, even though most new unit constructions and modifications will occur at existing refineries, the major focus of this analysis is upon the extent to which NSPS costs will increase the total per unit cost of new refineries.

The estimation of the extent to which the cost/price structure of a new refinery will be affected, entails the approximation of the annual capacity of a new refinery, the number of process units that will comprise

such a refinery, and the total annualized costs to the refinery to control VOC emissions from all process drain systems, the oil-water separator, and the air flotation system. In this regard it has been assumed that any new refinery will be relatively small with daily capacity of 4,000 m³ (about 25,000 Bbl), and will require controls on drains at six process units, two each for Model Units A, B, and C. The refinery is also assumed to have one oil-water separator and one air flotation system. It should be noted that in summarizing NSPS control costs for the refinery, three "worst case" assumptions are made. That is, it is assumed that dedicated control devices are needed for both the oil-water separator and air flotation systems, and that these systems are of the API and DAF types respectively. All three assumptions imply higher NSPS control costs.

Both the average size of the expected new refinery and number of process units were selected after review of the capacity and complexity of those new refineries currently under construction, as reported in published summaries of new refinery construction activities.³³ To the extent that a new refinery may have fewer process units, total costs to the refinery will be lower. Finally, per unit annualized costs are estimated through the division of total annualized NSPS control costs for the refinery by its expected annual volume of output.

The next step in this method entails the estimation of price per unit and total domestic refinery output for the year 1989. This year is of concern because it represents the fifth complete year after proposal, and because the current planning horizon of the industry extends to about that point, given the time required to plan, design and construct completely new refineries.

The estimation of 1989 price and output, as well as the demand curve for refined products in that year, has been made possible through the results of DOE econometric models. In particular, published results generated by DOE's Intermediate Future Forecasting System (IFFS) allow the estimation of equilibrium price and quantity under several assumptions regarding future world crude oil prices.³⁴

Some results of the IFFS model have been noted in Table 9-8 and are used in the following section to approximate the demand curve for refined

products as it might exist in 1989. The equation for the demand curve for refined petroleum products in 1989, has been estimated in this analysis by observing two points that lie on the curve, and solving for the straight line that includes those two points. As shown in the following section, the points selected are quantity demanded at the most likely 1989 price and quantity demanded if the 1989 price is about 25 percent higher. The straight line connecting these two points provides an approximation of the 1989 demand curve because the two points estimate the level of demand expected in that year if all factors other than price are held constant. In reality the demand curve is probably not linear, but for the purpose of this analysis linearity is assumed because the control costs will add very little to 1989 baseline prices. Consequently, the movement up the demand curve that will result as consumers respond to slightly higher prices will be very small, thus reducing the significance of the precise shape of the demand curve in that area.

Finally, estimates of prices and the demand curve for the industry in 1989, together with estimates of the costs per unit attributable to the NSPS, will allow approximations of the degree to which industry-wide output will fall short of the output level that would be expected without the NSPS. Such lower industry-wide output will have implications for the amount of new capacity required to meet the future demand for refined petroleum products. Estimates of 1989 demand under the two regulatory alternatives are made by simply solving the equation for the 1989 demand curve, under the assumption that 1989 prices will be higher by the amount of the NSPS control costs. A horizontal supply curve is implicitly assumed by this part of the analysis, and the extent to which the NSPS costs shift this curve upward is determined by the annualized control costs. The following section details the quantitative application of the method outlined above.

9.2.3 Analysis

As explained in the previous section the focus of this analysis is upon the cost structure of a hypothetical new refinery, and in particular the extent to which the NSPS costs will increase the per unit cost of the refinery, and ultimately the market clearing price of all refined petroleum products. Tables 9-16 and 9-17 demonstrate the calculation of annualized cost on a

Table 9-16. TOTAL ANNUALIZED CONTROL COSTS FOR A NEW REFINERY, REGULATORY ALTERNATIVE IIa

(\$1,000 1983)

Model Unit	Annualized Cost/Unit	Number of Units	Annualized Cost/Refinery
Process Drain Systems	<u>i</u>		
Α	\$5.34b	2	\$10.68
В	2.54b	2	5.08
С	1.61 ^b	2	3.22
Oil-Water Separator	5.67 ^c	1	5.67
Air Flotation System	1.85 ^d	1	1.85
		TOTAL	26.50

acapacity = $4,000 \text{ m}^3$.

bTable 8-4.

CTable 8-9.

dTable 8-13.

Table 9-17. TOTAL ANNUALIZED CONTROL COSTS FOR A NEW REFINERY, REGULATORY ALTERNATIVE IIIa

(\$1,000 1983)

Model Unit	Annualized Cost/Unit	Number of Units	Annualized Cost/Refinery
Process Drain Systems	<u>i</u>		
Α	\$47.62b	2	\$ 95.24
В	32.30b	2	64.60
С	26.21 ^b	2	52.42
Oil-Water Separator	38.46 ^c	1	38.46
Air Flotation System	34.64d	1	34.64
		TOTAL	285.36

^aCapacity = $4,000 \text{ m}^3$.

CTable 8-9. API separator with emissions vented to a dedicated control device.

bTable 8-4.

dTable 8-13. DAF system with emissions vented to a dedicated control device.

refinery basis assuming that the new refinery will have daily capacity of 4,000 m³ (about 25,000 Bb1/day) and will have six process units and both an oil-water separation and an air flotation system. According to the data shown in these tables, total annualized control costs for the refinery are \$26.50 thousand and \$285.36 thousand for Regulatory Alternatives II and III respectively.

In order to express these costs on a per unit output basis, the annualized costs are divided by total annual output. Assuming the refinery operates 350 days per year and at 60 percent of the designed capacity, annual output is 840,000 m³ (5,283,600 Bbl). Thus on a per unit basis the annualized cost are \$0.03 and \$0.34 per m³ for Regulatory Alternatives II and III respectively (\$0.005 and \$0.05/Bbl).

As noted in the previous section, the results of DOE modelling activities have allowed the estimation of equilibrium prices and quantities in 1989. While DOE has projected United States refinery demand under three possible world crude oil prices (in 1982 dollars) these prices have been converted to domestic wholesale prices for refined products to allow the approximation of the 1989 demand curve.

The relevant price and quantity data are summarized in Table 9-18. The world crude oil prices are those reported by DOE, and are also noted in Table 9-8 of Section 9.1. To convert crude prices to wholesale prices for refined products, the crude prices have been increased by 8.55 percent according to recently observed price differences between the two products. The 1989 wholesale price estimates (in 1982 dollars) are presented in the third and fourth columns of Table 9-18. Finally, because the control costs presented in Chapter 8 are expressed in terms of third quarter 1983 dollars, the 1989 wholesale prices (in 1982 dollars) are updated according to the GNP price deflator.

The equilibrium price and quantity for 1989 are assumed to be those represented by the mid-level price scenario. Table 9-18 shows this equilibrium price and quantity level to be \$257.16 per m³ (\$40.88/Bbl) and 2,514.29 thousand m³ per day (15,814.90 thousand Bbl/day). The slope of the demand curve in the immediate area of this equilibrium can be approximated from the data provided by Table 9-18. Because the table summarizes demand levels expected when all factors other than price are held constant,

Table 9-18. DOE PROJECTED PRICES AND DOMESTIC REFINERY DEMAND UNDER THREE WORLD OIL PRICE SCENARIOS, 1989

	World Crude Oil Price, 1989 ^a (1982 \$'s)		Prices	nolesale s 1989 ^b ? \$'s)	Prices	olesale 1989 ^c \$'s)	Total U.S. Refinery Demand 1989 ^d (1,000 m3/day)	
	\$/Bb1	\$/m ³	\$/Bb1	\$/m ³	\$/Bb1	\$/m ³	1,000 Bb1	1,000m ³
Low	26.00	163.54	28.22	177.52	29.52	185.72	17,591.09	2,796.68
Mi d	36.00	226.44	39.08	245.80	40.88	257.16	15,814.90	2,514.29
High	45.00	283.05	48.85	307.25	51.11	321.45	14,389.40	2,287.66

aTable 9-8.

^bCrude prices converted to wholesale prices for refined products, by applying a factor of 1.0855.

 $^{^{\}rm C}$ Prices converted to 3rd quarter 1983 dollars through GNP Implicit Price Deflator where 1982 = 206.88, and 3rd quarter 1983 = 216.44.

dTable 9-8.

the demand curve in the area immediately above the mid-price equilibrium can be approximated by solving for the straight line between the price/quantity points defined by the high and mid-price scenarios. When the two points (\$257.16, 2,514.29 thousand $$m^3/day$) and (\$321.45, 2,287.66 thousand $$m^3/day$) are considered the following equation for the demand curve is obtained;

Quantity $(1,000 \text{ m}^3/\text{day}) = 3,420.811 - 3.525125 \text{ Price},$

where price and quantity are the independent and dependent variables respectively.

The final step in the analysis is to add the NSPS costs per refinery to the 1989 equilibrium price for refined products, and estimate 1989 demand levels from the demand equation noted above. With regard to prices, it has been shown that the 1989 industry baseline price of \$257.16 per m³ would increase to \$257.19 and \$257.50 per m³ under Regulatory Alternatives II and III respectively, if all costs are passed through in the form of higher prices. Solving the demand equation for these prices decreases the estimate of 1989 quantity demanded from the 1989 baseline of 2,514.29 thousand m³ per day to 2,514.18 thousand m³ per day and 2,513.09 thousand m³ per day under Regulatory Alternatives II and III respectively. All 1989 prices and demand levels are summarized in Table 9-19.

9.2.4 Conclusions

The general conclusion to be derived from the preceding analysis is that the NSPS for refinery wastewater systems will have very little impact upon either the firms that refine petroleum products or the consuming public. Table 9-20 summarizes the changes in price and quantity demanded that can be expected as both the demand for and supply of petroleum products from domestic refineries grows until the year 1989. As indicated, market forces alone will increase the price of refined products by about \$42.86 per m³ (\$6.81/Bb1) over that period (i.e., from \$214.30/m³ in 1983, to \$257.16/m³ in 1989 as shown in Table 9-19). Such forces will determine the market clearing price and quantity in 1989 and include such factors as: the price of imported and domestic crude oil and the proportions of each used by domestic refineries; the prices of alternative sources of energy; the growth of the United States

Table 9-19. PRICE AND TOTAL DEMAND UNDER REGULATORY ALTERNATIVES II AND III

(3rd quarter 1983 dollars, 1,000 m³/day, 1,000 Bb1/day)

	1983 B	1983 Baseline ^a , ^b		1989 Baseline ^C		Reg. Alt. II		Reg. Alt. III	
	Price	Demand	Price	Demand	Price	Demand	Price	Demand	
Cubic Meters (m3)	\$214.30	2,320.79	\$257.16	2,514.29	\$257.19	2,514.18	\$257.50	2,513.09	
Barrels (Bbl)	\$ 34.07	14,597.79	\$ 40.88	15,814.90	\$ 40.89	15,814.19	\$ 40.93	15,807.34	

aTable 9-8, prices converted to 3rd quarter 1983 dollars through GNP Implicit Price Deflator where 1982 = 206.88, and 3rd quarter 1983 = 216.44.

^bCrude prices converted to wholesale prices for refined products by factor of 1.0855.

CTable 9-18.

Table 9-20. CHANGES IN 1989 PRICE AND DEMAND COMPARED WITH 1983 BASELINE LEVELS

(3rd quarter 1983 dollars, 1,000 m³/day, 1,000 Bb1/day)

	Changes Under Reg. Alt. I ^a		Changes Under Reg. Alt. II		Changes Under Reg. Alt. III	
	Price	Demand	Price	Demand	Price	Demand
Cubic Meters (m ³)	\$42.86	193.50	\$42.89	193.39	\$43.20	192.30
Barrels (Bbl)	\$ 6.81	1,217.11	\$ 6.82	1,216.40	\$ 6.86	1,209.55

 $^{{}^{\}rm a}{\rm No}$ NSPS control, thus these increases in price and quantity demanded are due to market forces alone.

and international economies; and the costs of other inputs into the refinery industry (e.g. labor-and capital).

If the NSPS costs are also considered in addition to the factors noted above, the prices of refined products would show very little additional increases. If the industry incurs the costs related to Regulatory Alternative II, the price of refined products would increase about \$42.89 per m³ (\$6.82/Bb1), or \$0.03 per m³ (less than \$0.01/Bb1) more than they would without the NSPS. If the higher costs of Regulatory Alternative III are incurred the increase would be about \$0.34 per m³ (\$0.05/Bb1).

Although the increases noted above are very low, and may in fact be imperceptible to the average consumer, the method used in this analysis allows some approximation of sales decreases that would occur as consumers encounter the slightly higher prices. Table 9-20 shows that in 1989, demand would be 193.50 thousand m³ per day (1,217.11 thousand Bb1/day) higher than in 1983, if the NSPS is not promulgated. However, with the standard, demand would be 193.39 thousand m³ per day (1,216.40 thousand Bb1/day) higher under Regulatory Alternative II, and 192.30 thousand m³ per day (1,209.55 thousand Bb1/day) higher under Regulatory Alternative III. Thus Regulatory Alternative II would reduce 1989 demand by about 110 m³ per day (about 710 Bb1/day) and Regulatory Alternative III by 1,200 m³ per day (about 7,560 Bb1/day). Under the competitive market and capacity utilization assumptions made in this analysis, it should be concluded that planned additions to industry-wide capacity would be reduced by these small amounts if either Regulatory Alternative II or III is promulgated.

9.3 SOCIOECONOMIC AND INFLATIONARY IMPACTS

The previous section has described how the petroleum refining segment of the national economy might be affected by this NSPS. In this section the scope of the analysis is expanded so that the probability of broader economic effects might be assessed. Among the issues examined are those related to inflation, employment, the balance of trade, and the potential for adverse impacts upon small businesses.

9.3.1 Executive Order 12291

According to the guidelines established by Executive Order 12291 "major rules" are those that are projected to have any of the following impacts:

- o an annual effect on the economy of \$100 million or more,
- o a major increase in costs or prices for consumers, individual industries, federal, state, or local government agencies, or geographic regions, or
- o significant adverse effects on competition, employment, investment, productivity, innovation, or on the ability of the United States based enterprises to compete with foreign-based enterprises in domestic or export markets.

Each of these topics are examined in the following sections.

9.3.1.1 Fifth-Year Annualized Costs. The determination of fifth-year annualized costs is demonstrated in Tables 9-21 and 9-22. Table 9-21 shows the expected fifth-year cost for each model unit under each regulatory alternative. The total costs noted in this table are determined through consideration of the annualized costs presented in Chapter 8 and the number of new unit constructions, reconstructions and modifications noted in Chapter 7. The costs presented in both tables are the highest that should be incurred under the regulatory alternatives, because it has been assumed that control devices do not exist at the refineries that will be affected by the NSPS.

Table 9-21. SUMMARY OF FIFTH YEAR ANNUALIZED COST BY MODEL UNIT AND REGULATORY ALTERNATIVE

(1,000 - 3rd quarter 1983 Dollars)

	Model Unit	Regulatory Alternative	Annualized Cost Per Unit	Number of Units	Total Annualized Cost
Process Drain Systems (New)a	Α	II	\$ 5.34	27	\$ 114.18
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		III	47.62	27	1,285.74
	В	II	2.54	27	68.58
		III	32.30	27	872.10
	С	II	1.61	51	82.11
		III	26.21	51	1,336.71
Process Drain Systems (Retrofi	t) ^b A	II	12.65	3	37.95
(- /	III	55.38	3	166.14
	В	II	5.97	3	17.91
		III	35.94	3	107.82
	С	II	3.78	9	34.02
		III	28.47	9	256.23
Oil-Water Separators (New) ^C	Α	II	10.47	5	52.35
,		III	43.26	5 5	216.30
	В	II	5.67	10	56.70
		III	38.46	10	384.60
	С	II	5.67	15	85.05
		III	38.46	15	576.90
Oil-Water Separators (Retrofit)d A	II	15.83	1	15.83
•	•	III	48.56	1	48.56
	В	II	8.59	1	8.59
		III	41.38	1	41.38
	С	II	8.59	1	8.59
		III	41.38	1	41.38

Table 9-21. (Continued)

	Model Unit	Regulatory Alternative	Annualized Cost Per Unit	Number of Units	Total Annualized Cost
Air Flotation (New) ^e	A	II III	3.69 36.48	5 5	18.45 182.40
	В	II III	1.85 34.64	10 10	18.50 346.40
	С	III	0.12 32.91	10 10	1.20 329.10
Air Flotation (Retrofit) ^f	Α	II III	3.69 36.48	1	3.69 [°] 36.48
	В	II III	1.85 34.64	î 1	1.85 34.64
	С	III III	0.12 32.91	1	0.12 32.91

aTable 8-4. bTable 8-5. cTable 8-9. dTable 8-8. eTable 8-13. fTable 8-13.

Table 9-22. RANGE OF FIFTH-YEAR ANNUALIZED COST OF AFFECTED FACILITIES

(1,000 - 3rd quarter 1983 Dollars)

		Regulatory Altern	ative
	I	IĬ	III
Process Drain Systems (New)	\$0	\$294.87	\$3,494.55
Process Drain Systems (Retrofit)	0	89.88	530.19
Oil-Water Separators (New)	0	194.10	1,177.80
Oil-Water Separators (Retrofit)	0	33.01	131.32
Air Flotation (New)	0	38.15	857.90
Air Flotation (Retrofit)	<u>o</u>	5.66	104.03
TOTAL	0	655.67	6,295.79

Table 9-22 summarizes the fifth-year costs in terms of extremes. Because Regulatory Alternative I entails no controls above those already employed, no incremental fifth-year costs are incurred. If Regulatory Alternative II is proposed for all model units, the total annualized costs in the fifth-year after proposal would be about \$0.7 million. Finally, under Regulatory Alternative III, the most stringent and costly alternative, fifth-year costs are about \$6.3 million.

It should be noted that the fifth-year costs under all regulatory alternatives are well below the \$100 million threshold specified in the Executive Order.

- 9.3.1.2 <u>Inflationary Impacts</u>. The proposal of this NSPS will have virtually no effect upon the rate of inflation in the domestic economy. Even if consumers eventually bear all of the fifth-year costs noted above, price increases would be imperceptable as the total annual value of the industry's output exceeds \$100 billion.
- 9.3.1.3 Employment Impacts. The costs related to this NSPS would have little effect upon the level of employment in the petroleum refining industry. Table 9-5 shows that about 169,600 persons were employed in the industry in 1981. Based upon industry capacity of about 3,000,000 m³ per day during that year, the approximate capacity per worker is 18 m³ per day. As reported in Section 9.2.4 the regulatory alternatives evaluated would reduce the need for planned expansions in capacity up to 1989 by 110 and 1,200 m³ per day for Regulatory Alternatives II and III respectively. Using the 18 m³ to 1 ratio of daily capacity to workers noted above, and the expected baseline increase in demand of 193.5 thousand m³ per day (Table 9-20), the growth in refinery employment over the next five years would be about 10,750 workers without the NSPS. Because the decreases in demand from the 1989 baseline are 110 and 1,200 m³ per day for Regulatory Alternatives II and III respectively, these alternatives could reduce the growth in employment by six and 67 workers.

9.3.2 Small Business Impacts - Regulatory Flexibility Act

The Regulatory Flexibility Act, which became effective on January 1, 1981, requires the identification of potentially adverse impacts of Federal regulations upon small entities including small businesses. The Act requires that a Regulatory Flexibility Analysis (RFA) be completed for all Federal regulations that could have a significant adverse economic impact on a substantial number of small entities. The following discussion will show that this NSPS will not affect a substantial number of small businesses.

For purpose of this discussion a small refinery is defined as one that has crude oil capacity of less than 3,180 m³ per day (20,000 Bbl per day). This level is based upon the recent definition of "small refiner" made by EPA in establishing lead content rules for gasoline refiners. In those rules a small refinery is defined as one that produces fewer than 1,590 m³ per day (10,000 Bbl per day) of gasoline. Because on a national level about half of total refinery throughput is gasoline, the crude oil capacity of the small refinery is in this analysis, assumed to be twice the gasoline output or $3,180 \text{ m}^3$ per day (20,000 Bbl per day).

According to the most recent OAQPS/Economic Analysis Branch guidelines, the NSPS must affect more than 20 percent of all small businesses in the industry in order to be defined as one that affects a "substantial" number of small businesses. Currently about one-third of all domestic refineries have crude oil capacity of less than 3,180 m^3 per day (20,000 Bbl per day). Because there are about 220 petroleum refineries operating (Table 9-1), about 75 are considered to be small refineries. However, the most recent survey of refinery construction and reconstruction activities shows that of about 75 current refinery construction and reconstruction projects, only five are being undertaken at small refineries as defined above. Therefore fewer than seven percent of the small refineries will be affected by the standard, if the current distribution of construction activity continues. Because there is no reason to presume that the current distribution of construction activity among firms of various sizes will change, it is concluded that this standard will not affect a substantial number of small refineries, and for this reason a Regulatory Flexibility Analysis is not required.

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APPENDIX A

EVOLUTION OF THE BACKGROUND INFORMATION DOCUMENT

The purpose of this study was to develop background information to support New Source Performance Standards (NSPS) for petroleum refinery wastewater systems. Work on this study was performed by Radian Corporation under contract to the United States Environmental Protection Agency (EPA), specifically, under the direction of the Office of Air Quality Planning and Standards (OAQPS), Emission Standards and Engineering Division (ESED).

In October 1982, Radian Corporation was contracted to develop a Source Category Survey (Phase I). This phase of the study was a screening study of refinery wastewater systems. From the screening study it was concluded that NSPS should be developed for this source category. Radian Corporation then began work on Phase II of this study, development of the Background Information Document (BID). Phase II entailed a more complete and up to date literature search and survey of the industry, including plant visits. The feasibility of conducting emissions testing was determined during the plant visits. Emissions testing was then conducted at three refineries.

The chronology which follows lists the major events which have occurred in the development of background information for New Source Performance Standards for petroleum refinery wastewater systems.

June 8, 1982	Plant Visit to Gulf Oil, Belle Chasse, Louisiana
June 8, 1982	Plant Visit ot Shell Oil, Norco, Louisiana
June 9, 1982	Plant Visit to Exxon, Baton Rouge, Louisiana
October 26-28, 1982	Plant Visit to Phillips Petroleum, Woods Cross, Utah
	Meeting held between Radian Corporation and the EPA to
	discuss Phase I of project

November 10, 1982	Outline for Source Category Survey Report Submitted to the EPA
January 25, 1983	Findings of Source Category Survey Report presented to the EPA
February 2, 1983	Workplan for Phase II submitted to the EPA
March 14, 1983	Plant Visit to Champlin Oil, Wilmington, California
March 15, 1983	Plant Visit to Tosco, Bakersfield, California
March 16, 1983	Plant Visit to Chevron U.S.A., El Segundo, California
March 16, 1983	Plant Visit to Union Oil, Wilmington, California
March 17, 1983	Plant Visit to Mobil Oil, Torrance, California
March 18, 1983	Plant Visit to Texaco, Wilmington, California
March 25, 1983	Plant Visit to Sun Oil, Toledo, Ohio
March 30, 1983	Meeting with the EPA to discuss Testing Program
April 6, 1983	Plant Visit to Phillips Petroleum, Sweeny, Texas
April 6, 1983	Test Request submitted to Emission Measurement Branch of
·	the EPA
May 3, 1983	Meeting with the EPA to discuss inclusion of air
	flotation systems and process drain systems in NSPS
May 11, 1983	Test Request sent to Phillips Petroleum, Sweeny, Texas
May 12, 1983	Test Request sent to Chevron U.S.A., Inc., El Segundo, California
May 13, 1983	Test Request sent Mobil Oil, Torrance, Calitornia
June 2, 1983	Meeting held with the EPA to discuss test plans
July 28, 1983	Test Request sent to Golden West, Santa Fe Springs,
	California
August 1-12, 1983	Emission Test at Chevron, U.S.A., El Segundo, California
August 15-19, 1983	Emission Test at Golden West, Santa Fe Springs, August
	California
August 30, 1983	Concurrence Memorandum submitted to the EPA for Model
	Plant Parameters and Regulatory Alternatives
September 19-23, 1983	Emission Test at Phillips Petroleum, Sweeny, Texas
October 7-8, 1983	Information requests sent to industry concerning fixed
	roofs installed on AP1 oil-water separators

November 23, 1983	BID Chapters 3-6 Sent to Industry
March 14, 1984	Concerrence Meeting on Regulatory Approach to NSPS
	Development
July 12, 1984	BID, Preamble, and Regulation sent to NAPCTAC Committee
	Members
August 29, 1984	NAPCTAC Meeting

DRAFT

April 20, 1984

APPENDIX B

INDEX TO ENVIRONMENTAL CONSIDERATIONS

This appendix consists of a reference system which is cross indexed with the October 21, 1974, Federal Register (39 FR 37419) containing EPA guidelines for the preparation of Environmental Impact Statements. This index can be used to identify sections of the document which contain data and information germane to any portion of the Federal Register guidelines.

APPENDIX B

CROSS-INDEX TO ENVIRONMENTAL IMPACT CONSIDERATION

Reg	ncy Guidelines for Preparing ulatory Action Environmental act Statements (39 FR 37419)	Location Within the Background Information Document (BID)
1.	Background and Summary of Regulatory Alternatives	The regulatory alternatives from which standards will be chosen for proposal are given in Chapter 6, Section 6.2.
	Statutory Basis for the Standard	The statutory basis for proposing standards is summarized in Chapter 2, Section 2.1.
	Industry Affected	A description of the industry to be affected is given in Chapter 3, Section 3.1.
	Processes Affected	A description of the process to be affected is given in Chapter 3, Section 3.2.
	Availability of Control Technology	Information on the availability of control technology is given in Chapter 4.
	Existing Regulations at State or Local Level	A dicussion of existing regulations for the industry to be affected by the standards are included in Chapter 3, Section 3.4.
2.	Environmental, Energy, and Economic Impacts of Regulatory Alternatives	
	Health and Welfare Impact	The impact of emission control systems on health and welfare is considered in Chapter 7, Section 7.2.
		Continued

CROSS-INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS (Concluded)

Agency Guidelines for Preparing Regulatory Action Environmental Impact Statements (39 FR 37419)	Location Within the Background Information Document (BID)
Air Pollution	The air pollutant impact of the regulatory alternatives are considered in Chapter 7, Section 7.2.
Water Pollution	The impacts of the regulatory alternatives on water pollution are considered in Chapter 7, Section 7.3.
Solid Waste Disposal	The impact of the regulatory alternatives on solid waste disposal are considered in Chapter 7, Section 7.4.
Energy	The impacts of the regulatory alternatives on energy use are considered in Chapter 7, Section 7.5.
Costs	The cost impact of the emission control systems is considered in Chapter 8.
Economics	Economic impacts of the regulatory alternatives are considered in Chapter 9.

APPENDIX C

EMISSION SOURCE TEST DATA

The purpose of this appendix is to present VOC emissions test data used in the development of this background information document. VOC emissions test data were obtained from three refineries by the U.S. Environmental Protection Agency. At one refinery, tests were conducted on a dissolved air flotation system (DAF), an induced air flotation system (IAF), and an equalization basin. At a second refinery, tests were conducted on an IAF system. At a third refinery, tests were conducted on two IAF systems. In addition to the emission tests, screening of process drains with a portable VOC analyzer was performed at three refineries. The results of the tests are described below along with the methodology used to conduct the tests.

C.1 EMISSION MEASUREMENTS

C.1.1 Chevron, U.S.A., Inc. Refinery - El Segundo, California. 1

The refinery wastewater system at Chevron is divided into segregated and unsegregated systems. The segregated system handles the majority of the oily wastewater while the unsegregated system handles mostly non-oily wastewater. Continuous monitoring of VOC emissions from the DAF and equalization basin in the segregated system was performed. Continuous monitoring of VOC emissions from the IAF system in the segregated system was also conducted.

The DAF and equalization basin are located in the Effluent Treating Plant (ETP) at Chevron. Two DAF systems are included in the effluent treatment system, but only one was in operation during the test. The DAF system treats oily wastewater from the API separators after the wastewater has been held in a storage tank preceding the ETP. Effluent from the DAF was discharged to the equalization basin before undergoing biological treatment.

Figure C-1 shows the DAF system tested at Chevron. The DAF is equipped with a fiberglass cover which consists of a series of ventilation holes around its side. The cover also has three access doors and a center ventilation hole. The DAF flotation chamber is connected to a vapor recovery system. Two blowers rated at 4,000 scfm create a vacuum which draws VOC and ventilation air from the flotation chamber. The captured VOC is vented to an activated carbon bed located near the system.

As shown in Figure C-1, continuous monitoring of VOC from the DAF was conducted at a sample point located between the DAF and the carbon house. EPA Method 25A was used to measure the VOC level. In addition, gas chromatography was used to identify the major volatile components of the vent stream. EPA Method 18 was used for this purpose. A summary of the results of the continuous monitoring of the DAF are shown in Table C-1. The total hydrocarbon increments include methane. Gas chromatography results are shown in Table C-2.

The equalization basin is shown in Figure C-2. As with the DAF, this basin is completely covered. Ventilation holes are located on one side of the basin and outlet ports are located on the opposing side. Two blowers rated at 4,000 scfm create a vacuum which draws VOC and ventilation air from the basin. The captured VOC is vented to an activated carbon bed similar to that on the DAF system. Continuous monitoring at VOC level was conducted at a sample point located between the equalization basin and the carbon house. The sample point is shown in the figure.

The same analytical methods used on the DAF were used to monitor the VOC and identify major volatile components being emitted from the equalization basin. A summary of the results of the continuous monitoring are shown in Table C-1. Gas chromatography results are shown in Table C-3.

The IAF at Chevron receives effluent from an API separator which handles mostly non-oily wastewater. The IAF is designed to be gas-tight and the gaseous emissions are vented to a 55 gallon drum of activated carbon. The IAF system is shown in Figure C-3.

The vapor space in the IAF was initially designed to be purged with plant air. Evaluations of the system by Chevron found that purging was not necessary to maintain safe operating conditions. Because of this, a steady

flow of gas from the IAF to the carbon drum was not maintained. A small flow of gas from the IAF did result from breathing losses in the system. This flow was recorded with a 4" vane anemometer. The positive gas displacement was calculated and used as the IAF outlet flow. Outlet VOC concentration could then be calculated using EPA Method 25A. The emission rates and gas chromatography results from the IAF are shown in Table C-4.

In addition to the gaseous samples taken at Chevron, liquid samples of the wastewater going to and from the API separators, DAF, IAF, and equalization basin were obtained. These samples were analyzed for chemical oxygen demand (COD), oil and grease, total organic carbon (TOC), and total chromatographic organics (TCO). The results of the analyses are shown in Tables C-5 to C-12. These samples were obtained in an attempt to correlate VOC emissions with conventions at wastewater pollutant parameters.

C.1.2 Golden West Refinery - Santa Fe Springs, California²

The refinery wastewater system at Golden West consists of two API separators followed by an IAF system. The IAF system is operated gas-tight and the vapor space is purged with plant air. The captured and purged VOC are vented to a fired heater located near the treatment system. A small blower serves to drive the VOC from the IAF to the fired heater.

Continuous monitoring of VOC from the IAF to the fired heater was conducted at a sample point located on the outlet duct of the IAF. The IAF system and sample point are shown in Figure C-4. EPA Method 25A was used in monitoring the VOC. Gas chromatography was used to identify the major volatile components of the vent stream. A summary of the results of the continuous monitoring of the IAF is shown in Table C-13. The total hydrocarbon measurements include methane. Gas chromatography results are shown in Table C-14.

In addition to the gaseous samples taken at Golden West, liquid samples of wastewater going to and from the API separators and IAF system were obtained. As with the samples acquired at Chevron, these samples were analyzed for COD, oil and grease, TOC, and TCO. The results of the analyses are shown in Table C-15 to C-18.

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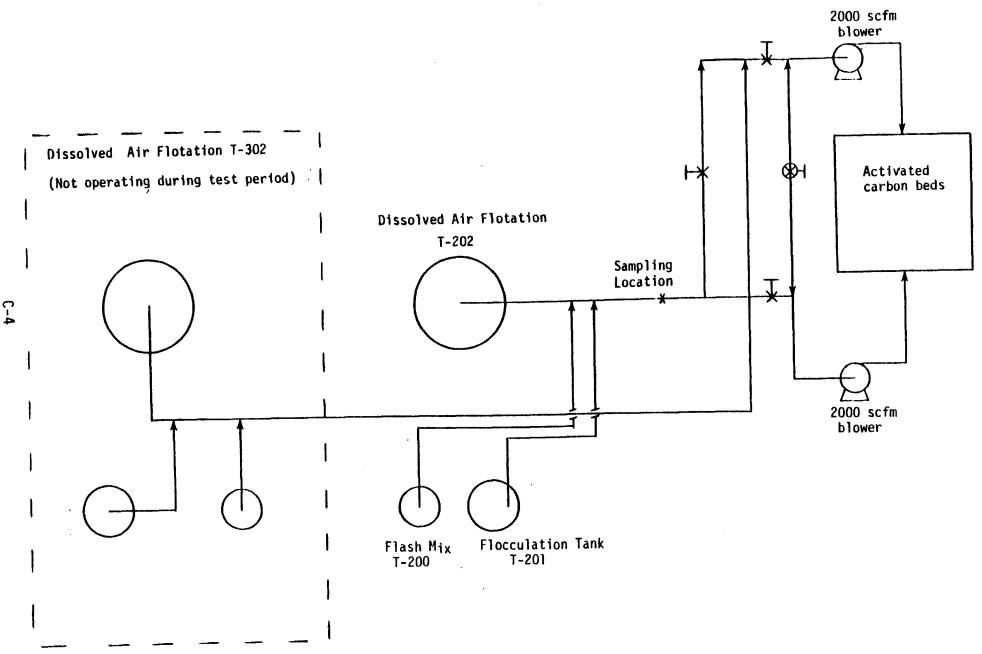


Figure C-1.) Dissolved air flotation system with sample location

TABLE C-1. SUMMARY OF DAILY EMISSION RATE AVERAGES: CONTINUOUS MONITORING RESULTS, CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

TEST DAY	8/3/83	8/4/83	8/5/83	8/8/83	8/9/83	8/10/83	8/11/83
SAMPLE LOCATION							
DAF Outlet (1bs/hr Total Hydro	ocarbon) 7.18	6.37	6.85	6.75	8.11	6.17	9.01
Equalization Tank (lbs/hr Total Hydro	carbon) 4.18	4.65	4.24				-

TABLE C-2. GAS CHROMATOGRAPHY RESULTS FROM DAF SYSTEM CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

DATE	8/3	8/3	8/4	8/4	8/5	8/5
TIME	1135- 1235	1445- 1545	930- 1010	1430- 1515	900 - 945	1500- 1530
ANALYTICAL RESULTS (ppmv as compound)						
C-1	46.8	46.5	53.6	45.5	53.8	58.3
C-2	5.7	7.0	6.4	5.3	6.7	6.5
C-3	6.8	8.1	8.3	6.2	7.1	8.3
C-4	3.8	5.0	4.9	4.4	4.2	
C-5	1.9	3.4	4.9	3.8	4.6	0.6
Hexane	10.1	16.9	23.0	15.1	10.7	18.0
Benzene	11.0	15.1	19.8	13.2	24.4	35.0
Heptane	10.0	11.8	21.3	6.6	2.6	
Toluene	39.2	45.3	55.5	32.4	46.7	44.4
m-Xylene	6.8	6.1	15.9	7.7	13.6	10.4
o-Xylene	3.4	3.0	7.9	3.0	5.0	3.8
TOTAL HYDROCARBON (ppmv as compound)	145	168	217	143	179	185
CONTINUOUS MONITOR DATA						
Hydrocarbon Level (ppmv as C_3H_8)	510	526	668	339	583	482
Emission Rate (1bs/hr Total Hydrocarbon)	6.69	6.88	8.59	4.35	7.82	6.38

(CONTINUED)

TABLE C-2. GAS CHROMATOGRAPHY RESULTS FROM DAF SYSTEM CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA (CONTINUED)

DATE	8/8	8/8	8/9	8/9	8/10	8/11
TIME	1100- 1300	1500- 1530	915- 1040	1400- 1455	904- 1004	1315- 1415
ANALYTICAL RESULTS (ppmv as compound)						
C-1	55.3	52.9	37.5	34.8	26.4	29.2
C-2	4.5	3.9	2.4	1.8	2.1	0
C-3	5.6	5.0	2.2	2.6	2.0	2.1
C-4	4.0	4.8	3.6	3.2	1.7	6.5
C-5 Hexane	3.4 16.1	4.0 26.2	4.8 12.8	4.8 0	0 6.7	9.2 19.1
Benzene	39.8	63.6	49.2	8.0	23.7	55.2
Heptane			28.3	44.4	7.0	0
Toluene	46.4	75.1	17.1	17.4	0	61.5
m-Xylene	11.3	20.7	6.0	7.0	12.7	10.0
o-Xylene	3.9	8.2	22.4	24.2	5.2	10.2
TOTAL HYDROCARBON (ppmv as compound)	190	264	186	148	87	203
CONTINUOUS MONITOR DATA						
Hydrocarbon Level (ppmv as C ₃ H ₈)	495	580	709	592	460	622
Emission Rate	c 70	7.87	9.68	8.09	5.28	8.2
(1bs/hr Total Hydrocarbon)	6.72	1.01	3.00	5.03	J. 20 ·	0.2

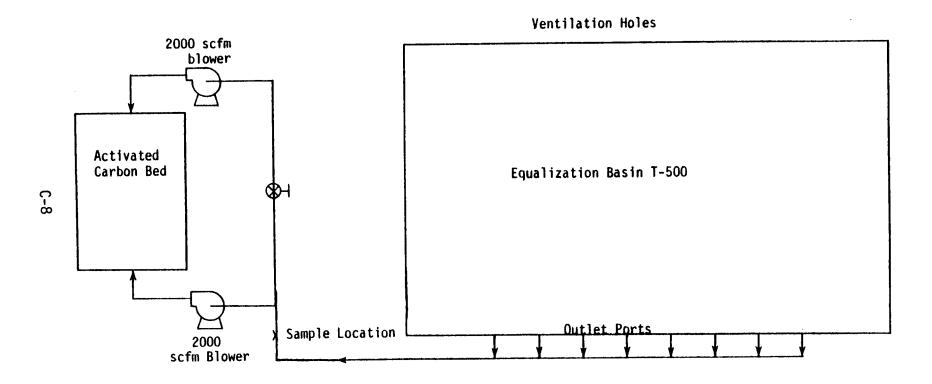


Figure C-2. Equalization Basin with Sample Location.

TABLE C-3. GAS CHROMATOGRAPHY RESULTS FROM EQUALIZATION BASIN CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

DATE	8/3	8/4	8/4	8/5	8/5	8/5
TIME	1600- 1700	1053- 1235	1431 - 1510	930- 1000	1228 - 1252	1400- 1510
LOCATION		Venti	lation air			Carbor house <u>outlet</u>
RUN NO.	1	1	2	1	2	OUT
ANALYTICAL RESULTS (ppmv as compound) C-1 C-2 C-3 C-4 C-5 Hexane Benzene Heptane Toluene m-Xylene o-Xylene	27.0 2.0 0 0 0 7.7 29.2 4.6 1.7	29.4 1.2 0 0 0 2.3 9.7 25.5 4.0 1.5	24.6 0 0 0 0 2.1 4.9 13.6 1.7	17.7 0 0 0 0 1.4 7.8 18.7 3.6 1.1	20.4 1.8 0 0 0 2.1 12.5 29.8 7.0 2.4	22.3 1.6 0 0 0 20.4 26.8 0
TOTAL HYDROCARBON (ppmv as compound)	72	74	47	50	76	72
CONTINUOUS MONITOR DATA						
Hydrocarbon Leve (ppmv as C ₃ H ₈)	1 150	182	167	155	155	179
Emission Rate (lb/hr)	4.07	4.87	4.45	3.98	3.98	4.65

TABLE C-3. (Continued)

DATE	8/12/83	8/12/83	8/12/83	
TIME				
LOCATION	Ventilation air	Carbon house exhaust		
RUN NO.	1	1	2	
ANALYTICAL RESULTS (ppmv as compound)				
C-1 C-2 C-3 C-4 C-5 Hexane Benzene Heptane Toluene m-Xylene o-Xylene TOTAL HYDROCARBON (ppmv as compound)	15.4 0 0 0 5.8 38.6 0 0 14.8 5.6	24.4 0 0 0 0 0 0 0 0	23.5 0 0 0 0 0 0 0 0	
CONTINUOUS MONITOR DATA				
Hydrocarbon Level (ppmv as C ₃ H ₈)	284		29	
Emission Rate (lb/hr)	7.54		0.77	

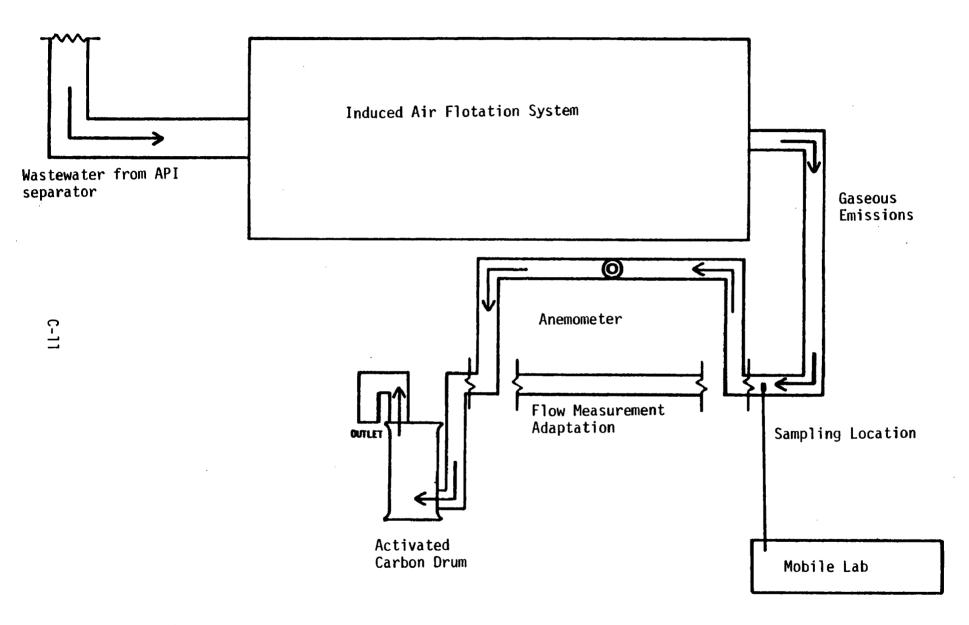


Figure C-3. Induced air flotation system at Chevron - El Segundo, California.

TABLE C-4. GAS CHROMATOGRAPHY AND EMISSION RATES FROM IAF SYSTEM CHEVRON REFINERY, ELSEGUNDO, CALIFORNIA

DATE	8/11	8/11	8/12	8/12
TIME	0924- 0942	1213- 1245	1213- 1254	1040- 1120
LOCATION	Ventilat	ion air	Carbon dru	ım outlet
RUN NO.	1	2	1	2
ANALYTICAL RESULTS (ppmv as compound) C-1 C-2 C-3 C-4 C-5 Hexane Benzene Heptane Toluene m-Xylene 0-Xylene	1602 7.6 18.2 42.0 283 1288 835 826 421 252 145	2818 3217 2913 80.5 220 6127 2642 938 0 105 31.7	2156 8.2 21.8 72.1 510 2005 2101 793 0 385 106	1762 4.5 12.8 36.4 110 2033 1074 449 0 168 67.8
TOTAL HYDROCARBON (ppmv as compound)	5720	19,092	8158	5717
CONTINUOUS MONITOR DATA				
Hydrocarbon Level (ppmv as C ₃ H ₈)	6950	7300	7222	6601
Emission Rate (1b/hr)	0.20	0.21	0.18	0.16

TABLE C-5. LIQUID SAMPLES TAKEN ON 8/3/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				· · · · · · · · · · · · · · ·
DAF-in	2,969	491	_	71.56
	3,008	535		
DAF-out	1,748	133	_	30.90
		144		
EQ-out	1,911	123		21.00
	1,870	120		
Volatile Organic Samples				
DAF-in #1 VOA (1650) ^a		_	611	_
DAF-out #1 VOA (1650)	_	_	365	
EQ-out VOA (1650)		_	661	_

^aTime sample taken.

TABLE C-5. LIQUID SAMPLES TAKEN ON 8/3/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA (CONTINUED)

	Compound	mg/l
iquid Composite Samples	Toluene	13.302
Iquia composite sampies	C ₈	2.278
	С́э	1.328
	Ç ₉	1.040
	C ₉	17.709
DAF Influent	C ₁₀	2.679
	C ₁₁	4.207
	C ₁₂	4.940
	C ₁₂	5.339
	C ₁₂	12.214
	C ₁₂	2.932
	C ₁₂ C ₁₂	1.436
	C ₁₂	1.930
	C ₁₂	1.487 10.496
	C ₁₃	3. 128
•	C ₁₃	4.838
	C ₁₄ C ₁₅	3.570
	C ₁₅	3.066
	-15	Ş. 000
	Toluene	3.643
DAF Effluent	C ₉	2.595
DRI LITTUENC	C ₉	15.412
	C ₁₀	4.972
	C ₁₀	5.549
	C ₁₁	0.828
	C ₁₁	1.383
	C ₁₁	2.679
	$\mathtt{C_{12}}$	2.232
	C ₁₃	2.257
	Toluena	2 201
m 191 11 B. 1 FEET	Toluene	3.301
Equilization Basin Effluent	Ce	2.460 11.538
	C ₉	3.927
	C ₁₀	3. 617
	C ₁₀ C ₁₂	1.180
	L ₁₂	1.100

Note: Benzene could not be determined due to a co-eluting peak in the solvent.

Note: These values were calculated using average response factors of C_7 – C_{11} , C_{11} – C_{16} , and C_{17} to C_{25} hydrocarbons. Due to the reduced response of C_{17} to C_{25} hydrocarbons as compared to C_7 – C_{11} , high values of some C_{17} – C_{25} compounds were found.

TABLE C-6. LIQUID SAMPLES TAKEN ON 8/4/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L
Liquid Composite Samples			
DAF-in	4,024	440	****
	4,228	441	_
DAF-out	1,545	125	
	1,585	94	_
	1,565	126	_
EQ-out	2,033	148	_
	2,155	142	_
Volatile Organic Samples			
DAF-in-VOA pm (1500)	-		484
DAF-in-VOA (1000)			a
DAF-out VOA pm (1500)	_	-	478
	_	_	475 550
	· —	_	542
DAF-out VOA (1000)	 .	-	464
EQ-out VPA (1000)		-	455
EQ-out VOA (1500)	_	_	511

 $^{^{\}rm a}{\rm Sample}$ lost; replaced with aliquot from DAF-in liquid composite samples. Result was 1,096 mg/L.

TABLE C-7. LIQUID SAMPLES TAKEN ON 8/5/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
DAF-in	8,056	6.14	_	
DAF-out	2,179	2.37	_	_
EQ-out	1,240	110	_	
	1,301	109		
Volatile Organic Samples				
DAF-in VOA (0915)		-	a	
DAF-in VOA (1530)		_	722	_
DAF-out VOA (0915)	_	_	578	_
DAF-out VOA (1530)	_		713	_
EQ-out VOA (1530)	_		600	
EQ-out VOA (0915)	_		, p	

 $^{^{\}rm a}$ Sample lost; replaced with aliquot from DAF-in liquid composite samples. Results are 849,940,860 mg/L.

 $^{^{\}rm b}$ Sample lost; aliquot from EQ-out liquid composite samples. Results are 416,398,476 mg/L.

TABLE C-8. LIQUID SAMPLES TAKEN ON 8/8/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
DAF-in	2,155 2,114	383 376	_	41.94
DAF-out	1,470	0.21	_	22.38
API-2 Inlet A (201)	20.3	6.4		1.74
API-2 Inlet B (202)	2,560	65.49	_	84.00
API-2 Inlet C (203)	463	20.9	_	9.30
API-2 Inlet D (204)	480	26.97		8.26
API-4	2,440	18.26	_	45.66
Volatile Organic Samples				
DAF-in VOA (1100)			538	_
DAF-in VOA (1500)		_	a	_
DAF-out VOA (1100)	_	_	622	
DAF-out VOA (1500)	_		b	

 $^{^{\}rm a}{\rm Sample}$ lost; replaced with aliquot from DAF-in liquid composite samples. TOC result is 016 mg/L.

 $^{^{}b}\mathsf{Sample}$ lost; replaced with aliquot from DAF-out liquid composite samples. TOC result is 774 mg/L.

TABLE C-8. LIQUID SAMPLES TAKEN ON 8/8/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA (CONTINUED)

-	Compound	mg/1
quid Composite Samples		
DAF Influent	Toluene C8 C9 C10 C10 C10 C12 C12 C12 C12 C12 C12 C15 C15 C15 C16	9.920 2.312 13.518 3.935 3.901 1.871 4.727 1.407 0.783 0.801 4.496 2.837 0.838 3.285 3.136
DAF Effluent	Toluene C ₉ C ₉ C ₁₀ C ₁₀	5.085 10.601 3.697 3.284 1.210
API #2 Influent (Site 202)	Toluene C8 C9 C9 C9 C10 C10 C11 C11 C11 C11 C11	2.571 1.005 2.065 23.039 1.858 7.464 12.990 5.835 0.932 0.051 1.153 4.145 14.226

(CONTINUED)

TABLE C-8. LIQUID SAMPLES TAKEN ON 8/8/83 - CHEVRON REFINERY EL SEGUNDO, CALIFORNIA (CONTINUED)

·	Compound	mg/l
	C ₁₃	13.544
	C ₁₃	4.316
	C ₁₄	8.411 2.306
	614 C	2.306 9.465
	C ₁₄ C ₁₅ C ₁₆ C ₁₇	7.679
	C ₁₇	59.638
	L ₁₈	45.744
	C ₁₉	65.488
PI #2 Influent	Toluene	2.165
(Site 203)	C ₈	1.034
	Toluene	6.595
PI #4 Influent	C ₈	1.848
	Co	12.555 3.390
•	C ₁₀ C ₁₀	3.291
	C ₁₀	3.341
	C ₁₂	8.448
	C ₁₂	2.436
	C ₁₂	1.395 1.447
	C ₁₂	7.986
	C ₁₂ C ₁₂ C ₁₂ C ₁₂ C ₁₃ C ₁₃	1.654
	€14	5.173
	C ₁₅ C ₁₅ C ₁₆ C ₁₇	1.388 5.558
	C15	4.977
	C16	46.394

TABLE C-9. LIQUID SAMPLES TAKEN ON 8/9/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
DAF-out	1,579	154		_
API-2 Inlet A (201)	693	61.56		_
API-2 Inlet B (202)	3,155	19.50		
API-2 Inlet C (203)	5,179	32.27	_	_
API-2 Inlet D (204)	2,230	18.28		_
API-4	620	23.90	-	
Volatile Organic Samples				
DAF-in VOA (0900)	_	_	482	-
DAF-in VOA (1342)	_	_	440	_
DAF-out VOA (0900)	_	_	341	_
DAF-out VOA (1340)	_	_	509	

TABLE C-10. LIQUID SAMPLES TAKEN ON 8/10/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
DAF-in	2,170	23.80		_
DAF-in	2,121	53.98		_
DAF-out	2,078	47.75	_	_
API-2 SP 201	594	33.80	~~	
API-2 SP 202	2,764	42.48	 -	_
API-2 SP 203	950	70.03	_	_
API-2 SP 204	2,635	32.62	_	
Volatile Organic Samples				
DAF-in VOA (0920)	_		619	
DAF-in VOA (1600)			471	
DAF-out VOA (0920)	_	_	546	
DAF-out VOA (1600)	_		511	_

TABLE C-11. LIQUID SAMPLES TAKEN ON 8/11/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

		·		
	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
DAF-in	2,316	43.74		95.26
DAF-out	1,410	54.92		22.42
IAF-in	811	61.58		12.58
IAF-out	201	46.73		11.06
API-4	1,616	43.59		96.20
API-2 SP 201	100	17.97		9.20
API-2 SP 202	1,700	37.24		30.68
API-2 SP 203	99	24.45		8.60
API-2 SP 204	450	33.06	_	51.98
Volatile Organic Samples				
DAF-in VOA (0900)	_	_	530	_
DAF-in VOA (1530)		-	355	_
DAF-out VOA (0900)			454	_
DAF-out VOA (1530)	_		343	
IAF-in VOA (1000)	-		64.5	-
IAF-in VOA (1600)			402	_
IAF-out VOA (1000)			134	
IAF-out VOA (1600)	_	-	52.0	

TABLE C-11. LIQUID SAMPLES TAKEN ON 8/11/83 - CHEVRON REFINERY EL SEGUNDO, CALIFORNIA (CONTINUED)

	Compound	mg/1
iquid Composite Samples		
DAF Influent	Toluene C8 C8 C8 C9 C9 C9 C10 C10 C10 C12 C13 C13 C14 C15 C16 C17 C18 C19	14.141 1.211 1.471 5.429 1.901 2.553 6.035 3.027 5.068 7.398 6.526 15.370 14.351 4.388 9.436 10.194 6.915 58.459 47.247
DAF Effluent	C ₂₀ Toluene C ₈ C ₉ C ₉ C ₁₀ C ₁₀ C ₁₁ C ₁₂ C ₁₃	28.031 4.430 0.838 0.805 7.528 4.021 3.658 1.375 0.852 0.920 1.549
IAF Influent	Toluene C ₈	1. 549 0. 668 1. 334
IAF Effluent	Toluene C ₈	0.581

TABLE C-11. LIQUID SAMPLES TAKEN ON 8/11/83 - CHEVRON REFINERY EL SEGUNDO, CALIFORNIA (CONTINUED)

	Compound	mg/1
44	Toluene	39.430
PI #4 Influent		28. 123
	C ₈ C ₉ C ₉ C ₉ C ₉	11.348
	Ç ₉	4.708
	C ₉	2.586
	Ce	0.954
	L ₉	13.200
	C ₁₀ C ₁₀	3.242 1.512
	C ₁₀	1. 126
	C ₁₀	4.686
	C ₁₀	3. 127
	C ₁₀ C ₁₀	2.379
	C ₁₁	1.349
	C ₁₁	1.502
	C ₁ ,	1.561
	C ₁₂ C ₁₃	1.976
	C ₁₃	1.679
	C ₁₅	1.832 2.025
	C ₁₆	2.023
DI #2 Influent	Toluene	2.221
(Site 202)	C ₈	1.434
(0.00 202)	Cg	1.188
	C ₉	3.697
	C ₁₀	3.205 3.147
	C ₁₀	1.684
	C ₁₁ C ₁₃	4.622
	C ₁₃	1.450
	C ₁₃	2.900
	C ₁₄	4. 285
	C ₁₅	3.544
ADI #2 Influent (Site 203)	Toluene	0.902

(CONTINUED)

TABLE C-11. LIQUID SAMPLES TAKEN ON 8/11/83 - CHEVRON REFINERY EL SEGUNDO, CALIFORNIA (CONTINUED)

	Compound	mg/1
API #2 Influent	Toluene	<0.5
(Site 204)		4.055
(0.00 00.7)	C ₁₁ C ₁₋₁	1.755
	C ₁₁	1.505
	C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₂ C ₁₂ C ₁₂ C ₁₃ C ₁₄ C ₁₅	1.002
	C ₁₁	1.395
	C ₁₁	2.130
	C ₁₂	12.261
	C ₁₂	3.872
	C ₁₂	4.312
	C ₁₃	10.914
	C ₁₄	7.363
	C ₁₅	3.839
	C ₁₆	70.078

TABLE C-12. LIQUID SAMPLES TAKEN ON 8/12/83 - CHEVRON REFINERY, EL SEGUNDO, CALIFORNIA

	COD mg/L	0il/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
IAF-in	320	14.14	_	
IAF-out	302	64.95	_	_
API-4	202	26.5	_	_
API-2 SP 201	405	12.0		_
API-2 SP 202	1,584	70.71	_	
API-2 SP 203	1,000	36.74	_	
API-2 SP 204	a	' a	a .	a
Volatile Organic Samples				
IAF-in VOA (0900)		_	86.0	
IAF-in VOA (1250)	_	_	57.0	*****
IAF-out VOA (0900)	_		162	_
IAF-out VOA (1330)	_		46.0	

^aSample broken in laboratory.

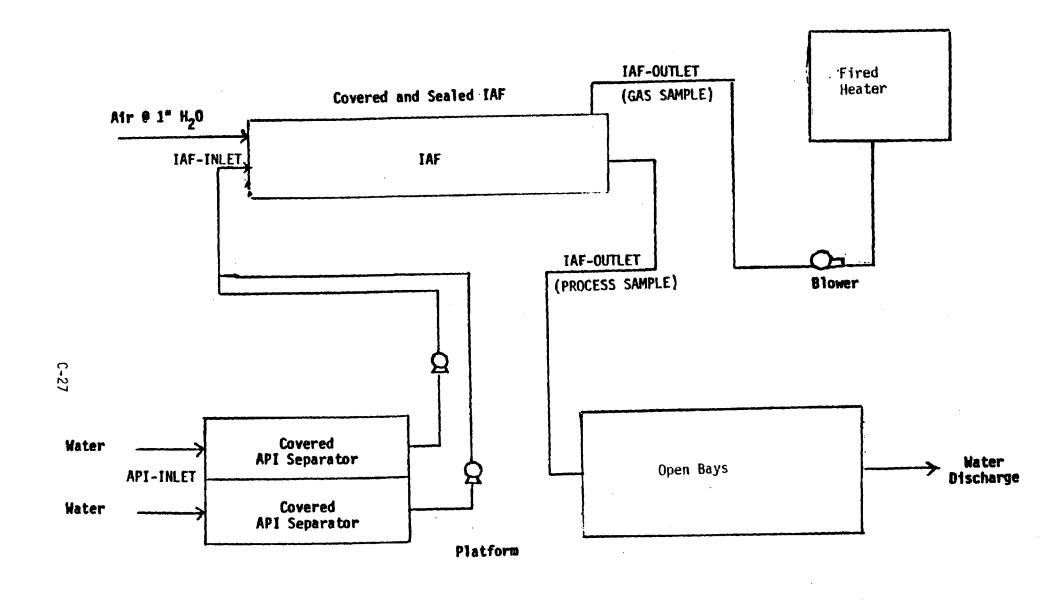


Figure C-4. Wastewater treatment facilities at Santa Fe Springs, California.

TABLE C-13. DAILY EMISSION RATE AVERAGES AT IAF OUTLET - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA

Test Day	Average Emission Rate (1b/hr Total Hydrocarbon as ^C 3 ^H 8)
3/15/83	1.40
3/16/83	1.39
8/17/83	1.14
3/18/83	1.23
8/19/83	1.39

TABLE C-14. GAS CHROMATOGRAPHY RESULTS FROM IAF SYSTEM - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA

DATE	8/16	8/16	8/16	8/17	8/17	8/17
TIME	735 - 835	1020- 1120	1235- 1335	0745- 0845	1000- 1100	1153- 1253
ANALYTICAL RESULTS (ppmv as compound)		•				
C-1	74.0	110	90.8	138	135	262
C-2	6.8	9.4	9.6	7.8	20.9	
C-3	14.2	22.1	14.4	19.0	78.5	122
C-4	38.6	269	108	140	315	365
C-5	52.0	250	130	183	685	341
Hexane	115	370	1068	180	577	524
Benzene	1357	2851	2424	1758	3638	3530
Toluene	1346	2486	2321	1629	2376	2476
m-Xylene	933	1458	1578	905	813	885
o-Xylene	326	467	510	305	283	308
TOTAL HYDROCARBON (ppmv as compound)	4262	8292	8253	5265	8921	8813
CONTINUOUS MONITOR DATA						
Hydrocarbon Level (ppmv as C ₃ H ₈)	6772	7104	7087	7008	8675	8811
Emission Rate (lbs/hr Total hydrocarben)	1.47	. 1.54	1.54	1.15	1.42	1.

(CONTINUED)

TABLE C-14. GAS CHROMATOGRAPHY RESULTS FROM IAF SYSTEM - COLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA (CONTINUED)

DATE	8/18	8/18	8/19	8/19
TIME	1030- 1146	1310- 1410	850 - 950	1030- 1130
ANALYTICAL RESULTS (ppmv as compound)				
C-1	44.5	94.7	66.0	72.8
C-2	3.0	4.1	5.3	6.8
C-3	4.2	8.0	8.1	10.9
C-4	10.5	96.5	28.4	50.7
C-5	14.9	71.0	90.3	78.9
Hexane	49.7	81.4	93.5	116
Benzene	547	1106	865	1236
Toluene	889	1661	1110	1785
m-Xylene	647	1164	640	890
o-Xylene	236	407	228	297
TOTAL HYDROCARBON (ppmv as compound)	2446	4695	3135	4544
CONTINUOUS MONITOR DATA				
Hydrocarbon Level (ppmv as as C_3H_8)	5975	6725	6205	6327
Emission Rate (lbs/hr Total Hydrocarbons)	1.08	1.21	1.37	1.4

TABLE C-15. LIQUID SAMPLES TAKEN ON 8/16/83 - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
IAF-in	2,323	11.31		104.46
IAF-out	909	21.89	-	40.78
API-in	2,020	23.37		25.64
Volatile Organic Samples				
IAF-in VOA (0805)	*******	_	344	
IAF-in VOA (1400)			411	.—
IAF-out VOA (0805)	_	_	237	
IAF-out VOA (1400)	_		304	_

TABLE C-15. LIQUID SAMPLES TAKEN ON 8/16/83 - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA (CONTINUED)

	Compound	mg/1
iquid Composite Samples		
	Toluene	7.611
IAF Influent	Cs	5.581
	C ₁₀	28.782
	C ₁₀	8.904
	C ₁₀	6.967
	C ₁₂	11.572
	C ₁₃ C ₁₃	12.999
	C13	3.990
	C ₁₄	6.041 11.920
	C ₁₅	5.032
	C ₁₆	229.816
	C ₁₇ C ₁₈	60.938
	C ₁₉	65.569
	C ₂₀	34.653
	C ₂₁	34.247
	C ₂₂	24.253
	Toluene	3.721
IAF Effluent	C8	1.841
	C ₉	0.899
	C ₉	21.115
•	C ₁₀	6.998
	C ₁₀	13.501
	C ₁₂	1.888
	Toluene	2.546
API Influent		1.632
	C ₉	5.749
	C ₁₀	3.522
	C ₁₀	4.173
	C ₁₂	2.765
	C ₁₃	2.646
	C ₁₄	1.699
	C ₁₅	2.621
	C ₈ C ₉ C ₁₀ C ₁₀ C ₁₂ C ₁₃ C ₁₄ C ₁₅ C ₁₆ C ₁₇	1.395
	C ₁₇	65.244

TABLE C-16. LIQUID SAMPLES TAKEN ON 8/17/83 - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
IAF-in	4,089	14.09		158.5
IAF-out	2,328	4.59	-	109.32
API-in	5,628	17.62	_	244.30
Volatile Organic Samples				
IAF-in VOA (0740)	_		554	
IAF-in VOA (1300)		-	426	
IAF-out VOA (1300)	_	_	323	_
IAF-out VOA (0740)			137	

TABLE C-16. LIQUID SAMPLES TAKEN ON 8/17/83 - GOLDEN WEST REFINERY SANT A FE SPRINGS, CALIFORNIA (CONTINUED)

	Compound	mg/1
iquid Composito Comples		
Liquid Composite Samples	Toluene	76.223
		1.835
	C ₇ C ₈	3.602
	C ₈	2.422
IAF Influent	C _a	2.066
	C-	5.420
	C _B	17.959
	C .	6.712
	C.	3.833
	C ₂	1.632
	Cs Cs Cs Cs Cs Cs	2.160
	C _a	2.644
	C _a	3.057
	C _a	4.577
	C	2.640
	C	5.201
	C	5.709
	Car	3.968
	C ₉ C ₉ C ₉ C ₉ C ₉ C ₁₀ C ₁₀ C ₁₀ C ₁₁	8.078
	C	11.172
•	C10	4.848
	Car	2.108
	Car	3.772
	C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₂	1.906
	C ₁₁	1.556
	C	2.039
	. C.	7.783
	C ₁₂	2.979
	Cia	2.162
	C ₁₂ C ₁₂ C ₁₂ C ₁₂	2.496
	C12	13.111
	C12	14.532
	C ₁₃	7.058
	C. o	3.105
	C ₁₃ C ₁₄ C ₁₄ C ₁₅ C ₁₅ C ₁₆ C ₁₆ C ₁₇	4.510
	C _{1.4}	3.376
	C ₁ E	10.791
	Cie	4.026
	Cie	5.481
	Cie	2.347
	C17	91.409
	C ₁₇	224.621

TABLE C-16. LIQUID SAMPLES TAKEN ON 8/17/83 - GOLDEN WEST REFINERY, SANTE FE SPRINGS, CALIFORNIA (CONTINUED)

****	Compound	mg/l
	C ₁₈	87.140
	C ₁₈	84.054
	C ₁₉	110.444
	C ₁₈ C ₁₉ C ₂₀ C ₂₁	73.046
	C ₂₁	90.032
	և 22	73.718
	C ₂₃	46.656
	C ₂₄	55.906
	C ₂₅	30.594
	Toluene	50.025
Effluent	C ₇	0.482
	C ₇	0.516
	C ₇	0.957
	Cg	0.688
	Ç ₈	0.563
	Cg	2.543
	Cg	10.277
	Cg	3.919
	Cs	1.296
	C7 C7 C7 C8 88 88 89 99 99 00 C10	0.628
	Cg	0.618 1.126
	Lg .	1.126
	Lg C	2.743
	Lg C	2. 743 1. 290
	Lg C	30.117
	Lg C	2.226
	C ₁₀	2.117
	C ₁₀	0.971
	C ₁₀	0.588
	C ₁₀	0.889
	C ₁₀ C ₁₀ C ₁₀	9.658
	C10	20.001
	C10	2.108
	C ₁₀	0.666
	C11	1.663
	C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁	2. 282
	C-11	0.674
	C	2.144
	C ₁₁	0.726
	C ₁₁	0.916
	C ₁₁	0.683
	Ç ₁₁	1.092
	C ₁₁	2.92

TABLE C-16. LIQUID SAMPLES TAKEN ON 8/17/83 - GOLDEN WEST REFINERY SANTA FE SPRINGS, CALIFORNIA (CONTINUED)

	Compound	mg/l
	C12 C12 C12 C12 C13 C13 C13 C14 C14 C15 C15 C16 C17 C18 C19 C20 C21 C22 C23 C24	1.337 1.231 1.445 7.804 8.226 1.390 1.850 2.598 1.808 5.846 2.174 84.094 105.381 39.690 50.973 36.077 29.241 20.598 23.798 14.621
API Influent	Toluene C7 C7 C8 C8 C8 C8 C9 C9 C9 C9 C9 C10 C10 C10 C10 C10 C10	23.873 1.593 2.085 2.157 5.764 24.131 9.263 2.470 3.303 4.726 6.821 3.696 1.205 4.956 9.215 5.188 2.297 2.867 1.772 8.807 4.265 2.081

TABLE C-16. LIQUID SAMPLES TAKEN ON 8/17/83 - GOLDEN WEST REFINERY SANTA FE SPRINGS, CALIFORNIA (CONTINUED)

Compound	mā/]
C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₁ C ₁₂ C ₁₃ C ₁₄ C ₁₅ C ₁₆ C ₁₇ C ₁₆ C ₁₇ C ₁₈	3.670 1.726 3.837 4.716 1.931 1.812 5.883 2.842 6.898 2.667 3.212 3.528 2.250 15.183 15.331 7.276 15.577 7.765 3.512 63.229 180.452 86.216

TABLE C-17. LIQUID SAMPLES TAKEN ON 8/18/83 - GOLDEN WEST REFINERY SANTA FE SPRINGS, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
IAF-in	1,162	31.83	_	46.48
IAF-out	1,111	16.71		34. 3 4
API-4 (1130)	1,364	15.16	_	36.04
Volatile Organic Samples				
IAF-in VOA (1050)	_		204	
IAF-in VOA (1500)	_		283	_
IAF-out VOA (1050)	-	_	_	_
IAF-out VOA (1500)	-	_	315	

TABLE C-17. LIQUID SAMPLES TAKEN ON 8/18/83 - GOLDEN WEST REFINERY SANTA FE SPRINGS, CALIFORNIA

	Compound	mg/l
IAF Influent	Toluene C8 C8 C9 C9 C10 C10 C12 C15 C18	9.752 4.435 1.832 1.299 22.145 7.012 14.987 2.081 1.203 29.697
IAF Effluent	Toluene C ₈ C ₉ C ₉ C ₁₀ C ₁₀ C ₁₂	5.949 2.174 1.071 16,975 5.575 10.822 0.853
API Influent	Toluene C ₈ C ₈ C ₉ C ₉ C ₁₀ C ₁₀ C ₁₂ C ₁₅ C ₁₈	5.477 2.531 0.971 1.052 17.101 5.889 12.505 1.399 0.976 25.959

TABLE C-18, LIQUID SAMPLES TAKEN ON 8/19/83 - GOLDEN WEST REFINERY SANTA FE SPRINGS, CALIFORNIA

	COD mg/L	Oil/grease mg/L	TOC mg/L	TCO mg/L
Liquid Composite Samples				
IAF-in	1,194	348		
IAF-out	830	332		_
	960	201-	_	_
API-in	3,482	1,321		_
Volatile Organic Samples				
IAF-in VOA (0830)		-	289	_
IAF-in VOA (1400)	_		509	_
IAF-out VOA (0830)		_	293	
IAF-out VOA (140)	_		607	_

C.1.3 Phillips Petroleum Company - Sweeny, Texas³

The refinery wastewater system at Phillips consists of two separate oil-wastewater separation facilities. Wastewater generated in the older sections of the refinery is first treated by dual API separators which are followed by a dissolved air flotation system. Wastewater generated by the new process units is treated in three corrugated plate interceptor (CPI) type separators which are followed by two IAF systems. The VOC emission tests were conducted on the two IAF systems.

The IAF systems operate in parallel and are identical in size and structure. Both are designed to be operated gas tight, and each has eight access doors located on the sides of the units. In order to test VOC emissions from the two systems, the access doors were tightly secured. A steady air flow was introduced into the units using a blower. An outlet location was fabricated so that continuous monitoring of the VOC concentrations from the IAF could be measured. Figures C-5 and C-6 show the IAF systems and sample locations.

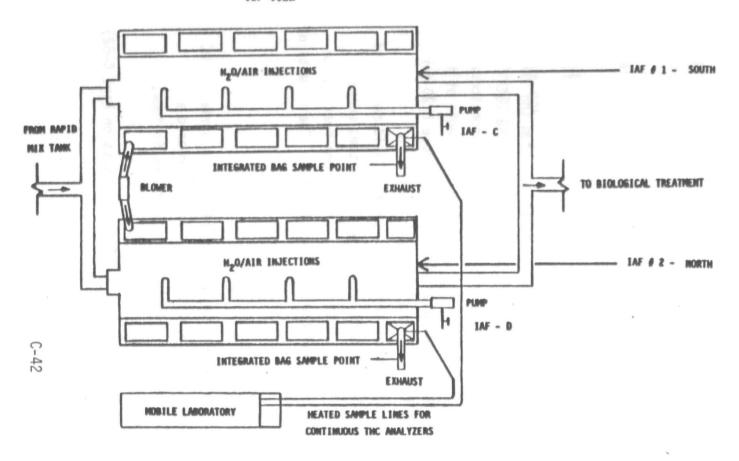
EPA Method 25A was used to measure VOC concentrations from the IAF systems. A summary of the results are shown in Table C-19. The total hydrocarbon measurements include methane. In addition, gas chromatography (EPA Method 18) was used to identify the major volatile components of the vent stream. The gas chromatography results are shown in Table C-20 for the south IAF system and in Table C-21 for the north IAF system.

In addition to the gaseous samples taken at Sweeny, liquid samples of wastewater going to and from the CPI separators and IAF systems were obtained. As with the samples acquired at Chevron and Golden West, these samples were analyzed for COD, oil and grease, TOC, and TCO. The results of the analyses are shown in Table C-22 to C-25.

C.2 VOC SCREENING OF PROCESS DRAINS

Process drains at three refineries were screened using a portable VOC analyzer (Century Systems OVA-108). Process drains were screened at Phillips Petroleum in Sweeny, Texas, Golden West in Santa Fe Springs, California, and Total Petroleum in Alma, Michigan.

(Text continues on Page C-52)



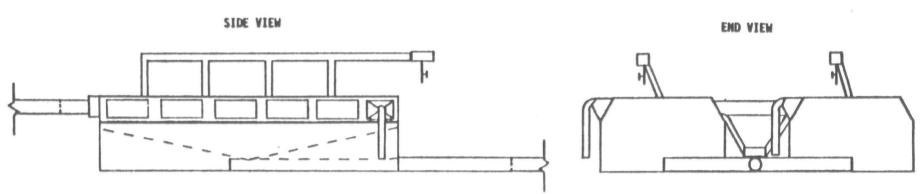


Figure C-5. Schematic representation of the IAF process with sample points and induced air system: Phillips Petroleum - Sweeny, Texas.

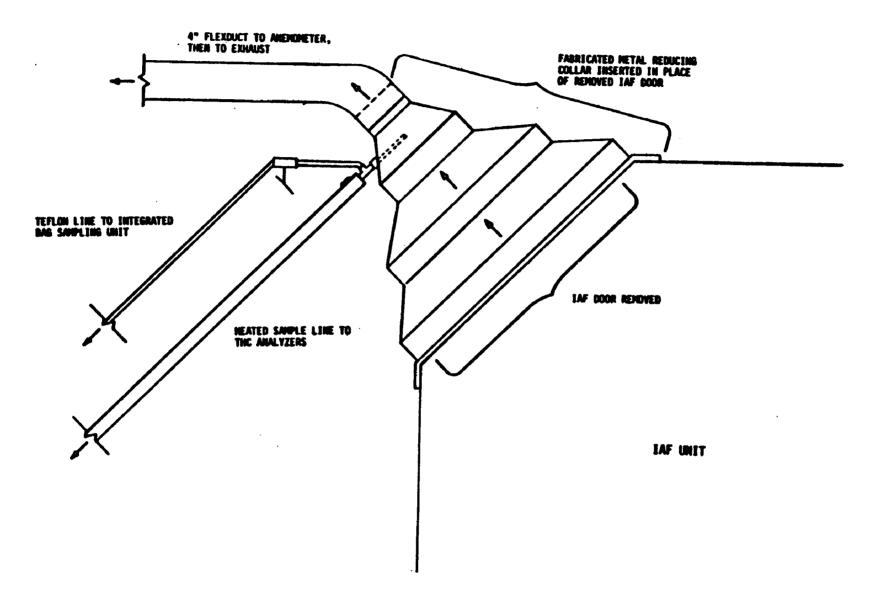


Figure C-G. IAF-outlet sample locations fabricated: Phillips Petroleum - Sweeny, Texas.

TABLE C-19. DAILY EMISSION RATE AVERAGES AT IAF OUTLETS - PHILLIPS PETROLEUM, SWEENY, TEXAS

Test Day	Average Em (lb/hr Total Hydi	ission Rate rocarbon as C _a H _o)
	IAF #1	IAF #2
8/15/83	0.51	a
8/16/83	0.47	0.34
8/17/83	0.71	0.54
8/18/83	0.93	0.80
8/19/83	0.36	0.42

aIAF #2 not on-line for monitoring on 9/19/83.

TABLE C-20. GAS CHROMATOGRAPHY RESULTS FROM IAF #1 (SOUTH IAF) - PHILLIPS PETROLEUM, SWEENY, TEXAS

				<u> </u>
DATE				
DATE	9/20/83	9/20/83	9/21/83	9/21/83
TIME	1500	1645	1100	1430
ANALYTICAL RESULTS (ppmv as compound)			·	
C-1	87.2	57.7	65.1	57.5
C-2	4.9	_	4.3	6.0
C-3	6.7	4.2	3.9	4.7
C-4	18.4	11.7	15.2	1.1
C-5	20.4	17.6	20.3	3.9
Hexane	145.3	85.9	110.0	63.6
Benzene	161.1	99.0	135.2	95.1
Heptane	25.9	16.8	37.0	21.1
Toluene	139.4	95.2	94.1	67.0
m-Xylene	45.4	34.2	33.3	21.1
o-Xylene	20.7	12.4	10.3	8.5
TOTAL HYDROCARBON (ppmv as compound)	675.4	434.7	528.7	349.6
CONTINUOUS MONITOR DAT	Γ Α			
Hydrocarbon Level (ppmv as C ₃ H ₈)	1834	1577	1625	1508
Emission Rate (lb/hr)(Total Hydro	carbon)0.72	0.62	0.67	0.62

TABLE C-20. GAS CHROMATOGRAPHY RESULTS FROM IAF #1 (SOUTH IAF) - PHILLIPS PETROLEUM, SWEENY, TEXAS (CONTINUED)

TIME 0930 1430 0915 ANALYTICAL RESULTS (ppmv as compound) C-1 218.2 197.5 115.7 C-2 6.2 5.7 4.0 C-3 5.6 6.0 2.7 C-4 21.2 15.5 4.6 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane - 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate				
ANALYTICAL RESULTS (ppmv as compound) C-1 218.2 197.5 115.7 C-2 6.2 5.7 4.0 C-3 5.6 6.0 2.7 C-4 21.2 15.5 4.6 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane - 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Leve1 (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	DATE	9/22/83	9/22/83	9/23/83
(ppmv as compound) C-1 218.2 197.5 115.7 C-2 6.2 5.7 4.0 C-3 5.6 6.0 2.7 C-4 21.2 15.5 4.6 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane — 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	TIME	0930	1430	0915
C-2 6.2 5.7 4.0 C-3 5.6 6.0 2.7 C-4 21.2 15.5 4.6 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane - 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate				
C-3 C-4 C-5 5.6 6.0 2.7 C-4 21.2 15.5 4.6 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	C-1	218.2	197.5	115.7
C-4 C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane	C-2	6.2	5.7	4.0
C-5 52.4 16.2 10.5 Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane — 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	C-3	5.6	6.0	2.7
Hexane 352.2 213.5 41.3 Benzene 353.4 201.1 60.9 Heptane — 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	C-4	21.2	15.5	4.6
Benzene 353.4 201.1 60.9 Heptane — 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C3H8) 3358 2087 1199 Emission Rate	C-5	52.4	16.2	10.5
Heptane — 78.7 20.2 Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	Hexane	352.2	213.5	41.3
Toluene 217.4 140.2 53.7 m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	Benzene	353.4	201.1	60.9
m-Xylene 118.4 62.4 26.2 o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	Heptane		78.7	20.2
o-Xylene 43.2 18.9 10.0 TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	Toluene	217.4	140.2	53.7
TOTAL HYDROCARBON (ppmv as compound) 1388.2 955.7 349.8 CONTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	m-Xylene	118.4	62.4	26.2
(ppmv as compound) 1388.2 955.7 349.8 CDNTINUOUS MONITOR DATA Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	o-Xylene	43.2	18.9	10.0
Hydrocarbon Level (ppmv as C ₃ H ₈) 3358 2087 1199 Emission Rate	7 - 7	1388.2	955.7	349.8
(ppmv as C_3H_8) 3358 2087 1199 Emission Rate	CONTINUOUS MONITOR DAT	`A		
		3358	2087	1199
(1b/hr) (Total Hydrocarbon)1.41 0.87 0.41		carbon)1.41	0.87	0.41

TABLE C-21. GAS CHROMATOGRAPHY RESULTS FROM IAF #2 (NORTH IAF) PHILLIPS PETROLEUM, SWEENY, TEXAS

DATE	9/21/83	9/21/83	9/22/83	9/22/83	9/23/83
TIME	0930	1545	1050	1550	1015
ANALYTICAL RESULTS (ppmv as compound)					
C-1	58.7	78.6	226.2	167.2	93.0
C-2	4.2	7.5	7.3	3.8	3.4
C-3	4.4	5.9	5.6	3.6	2.2
C-4	17.5	22.6	21.5	8.6	3.5
C-5	21.5	10.5	59.5	7.7	8.9
Hexane	128.5	133.7	292.5	109.7	33.1
Benzene	134.3	171.8	287.0	122.4	53.4
Heptane	35.9	46.6	113.1	50.2	20.3
Toluene	84.0	116.5	178.2	96.5	52.2
m-Xyłene	26.1	43.9	73.9	46.9	26.1
o-Xylene	8.1	13.6	20.0	14.5	8.5
TOTAL HYDROCARBON (ppmv as compound)	523.2	651.2	1284.8	631.1	251.2
CONTINUOUS MONITOR D	ATA				
Hydrocarbon Level (ppmv as C ₃ H ₈)	1739	2319	3428	2892	1278
Emission Rate (lb/hr)(Total Hydrocarbon)	0.55	0.74	1.11	0.94	0.52

^aIAF #2 not monitored on 9/20/83 during Run No. 1 and Run No. 2.

TABLE C-22. LIQUID SAMPLES TAKEN ON 9/20/83 - PHILLIPS PETROLEUM, SWEENY, TEXAS

	COD mg/1	Oil/grease mg/l	TOC mg/l
Liquid Composite and Grab Samples			
IAF #2-out-D	539.3	40.6	
IAF #1-out-C	628.4	150.1	
IAF-inlet-A'	4221.8	3059.5	
CPI-3-in (1700)	2061.4	1065.1	
CPI-2-out (1700)	681.2	69.6	
CPI-2-out (1700)	2267.1	121.0	
CPI-3-in (1700)	2810.7	339.9	
Void of Air Samples			
CPI-2-out (1813)			502.5
IAF #2-out-C (1830)			308.5
CPI-3-in (1700)			205
IAF-in-A (1830)			478.5
IAF #2-out-C (1030)			107
CPI-2-in (1700)			664.5
IAF-in-A (1030)			358
CPI-1-in (1700)			478.
CPI-3-out (1700)			204
IAF #2-out-D (1830)			138
IAF #1-out-C (1030)			229.

TABLE C-23. LIQUID SAMPLES TAKEN ON 9/21/83 - PHILLIPS PETROLEUM, SWEENY, TEXAS

	COD mg/l	Oil/grease mg/l	TOC mg/l
Liquid Composite and Grab Samples			
CPI-3-out (0930)	1991.0	269.6	
CPI-2-in (0945)	2149.1	267.4	
CPI-1-in (0945)	2697.8	687.7	
IAF-in-A'	1476.6	126.0	
IAF #2-out-D	2300.7	34.2	
IAF #1-out-C	1369.5	58.0	
CPI-2-inlet (0945)	1042.7	40.5	
CPI-1-out (0930)	2114.8	168.3	
CPI-3-out (0930)	2395.0	209.4	
Void of Air Samples			
CPI-1-in (1600)			310
CPI-3-in (1600)			259
CPI-2-in (1600)			250
CPI-2-out (1600)			157.5
CPI-3-out (1600)			198
CPI-1-out (1600)			549
CPI-2-inlet (0945)			36
IAF #2-out-D (1445)			218.5
IAF #1-out-C (0855)			129.5
CPI-1-inlet (0945)			155.5
IAF-in-A (0855)			237
IAF #2-out-D (0855)			226.
CPI-2-outlet (0930)			223.5
CPI-3-outlet (0930)			194.5
CPI-3-inlet (0945)			451.5
IAF #1-out-C (1445)			242
IAF-in-A' (1445)			278
CPI-1-outlet (0930)			262.5

TABLE C-24. LIQUID SAMPLES TAKEN ON 9/22/83 PHILLIPS PETROLEUM, SWEENY, TEXAS

	COD mg/1	Oil/grease mg/l	TOC mg/1
Liquid Composite and Grab Samples			
CPI #3-outlet (0930)	3000.5	232.5	
IAF-in-A'	2941.7	262.8	
IAF-#1-out-C	1312.9	152.3	
CPI-#1-inlet (0940)	1811.2	32.1	
CPI-#1-outlet (0930)	3400.2	705.3	
CPI-#3-inlet (0940)	2290.5	31.7	
CPI-#2-inlet (0940)	2065.1	34.8	
CPI-#2-outlet (0940)	5045.2	4293.6	
IAF-#2-out-D	1140.3	74.4	
Void of Air Samples			
CPI-#3-outlet (0920)			192.5
IAF-#2-out-D (0920)			410
CPI-#2-outlet (1600)			80
CPI-#2-inlet (1600)			199.
CPI-#2-inlet (0930)			302.5
IAF-#1-out-C (0920)			366
IAF-#1-out-C (1600)			688.
IAF-in-A' (0920)			531.
CPI-#1-outlet (0920)			146.
CPI-#2-outlet (0920)			194.
CPI-#1-inlet (1600)			166
IAF-in-A' (1600)			274
CPI-#3-outlet (1600)			242.
IAF-#2-out-D (1600)			335
CPI-#1-outlet (1600)			396
CPI-#3-inlet (1600)			210.
CPI-#1-inlet (0930)			297
CPI-#3-inlet (0930)			208

TABLE C-25. LIQUID SAMPLES TAKEN ON 9/23/83 PHILLIPS PETROLEUM, SWEENY, TEXAS

	COD mg/l	Oil/grease mg/l	TOC mg/l
Liquid Composite and Grab Samples			
CPI-#3-outlet (1000)	1503.3	469.4	
IAF-in-A'	160.9	250.0	
CPI-#1-inlet (0930)	1604.4	107.4	
CPI-#2-inlet (0930)	29194	10617	
CPI-#3-outlet (1000)	1352.2	90.0	
CPI-#3-inlet (0930)	1135.2	48.3	
CPI-#1-outlet (1000)	2230.3	405.6	
CPI-#2-outlet (0930)	2354.4	336.2	
IAF-#2-out-D	1927.6	21.2	
IAF-#1-out-C	1910.7	26.6	
Void of Air Samples			
CPI-#3-in (1000)			204.5
CPI-#1-outlet (1000)			105
IAF-in-A' (0900)			224.5
CPI-#2-outlet (1000)			444.5
IAF-#2-out-D (0900)			248
IAF-#1-out-C (0900)			225.5
CPI-#3-outlet (1000)			251
CPI-#1-in (1000)			107
CPI-#2-in (1000)			153.5

At Phillips Petroleum, the process drains are sealed with steel caps. The caps have a handle for manual removal and rest on supports over the drain inlet. The drain inlet consists of a circular sump about 6-8 inches deep and about 12 inches in diameter. Within the sump is the opening of the vertical drain pipe which connects below grade to the drain line for the process unit. A water seal is formed between the inside annulus formed by the drain pipe and the side of the cap, and the cap side and circular watts of the sump.

Screening values were taken at each drain while the drain was capped. These screening values represent emissions from controlled drains. The caps were then removed and left off for a period of time. The screening values recorded after the cap had been removed for a period of time represented emissions from uncontrolled drains. Only drains that were properly sealed and maintained were included in the analysis.

The screening values of the controlled and uncontrolled drains can be converted to leak rates (lbs VOC/hr) using the correlation established in am EPA study of atmospheric emissions from petroleum refineries. This correlation is as follows:

 Log_{10} (Non Methane Leak) = -4.0 + 1.10 Log_{10} (Max. Screening Value)

A summary of the screening values is given in Table C-26.

Process drains were also screened at Golden West (Santa Fe Springs, California) and Total Petroleum (Alma, Michigan). The process drains at Golden West are designed with water seals. However, it was difficult to determine if the water seals were being maintained at the time of the screening. The process drains at Total Petroleum were not sealed. Summaries of the screening results from these refineries are given in Tables C-27 and C-28.

C-5:

TABLE C-26. SUMMARY OF EMISSION RATES AND EMISSION REDUCTION FOR DRAINS WITH A LEAK RATE >100 PPM

	Drain	Drain Screening Values		Estimated Emission Rate, LB/HR		Est. Emission Reduction	
Unit	No.	Cap On	Cap Off*	Cap On	Cap Off*	LB/HR	<u> </u>
27.1	6	12	1,000	0.00019	0.02512	0.02493	99.
	7	10	100	0.00016	0.00200	0.00184	91.
	17	10	120	0.00016	0.00244	0.00228	93.
26.2	3	4	100	0.00005	0.00200	0.00195	97.
27.2	1	40	110	0.00073	0.00222	0.00149	66.9
	2	2,000	1,750	0.05384	0.04649	-0.00735	-15.
	2 3	7	300	0.00011	0.00668	0.00657	98.
	11	50	300	0.00083	0.00792	0.00709	89.
	- -	40	400				
	12	10	178	0.00016	0.00376	0.00360	97.
25	11	8	300	0.00012	0.00668	0.00656	98.
•	19	120	400	0.00244	0.00917	0.00673	73.
	23	20	120	0.00034	0.00244	0.00210	86.
	69	12	150	0.00019	0.00312	0.00293	93.
	. 83	7	200	0.00011	0.00428	0.00417	97.
	84	70	100	0.00135	0.00200	0.00065	32.
	85	70	300	0.00135	0.00668	0.00533	79.
	86	1,000	1,500	0.02512	0.03924	0.01412	36.
	94	8	150	0.00012	0.00312	0.00300	96.
				0.08737	0.17536	0.08800	50.

^{*}Reading(s) taken after cap had been removed for a while.

TABLE C-27. SUMMARY OF PROCESS DRAIN SCREENING - GOLDEN WEST REFINERY, SANTA FE SPRINGS, CALIFORNIA

Drain	Screening Value (ppmv)
1 2 3 4 5 6 7 8	30 30
3	70
4 E	20
6	15 15
7	20
8 9	10 10
10	70
11	700
12 13	700 15
14	30
15 16	70 10
17	20
18	10
19 20	50 -
21	•
22 23	>10,000
23 2 4	>10,000 >10,000
25	300
26 27	200 50
28	700
29 30	500 1,000
31	30
32	150
33 34	>10,000
35	20
36 37	15 20
38	15
39 40	10 80
40 41	20
42	20
43 44	40 50
45	10
46 47	10 15
48	10
49	10
Total Drains Screened	= 49
Average Screening Value	= 725
Avg. Non-Methane Leak Rate	= 0.14 lbs VOC/hr

TABLE C-28. SUMMARY OF PROCESS DRAINS SCREENING - TOTAL PETROLEUM, ALMA, MICHIGAN

Drain -	Screening Value (ppmv)
1	800
2	0
3 4	0
1 2 3 4 5 6 7 8 9	120
5	260
7	0
ά	0
a a	
10	0
11	180
12	>10,000 >10,000
13	4,500
14	1,000
15	>10,000
16	>10,000
17	0
18	Ö
19	640
20	450
21	3,500
22	>10,000
23	0
24	3,000
25	60
26	1,000
27	10
28	10
29	10
30	50
31	3,500
32	150
33	10
34	10
35	10
36	10
37	10
38	10
39	10
40	10
41	10
42	10 10
43 44	100
44 45	600
45 46	10
47	50
48	200
Total Drains Screened	= 48
Average Screening Value	= 1470
Avg. Non-Methane Leak Rate	= 0.30 lbs VOC/hr

C.3 References

- 1. Stackhouse, C. and M. Hartman. Emission Test Report Petroleum Refinery Wastewater Treatment System, Chevron U.S.A., Incorporated (El Segundo, California). TRW Environmental Operations. Research Triangle Park, North Carolina. EMB Report No. 83WWS2. March 1984.
- 2. Stackhouse, C. and M. Hartman. Emission Test Report Petroleum Refinery Wastewater Treatment System, Golden West Refining Company (Santa Fe Springs, California). TRW Environmental Operations. Research Triangle Park, North Carolina. EMB Report No. 83WWS4. March 1984.
- 3. Stackhouse, C. and M. Hartman. Emission Test Report Petroleum Refinery Wastewater Treatment System, Phillips Petroleum Company (Sweeny, Texas). TRW Environmental Operations. Research Triangle Park, North Carolina. EMB Report No. 83WWS3. March 1984.

PETROLEUM REFINERY WASTEWATER TREATMENT SYSTEMS

APPENDIX D: EMISSION MEASUREMENT AND CONTINUOUS MONITORING

D.1 INTRODUCTION

This appendix describes the measurement method experience that was gained during the emission testing portion of this study, the potential continuous monitoring procedures, and the recommended performance test procedures. The purpose of this appendix is to define the methodologies used to collect the data to support a new source performance standard, to recommend procedures to demonstrate compliance with a standard, and to describe alternatives for monitoring either process parameters or emissions to indicate continued compliance with a standard.

D.2 EMISSION MEASUREMENT EXPERIENCE

The purpose of the field study in this project was to provide estimates of the organic compound release rates from several types of devices used in wastewater treatment plants. There was insufficient information available to estimate the uncontrolled volatile organic compound emission rate from induced air flotation devices, dissolved air flotation devices, and equalization basins. Testing was performed at three refineries that use these devices. However, the true "uncontrolled" emission rate could not be measured because none of the devices were open directly to the atmosphere. All of the devices were equipped with a cover, and four of the six devices tested were equipped with an add-on emission control system. These devices were selected for testing because the

organic compounds released from the wastewater in the device were or could be collected in a duct or vent and the mass flow rate could be measured. This approach was used to estimate what the emission rate would have been from an uncovered device because of the difficulty of measuring a dispersed fugitive emission. It is necessary to assume that the dominant factors affecting the organic emission rates from these type devices are wastewater and device-related, and that meteorological variables such as air temperature and wind speed are secondary parameters.

Tests were conducted at one dissolved air flotation (DAF) unit, three induced air flotation (IAF) units, and one equalization basin. These tests included measurements of the gaseous flow rate and organic content, and various tests to characterize the wastewater organic content before and after the treatment units. Screening surveys were conducted on the drain systems in various process units at three refineries to estimate the occurrence of the fugitive emissions for various drain designs. Emission rate measurements were not made for drains, junction boxes, oil/water separators, and uncovered or open primary or secondary treatment processes.

D.2.1 Air Flotation and Equalization Basin Tests

The procedures used to characterize the emissions prior to control at the two types of air flotation devices and the covered equalization basin were similar and are discussed below in terms of the parameters that were measured.

D.2.1.1 Vent Gas Flow Rate

At the dissolved air flotation unit, the equalization basin, and one of the induced air flotation devices, the covered head spaces were ventilated by induced draft blowers. At the units with relatively high flow rates, EPA Method $2^{(1)}$ was used to measure the gas velocity. This method is based on the use of a pitot tube to traverse the flow area to calculate an average gas velocity. The gas density was calculated based on a fixed gas $(0_2, C0_2, N_2, C0)$ analysis by gas chromatography with thermal conductivity detection. Using the duct area, the gas volumetric flow rate was calculated. Since the blowers operated at constant speed with no changes in the ventilation area, the measured flows were relatively constant. No problems were experienced using Method 2 at these sources.

At one IAF that was equipped with an induced draft blower, the flow rate was expected to be too low to measure with a pitot tube, so a positive displacement volumetric flow meter was installed. This procedure is essentially EPA Method 2A. Due to a small pressure head and large amounts of water condensate, the flow meter approach did not work. At another IAF where no induced blower was used, a similar volumetric flow meter (a turbine meter) was installed. It was found that the actual flow was less than the minimum rating of the smallest meter that was commercially available.

The procedure finally used at these two sites was to construct a flow meter system using a vane anemometer in a housing of the same diameter. This system routed all of the vent stream through the anemometer at velocities sufficient to be detectible by the anemometer, with a negligible meter pressure differential. This measurement system is described in more detail in Reference 2.

The final type flow measurement was at an induced air flotation unit that normally did not have an induced or a forced ventilation system. The inspection doors on the unit cover were temporarily sealed and a portable blower was used to establish positive ventilation. Flow measurements were made using the

⁽¹⁾ See Reference 1.

anemometer system described above. No problems were encountered in the actual measurement of the flow rate, but it was found that the doors could not be perfectly sealed and that the flow supply and exhaust rates had to be measured to account for the leakage at the doors.

In summary, it was found that for systems equipped with large capacity blowers, EPA Method 2 (pitot tube traverses) can be used successfully to determine volumetric gas flow. Where there is no forced ventilation or the ventilation rate is deliberately maintained at low levels, large volumes of condensate can be present, low pressure heads may not drive a flow meter, and the flow rate may be below the range of commercially available volumetric flow meters. These conditions existed at several facilities and commercially available meters could not be used. A fabricated meter based on an anemometer normally used for low velocity air flows was used with success at these difficult sources.

D.2.1.2 Total Organic Concentration Measurement

Procedures similiar to EPA Method 25A were used to measure the total organic or hydrocarbon concentration in the vent stream. A sample was continuously withdrawn from the vent stream through a heated Teflon® sample line to a flame ionization analyzer. Propane in nitrogen mixtures were used to calibrate the analyzers. For aliphatic and aromatic hydrocarbons, such as are expected at a refinery, the total instrument response is relatively proportional to carbon content and can be used as a measure of total hydrocarbon concentration. The result of this measurement is a gaseous hydrocarbon equivalent concentration as propane. The molar density of propane was used to calculate a mass per unit volume result.

The analyzers were zeroed and calibrated with propane standards before, during, and after testing each day. For those systems that operated continuously during a multiple-day test, calibrations were performed at 4- to 8-hour intervals. The zero and calibration drifts were within the acceptable range in Method 25A.

The only problems encountered with the use of this method was the eventual condensation of high molecular weight organic aerosols in the instruments which led to instability, noise, and flameout. When these conditions occurred, the instruments had to be purged with clean air until the signal stabilized. This problem was minimized when an instrument equipped with a totally heated enclosure was used.

D.2.1.3 Gaseous Organics Speciation

Gas chromatographic techniques were used to identify the major volatile components of the vent streams prior to control. The basic techniques described by EPA Method 18 were used. An integrated sample was collected into an inert, flexible plastic bag and these samples were analyzed by two chromatograph systems. The purpose of these determinations was to identify the major components and to estimate an average flame ionization response factor to evaluate the carbon proportionality of the total hydrocarbon analyzer result.

One of the gas chromatograph systems was used to separate methane through pentane. The calibration mixture for this analyzer consisted of C_1 - C_5 species so that specific identification and quantification was possible. The second system was used to separate higher boiling point compounds in the range of C_6 to C_9 . Benzene and m-xylene were used as calibration species. Specific identification and quantification was possible for these two compounds. The other

compounds were identified by retention time and quantified by using the closer (benzene or xylene) calibration factor based on the number of carbon atoms in the molecule.

No specific problems were encountered in conducting these tests. The collection of the samples into bags was straightforward. In some cases, condensate was observed in the bags, but analysis of this material indicated negligible organic content. The only uncertainty is whether or not any significant amounts of compounds with a higher boiling point than C9 were present.

This is unlikely because of the relatively high boiling points of compounds heavier than C9, and the relatively low source temperatures.

D.2.1.4 Wastewater Sampling and Analysis

Water samples were collected before and after the wastewater treatment devices that were tested in order to characterize the wastewater and to determine if there were any simple tests that could be used as an indicator of expected hydrocarbon emission rates.

Samples were collected using techniques similar to those used by the refineries for process operation control. Composites were made from individual grab samples taken periodically during in the test day. The composite sample volume was approximately 1 gallon. The samples were stored and shipped on ice to minimize the loss of volatile components. Additional samples were collected into void-of-air (VOA) vials where all the head space could be eliminated to obtain a sample for total carbon analysis.

No specific problems were encountered with the collection of samples from flowing streams in pipes. Where samples had to be collected from a quiescent pool (e.g., an API separator forebay), there is some uncertainty about the

representativeness of a dipped grab sample. During sample shipment, several of the void-of-air (VOA) sample vials were broken because of freezing. Since no expansion area was left in the bottle, the container broke when the sample remained in direct contact with ice for extended periods. Also, it is possible that during a storage period of several weeks, coagulation and settling occurred so that a homogenous mixture could not be regenerated for analysis. This problem may not have occurred if the analysis had been performed within 1 day and the samples could have been stored at nearly ambient conditions.

The water samples were analyzed for total organic carbon, chemical oxygen demand, oil and grease, total chromatographical organics (organic speciation), and volatile organics by a purge and trap technique.

Total organic carbon was determined using an automatic analyzer that measures the carbon dioxide resulting from the photochemical oxidation of organic carbon after the inorganic carbon has been removed by purging. This procedure does not measure the volatile compounds that are removed by the purge stream. Variation can also be caused by nonrepresentative collection of heavy organics in the aliquot transfer syringe used to inject the sample into the analyzer.

The chemical oxygen demand method is based on the quantity of oxygen required to oxidize the organic matter in the sample under controlled conditions. Organic and oxidizable inorganic carbon is measured. Volatile straight chain aliphatics are not appreciably oxidized, partly due to their presence as volatiles in the head space where they do not come into contact with the oxidizing liquid.

Oil and grease content was determined by a gravimetric determination of fluorocarbon-113 extractible compounds. The solvent evaporation step of the process removes short chain hydrocarbons and simple aromatics due to evaporation.

Total chromatographicable organics was performed by gas chromatography with flame ionization detection. The sample was prepared by extracting the water with methylene chloride and injecting the extract to the chromatograph. This procedure allowed speciation of C_7 to C_{25} compounds. A solvent volume reduction step in the analysis tends to volatilize short straight chain aliphatics and simple aromatics with a boiling point less than $100^{\circ}C$.

The purge and trap procedure used was EPA Method 624 (see Reference 5) with component identification by mass spectrometry.

The results of all the analyses were highly variable from day-to-day. There did not appear to be any one procedure that yielded consistently reasonable results. These were also significant variations from the results obtained by the treatment system operators for those parameters that were measured for process control. The sample storage time and storing the sample on ice may have contributed to the inconsistencies. Also, all of the routine procedures that were performed tend to exclude the more volatile compounds from the result. Because of these inconsistencies, it is not possible to determine if any of the test procedures would yield results that would predict hydrocarbon emission factors.

Further studies would be necessary to determine if the inconsistencies were caused by field sampling, storage, or analysis techniques.

D.2.1.5 Process Drain Screening Surveys

Portable analyzers were used at three refineries to survey the unit drain systems. The purpose of these surveys was to determine if there was a significant

difference in the occurrence of fugitive emissions from drain systems of different designs. EPĀ Method 21 techniques were used. The meter reading at the centroid of the cross-sectional opening to atmosphere was recorded. A leaking source was tentatively identified when the meter reading at the source exceeded the ambient meter reading.

There were no problems encountered in conducting the field tests.

However, the identification of the source of some detected emissions was difficult.

In some cases it was found that the source of a detected emission was an openended line that terminated at the drain, rather than from the underground drainage system. Also, since the source of the detected emission was not necessarily concentrated or steady, the variability of a meter reading at a source was more than was observed at other types of fugitive emission sources.

D.3 PERFORMANCE TEST METHODS

The specific combination of measurements that would be necessary to demonstrate compliance depends on the format of a standard. The options include specification of a VOC emission concentration limit, a VOC mass rate limit, or a minimum VOC removal efficiency requirement. The procedures recommended for determination of each of these values are described in this section. The estimated cost of each type of performance test is also presented.

D.3.1 VOC Concentration Measurement

The recommended VOC measurement method is Reference Method 25A or 25B.

Method 25A, "Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer," applies to the measurement of total gaseous organic concentration of vapors consisting of alkanes and aromatic hydrocarbons. The

instrument is calibrated in terms of propane or another appropriate organic compound. A sample is extracted from the source through a heated sample line and glass fiber filter and routed to a flame ionization analyzer (FIA). Provisions are included for eliminating the heated sampling line and glass fiber filter under some sampling conditions. Results are reported as concentration equivalents of the calibration gas or organic carbon.

Method 25B, "Determination of Total Gaseous Organic Concentration Using a Nondispersive Infrared Analyzer," is identical to Method 25A except that a different instrument is used. Method 25B applies to the measurement of total gaseous organic concentration of vapor consisting primarily of alkanes. The sample is extracted as described in Method 25A and is analyzed with a non-dispersive infrared analyzer (NDIR).

In both the FIA and NDIR analysis approaches, instrument calibrations are based on a single reference compound. For refinery wastewater systems propane is the recommended calibration compound. As a result, the sample concentration measurements are on the basis of that reference and are not necessarily true hydrocarbon concentrations. Calculation of emissions on a mass basis will not be affected because the response of the instruments is proportional to carbon content for similar compounds, which in this case, are crude petroleum components. Mass results would be equivalent using either the concentration and molecular weight based on a reference gas or the true concentration and true average molecular weight of the hydrocarbons. The advantage of using a single component calibration is that chromatographic techniques are not required to isolate and quantify the individual compounds present.

The VOC analysis techniques discussed above measure total hydrocarbons including methane and ethane. Chromatographic analyses during prior field tests have indicated that significant quantities of methane and ethane may sometimes be

present in the vapors emitted. If it is expected that methane or ethane is present in significant quantities, appropriate samples are required for chromatographic analysis to adjust the results to a nonmethane-nonethane basis. "Reference Method 18: Measurement of Gaseous Organic Compounds by Gas Chromatography" would be applicable for this measurement.

D.3.2 Gas Flow Measurement

Reference Methods 2. 2C. 2A. and 2D are recommended as applicable for measurement of gaseous flow rate. "Method 2: Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)" applies when the duct or pipe diameter is larger than 12 inches and the flow is constant and continuous. "Method 2C: Determination of Stack Gas Velocity and Volumetric Flow Rate from Small Stacks or Ducts (Standard Pitot Tube)" applies when the duct diameter is less than 12 inches and the flow is constant and continuous. "Method 2A: Direct Measurement of Gas Volume Through Pipes and Small Ducts" applies to the measurement of volumetric flow where a totalizing gas volume meter is installed in the duct and a direct reading is obtained. This method can be used in the general temperature range of $0-50^{\circ}\text{C}$, with a flow range dependent on the meter size. Temperature and pressure measurements are made to correct the volume to standard conditions. "Method 2D: Measurement of Gas Volume Flow Rates in Small Pipes and Ducts" applies when Method 2A cannot be used because the vent size is too large or when pressure drop restrictions prevent reducing the duct size to that of a volumetric meter. This method incorporates the use of a device to measure gas flow rate, such as an orifice, a venturi, or a rotameter. The flow rate is integrated with time to compute an average volume flow. This method must be applied with caution to intermittant or variable gas flow rates.

D.3.3 Mass Flow

The VOC concentration and volume measurements are combined to determine the mass flow. To determine the total VOC mass during the entire test period, the VOC mass flow is determined for small incremental periods; each 5-minute interval and increment thereof when the processor is operating, and each 15-minute interval and increment thereof during non-operation. These incremental flows are then summed for the entire test period. Because VOC concentrations and flow rate may vary significantly within a brief time period, these short incremental calculation intervals are needed so that short-term variations in flow rates can be properly weighted in the calculations.

D.3.4 Emission Reduction Efficiency Determination

The recommended procedures for determining the VOC concentration and gas flow would be performed simultaneously at the control device inlet and outlet. The measurements would be combined to compute a VOC mass flow before and after the control device. The mass flows would be used to calculate a VOC removal efficiency.

D.3.5 Performance Test Time and Costs

The length of a performance test is specified in the applicable regulation and is selected to be representative for the process being tested. Wastewater treatment operations are generally steady, although there may be periods where intermittent high organic content wastes are treated. In general, a performance test would consist of three to six runs, each lasting about 2 hours.

It is estimated that for most operations, the field testing could be completed in 2 to 3 days (i.e., two or three 8-hour work shifts) with an extra day for setup, instrument preparation, and cleanup.

The cost of the testing varies with the length of the test and the number of vents to be tested. The cost is estimated at \$6,000 - \$10,000 for VOC concentration determination at one vent, and \$12,000 - \$15,000 for the determination of VOC removal efficiency.

D.4 MONITORING SYSTEMS AND DEVICES

The purpose of monitoring is to ensure that the emission control system is being properly operated and maintained after the performance test. One can either directly monitor the regulated pollutant, or instead, monitor an operational parameter of the emission control system. The aim is to select a relatively inexpensive and simple method that will indicate that the facility is in continual compliance with the standard.

The use of monitoring data is the same regardless of whether the VOC outlet concentration or an operational parameter is selected to be monitored. The monitor should be installed and operating properly before the first performance test. Continual surveillance is achieved by comparing the monitored value of the concentration or parameter to the value which occurred during the last successful performance test, or alternatively, to a preselected value which is indicative of good operation. It is important to note that a high monitoring value does not positively confirm that the facility is out of compliance; instead, it indicates that the emission control system is operating in a different manner than during the last successful performance test.

Two types of emission reduction systems can be used to control vent streams from covered water treatment devices. These are combustion and vapor processing. Potential monitoring approaches for these control systems are discussed below.

D.4.1 Monitoring of Vapor Processing Devices

There are presently no demonstrated continuous monitoring systems commercially available which monitor vapor processor operation in the units of VOC removal efficiency. This monitoring would require measuring not only inlet and exhaust VOC concentrations, but also inlet and exhaust volumetric flow rates. An overall cost for a complete monitoring system is difficult to estimate due to the number of component combinations possible. The purchase and installation cost of an entire monitoring system (including VOC concentration monitors, flow measurement devices, recording devices, and automatic data reduction) is estimated to be \$25,000. Operating costs are estimated at \$25,000 per year. Thus, monitoring in the units of efficiency is not recommended due to the potentially high cost and lack of a demonstrated monitoring system.

Monitoring in units of mass of VOC emitted would require measurements only at the exhaust location, as discussed above. The cost is estimated at \$12,000 for purchase and installation plus \$12,500 annually for operation, maintenance, calibration, and reduction.

Monitoring equipment is commercially available, however, to monitor the operational or process variables associated with vapor control system operation. The variable which would yield the best indication of system operation is VOC concentration at the processor outlet. Extremely accurate measurements would not be required because the purpose of the monitoring is not to determine the exact outlet emissions but rather to indicate operational and maintenance practices regarding the vapor processor. Thus, the accuracy of a FIA (Method 25A) type instrument is not needed, and less accurate, less costly instruments which use different detection principles are acceptable. Monitors for this type of continuous VOC measurement, including a continuous recorder, typically cost about \$6,000

to purchase and install, and \$6,000 annually to calibrate, operate, maintain, and reduce the data. To achieve representative VOC concentration measurements at the processor outlet, the concentration monitoring device should be installed in the exhaust vent at least two equivalent stack diameters from the exit point, and protected from any interferences due to wind, weather, or other processes.

The EPA does not currently have any experience with continuous monitoring of VOC exhaust concentration of vapor processing units at wastewater treatment units in petroleum refineries. Therefore, performance specifications for the sensing instruments cannot be recommended at this time. Examples of such specifications that were developed for sulfur dioxide and nitrogen oxides continuous instrument systems can be found in Appendix B of 40 CFR 60.

For some vapor processing systems, there may be another process parameter besides the exhaust VOC concentration which is an accurate indicator of system operation. However, all acceptable process parameters for all systems cannot be specified. Substituting the monitoring of vapor processing system process parameters for the monitoring of exhaust VOC concentration is valid and acceptable if it can be demonstrated that the value of the process parameter is an indicator of proper operation of the processing system. Monitoring of any such parameters would have to be approved by enforcement officials on a case-by-case basis. Parameter monitoring equipment would typically cost about \$3,000 plus \$3,000 annually to operate, maintain, periodically calibrate, and reduce the data into the desired format.

D.4.2 Monitoring of Combustion Devices

D.4.2.1 Incinerators

Incinerators used to comply with a standard need to be maintained and operated properly if the standard is to be achieved on a continuous basis. Continuous inlet and outlet emission monitoring would be the preferred method of monitoring because it would provide a continuous, direct measurement of actual emissions and destruction efficiency. However, no continuous monitor measuring total VOC has been demonstrated for incinerators controlling vent streams. Moreover, such a monitoring system would be extremely complex and labor-intensive, and it would be relatively expensive when two monitors are required to ensure that a certain destruction efficiency is maintained.

The incinerator operating parameters that affect performance are temperature, type of compound, residence time, inlet concentration, and flow regime. Of these variables, the last two have the smallest impact on incinerator performance. Residence time is essentially set after incinerator construction unless the vent stream flow rate is changed. Moreover, at temperatures above 760°C, compound type has little effect on combustion efficiency.

Test results and theoretical calculations show that lower temperatures can cause significant decreases in control device efficiency. Test results also indicate that temperature increases can also adversely affect control device efficiency. In terms of cost, temperature monitors are relatively inexpensive, costing less than \$5,000 installed with strip charts, and are easily and cheaply operated. Given the large effect of temperature on efficiency and the low cost of temperature monitors, this variable is clearly an effective parameter to monitor.

Where a combustion device is used to incinerate waste VOC streams alone, flow rate can be an important measure of destruction efficiency since it relates directly to residence time in the combustion device. Flow rates of fugitive

emission vent streams are typically small in comparison to other streams that may be ducted to the same incinerator. As a result, flow rate may not always give a reliable indication of the vent stream residence time in the incinerator. But an indication of emission vent stream flow rate to the incinerator gives assurance that VOC is being routed for proper destruction. Flow rate monitors, at an estimated installed cost of less than \$2,000, are inexpensive and easy to operate. Therefore, since flow rate monitors give an indication that organics-laden streams are being routed for destruction and since they are inexpensive, flow rate is also an effective parameter to monitor for incinerators. Flow rate meters should be installed, calibrated, maintained, and operated according to the manufacturer's specifications and should be equipped with a continuous recorder. They should have an accuracy of 5 percent of the flow rate being measured and should be installed on combustion device inlets.

D.4.2.2 Boilers or Process Heaters

If an emissions vent stream is introduced into the flame zone of a boiler or process heater, it is necessary to know that the boiler or heater is operating and that the waste gas is being introduced into the boiler or heater. Maintenance of records such as steam production records would indicate periods of operation. Flow indicators could provide a record of flow of the vent stream to the boiler or heater. For smaller heat producing units less than 44 MW (150 million Btu/hr heat input), temperature should also be measured to ensure optimum operation. Monitoring temperature for boilers or heaters with heat design capacities greater than 44 MW would not be necessary. These larger units always operate at high temperatures (>1100°C) and stable flow rates to avoid upsets and to maximize steam generation rates. Maintenance of records that indicate periods of operation would be sufficient for these larger boilers or heaters.

D.4.2.3 Flares

Because flares are not enclosed combustion devices, it is not feasible to measure combustion parameters. Moreover, temperatures and residence times are more variable throughout the combustion zone for flares than for enclosed devices and, therefore, such measurements would not necessarily provide a good indicator of flare performance even if measurable.

The typical method of monitoring continuous operation of a flare is visual inspection. However, if a flare is operating smokelessly, it can be difficult to determine if a flame is present, and it may take several hours to discover. The presence of a flame can also be determined through the use of a heat sensing device, such as a thermocouple or ultra-violet (U-V) beam sensor on a flare's pilot flame. If a flame is absent, the temperature probe can be used to alert the plant operator. The cost of available thermocouple sensors ranges in price from \$800 to \$3,000 per pilot. (The more expensive sensors in this price range have elaborate automatic relight and alarm systems.) One drawback of thermocouples is that they burn out if not installed properly. The cost of a U-V sensor is approximately \$2,000. However, the U-V system would not be as accurate as a thermocouple in indicating the presence of a flame. The U-V beam is influenced by ambient infrared radiation that could affect the accuracy. Interference between different U-V beams would make it difficult to monitor flares with multiple pilots. U-V sensors are designed primarily to monitor flames within enclosee combustion devices. Therefore, thermocouples are a superior monitoring methodology for flares. To ensure that a vent stream is being continuously vented to a flare, a flow indicator can be installed on the vent stream.

D.5 References

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