

PETROLEUM REFINING AND AIR QUALITY MANAGEMENT

by

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(ABSTRACT)

Management of the air quality surrounding Petroleum Refineries deserves attention because the industry contributes almost five percent of the total emissions from all anthropogenic sources. A document containing a complete set of guidelines for use in the refining industry which satisfies the current and anticipated air quality legislations and regulations in the U.S. is necessary. In the past, several documents have been prepared, but have not included a complete coverage of the air quality management as currently needed. Furthermore, due to the continuing revisions of the Clean Air Act, a document with current, updated regulations and air quality management principles is necessary. This study dealt with a broad range of topics including characteristics of emissions, control technology applied, regulations and legislative issues, monitoring and modeling practices, and issues of the 1980s together with future projections and implications. Air quality regulations and standards are periodically revised and are becoming more

stringent with time. Issues like acid rain may lead to even more stringent emission standards if investigations carried out currently reveal that the refineries are significant contributors. Great measures are taken to control emissions from the refineries either by using good control equipment or using other alternative control strategies. Small operating refineries are closing down due to changing conditions. An agglomeration and or expansion of the existing refining capacity is occurring. The air quality trends associated with this transition in the industry are discussed.

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I. INTRODUCTION

Oil, the single largest source of energy in the world, has grown rapidly to its position at present as a result of its competitiveness of price, versatility, relative cleanliness, and ease of handling. Such a wide global growth has contributed significantly to the welfare of the society, but the scale of operations involved has inevitably brought about associated environmental problems such as those arising from exploration and production, ocean transportation, refining, distribution, and the usage of the products.

Environmental management of air quality surrounding petroleum refineries encompasses the understanding of several interacting factors that include adverse effect assessment, meteorology, atmospheric chemistry, emissions sources, legal requirements, control technology, and costs. The management of air quality around the refineries in particular deserves a fair attention because the petroleum refining industry has been shown to contribute approximately five percent of the total anthropogenic emissions from the industrial, commercial, residential, and transportation sectors (6).

A single document encompassing several disciplines pertinent to air quality management around the refineries such as the basic chemical processes occurring in a refinery, characteristics and technologies applied to control the emissions, current regulations and legislations, permits involved in constructing, expanding, or maintaining refineries, methodology involved in monitoring and modeling, environmental related issues of the 1980s, and the current research being conducted is essential in managing the air quality at the refineries. Prior to this thesis, although the information on the various aspects outlined above was available, it was scattered all over and the acquisition of several documents was necessary to understand the basic methodology involved in air quality management around the refineries. Furthermore, it was desirable to integrate the revisions of the Clean Air Act Amendments of 1977 and the resulting EPA promulgated regulations and standards enacted until the time the thesis was written.

In short, it can be said that the thesis is intended for the person interested in knowing the various disciplines outlined above and the methodology involved in managing the air quality around the refineries. Without this thesis, a person will have to spend a considerable amount of time gathering the relevant documents.

It is imperative to point out that this document is not design oriented containing high technical areas pertinent to design parameters at the refineries. Reference to such technical aspects is however included in the various sections of the document.

The basis of this guideline document demanded the acquisition of relevant data and information from different sources dealing with the air quality management of the refineries. The objectives of the study conducted are outlined by the following summary type statements:

1. Examine the characteristics of refineries mainly in the U.S. from an air quality point of view with emphasis on the emissions from the chemical and physical processes being employed.
2. Examine the air quality permits and the steps involved in acquiring those permits to construct or expand a refinery.
3. Investigate the various methods used in the control of refinery emissions.
4. Determine typical limits, standards, and regulations as they apply to refineries.

5. Investigate the criteria involved in setting up Environmental Impact Statements (EIS) and Prevention of Significant Deterioration (PSD) permits.
6. Discuss the air quality monitoring practices and the use of measuring instrumentation at the refineries.
7. Explain the use of air quality modeling at refineries.
8. Briefly compare air quality regulations and steps involved in setting up a refinery in U.S. to that in a third world country like Malaysia.
9. Relate economic-environmental inter-relationships as they relate to refinery air quality management. For example, the closing in recent years of some refineries which are no longer competitive and the construction of new larger ones will change the impact of refineries on air quality.
10. Discuss important environmental issues of the 1980s as they apply to refineries.
11. Identify research in progress and expected future developments that will effect refinery air quality management.

Chapter II is used to summarize the results of the literature review carried out to set the stage for accomplishing the objectives. It contains a discussion on research that has been carried out in the management of air quality of refineries and other areas that deserve further attention and work.

To be able to quantify air quality at refineries, it is imperative to know the chemical processes used in the refineries. This, together with some information on an overview of refinery capacity and growth, and classification of refineries is discussed in Chapter III.

Chapter IV deals with acquiring the necessary permits such as Prevention of Significant Deterioration (PSD), other documents, and other air quality steps required prior to operating a new refinery. Applicable air quality legislations and regulatory policies, application of alternative regulatory strategies in U.S., too, are, presented in the Chapter. A discussion on the PSD permit of the proposed Hampton Roads Energy Company Oil Refinery (here after referred as Portsmouth Refinery) in Portsmouth, Virginia and Kenai Refinery (Kenai, Alaska) is included. The purpose of discussing the Environmental Impact Statements (EISs) and PSDs of the refineries is to develop an overview of the methodology involved in setting up and managing the air quality aspects of

refineries. It, too, contains a discussion on implementation and the procedure involved in setting up a small refinery by Petroliam Nasional Berhad (PETRONAS) at Kerteh Industrial Area, Trengganu, Malaysia.

Chapter V includes a comprehensive discussion on the types and magnitude of emissions generated by refineries. It includes the magnitude, survey of the emissions, air pollution controls and their cost effectiveness utilized at modern refineries. Pollutants emitted include oxides of sulfur (SO_x), oxides of Nitrogen (NO_x), hydrocarbons (HC), carbon monoxide (CO), total suspended particulates (TSPs), acidic and airborne sulfates, hazardous gases, mercaptans, and other offensive odors.

Chapter VI deals with the application of air quality measurement,

monitoring, modeling, and instrumentation for both the ambient levels and stack pollutant discharges at the refineries.

Economic-environmental inter-relationships and environmental issues of the 1980s are discussed in VII. A discussion on the environmental expenditure due to air pollution contributed by refining industry has been included. The reasons for closing down of some young and old refineries is

also addressed in the Chapter. Furthermore, information on the treatment of gases into possible marketable products and global environmental issues related to emissions from refineries such as acid rains, carbon dioxide 'green house effects' are also covered in the Chapter.

Chapter VIII deals with a discussion on research in progress in environmental management of refineries and its future developments. It, too, focuses on general comments regarding the literature and study as a whole projecting the future of oil refineries in being able to enhance the air quality management of the refineries.

Chapter IX which is the conclusion, focuses on the generalizations and a few recommendations made of the study.

II. LITERATURE REVIEW

Environmental management of refineries has developed from early efforts to reduce local citizens' complaints about offensive pollution problems to its present status. The air quality aspects of design, siting, and operation of refineries now consists of major activities. These have emerged as a consequence of the concerns of modern society which have the following underlying goals:

1. Protecting the environment for succeeding generations.
2. Assuring safe, healthy, productive and satisfying surroundings for all people.
3. Attaining the widest range of beneficial uses of the environment without degradation, risk to health or safety, or other undesirable and unintended consequences.
4. Preserving important historic, cultural, and natural aspects of national heritage, and maintaining, wherever possible, an environment which supports diversity and variety of individual choice.

5. Achieving a balance between population and resource use which permits high standards of living and a wide sharing of life's amenities.
6. Enhancing the quality of renewable resources and approaching the maximum attainable recycling of depletable resources.

To attain these goals, regulations and standards based on limiting emissions or using specified technologies have been used. Unfortunately, this resulted in inflexibility as it did not allow for alternative approaches as technology and experience developed. In addition, it was found that many standards undoubtedly failed to balance benefits derived from pollution control and costs of installing and operating pollution control equipment.

Today, air quality controls are usually based on specifying environmental parameters to achieve the required objectives. The factors taken into account include the ecosystem, the total pollution load from all sources, and the pollution load from the specified refinery (87). The emphasis placed by such parameters is geared towards the preservation of air quality, generation of a minimum degree of air quality degradation, or air quality improvement. Such parameters are not normally set without considering the cost

of achieving them. If the cost is too high, it may force closure of existing facilities or abandonment of proposed projects. It is important to view the air quality management of refineries as a site-specific security.

The U.S. can be regarded as the historical heart of the refining industry for it has far more distillation capacity, cracking capacity, desulfurization capacity than any other nation. It is also the center of technological innovation in refining; disproportionate demands for gasoline fostered the development of catalytic cracking, the need for flexibility in processing brought about hydrocracking technology.

The control of atmospheric emissions from petroleum refineries historically has been reasonably good in the context of the total emissions from all industrial sources. The conservation of resources was an industry practice for many years before the upsurge of interest in the environment in the 1970s. Floating roof tanks and recovery systems have for some time conserved hydrocarbons. The recovery of catalytic cracking catalyst dusts through the use of high efficiency cyclone separators, is another example of a long standing industry practice. It can be said that the petroleum refining industry has always been technologically progressive. Today, new processes for the reduction of sulfur oxide emissions from refineries are in advanced stages of development

or commercial evaluation (5, 6). Technology for CO, TSP, and HC emissions control used sparingly earlier is now available and is widely used in refineries throughout the world (6).

The volume and components of energy production and consumption have a direct bearing upon the nature and extent of the environmental protection mechanisms.

During the decade of the 1980s, U.S. energy consumption is expected to experience a 1.5 percent annual rate of growth, while comparable real Gross National Product (GNP) growth is expected to be 2.1 percent per year (73). During the 1960s and 1970s, the annual average increase in consumption was 4.2 and 1.3 percent respectively, whereas the annual average GNP growth was 3.8 and 3.3 percent respectively (73). According to statistics published by the Energy Information Administration, it has been projected that the total U.S. energy consumption will increase from 76.3 in 1980 to 88.6 quadrillion British Thermal Units (Btu's) in 1990 (73). These data together with the historical and projected total energy consumption per dollar of real GNP are presented in Table 1 (73) and Fig. 1 (73). A greater use of energy in the form of fuel will demand an increased use of control technology in the industry.

The challenge of air quality management in the refining industry has been mitigated to an enhanced degree by the limited research carried out. Two sources that contained a considerable amount of information pertaining to this study are Environmental Conservation(73) prepared by the Oil and Gas Industries National Petroleum Council and Environmental Management of Refineries and Terminals(87) prepared for the International Petroleum Industry Environmental Conservation Association (IPIECA) by Standard Oil Company (Indiana). Unfortunately, most of the research results dealt with the management of refinery wastewaters and the management of oil spills. Only about 15-20 percent of these two references dealt with the air quality management of refineries. Furthermore, the documents did not include a complete coverage of the air quality management around refineries. In addition to the literature available at the library, information for preparing the thesis was also gathered from correspondence in form of letters, purchasing relevant documents, and telephone calls.

Letters were written to large oil companies such as Exxon, Shell, Mobil, Texaco, Standard Oil Co. (Indiana), Caltex, Marathon Oil Co., and others to inquire and gather information dealing with the control of air quality near refineries. Exxon, Texaco, and Standard Oil Co. (Indiana) were

very cooperative in sending literature on the environmental control practices carried out by them (49, 95-98).

A very important source of information for the study was the American Petroleum Institute, Washington D.C. Several volumes of documents pertaining to topics such as the Atmospheric Disposal of Refinery Wastes, Atmospheric Emissions, and Environmental Control Expenditures were examined (1-9). These references covered some areas of refinery air quality management not covered by the two other major sources of information. Although the references especially the 'Manual on Disposal of Refinery Wastes Volume on Atmospheric Emissions' contained considerable amount of information, the document was prepared prior to the introduction of the Clean Air Act Amendments of 1977 (1977 CAAA). Much of the information contained had to be updated to be applicable to the 1977 CAAA. Letters were also sent to Meteorology and Environmental Protection Agency (MEPA) of Saudi Arabia to find out the standards and controls used in Saudi Arabia. Unfortunately, very little information was provided by MEPA to be used in the study. Furthermore, the standards used were exactly like those set by the Environment Protection Agency (EPA) of U.S.

As the study includes a brief survey of some of the important steps and procedures involved in setting up modern

refineries, information on PSD permits and EISs were sought from the Department of Environmental Conservation (Poucho, Juneau, Alaska) and the EIS of the proposed, but abandoned Portsmouth Refinery from the State Air Pollution Control Board (SAPCB) of Virginia (Richmond, Virginia). The main reason for getting an access to the EIS and PSD of the proposed Portsmouth Oil Refinery was that the facility was among one of very few modern refineries proposed after 1975 which made both EIS requirements and 1977 CAAA applicable. Furthermore, the PSD and EIS prepared for the facility contained current technological innovations used in managing refinery air quality.

Since a small section of the thesis was devoted to a discussion on management of refinery air quality of refineries of Malaysia, information was obtained from Petroliam Nasional Berhad (PETRONAS) of Malaysia. PETRONAS recently built a small refinery having a capacity of 30,000 b/d a day at Kerteh Industrial site (Trengganu, Malaysia) (80). An EIS prepared for that facility was examined and briefly compared with the EIS of the Portsmouth refinery which is typical of those required of new refineries proposed for U.S. construction. To be able to understand and familiarize with some of the limits, standards, and regulations that apply to refineries in Malaysia, the Environmental Quality (Clean Air) Regulations of 1978 were obtained from the Division of Envi-

ronment (Malaysia) (40). Articles pertaining to environmental management of air quality were also obtained from the libraries in Malaysia namely Universiti Pertanian Malaysia (Agriculture University of Malaysia), Universiti Kebangsaan Malaysia (National University of Malaysia), and Universiti Malaya (University of Malaya). Unfortunately, a great deal of the literature was on water quality management and was therefore of only a little use.

III. OVERVIEW OF REFINERY OPERATIONS

REFINERY CAPACITY AND GROWTH

From 1940 to the early 1970s, refining capacity grew rapidly with demand. An overview of the growth in global refining capacity and oil product demand for the period 1940-1980 is shown in Table 2 (55). The ratio of product consumption to refinery capacity indicates the capacity utilization achieved over those years. Table 2 shows both the refining capacity and consumption grew rapidly during 1940 to 1973. In the 1950s, the trend towards concentrating refineries near consumers rather than near centers of oil production began. The number and quality of products marketed changed as did the cost of moving crude oil in large quantities relative to the cost of moving finished products decreased. These trends led to atmospheric emissions being increased, but originating however, from fewer refineries (81).

In the U.S., from the 1860s until 1920, refining operations were generally limited to crude oil distillation for the production of kerosene. By 1960, refining capacity stood at 9.9 million barrels per day (Mn b/d). Capacity nearly doubled over the next 20 years; by 1980 operating capacity

was 17.6 Mn b/d (73). According to the Weekly Petroleum News Status Report (38), crude oil input to refineries averaged only 11.1 Mn b/d for the four weeks ending on January 6, 1984. It can be said that the operating capacity of refineries has slightly fallen over the years. Atmospheric emission trends follow refinery capacity trends. The closing down of refineries unable to compete economically has been for, the most part, those refineries with the lower efficiency air pollution control facilities.

WORLD WIDE DISTRIBUTION OF REFINERIES

A list of distribution of refineries is presented in Table 3 (107). In 1981, there were 834 refineries operating in the world. The refinery capacity levels varied from 190 b/d (C&H Refinery Inc., Wyoming) to as high as 728,000 b/d (Hess Oil Virgin Islands Corp., St.Croix, Virgin Islands). The three countries with the largest number of refineries in ascending scale in 1981 were Canada (41 refineries), Japan (50 refineries), and U.S. (330 refineries). Surprisingly, the Middle-east being among the world's largest producer of crude oil had a total of only 37 refineries. Almost 40 percent of the world's total refining capacity was in the U.S. The 15 largest U.S. oil companies are listed in Table 4 (78). These companies refined approximately 74 percent of the total crude oil refined in the U.S. in 1976.

MANUFACTURING OPERATIONS

Crude oils are complex mixtures of thousands of chemical compounds ranging from methane and ethane which are dissolved gases, to compounds which are solids at room temperature. Chemists have identified more than 3,000 different compounds in crude oil, and these are only a small part of the total. Although crude oils contain thousands of different compounds, the compounds (other than water and trace contaminations) are all composed mostly of carbon and hydrogen called hydrocarbons (65).

Typical crudes also contain small amounts of sulfur (up to five percent) nitrogen (up to 1 percent), oxygen (up to 5 percent), and metals (up to 0.1 percent). The metals are primarily iron, nickel, and vanadium (87). Most of the non-hydrocarbon constituents are chemically combined with carbon and hydrogen and are impurities and contaminants that must be removed, or reduced in concentration in the refining process (90). As a result, air and water pollution result from refining.

Crude oil can range from an almost clear liquid, similar to gasoline, to a pitch, tar-like material that is viscous and must be heated before it can flow through a pipeline. Crude oil is typically designated as either sweet or sour,

and either heavy or light. Usually, sweet crude oil contains 0.5 weight percent or less total sulfur, and sour crude oil contains more than 0.5 weight percent sulfur (90). Light crude oil is defined as having an American Petroleum Institute (API) gravity greater than 25° whereas heavy crude oil has a gravity of 25° or less (14) (see Appendix C).

The purpose of refineries is to change the crude oil into fuels such as gasoline and diesel oil, lubricants such as oil and grease, and chemical feed stocks such as olefins (mainly ethylene, propylene, butadiene, etc.), and aromatics (mainly benzene, toluene, and xylene) (49). Crude oils from different sources vary considerably, and refineries are often designed to process crude from a particular source. Refineries differ widely in size, number and sophistication of the processes they employ and the variety of products they produce. More complex refineries can produce a wide range of items from fuel gas and liquefied petroleum gas (LPG) through gasoline and olefins to greases, asphalt, and coke; the simpler operations of the other may limit their output to a few items such as fuel gas, gasoline blending stocks, and heavy fuel oil (14). A list of products of the refineries together with the sector utilizing it is further illustrated in Table 5 (37).

REFINERY CLASSIFICATION

EPA categorizes the various petroleum refineries into groups based on raw waste land, product mix, refinery process, and wastewater generation characteristics. Such a classification system, which includes five divisions, is based on the components of a classification system proposed by the American Petroleum Institute (API) in the mid 1960s. The five classifications used by EPA for refining industry are given below (90). Flow diagrams of these five refinery types are shown in Figs. 2 through 6 (87).

Air quality impact is a function of the types of refineries. The following discussion focuses on types of refineries all over the world.

1. Topping .

Includes topping (distillation) and catalytic reforming besides any other processes in addition to these. This category is not applicable to facilities which include thermal processes (like coking, visbreaking, etc.) or catalytic cracking.

2. Cracking .

Includes topping and cracking in addition to other processes as specified in the diagram (Fig. 3).

3. Petrochemical.

Includes topping, cracking, and petrochemical operations besides any other processes in addition to these. This does not include lube oil manufacturing processes.

4. Lubricating oil.

Includes topping, cracking and lube oil manufacturing processes besides any other processes in addition to these, except petrochemical operations.

5. Integrated.

Includes topping, cracking, lube oil manufacturing processes and petrochemical operations besides any other processes in addition to these.

REFINERY PROCESSES

The type and number of refinery process units in a given plant depends upon the type of crude oil to be processed, product values and availability and cost of utilities and

equipment. In order to characterize air quality emissions from the various types of refineries, it is necessary to investigate in briefly those refinery processes which result in atmospheric emissions. The type and size of processing units thus varies greatly. Generally, the operation of a refinery can be divided into seven steps (73) :

1. Separation of crude oil.

The most widely used method for separating crude oil are atmospheric and vacuum distillation. Solvent extraction, absorption and crystallization are also used, but to a much smaller degree. Pretreatment of the crude oil in a desalter is typically included as a part of the separation processes.

2. Conversion of hydrocarbon molecules.

Conversion processes, which change the size or structure of the hydrocarbon molecule, convert some of crude oil fractions into higher value products. The most common conversion processes are cracking (thermal, catalytic, viscosity breaking, hydrocracking and coking), combining (alkylation and polymerization), and rearranging (catalytic reforming and isomerization).

3. Treating crude oil fractions.

Some of the original sulfur compounds are converted to hydrogen sulfide (H_2S), which can be separated and converted to elemental sulfur. Undesirable sulfur compounds are removed by treating processes such as hydrodesulfurizing and chemical treating. Other compounds removed include nitrogen, olefins, metals, asphaltenes, naphthenic acids, and phenols.

4. Blending Hydrocarbon products.

Most petroleum products are a blend of hydrocarbon fractions or components produced by various refinery processes. Motor gasoline is a blend of various gasoline blending stocks, including reformate, alkylate, straight run naphtha, thermally and catalytically creaked gasoline, and necessary additives. The vast number of fuel oils, lubricants, and asphalt products are blends of refinery stocks.

5. Auxiliary Operating Facilities.

A number of refinery units are used to maintain normal operating conditions. These units support processes such as hydrotreating, improve efficiency by al-

lowing reuse of water, and the use of sour gas as fuel and help the refinery meet environmental standards. Included among the functions of auxiliary operating facilities are hydrogen production, light ends recovery, acid gas treating, low water stripping, sulfur recovery, and tail gas treating.

6. Refinery Offsite Facilities.

Refinery offsite facilities are equipment and systems used to support refinery operations. These include storage tanks, steam generating systems, floor, and blowdown systems, circulating water systems, receiving and distribution systems, and refinery fire control systems. In addition, garages, maintenance shops, storehouses, laboratories, and recovery office buildings are considered as offsite facilities.

7. Emissions Control.

Refineries generate air emissions which must be controlled for efficient processing and environmental protection. The control of pollutants that can damage the environment is an important part of refinery operations. In this Chapter, the discussion of emission control is not presented and has been deferred to Chapter

V as it happens to be an important section; hence it deserves a more thorough attention. Previous sections have been included so that the reader has an insight into those factors or processes that govern the air pollution emissions.

The general flow of crude oil and petroleum products through a complex refinery and the processes involved are shown in Fig. 7 (87). The individual processes used in a modern complex refinery are described in the following section (73) :

Separation of Crude Oil (Distillation)

Distillation is used to separate the crude oil into various boiling range fractions or 'cuts'. The basic process involves feeding the hot crude to a vertical distillation column where the lighter (lower boiling point) fractions condense toward the top of the column and the heavier (higher boiling point) fractions condense or remain at the bottom. The current trend is towards the use of multiple atmospheric and vacuum distillation unit configurations.

Desalter. The desalter is normally the starting point of the separation process. As shown in Fig. 8 (87), the crude oil is pumped from 'tankage' preheated by heat exchanged with various product streams (fractions) and sent to the desalter.

Desalting removes inorganic salts from crude oil so that these salts will not contribute to the fouling and corrosion of process equipment. The process also removes the soluble trace metals present in the water phase which can poison downstream process catalysts. Chemicals and water are added to the crude oil, and oil/water separation occurs by gravity in the presence of a high voltage electrostatic field. This helps agglomerate the water droplets, which contain the salts and separates the water from the oil. The oil is removed from the top of the desalter vessel, and the water from the bottom. The water is then sent to the wastewater treatment plant.

Atmospheric Distillation Unit (Fractionation). Crude oil is then pumped from the desalter to a furnace where the oil is further heated and fed to the atmospheric distillation unit. All petroleum distillation processes are fundamentally the same and require the following equipment: heat exchangers; furnaces or other heaters; a fractionating tower or column; condensers and coolers; pumps and connecting lines; storage and accumulator tanks , and instrumentation. Some of the factors considered in adapting these units of equipment are boiling range of the stocks, heat stability of the stocks, and product specifications.

As shown in Fig. 8 (87), the atmospheric distillation tower separates the crude oil into fractions having specific boiling point ranges. The fractions with the lowest boiling range are recovered as overhead streams and are either fuel gas, light naphtha or gasoline. These fractions are used as reformer feedstocks, gasoline blending stocks, petrochemical feed stocks, solvents, and LPG. The intermediate boiling range fractions are gas oil, heavy naphtha, and distillates. These fractions are used to produce kerosene, diesel fuel, fuel oil, jet fuel, blending stocks, and catalytic cracker feedstocks. The high boiling point stream or atmospheric bottoms is used to produce asphalt or No.6 fuel oil, or as feed to a vacuum distillation unit for the production of lubricants.

Vacuum Distillation Unit. The charge stock for the vacuum distillation unit shown in Fig. 9 (87) consists of heated atmospheric bottoms from the crude oil distillation unit. Vacuum can be applied by using steam educators or pumps. The equipment commonly used are two-stage steam-jet educators, and surface condensers. At reduced pressure, the oil vaporizes at a lower temperature allowing the distillation to occur at a minimum temperature.

The product streams from the vacuum tower include light vacuum gas oil, heavy vacuum gas oil, and vacuum tower bot-

toms or residue. These streams can be further processed depending upon the desired products. The vacuum gas oil is then usually sent to the catalytic cracker to produce gasoline blending stocks or it may be recovered for heating fuel. The vacuum bottoms may be used as fuel oil, used for the production of asphalt and lubricants or sent to a coker for conversion to gasoline components, coke, and gas. If low sulfur fuel oil is required, the vacuum bottoms may have to be desulfurized prior to blending.

Conversion of Hydrocarbon Molecules

Conversion processes change the size or structure of the hydrocarbon molecules, converting them into higher value products. Common conversion processes are :

Cracking Processes. Cracking processes break large hydrocarbon molecules into smaller, lower boiling point molecules. During the process, some of the molecules combine (polymerize) to form larger molecules. Common products are gaseous hydrocarbons, gasoline blending stocks, gas oil, fuel oil, and coke. Sour water generated during the process is sent to the sour water stripping unit. The off-gases from the fractioning column are treated by amine scrubbing, which removes the H_2S . The H_2S is then sent to the sulfur recovery unit.

Thermal cracking. In modern refineries, thermal cracking is used mostly in two of its extreme forms namely coking and viscosity breaking.

a. Coking. Two coking processes employed extensively are delayed and fluid coking. Coking is accomplished at a high temperature and low pressure. It is an important process for upgrading heavy crude oils. In the coking unit, atmospheric bottoms or vacuum residuals are cracked to produce fuel gas, gasoline blending stocks, distillates, and petroleum coke as shown in Fig. 10 (87).

The coke charge is fed directly to the fractionator where the feed combines with the heavy recycle oil from the coke drums. The combined feed is pumped to the coke furnace where it is heated. This heating produces partial vaporization and mild cracking. The liquid/vapor mixture then enters the coke drum where the liquid undergoes further cracking until it is converted to hydrocarbon vapors and coke.

The coking unit typically has one or more pairs of coke drums. In normal operation, one drum is in service while the other is being decoked. Decoking involves cooling the coke, and then cutting it from the drum with a high pressure water drill. The coke and water drop from the drum into a pit where

the coke dewater, and the cutting water is recovered for reuse. The coke is then stored offsite.

Fluid coking is a similar thermal cracking process, producing similar products except that coking occurs in a fluid bed. This is a continuous process unlike delayed coking.

b. Viscosity breaking. Viscosity breaking is a mild form of thermal cracking that is used primarily to improve the quality of fuel oil by lowering the viscosity of temperatures from 460 to 482°C (73). This process produces small amounts of gasoline blending stocks, gas oil, and fuel oils.

Catalytic cracking. Catalytic cracking uses a catalyst at high temperatures to convert atmospheric and vacuum oils, and stocks derived from other refinery operations into fuel gases, light gases, and gasoline and distillate fuel components. This process normally takes place in the Fluid Catalytic Cracking unit (FCCU). Olefin-rich light gases are normally directed to alkylation or polymerization operations to produce high octane gasoline blending stocks. Typically, yields of gasoline boiling range products will exceed 50 to 65 volume percent of the FCCU feed (87).

A typical FCCU is shown in Fig. 11 (87). The catalyst used in the process must be regenerated to remove coke that forms on its surface during the reaction. This is done in separate regenerating vessel by passing air through the catalyst. The catalyst regeneration produces CO, SO_x, NO_x, and particulates.

Hydrocracking. Hydrocracking differs from catalytic cracking in four distinct ways:

1. Hydrogen is utilized in the process.
2. Operating pressures are substantially higher.
3. Temperatures are somewhat lower.
4. A different type of catalyst is used.

The yield of specific products will depend upon how the hydrocracking unit is operated. For example, yields of jet fuel plus diesel fuel equal to approximately 85 to 90 volume percent of feed can be achieved with concurrent production of LPG and gasoline (87). The process produces high quality gasoline and distillates and accepts a wide variety of feedstocks including naphthas, gas oils, and heavy aromatic feedstocks. Hydrogen used for this purpose is generated by

a hydrogen plant or is a by-product from the catalytic reformer. Fig. 12 (87) shows a typical Two-Stage hydrocracker unit.

Combining processes. These processes join together small hydrogen deficient molecules (olefins) that are recovered from thermal and catalytic cracking to produce more valuable gasoline blending stocks. Two processes, alkylation and polymerization are normally utilized for combining the olefins with isobutane.

Alkylation. The alkylation process combines light olefins, primarily a mixture of propylene and butylenes, with isobutane to produce a blending stock that is one of the lightest quality components of motor gasoline. The final product, alkylate, has excellent 'antiknock' (detonate) properties. It has a clear burning, high-octane number ratings, and has an excellent performance ratings. The union of the olefins and isobutane takes place in the presence of a catalyst, either hydrofluoric or sulfuric acid, under conditions selected to maximize product yield and quality. Such a process is shown in Fig 13. (87).

The unit feed, consisting of C₃ and C₄ olefins and isobutane, is mixed with recycled acid and fed to the reactor settler where the alkylation reaction takes place. The com-

bined products are sent to a fractionator where the alkylate product is separated from the unreacted fuel, catalysts that carry over, and propane and butane that was formed by the reaction. The product or alkylate may first be debutanized before being sent to storage for gasoline blending.

The hydrofluoric acid alkylation unit includes a hydrofluoric acid regenerator, which continuously purifies a small side stream of the acid. The tar like substance that is formed in the regenerator may be disposed of by incineration or neutralized with lime and handled as solid waste.

Polymerization. Polymerization combines light olefins from thermal and FCCU to form hydrocarbons of higher molecular weight. Two molecules of isobutylene (C_4H_8) may be combined to form one molecule of molecule of di-isobutylene (C_8H_{16}). This product, formed by the union of two olefin molecules, is referred to as a dimer. That formed by three such molecules is known as a trimer. Two unlike olefins may also combine resulting in a product known as a copolymer. By-product gases are used to produce a wide variety of products ranging from gasoline blending stocks to solids that can be used as plasticizers. Polymerization of a mixture of propylene and butylene to produce a blending stock for gaso-

line is the most common polymerization operation. Usually, phosphoric acid is used as a catalyst.

Rearranging Processes. Rearranging processes are those in which the molecule is changed to produce a product of different characteristics. Two such widely used processes are catalytic reforming and isomerization.

Catalytic reforming. Catalytic reforming is a process used to upgrade low octane naphthas to produce high octane blending stocks or high yields of aromatic hydrocarbons for petrochemical feedstocks (i.e. benzene). The final product will depend on reactor temperature and pressure, catalyst used and the hydrogen recycle rate. Reforming catalysts contain platinum and are readily deactivated (poisoned) by sulfur and nitrogen, so the feedstock must be pretreated prior to being charged to the reforming unit.

In the operation, as the octane number increases gasoline yield decreases. This process also yields hydrogen that is required for many of the operations employed in modern refineries. Fig. 14 (87) shows the catalytic reforming unit. The naphtha feedstock is mixed with recycled hydrogen rich gas, heated in a furnace and fed to the first reactor. The liquid product passes to a separator to remove the hydrogen-rich gas and then to a stabilizer for final separation of

light gases and product. The reformate product then goes to storage for blending into gasoline. The light gases, consisting mostly of propane and butane, are sent to the light ends recovery unit (discussed in Chapter V).

The catalyst requires regeneration, which may be accomplished by utilizing a swing reactor. Coke deposited on the catalyst surface is burned off under controlled conditions.

Isomerization. Isomerization units are employed to convert n-butane, n-pentane, n-hexane (low-octane, straight chain hydrocarbons) to high octane, branched chain isomers (isoparaffins) as shown in Fig.15 (87).

Treating Crude Oil Fractions

To produce higher yields of octane gasoline and low sulfur fuel oil, it is necessary to upgrade materials that are used directly as gasoline components or blended into fuel oil. Components such as thermal naphthas derived from thermal cracking, visbreaking and coking operations, as well as high-sulfur naphthas and distillates from crude oil distillation containing sulfur and nitrogen, require treating.

Hydrotreating (Hydrodesulfurization). Hydrotreating is a catalytic process used to remove sulfur, nitrogen, olefins, arsenic, and lead from liquid petroleum fractions. Hydrotreatment units are usually employed before processes such as catalytic reforming because the process catalysts used in reforming become inactive if the feedstock contains impurities. These units can also be used prior to catalytic cracking to reduce the sulfur emissions from the regenerator and improve product yields. It may also be used to upgrade petroleum fractions into finished products such as kerosene, diesel fuel, and fuel oils.

Generally, hydrotreatment of process streams from sour crude oil requires greater quantities of hydrogen than similar treatment of sweet crude oil fractions. As shown in Fig.16 (87), the feed is mixed with make-up hydrogen from the reformer or hydrogen manufacturing plant. The mixture is heated and fed to the catalyst reactor, where sulfur and nitrogen are converted into H_2S and ammonia (NH_3).

Product from the reactor goes to the high pressure separator where excess hydrogen is 'flashed' off and returned to the reactor. The product then passes to the low pressure separator where H_2S , NH_3 , non-condensable hydrocarbon gases, and hydrogen are removed. The gases from the low-pressure separator are sent to the gas treating system to remove H_2S .

The liquid product is then sent to the stabilizer where the remaining light material is stripped and sent to the fuel gas treating system. The sour water generated during the process is sent to the sour water stripping unit.

Chemical Sweetening. Sweetening processes remove sulfur compounds, primarily hydrogen sulfides, thiols (mercaptans) and thiopenes to improve odor, color, and oxidation stability; to lower fuel sulfur content to comply with environmental regulations; and to lower the amount of tetraethyl lead required to boost gasoline octane ratings. There are at least eleven different processes for sweetening hydrocarbons. Some processes remove the mercaptans from the hydrocarbon stream by extraction with caustic. The caustic solution often contains solubility promoters such as alkyl phenols and naphthenic acids. Extraction is generally confined to lighter mercaptans (methyl and ethyl mercaptans). Conversion process oxidize higher molecular weight mercaptans to the less odoriferous sulfides in presence of air, alkali, and a catalyst.

Fig. 17 (87) shows a typical gasoline sweetening process that employs a sodium hydroxide solution (caustic) containing a dissolved catalyst. This process is conducted at ambient temperature in the range of 32 to 38°C. Sour gasoline is fed to the extractor where it is brought into contact with recy-

bled, regenerated caustic solution. The two streams are immiscible and the mercaptans are removed through liquid-liquid (phase) extraction. Only a portion of the mercaptan is removed in the extractor and the partially sweetened gasoline flows from the top of the extractor to the sweetener where it is contacted with additional recycled caustic solution and air. The remaining mercaptan is oxidized to disulfide in the sweetener. Caustic solution is separated from the treated gasoline in the solution settler and is recycled to the sweetener.

Lube Oil Processing. Narrow boiling range fractions from the vacuum distillation of reduced crude are used for lubricating oil base stocks. These are refined to increase viscosity indices, oxidation stability, and resistance to sludge and gum formation by removing aromatics, unsaturates, naphthenes, and asphalts. Some lube oil stocks are then dewaxed and the wax deoiled. Solvent treating processes are the most effective and widely used for lube oil refining, oil refining, oil dewaxing, and wax deoiling.

Deasphalting. Deasphalting is applied primarily for the separation of asphaltic materials from heavy oil and residual fractions. This separation, called decarbonizing, recovers oil for use as a feed to catalytic cracking and hydrocracking processes and production of both lube oil stocks, and a raw

asphalt material. Deasphalting removes some sulfur and nitrogen compounds, metals, carbon residues, and paraffins from the feedstock.

Asphalt Blowing. The purpose of asphalt blowing is to oxidize those residual oils containing polycyclic aromatic rings. These heavy residual oils, called asphalt, along with asphalt from the deasphalting unit, are oxidized by blowing air or nitrogen through a batch heated mixture. The reaction is exothermic and blowing is stopped when the asphalt reaches the desired penetration specification.

Wax Manufacture. The separation process currently in wide use in production of paraffin, and occasionally of microcrystalline waxes of low oil content is similar in most respects to dewaxing used in lube oil processing.

In the most common method of wax finishing, the feedstock is dissolved in a solvent and chilled in double pipe, scraped-surface chilling equipment to a temperature required to crystallize only the deoiled wax components having the desired melting point. Wax crystals are vacuum filtered and oils in the wax cake are washed out with cold solvent. The resulting wax cake is removed and refiltered and the filtrates are recycled.

Grease Manufacture. Grease primarily consists of mixtures of soaps and lubrication oils. Sodium, calcium, aluminium, lithium, and barium soap bases are produced by saponification of fatty acids. Soaps are manufactured by saponification i.e. through the heating and mixing of fatty acids and alkali metal hydroxides. Lubricating oils, waxes, and additives are mixed with the soap base in a heated kettle and the resulting grease may be further processed to final specifications.

Blending Hydrocarbon Products

The last major step in the refinery operation is the blending of various fractions into finished products. A large volume operation is the blending of various gasoline stocks, including alkylates and other high-octane components, with 'antiknock' compounds such as tetraethyl lead, anti-rust, anti-icing, and other additives. Of particular interest is addition of tetraethyl lead to improve the octane number of motor gasoline. Problems associated with it will be discussed later in Chapter VIII.

In gasoline blending, the components or blending stocks from the process unit such as butane, alkylate, isomerization stock, reformate, catalytic gasoline, naphtha or straight-run gasoline, coker gasoline, and additives are blended to meet

gasoline specifications. The mixing of the components is normally accomplished by automated in-line blending as shown in Fig. 18 (87). Gasoline blending components are fed into a system of proportional metering pumps and control valves to the gasoline header. The metering pumps ensure that each component is fed in the proper proportion. The components are then mixed by the flow turbulence in the header and sent to a series of on-stream analyzers which continually monitor the product for octane number and vapor pressure. The monitors automatically control the metering system to ensure proper portions of each component.

Auxiliary Operating Facilities

Auxiliary operating facilities are necessary to support process units requiring hydrogen, collect, and treat gases for refinery fuels and petrochemical related operations.

Hydrogen Production Unit. Hydrogen is required for a number of refinery units such as hydrodesulfurization, hydrocracking, and isomerization. The primary source of hydrogen is the catalytic reforming process. It can also be produced by the steam reforming of available hydrocarbons such as methane, refinery fuel gases, propane, butane or desulfurized light naphtha, or by the partial oxidation of heavier hydrocarbons.

Fig. 19 (87) shows the manufacturing of hydrogen using reforming process. The feed to the unit contains traces of sulfur which are removed by activated carbon. The removal of sulfur is necessary to avoid poisoning the process catalyst.

Desulfurized naphtha and natural gas are mixed with steam passed through catalyst filled tubes in the reformers. The reformer gas containing H_2 , CO, CO_2 , and excess steam is passed through a shift converter where CO and steam are converted to hydrogen and CO_2 . The CO_2 rich gas is scrubbed

to remove practically all the CO₂, yielding 95 to 98 percent pure hydrogen (73).

In the manufacture of hydrogen by the partial oxidation process, the feed to the units is typically bottom products from the vacuum tower or heavy coker gas oil.

In the partial oxidation process, the residual oil is fed to a combustion chamber where it is partially burned in the presence of steam and oxygen. Gases leaving the combustion chamber are composed primarily of hydrogen and CO and have a temperature of 1093° to 1538°C. The gases are then quenched with water and steam and fed to a shift converter for further conversion of the CO and steam to hydrogen. The gases purified by absorption are then sent to storage or process units.

Although the offsite equipment and facilities do not enter directly into the operations of the various process units, they are critical to the operation of the refinery. These operations are discussed in Chapter V as related to air pollution control.

IV. AIR QUALITY LEGISLATIVE, REGULATORY, AND OTHER RELATED POLICIES

OVERVIEW

Federal, State, and local governments have placed stringent air quality standards on petroleum refining and processing facilities (73). Two major pieces of legislation governing air quality that were passed during the 1970s were the National Environmental Policy Act (NEPA) and Clean Air Act Amendments CAAA (73).

NATIONAL ENVIRONMENTAL POLICY ACT (NEPA)

On January 1, 1970, NEPA was signed into law (105). It was formulated to promote efforts to prevent or eliminate damage to the environment, promote the health and welfare of man, encourage a better understanding of ecological systems and natural resources, and to create a Council On Environmental Quality (CEQ).

An important element of NEPA is its action forcing provision which is the requirement that no major federal action affecting the environment may be taken by a federal agency until it has analyzed the environmental consequences of the

proposed action and possible alternatives. Section 102 (2) (c) of that Statute requires all agencies of the Federal government to prepare detailed EISs on proposals for legislation and other major Federal actions significantly affecting the quality of the environment (105).

Environmental Impact Assessment (EIA) / Environmental Impact Statements (EIS)

An EIS is a detailed statement on the effects (impacts) of proposed actions on the environment and is intended to be an information source from which decisions can be drawn. A project can have positive, negative or even no significant impacts at all. Such a statement is officially prepared by each concerned Federal or State agency under the guidance of CEQ. Only a few States as shown in Fig. 23 (88) have adopted laws or regulations similar to NEPA requiring State EIS or similar documentation.

One primary role of CEQ is to supervise the enforcement of NEPA functions and to publish broad guidelines for use by Federal agencies in developing and disseminating specific guidelines on EIS preparation (35). Detailed documentation leading to the final EIS is performed by Federal agencies. Evaluation of the EIS is conducted by Federal, State, and local agencies as well as special interest groups.

Usually, if a petroleum company is required to supply data on a project because of Federal involvement, the information is usually in the form of an environmental report called Environmental Impact Assessment (EIA). An EIA is a document reviewed by the Federal agency as basis for administrative action such as the issuance of a permit. Depending on company supplied data contained in the EIA, and upon other factors, an agency will either undertake to prepare an EIS or issue a 'negative declaration', stating that an EIS is not required. Not all Federal agency actions require an EIS. It is only prepared if some kind of impact such as that which can deteriorate air quality arises.

EIA is the applicant's report to the concerned Federal agency which describes the project and its potential impacts upon the physical, social, and economic facets of the environment. A few of the guidelines used in Guidelines For Preparation of EIS by CEQ (35) include the following:

1. A detailed description of a proposed action information and technical data needed to permit a careful assessment of environmental impact.
2. Discussion of the probable impact upon the environment including any impact on ecological systems and any direct

or indirect consequences that many result from the action (possible mitigating measures are also discussed)

3. Any adverse environmental effects that cannot be avoided.
4. Alternatives to the proposed action that might avoid some or all of the adverse environmental effects, including cost analysis and environmental impacts of the alternatives.
5. An assessment of the cumulative, long term effects of the proposed action including its relationship to the short term use of the environment versus the long term productivity of the environment.
6. An irreversible or irretrievable commitment of resources that might result from the action or which would curtail beneficial use of the environment.

Fig. 21 (86) shows inter-relationships between EIA, EIS, and Finding Of No Significant Impact (FONSI) document. The preparation of an EIS is a time consuming process. As indicated in Environmental Conservation (73), preparation of EIA for a complex refinery takes about six months followed by two months for agency review, and conversion to EIS itself takes another six additional months. Further details are also

provided in Fig. 26 (73). Early in the process, the agency either Federal or State publishes a notice of intent to prepare an EIS and invites public input to determine the scope of issues that will be addressed. A draft EIS (DEIS) is then prepared and made publicly available. Public participation after the initial EIA and throughout the preparation of DEIS is desirable for it permits contribution from those who are directly affected by a proposed project or individuals with expertise in environmental fields that may be affected by government action (13). Comments made on the draft by any party must be specifically addressed in the final EIS.

Agency action on the proposed permit or other action cannot be made before publication of the final EIS and preparation of the public record of decision, indicating the factors that lead to its final choice. If an agency fails to meet the procedural requirements of NEPA, any party may go to Federal courts and obtain an injunction preventing action until an adequate EIS has been prepared.

Since preparation of EIA/EIS consumes a lot of time, they should be properly prepared and well presented in a form that can be understood and accepted by all participants. It can insure that the debits, credits, and net value of the project are presented properly and it can make certain the alternative projects are investigated. Such information can

speed the making of decisions and help in reaching proper conclusions (59). If not, a delay can generally increase cost of the project. Although this activity has been incorporated into most of the planning processes, the delay can become critical at times and can add to the uncertainty of certain high-risk projects.

Fig. 22 (88) and Fig. 23 (88) show the basic guidelines generally followed in EIS preparation. Fig. 22 outlines the basic steps that can be followed for preparation of any general EIS whereas Fig. 23 specifically refers to the air quality aspect of EIS preparation. The discussion below outlines a summary of some of the basic steps, measurements, considerations, and approaches used in preparing EISs by two oil refineries namely the proposed but abandoned Portsmouth Refinery and PETRONAS Refinery.

Summary of EIS of Portsmouth Refinery. An EIS of the Portsmouth Refinery was prepared to assess the environmental impact (57). The refinery was proposed by the Hampton Roads Energy Company of Portsmouth, Virginia for construction in 1978. An DEIS was filed with CEQ on November 28, 1975. The proposed final EIS was released

around March, 1976 and the final EIS was submitted to CEQ on September 30, 1977. The discussion below includes various considerations and aspects of the EIS of the refinery. Only

the air quality aspects of the proposed refinery were examined.

Both the EIA and EIS were prepared for the facility. The EIS was prepared by the Norfolk District Engineer with input from the environmental assessment prepared by NUS Corporation of Rockville, Maryland under contract with Hampton Roads Energy Company. State agencies having permitting authority involved in the project were the Department of the Army, State Water Control Board (SWCB), Virginia Marine Resources Commission (VMRC), and of utmost importance, the State Air Pollution Control Board (SAPCB) of Virginia. SAPCB (Virginia) approved the permit application of the refinery on October 7, 1975.

A 623 acres site was proposed for the refinery in the city of Portsmouth along the west bank of Elizabeth river. The refinery was to process 175,000 b/d crude oil initially with the capability to expand eventually to 250,000 b/d. The feedstock of the refinery was supposed to be Middle-Eastern crude. A combined total of more than seven million gallons per day such as low sulfur (0.3 percent sulfur), gasoline, jet-fuel (A-1), fuel oil (No.2), and liquefied petroleum gas (butane and propane) were to be produced by the refinery. The purpose of building the refinery was to help offset some

of the escalating demands for low sulfur petroleum products and to cope with the energy demands of the U.S.

The site selected was lightly populated and furthermore had been zoned for industrial development for at least 20 years, as have some adjacent properties. Within a twenty mile radius of the site lie the cities of Norfolk, Virginia Beach, and Chesapeake.

The section on 'project description,' included a list of process units incorporated within the refinery such as atmospheric distillation, hydrodesulfurizer, catalytic reformer, etc. Tank dikes, storage tanks, and their foundations, too, were briefly mentioned.

A discussion on climatological and meteorological aspects were presented. The locality had fairly good records of temperature; high extremes ranging from 50°F in January to 88°F in July; low temperatures ranging from 32°F in January to 70°F in July. Fogs, hail and ice-storms, extreme winds, average wind-speed and direction persistence, and restrictive dilution conditions were indicated in the section.

Air quality information in the vicinity of the refinery was obtained from the Virginia Air Pollution Control Board's (VAPCB) air quality monitoring network and on-site informa-

tion collected by Atmospheric Research Group Of the Old Dominion University. VAPCB sampled pollutants such as TSPs, SO₂, CO, and O₃.

Data from sampling stations located in Norfolk, Chesapeake, Virginia Beach, Portsmouth, and Suffolk were reviewed for ambient air quality. The on-site monitoring program (an extremely important operation) to determine background ambient air quality was conducted by Old Dominion University's Atmospheric Research Group at the proposed refinery site. The program was conducted for a short period of time when meteorological conditions tended to disperse the pollutants. Another short-term monitoring program was also conducted at the previously considered 'Nansemond River' site for the proposed refinery. Four sites were chosen for on-site monitoring programs. High volume suspended particulate air samples were used to collect 24-hour samples daily at the four sites.

Specific measurements of SO₂ were not carried out by Old Dominion University. Instead, total sulfur was measured; therefore direct comparison with the Virginia Air Quality standard could not be made. The basis used was that if the total sulfur concentrations were less than the SO₂ ambient, air quality standards, then it follows that the SO₂ concentrations would also be less than the standards since the

total sulfur includes the reduced sulfur component as well as the oxidized sulfur component.

An 8-hour concentration of CO was measured. Monitoring of O₃, hydrocarbons, and NO₂ was also carried out. On-site monitoring results of the short-term ambient air quality surveys indicated that most pollutant concentrations were within existing standards.

Air quality modeling of dispersion of plumes (contaminants) were calculated. The purpose of the dispersion analysis was to assess the contribution of various air contaminants expected to be emitted through three stacks to the environment. Emissions concentration were calculated using computer models, assumptions, and dispersion equations. Plume rise calculations using Briggs equations, short-term dispersion analysis using Tennessee Valley Authority (TVA), coning plume conditions, too, were carried out (82). Limited layer mixing (trapping conditions) inversion break up (fumigation conditions), and Pasquill-Gifford's dispersion models were extensively applied in the study (77).

It took almost five years to carry out surface meteorological observations from the Norfolk Regional Airport (87). Computer programs were used to calculate annual aver-

age ground level concentrations employing stability wind rose data and a constant pollutant emission rate as input.

Construction emissions i.e. those attributed to earth moving activities, open burning during site clearing, increased traffic, and miscellaneous operations such as painting were also evaluated. Emissions from other point sources within the refinery were also evaluated. The total regional emissions of ambient air quality criteria pollutants from man-made sources in the region projected to 1980 were made using the 1972 emission values as the base projected accordingly to the Population Growth Factors for the region.

Trace element emission impacts of elements such as vanadium, nickel, iron, and manganese were considered as they act as sites on which SO_2 can be converted to sulfuric acid.

Hydrocarbon and oxidant impacts were investigated as they play an important role in the formation of photochemical oxidants such as O_3 and peroxyacetyl nitrate (PAN). Other emission impact areas considered were on health and odor.

Summary of EIS of PETRONAS Oil Refinery. A draft version of the EIS of the Oil Refinery submitted to Division of Environment (DOE) of Malaysia was examined (80). As with the EIS of the Portsmouth refinery, only the air quality aspects

were viewed. Approval for construction of the refinery from DOE was granted in 1981.

The refinery is located in the planned industrial complex in Kerteh in the State of Trengganu. It has a capacity of 30,000 b/d topping unit with associated side strippers, an LPG recovery unit and other facilities such as crude tank, diesel tank, heavy naphtha tank, reformate tank, gasoline tank, etc.

An attractive feature of the refinery was that it would process low sulfur content crudes (namely Pulau, Bekok, and Tapis) drilled off the platforms offshore the State of Trengganu. As a result, the finished products contain very little (negligible) sulfur content. An advantage of the refinery is that the flue gas vented the boilers and furnaces has negligible sulfur. As the crudes are sweet, they should contribute very little pollution impacts on the environment due to SOx

The refinery can be classified as a 'topping' plant (see Chapter III) designed to process three light, sweet crudes run individually or in combinations. Other processing functions of the refinery include blending reformate into gasoline imported from other refineries. Finished products of the refinery include fuel oil, diesel, kerosene, naphtha, and

LPG. Since the crude contains very little sulfur, no sulfur removal treatment is employed.

A brief discussion on the atmospheric quality covered aspects on gaseous pollutants, fuel requirements, flue gas emissions, and hydrocarbon emissions. Pollutants present in the combustion gases from process heaters and boilers include SO₂, CO₂, NO, and NO₂. Uncondensable hydrocarbons ranged from C₁ to C₄ together with small quantities of hydrogen sulfides. Uncondensable and unrecovered refinery gas is diverted and used as fuel in the heater and boilers. H₂S traces are generally burnt and released as SO_x

Fuels used for the refinery include lean gases, fuel gases, diesel, and fuel oil. Hydrocarbon emissions were viewed from three aspects namely relief valves, tankage, and oil/water separator. Since all the pressure reliefs in the refinery are routed to flare stacks via knock out vessel, no hydrocarbons are routed from the pressure relief to the atmosphere. Floating roof tanks were utilized to minimize emissions of hydrocarbon vapors to the atmosphere.

A brief review of the comparison in approaches used in preparation of each EIS are included in the discussion.

CLEAN AIR ACT AMENDMENTS (CAAA)

Although the government first assumed responsibility for controlling air quality under the Air Pollution Control Act of 1955, the basis for the nation's present approach to air quality management came from the 1970 and 1977 amendments to the CAA. These are responsible for establishing the requirement that National Ambient Air Quality Standards (NAAQS) for criteria pollutants be attained and maintained at all locations in the country.

The CAA serves the basis for regulatory promulgation by EPA in the air quality area. EPA is responsible for generating the requirements that the States follow in managing the nation's air quality. The 1977 CAA mandates that all States develop control plans referred to as State Implementation Plans (SIPs) describing enforcement strategy for meeting and maintaining NAAQS. SIPs approved by the EPA also function to bring non-attainment and attainment areas maintained to the NAAQS level (discussed in the following section). In relation to petroleum refining, each SIP is required by the law to include a construction permit program for the facility to ensure that NAAQS are achieved and maintained. Enactment and promulgation of regulations of the States can be more stringent than the Federal mandates, but not the reverse. State laws and regulations govern the operation of air pol-

lution control activities at the local level, and these laws and regulations will meet Federal requirements.

With the authority vested in States, the States carry out much of the emissions control progress with the local air pollution control agencies organized in a county, district, or other regions. The local offices insure that the Federal and State regulations for control of existing, new, and modified stationary sources are enforced in their jurisdictions.

Limits and Standards

The petroleum refineries are subjected to the regulations and standards set by either the EPA or the SAPCBs. The facilities have to ascertain they achieve the attainment status for each pollutant emitted (73). Three important categories of standards that apply to the refineries are the NAAQS, Emission standards such as New Source Performance Standards (NSPS), and National Emissions Standards for Hazardous Air Pollutants (NESHAPS) (73).

National Ambient Air Quality Standards (NAAQS). In 1971, the U.S. EPA established NAAQS for six criteria pollutants namely SO_x, TSP, CO, NO_x, O₃, and non-methane hydrocarbons. NAAQS prescribe for the designated air pollutants the average concentration levels and exposure

times that cannot be exceeded legally in the ambient air during a specified time (17).

NAAQS are classified into two different groups namely the primary and secondary standards. Primary NAAQS are promulgated to protect human health whereas the secondary NAAQS are designed to protect the public from adverse effects other than those affecting health. As shown in Table 7 (32,17), NAAQS have been set for seven pollutants, lead being added recently. The concentration level for each standard has associated with it time period over which the concentration was averaged.

The 1977 CAAA required EPA to re-examine the NAAQS by December 31, 1980, and to re-examine each NAAQS every five years thereafter. Such ongoing review of the NAAQS is an important activity relative to the nation's air pollution control program. Any change in a standard could potentially affect other CAA requirements since all stationary source requirements have been designed to provide for compliance with the standards.

New Source Performance Standards. In addition to a State's regulation as defined in their SIP's, new and modified sources are subjected to NSPS. Petroleum refineries are on industrial category covered by Federal NSPS, which are

national standards for new major industrial sources (31). Three NSPS govern the construction or the expansion of a new refinery and two exist for liquid petroleum storage vessels (31).

NSPS for petroleum refineries are applicable for units such as the FCCU catalyst regenerators (see Chapter III), fuel gas combustion devices, and for all Claus sulfur recovery plants generating more than twenty long tons (2240 lbs) of sulfur per day (31). A summary of the applicable NSPS is shown in Table 8 (31). Other NSPS include those set for petroleum liquids contained in vessels with a capacity of 40,000 gallons or more and utilizing floating roofs and vapor recovery system to control hydrocarbon emissions depending upon the true vapor pressure of the hydrocarbon stored (73).

The cost involved to abide by the NSPS can be very expensive. According to an article on NSPS sets for oil refineries, pulp mills, and lime plants (76), EPA estimated in 1978 that about 80 new petroleum sulfur recovery plants would then have been subjected to the standards in 1980. It was also expected then that a capital investment of U.S. \$100 million would be required until the projected year 1985. An estimation was also made that an operating cost of \$16 million would plummet annually.

National Emission Standards for Hazardous Air Pollutants. Volatile organic compounds (VOCs) emitted from pumps are mostly criteria pollutants i.e. regulated under NAAQS. However, one of the VOCs, benzene, has been identified as a hazardous air pollutant under Section 112 of CAA (NESHAPS) (73). Standards and steps are still being considered for regulation of such emissions (64). Others such as toluene and xylene are, too, beginning to receive attention.

Two areas namely the attainment and non-attainment areas are often considered in discussing the maintenance of the NAAQS levels. An attainment area is defined as an air quality region that meets the NAAQS whereas a non-attainment area refers to an area or a region where the NAAQS for a particular pollutant is being violated (73).

Attainment Area Preservation of air quality in less polluted regions was included into the 1977 CAAA. Prevention of Significant Deterioration (PSD) is the review process for sources in attainment areas and is required for both SO₂ and TSP (52). PSD policies function to preserve special air quality characteristics of national parks and other identified areas, and to allow moderate growth of well-controlled facilities at suitable locations in other clean areas. Such a goal is met by establishing emission control and siting requirements on all new and expanded emitting facilities in-

cluding refineries in Clean air areas. These rules can limit the size of individual plants as well as the total number of sites potentially suitable for industrial development.

As discussed in Federal Register (52) and in the Code of Federal Regulation (CFR) (30), three classes of Clean Air areas have been established and maximum increases of SO₂ and TSP concentrations have been specified for each area as follows:

1. Class I - Largely undeveloped and unpolluted where only minimal increases in pollutants are allowed.
2. Class II - Lightly polluted where slightly greater increases will be accepted.
3. Class III- Moderately polluted where pollutants are permitted to rise to the level of the NAAQS.

Table 6 (104) shows a list of limits of increments of TSP and SO₂ applicable to specific Classes of Clean Air areas as listed above. Class III areas are limited to limited to concentrations of TSP and SO₂ no greater than the NAAQS. Class III is applicable only in some States, State of Virginia being a good example of an exception where Class III designation does not occur (104).

The PSD process used for the proposed Portsmouth Refinery (82) and that of Kenai Refinery (83) illustrate how the PSD policy applies to petroleum refining. The PSD of the Portsmouth Refinery and the Kenai Refinery are examined since they happened to be among the few proposed modern refineries subjected to the 1977 CAAA.

Summary of PSD Application of Portsmouth Refinery. A PSD application permit prepared by NUS Corporation (Rockville, Maryland) for the refinery was submitted to U.S. EPA and SAPCB (Virginia) for approval. The application submitted complied with the provisions of the 1977 CAAA.

The purpose of getting the approval under the PSD was because the refinery was considered a major source of air pollutants (defined as a source that is capable of emitting 100 tons of pollutants per year before applying any control technology) (30). The locality of the refinery was classified as an attainment area for TSP, SO₂, NO₂, CO, but non-attainment for oxidants and hydrocarbons (73). The refinery was under constraints as the site was about 100 miles from the nearest Class I PSD area. Fortunately, the distance involved precluded any measurable air quality impacts on the areas associated with the proposed refinery.

The refinery was required to obtain non attainment off-sets (discussed later on) and install controls that conform with Lowest Achievable Emission Rate (LAER). It was also subjected to control technology review for TSP, SO₂, and NO₂. Allowable emissions from this refinery with Best Available Control Technology (BACT) were 706.6 tons per year for TSP, 4642.2 tons per year for SO₂, and 4081.7 tons per year for NO₂. The allowable emissions after application of BACT subjected the refinery to an air quality impact review as required by 1978 amendments to CFR (30).

There were numerous exceedness of the primary 24-hour standards for SO₂ and TSP in the region caused by low level releases (between 7-21 meters) due to two other pollutant emitting sources. Secondary 3-hour standards for SO₂ in the region, too, were exceeded.

In preparing the PSD, the air quality status of the region was studied. Attainment and non-attainment designations for various pollutants were determined. Siting of the monitoring stations for pollutants was carefully carried out using monitoring network as discussed in Chapter VI. Climatological aspects including regional data sources, topography, and other possible aspects were designated.

Since the refinery was considered as a major stationary source, studies pertinent to allowable emissions from the refinery were carried out. As the refinery was considered as a major emitting source of hydrocarbons, it was given a non-attainment status for oxidants. That subjected the refinery to non-attainment offset requirements under 1977 CAAA. Due to its refinery non-attainment status, it had to install hydrocarbon emission offsets that conform LAER to obtain hydrocarbon emission offsets within the region.

Two important sections i.e. applicable regulations on emissions standards, limitations, and allowable emissions with BACT were presented. EPA regulations on Standards of Performance for Petroleum Refiners (31) were incorporated in the control technology. An example of the new regulation applied to the refinery was the Claus Sulfur Recovery Plant Standards.

Good engineering practice stack height was also considered as required by the 1977 CAAA. The purpose was to avoid excessive concentrations of any air pollutants in the immediate vicinity of the source as a result of downwash and eddies created by the source itself, terrain, or tall structures.

Air quality modeling under PSD review was necessary as there had been two other PSD permits for two other emission sources. Meteorological considerations, topography, ocean-bay effects, data base, and mixing heights were studied.

Air quality modeling for PSD increments and air quality modeling for NAAQS compliance were emphasized and thoroughly investigated. Several dispersion models such as single source (CRSTER) model, Gaussian-Plume Multiple Source Air Quality Algorithm, and Climatological Dispersion model (CDM) were used for the analysis of the PSD increments associated with the proposed refinery.

A section on hazardous and toxic emissions, too, were included. Two important toxic gases to be released from the refinery operation were H_2S and benzene (C_6H_6). H_2S is a malodorous and highly toxic substance carried in the fuel gas stream whereas benzene is a carcinogen present in the gasoline products of the refinery.

Impact on soil, vegetation, and visibility, too, was investigated. Air quality impact especially of the possible traffic growth i.e. vessels associated with the refinery, too, was considered as part of the assessment.

Summary of PSD Application of Kenai Refinery. A PSD application permit prepared by Radian Corporation (Austin, Texas) for Tesoro Alaska Petroleum Company was submitted to U.S. EPA and Alaska Department of Environmental Conservation on April, 21, 1983 (83). PSD application was submitted because of its modification to increase refining capacity from 48,500 to 80,000 b/d involving an expansion cost between US \$90 to \$100 million. The refinery located in the southern part of Alaska on the Cook Inlet needed an expansion to handle the growing trend towards the use of Alaska North Slope (ANS) crude which is 'sour' or high in sulfur content (85). The capability was necessary because of the declines in the production of Cook Inlet crude oil and Tesoro's inability.

To process ANS crude oil, a two-phased construction program was necessary. Phase I included re-alloying the crude unit, expanding hydrocracker capacity installing storage tanks for residual and diesel fuels and Phase II included increasing hydrogen (H₂) production and replacement of Sulfur Recovery Plant. Due to these, emissions were expected to increase at the refinery. PSD review was necessary as it would then be a major source resulting in eventual increases of SO₂, NO x emissions, and was therefore subjected to Federal PSD Regulations.

Emissions increases from the proposed expansion of the existing contemporaneous equipment was compared in tons per year. Primary source of SO₂ would be the sulfur plant whereas hydrogen plant process heater was the primary source of NO x emissions.

Existing environment of the site was briefly discussed. The nearest Class I area was Tuxedni Wilderness area which was approximately 58.5 miles south west of the refinery.

Tesoro Refinery is located in an area designated PSD Class II attainment area. Monitoring by Radian Corporation took almost a year. Ambient pollutant levels in the area were found to be well within the limits. Climatic conditions and other related factors were considered in preparation of the permit.

Since the plant expansion was expected to have controlled emissions of SO₂ and NO x in excess of 40 tons per year, Best Available Controlled Technology (BACT) as specified by the 1977 CAAA was used to control the SO₂ emissions.

Assessments such as Environmental Impact , Energy Impact, reliability of control technology, too, were investigated. No impacts were prevalent as estimated air quality

impacts from control systems were estimated to be well below all applicable standards and increments.

Air quality impact analysis was performed to evaluate the impact of the proposed modification on ambient air quality. Stacks were examined to insure that they were of sufficient height to avoid emitting pollutants into the wakes of nearby buildings. A dispersion modeling analysis of the proposed sources was performed and the results were combined with monitored air quality levels to estimate total impacts on the applicable air quality standards. Included in the investigation were aspects such as stack height analysis, impacts on NAAQS, PSD increments, use of modeling, and meteorology, and emissions from sources other than the proposed modified refinery.

Various other assessments pertaining to general welfare carried out were such as the impacts on visibility due to emissions, impacts on soils, vegetation, and impact of associated growth (e.g. residential, industrial, and commercial expansions).

Non-attainment

CAA of 1977 also established specific provisions to permit limited industrial growth in areas of the county des-

ignated as non-attainment in order to foster improvement in air quality (73). A non-attainment area might be non-attainment in one pollutant, but can be attainment in another (43).

Under the CAA, States were required to revise their SIPs by January 1, 1979 to include detailed strategies for bringing non-attainment areas into compliance by December 31, 1982 (attainment date was extended to 1987 in a few cases). EPA has also been authorized by the act to impose 'no-growth' sanctions in areas of States for which there is no approved SIP. At present, EPA has strong impositions on the construction of major new or modified facilities including petroleum refineries.

REGULATORY CONTROL STRATEGIES

Control technology as defined by 1977 CAAA aimed at reducing emissions from existing, new or modified sources. A definition list of various sources include (43):

1. A new source is one which is contracted and installed at a facility after the date emission standards are proposed for that industry.

2. Existing source refers to an air pollution source which was constructed before the proposed date of the emission standards.

3. Modified source (e.g. expansion of a refinery) refers to any physical change in operation of an existing facility which increases the amount of an air pollutant emitted, or results in the emission of an air pollutant not previously emitted into the atmosphere to which a standard applies.

Control technologies include Reasonably Available Control Technology (RACT), Best Available Control Technology (BACT), and the Lowest Achievable Emission Rate (LAER). These classes describing technological methods to reduce pollution can also be applied to petroleum refineries. A few examples of the technologies include Shell Claus Off-Gas Treating (SCOT), Beavon-Stretford processes as BACT, and vapor recovery systems from storage tanks as LAER. These control methods will further be dealt in Chapter V. The use of such control technology to a certain degree also depends on its location (11).

Existing sources in non-attainment areas are subjected to RACT. RACT emission limits are designated in SIP and can apply to sources located in attainment areas, but are gener-

ally required only in non-attainment areas. RACT considers both the cost and technology available for emission control. This control is usually less stringent than both BACT or LAER (11). This is because there are more existing sources and the cost of applying BACT or LAER to all of the sources would not be cost effective.

New sources are subjected to a number of control technologies depending on where the source is located. A new source installed in an attainment area is subjected to NSPS, BACT, and a PSD review. But, if a new source is installed in a non-attainment area, it is subjected to NSPS, LAER, and offset emission reduction (11). BACT considers cost, energy use, emission reduction achieved, and several other factors. LAER is the most stringent emission limitation contained in the SIP of any State or the most stringent emission achieved in practice by that source. It is generally considered as technology forcing involving the transfer of technology from one source category to another (43). However, from a practical viewpoint, the cost of LAER must not be so high as to cause the industry to be economically uncompetitive. In addition, all new sources are sources are also controlled by NSPS.

BACT and LAER emission limitations cannot be less stringent than the NSPS limitations for any new or modified source if NSPS source categories have been promulgated.

ALTERNATIVE CONTROL POLICIES IN EMISSION REDUCTIONS

U.S. EPA has taken great steps to enhance the air quality management and limitations since CAAA was passed in 1970. This has been achieved by developing a number of innovative and administrative procedures for stationary emissions. Moves were also made around July 1979 when alternative control strategies such as emission reductions were established. Such reforms function to reduce the overall cost of pollution control (47).

Vested within the framework of emission reduction policies are strategies such as emissions trading programs which further involve policies, offset policies, netting, and emissions banking.

The emissions trading program was one of the first major regulatory reform efforts passed by the EPA under the present Reagan Administration. It consists of a set of guidelines for the States to develop Federally approved transactions in discharge permits called Emissions Reduction Credit (ERC) (47). Such a policy is believed to provide a

much more cost effective set of implementation incentives in comparison to a 'command and control' regulatory system (18). Some of the terms associated with emissions trading are defined as below:

1. Emissions banking - Storing of ERC for future use within the industry or for sale or trade to another (47).
2. Bubble policy - A concept placing an imaginary bubble over a facility and developing a cost-effective plan under which total emissions from a point at the top of the bubble are at least as low as the emissions under conventional regulations. It allows provisions for reduction in discharge at another point source within the same activity (70).
3. Marketable discharge permit system - An environmental quality management strategy based on the determination of a total permissible discharge limitation (pollution budget) for a region and the sale of rights to discharge units of permissible discharge by activities within the region.
4. Netting - A set of administrative procedures that allow an existing source which increases discharges through modification to apply the bubble concept in order to

avoid new source review, BACT determination, or construction ban. It is allowed in non-attainment and PSD air quality management regions.

5. Offset procedures - New or modified sources expand in non-attainment or PSD regions through inter-firm trading of discharge reductions.

Emissions trading is a consolidation of the administrative procedures to the components listed above. The transactional mechanism that draws these programs into a common framework is called the Emissions Reduction Credit (ERC). ERC is the legal entity to satisfy legal requirements for discharge permits by existing, modified, and new point activities (17). It is also credited in excess of the legal requirements for existing sources specified in SIP or by technological performance such as RACT.

Fig. 24 (47) shows an overview of the process by which emissions reduction becomes amenable to banking and trading whereas Fig. 25 (47) illustrates the conversion of ERCs back into allowable emissions. ERCs can be used by converting back into physical pollution units through the permit system. Both of the figures show an important relationship existing between the emissions reduction and ERCs and their uses.

An important advantage of the emissions trading system is that it is an important step towards more flexible and efficient air quality management. For example, as discussed earlier, permitting of a new facility in a non-attainment area requires offsets of emissions reduction from other sources in the area. The proposed Portsmouth Refinery supposed to be built in a non-attainment area for hydrocarbon was granted approval for construction by providing hydrocarbon offsets changing the materials used for paving the roads. The asphaltic material used previously caused the evaporation of hydrocarbons in large quantities. Therefore, emissions reduction as an offset was applied by using different paving materials (73). Furthermore, it places greater regulatory emphasis on the activity level than under the command and control system which prescribes emissions requirements on a point source basis. This is of an advantage to the refineries as they have several emission emitting sources.

Since legislative, regulatory, and permits of various kinds were focused in the Chapter, it would be interesting to know the approximate time involved in obtaining permits pertinent to air quality in refineries.

CONSTRUCTION AND PERMIT TIMING

Fig. 26 (73) shows a flowchart for obtaining the major permits for a new refinery in an area classified as attainment for air quality standards . Permit timing shown refers specifically to the permits obtained in relation to air quality management. As shown, the flow-chart timing is self explanatory as the various sections have been covered earlier in Chapter.

Getting approvals of permits relevant to air quality itself takes about four years. On the whole, the construction of a large, new refinery takes about five years from the time engineering considerations are made. Normally, if selected site does not pose any critical environmental or social problems and the project receives support from State government and local community, all permits could be expected in two to four years.

V. EMISSIONS, AIR POLLUTION CONTROL, AND MANAGEMENT GUIDELINES

CHARACTERISTICS OF EMISSIONS

Although the U.S. has a fairly large number of refineries (as illustrated in Chapter III), the atmospheric emissions from the refineries to an extent have contributed a fair amount of impact to the environment (73). Petroleum industry operations emissions have been estimated to contribute almost five percent of the total atmospheric emissions from all anthropogenic sources (6). The breakdown of the emissions as reported by the National Petroleum Council (73) in 1981 was 0.9 percent of CO emissions, 3.9 percent of HC which was mainly in the form of Volatile organic compounds (VOCs). On the whole, the emission statistics are relatively low compared to other pollution emitting sources such as commercial, residential, and transportation sectors as shown in Fig. 27 (73). Yet, the refining industry receives a great deal of regulatory constraints from regulatory and other related agencies such as the EPA, SAPCB, and other public opinion bodies.

The major types of pollutants emitted or associated with refineries can be categorized into 4 major categories as

listed in Table 9 (6). They are namely the oxides of sulfur, nitrogen, and carbon, hydrocarbons, particulates, and malodorous materials.

Table 9 further shows the various sources (including refinery processes and the equipment) that tend to produce the air pollutants. Hydrocarbon emissions (mainly in the form of VOCs) are generally considered as the largest type of emissions emitted from refineries. This is followed by CO, SOx, NOx, TSP, and malodorous materials in a descending scale. This is further illustrated in Table 10 (73) which indicates the magnitude of the emissions from refineries in 1970 and 1979. Hydrocarbon emissions in the form of VOCs constituted the largest fraction of the total emissions, approximately 33 percent of the total in 1979. A reduction in emissions over the years could possibly be due to the use of sophisticated and innovative technology such as BACT in combating pollution.

Although the crude oil runs increased from 35 percent during the period from 10,870 Mn b/d in 1970 to 14,648 Mn b/d in 1979, some substantial reductions were made in emissions per barrel of crude oil run as shown in Table 10(73). The reductions per barrel were were 50 percent for TSP, 19 percent for SOx, 18 percent for NOx, and 68 percent for CO (73).

STATES OF EMISSIONS

Before discussing the various control technologies applied in air pollution control in refineries, it is necessary to have an insight of the various states of emissions as the methods employed to control refinery depend on their various states of occurrences. The states are briefly defined as follows (9)

1. Gases are fluids above their boiling points and they have neither shape nor volume, and tend to expand indefinitely (for e.g. methane, nitrous oxide, and carbon monoxide).
2. Vapors are fluids that exist like gases in the atmosphere, but at temperatures below their boiling points (for e.g. mercaptans, and phenolic compounds).
3. Aerosols are suspensions of finely divided solid or liquid particles in air or gas, such as smoke, fumes, and mists.
4. Smoke is a product of incomplete combustion of hydrocarbons and particle size ranges from 0.001 to 1.0 micrometer in diameter.

5. Fumes consist of solid particles, less than 1 micrometer in diameter commonly formed by the condensation of vapors of solid matter after volatilization from molten state. Fumes can be generated by chemical reaction such as distillation that can create airborne particles.

6. Mists and Fogs consist of particles formed by condensation of vapors. In mists, particle size ranges from 40 to 500 micrometers. In fogs, the particles are less than 40 micrometers in diameter.

7. Dusts consist of solid particles blown into the air by wind, released by other natural forces, or generated by mechanical processes such as demolition or the crushing, grinding, and conveying of solids. Difference between dusts and aerosols is that dusts are much coarser in texture.

ESTIMATING WITH EMISSION FACTORS

Emissions from refinery unit processes are determined by the type of fuel burned and the EPA emission factors (91). Emission factors define the amount of pollutants that would be generated for a specific amount of fuel used. Several emission factors are available for estimating emissions of hydrocarbons, nitrogen oxides, carbon monoxide, aldehydes, cyanides, ammonia, and particulates (6). Such factors are carefully applied to refineries as the emissions vary tremendously depending upon the maintenance standards of the equipment of the refineries. Table 11 (41) illustrates a few of the emission factors used for estimating emissions from petroleum refineries. Included within the table is a description on the various processes occurring in the refinery together with the dimensions of the emission factors. It is important to note that emission factors differ for the same pollutant emitted from two sources. For example, as shown in Table 11, 840 lbs of particulates would be emitted from boilers and process heaters if 1000 barrels of oil are burned whereas only 61 lbs of particulates would be released from FCCU if similar amounts of feed is used. Using proper precautions, estimates from emission factors can be made as below (6):

1. Although there are many sources of emission with a wide variety of control methods in a refinery, reliable factors using proper account of variables have been developed for calculating the emissions for the major sources of pollution.
2. Estimates of emissions of certain hydrocarbons, ammonia, aldehyde, hydrogen sulphide, etc. are necessary as they are the main causes of complaints of refinery odors. Although the quantities emitted are extremely small, yet adverse public reaction to the odors often occurs.
3. Emissions of oxides of sulfurs can be estimated from the sulfur contents of the fuels burned for process operation, regeneration of spent catalysts or incineration of waste gases.

SITING REFINERY

The siting of a refinery takes into consideration the type and quantity of pollutants emitted and their effects on the surrounding environment and community.

Important factors that strongly have an effect on air quality of an area include terrain of the site, air pollutants that will be emitted, and local climatological and

meteorological conditions such as precipitation, temperature, humidity, wind direction, fog occurrences, etc.(94). For example, where conventional cooling towers for recirculating water are planned the drift from such towers can contribute to increased fog adversely impacting nearby areas relying on visibility (i.e. airports, highways, etc.). Also, local meteorology can affect dispersion of pollutants causing unhealthy or annoying levels of pollutants present in the area. Important steps considered while siting a refinery include:

1. The transportation and the diffusion of the pollutants and resulting ground level concentrations of various locations.
2. Environmental and health effects of varying concentrations of the pollutants.
3. The results of increased pollution due to other sources emitting pollutants in the vicinity.
4. Presence of odorous compounds or other pollutants that will either cause annoyance or degrade the aesthetics of the atmosphere. (e.g. fog or smog)

A basic goal in designing a refinery is to minimize or eliminate the emission of pollutants to the atmosphere. The methods necessary to implement this goal are based on types of crude oil processed, the types of products, availability of water and fuel supplies, and most important the decrease in pollution emissions required. In addition, the processes and equipment used in the facility should be designed to maximize the recovery of materials for reuse or recycling. The section below covers a broad aspect of the control technology utilized to reduce or eliminate different types of pollutants.

AIR POLLUTION CONTROL TECHNOLOGY

The amount and type of emissions from a refinery depends upon many factors, such as type of crude oil feed stocks, chemical processes, equipment utilized, air pollution control measures applied, maintenance practices, and finally the age and the category (see classification of refineries discussed in Chapter III) of refinery.

This section as the subtitle suggests deals with the major air pollution control processes in a refinery and the related control methods often employed in a modern refinery. It is basically viewed from two aspects namely the major equipment utilized and emission sources and control methods

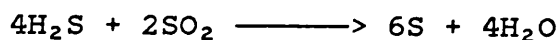
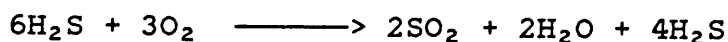
employed. It is actually a follow up of the section on refinery processes discussed in Chapter III. The reason for including it here is mainly because it deserves a great deal of attention as the final emissions emitted into the atmosphere are greatly dependant upon the control equipment and technology utilized. Important sources of information for the following section include Environmental Management of Refineries and Terminals (87), Environmental Conservation (73), and API Manual on Disposal of Refinery Atmospheric Wastes (6). Those sources had the most updated information on the control technology utilized in modern refineries.

Major Equipment

The following are major refinery processes used either partially or totally for control of major air pollutants which include sulfur and hydrocarbons.

Sulfur Recovery Unit. The most widely used recovery system is the Claus Process which uses both thermal and catalytic conversion reactions (87). The feed used in the plant includes the concentrated gas streams from the recovery unit and sour water strippers located in the waste treatment section.

In the process as shown in Fig.28 (87), H₂S is converted to elemental sulfur in two steps. In the first step (i.e. Thermal), one-third of the H₂S in the feed is burned to SO₂ at about 980°C in a sulfur boiler recovering about 80 percent of the overall heat of reaction in the form of steam. The resulting mixture which is four parts of H₂S to two parts of SO₂ forms sulfur as shown by the reaction below:



Usually a series of two to four catalytic converters with beds of bauxite or alumina at 190-260°C are utilized. Shift conversion reactors as shown in Fig.28 allows more efficient sulfur removal with much lower operating temperatures. The sulfur that condenses is removed from the boilers and the convertors. Conversion efficiency increases 92 percent, 92 to 95 percent, and 96 to 97 percent using two, three, and four catalytic stages respectively.

The unconverted H₂S leaves the process in a tail gas stream and is either further processed or incinerated to remove the last traces of reduced sulfur compounds. Sulfur

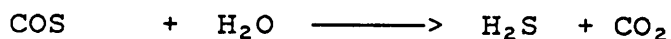
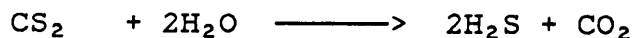
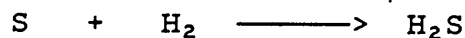
recovered by the process is usually sold as a refinery by-product.

Claus Tail Gas Treating Unit. The compositions of typical Claus tail gases fall in the ranges shown in Table 12 (73). If all the sulfur compounds are converted to SO_2 by incineration, the tail gas will contain up to 15,000 parts per million (ppm) of SO_2 . Such a quantity is not usually acceptable, and because of this a number of proprietary processes have been developed to limit the sulfur content of the Claus Tail Gas to acceptable levels.

Processes used to treat tail gas from Claus Sulfur Recovery Unit consist of reduction and oxidation processes. Both types have been successfully used in refinery operations; the choice depending upon the tail gas composition and process economics. Reduction processes convert sulfur compounds to H_2S whereas in the oxidation process, the sulfur recovery tail gas is incinerated to convert all sulfur compounds to SO_2 . The hot flue gases produced are then sent to an absorber where the SO_2 is absorbed with a solution of sodium sulfite. The clean gas contains very slight concentrations of sulfur compounds and can be released to the atmosphere. Examples of the reduction process include the Beavon-Stretford shown in Fig. 29 (87) and the SCOT Process as illustrated Fig. 30 (87). Oxidation processes include

the Wellman-Lord process illustrated in Fig 31 (87). A fourth tail-gas treatment unit is the Cold Bed Absorption (CBA) process shown in Fig. 32 (87) where sulfur is reduced and then absorbed on a catalyst.

Beavon-Stretford process. It employs a reactor containing cobalt molybdate to convert the sulfur compounds in the Claus tail gas to H₂S. Sulfur, SO₂, and mercaptans are hydrogenated by hydrogen in the feed which is supplied by the water/gas reaction with feed carbon disulfide (CS₂) and carbonyl sulfide (COS) are hydrolyzed by water in the feed to residuals of about 25 ppm each. Reactions included are:



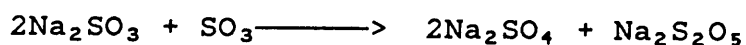
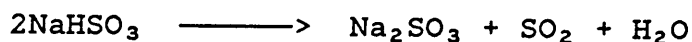
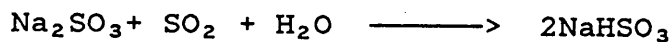
A tail gas containing less than 200 ppm of sulfur compounds is yielded after incineration. An advantage of the process is that it is not sensitive to CO₂ in the feed.

SCOT process. This process reduces the tail gas to H₂S by hydrogenation over a cobalt/molybdenum catalyst at about 299°C. The H₂S is cooled, absorbed in a alkanolamine solution, usually mono or di-ethanolamine or diisopropanolamine, which is regenerated by reboilin released is returned to the Claus unit feed.

It is typical for the absorber tail gas to contain between 200 to 500 ppm of H₂S before being incinerated and released. No conversion of the H₂S to elemental sulfur occurs in the process. Since the absorbing solution tends to absorb between 20 to 30 percent of CO₂ in the Claus tail gas, a build up of CO₂ occur if the initial concentration exceeds 20 percent.

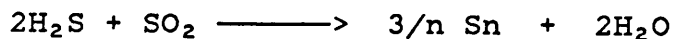
Wellman-lord process. It incinerates the tail gas and absorbs the SO₂ sodium sulfite (Na₂SO₃) to form sodium hydrosulfite (NaHSO₃). The absorbing solution is regenerated in an evaporator-crystallizer, which returns the freed SO₂ to the Claus plant.

Reactions are:



A purge stream is required to control the concentration of sodium sulfate. This process can yield a tail gas containing less than 200 ppm of SO_2 .

Cold bed absorption. The process provides a final catalytic convertor at low temperature to shift reaction equilibrium to increase conversion by the Claus reaction:



The CBA process generally involves the treatment of the tail gas from the Claus process to convert additional H_2S and SO_2 to sulfur. The oxidation process produces elemental sulfur which gets adsorbed onto the catalyst. The upper portion of Fig.32 (87) shows the conventional Claus plant whereas the

lower portion shows a simplified diagram of the CBA process equipment.

The overall conversion for the Claus plus CBA process increases up to 98.0-99.3 percent. As shown in Fig.32, the tail gas from the CBA convertor goes directly to the incinerator. Therefore, the pressure drop added to the Claus train for a CBA unit is only that required for one additional convertor and additional piping.

The catalyst is periodically regenerated to remove adsorbed sulfur and to insure continued activity.

Flare and Blowdown Systems. Pressure and flare systems are used to control discharges of vapors and liquid from over pressure line, furnace blowdowns, and blowdowns from process units during start-ups, shut-downs, or emergencies. Although some pressure relief and safety valves discharge to the atmosphere, environmental and safety considerations generally require the use of a closed loop blow down system. A typical refinery flare system is shown in Fig.33 (87)

Blow down system consists of a gathering system for all discharges, a knockout drum to separate vapors and liquids and a flare to insure combustion of vapors vented to the atmosphere. Liquid collecting in the blow down drum is pumped

away to an oil recovery system. This system prevents the uncontrolled discharge of hydrocarbons into the wastewater treatment system, the release of hydrocarbons to the air, and the loss of valuable petroleum materials.

Flares are commonly equipped with pilots and ignition systems to insure continuous combustion of hydrocarbons. Steam is usually injected into the combustion zone to further promote combustion in order to reduce or eliminate smoke from forming. Most flares are designed as vertical stacks with the flare tip 6-90 meters (20 to 300 feet) above the ground. Flare heights are determined by considering factors such as heat liberation, combustion product dispersion, and noise. Another commonly used flare is the ground flare which utilizes a series of burners at ground level. The burners are designed to induce large quantities of air into the combustion zone to eliminate smoking.

Emission Sources and Controls

Table 9 (6), as indicated earlier shows the major types of air pollutants together with their sources associated with refining. Methods of controlling the emissions of pollutants such as hydrocarbons, carbon monoxide, sulfur oxides, nitrogen oxides, total suspended particulates, odors, and hazardous compounds are discussed. A summary of the sources

together with some design parameters for air quality control is provided in Table 17 (6, 87).

Sources and Control of Hydrocarbons. Hydrocarbon emissions usually in the form of VOCs are potentially the largest type of emission from a refinery and considerable attention is given to reduce the emissions (87). The potential sources of hydrocarbon emission in a refinery include fixed roof storage tanks, loading operations, oil/water separators, relief valves, blow down stacks, asphalt oxidizing pumps and compressors, vacuum distillation vents, sewers, cooling towers, furnaces, and sampling.

Storage tanks. A major source of hydrocarbon emissions to the atmosphere from a refinery is the evaporation loss from tankage. Another similar method employed in storing is using fixed roof tanks, which are used mainly for temporary storage purposes e.g. at the producing oil field and low volatility stocks. A vapor space existing in a fixed roof tank tends to become saturated with hydrocarbons. The tank subsequently loses the vapors to the atmosphere primarily due to breathing loss (due to thermal action and daily expansion and contraction) and filling or withdrawal loss. Usually to minimize the hydrocarbon emissions with the fixed roof tanks, scrubbed flue gases are supplied to the vapor spaces above the crude oil. The flue gases containing some hydrocarbons

are then sent to an incinerator as these gases are expelled from the tank by incoming crude.

In either of the fixed roof or floating roof, a few important factors affecting evaporation losses include true vapor pressure, temperature changes in the tank, tank outage (height of the vapor space), tank diameter, schedules of filling and emptying, mechanical conditions of tank and seals, type of tank and paint applied to outer surfaces, type of tank seal, fugitive emissions due to vapor and/or liquid leaks, and wind speed.

The purpose of installing a floating roof or using a fixed roof tank is to reduce storage tank losses (73). Besides these, vapor recovery systems having interconnection with the vapor spaces of cone roof tanks are also used. The individual tank is usually repressurized with natural gas or nitrogen and is operated at a slight pressure. Unfortunately, the system has been limited by safety and corrosion considerations which present a maintenance problem. Safety is an important factor, particularly in areas of frequent electrical storms.

Variable vapor space tanks are equipped with expandable vapor reservoirs to limit vapor volume fluctuations due to temperature, barometric, and pumping-induced changes. A

variable vapor space tank normally is connected to the vapor spaces of more than one tank, usually fixed-roof tanks. Two most common variable space tanks are lifted roof tanks and flexible diaphragm tanks. Lifted roof tanks have a telescoping, sealed roof that fits around the outside of and over the main tank wall. Local natural gas supplies are frequently held in simple tanks called gasholders.

Pressure tanks designed to withstand relatively large pressure variations without vapor loss are generally used to store highly volatile refinery products. These tanks are usually spherical or cylindrical in shape and can withstand pressures up to 19 kg/cm² (265 psia).

Flares. An avoidable emissions of hydrocarbon and other combustible gases are destroyed or eliminated by using special burners called refinery flares. Such gases are burnt to prevent deleterious effects on people, animals, and plants. Furthermore, it is done to comply with the Federal, State, and local regulations.

The refinery flare must be capable of handling voluminous releases of hydrocarbons that exceed the capacity of the system for control and recovery. Such releases occur in emergencies resulting from the failure of equipment or from fires.

Primary gravity sedimentation devices. The primary gravity sedimentation device employed to separate oil from wastewater is normally an API separator. In the process of sedimentation, oil contained in the wastewater rises to the top of the separator and, if the area is uncovered, evaporation occurs, and hydrocarbon vapors are emitted.

There are two basic methods of emission control. The first involves design modifications towards suitable maintenance of the wastewater collection system upstream of the separator to reduce the total amount of oil. The second method involves covering the separator, utilizing either a fixed or a floating cover.

Leakage. The principal control of equipment leakage from valves, flanges, vessel drains, and pump drips is a periodic inspection and maintenance program.

Furnaces. In a survey carried out, the National Petroleum Council (73) revealed that burner emissions were insignificant and were all in concentrations less than 100 ppm, including samples taken from the first few seconds of operation. The studies also concluded that under more normal burning conditions, the concentration of hydrocarbons, aldehydes, and organic acids in the gaseous emissions products does not usually exceed 20 ppm when burning e.g. No.6

fuel oil. Such emissions cannot be measured by quantitative techniques available at present.

As the hydrocarbon emissions from furnaces are very low, the only method of control would be by making sure that the burners are well maintained.

Cooling towers. Cooling towers are used in refineries to cool water so that the water may be used and reused for heat transfer purposes, e.g. cooling condensation of petroleum products. Newer refineries, especially where favorable atmospheric conditions exist, tend more to air cooling, but water cooling is still required under certain conditions.

Hydrocarbon emissions occur only as a result of the contamination of the cooling water. If the cooling water is oil contaminated, no practical method of hydrocarbon emission control is available. Therefore, efforts are directed to inspection and detection of leaks and maintenance as and when required.

Pressure relief valves. Pressure relief systems are required to protect refinery process equipment against excessive pressures caused by fires, accidents, and process upsets. They consist of pressure relief valves for gases. These valves can be spring loaded, pilot operated, or weight

loaded, but all are designed to open at a pressure set to protect the vessel and to close when relief is obtained. Control of these emissions maybe obtained by minimizing leakage or by using closed relief systems.

Vacuum distillation. Heavy oils boiling at temperatures up to about 566°C are distilled from crude oil residues under reduced pressure in vacuum towers. The very low pressure is maintained by steam-actuated vacuum jets followed by surface condensers.

Some cracking occurs during distillation producing non-condensable decomposition products. Emission rates depend upon the feedstock and operating conditions. As they often have fuel odors, these gases are usually burned in one of the unit furnaces.

Air-blowing (Asphalt Oxidizing). Air blowing of petroleum products is confined largely to the manufacture of asphalt although air is occasionally blown through heavier petroleum products for the purpose of removing moisture. Exhaust air from the process usually contains hydrocarbons and aerosols.

Asphalts are generally used for roofing purposes and in producing high quality asphalts, the crude oils vacuum still

asphaltic resids must be further refined to the desired consistency, which is accomplished by air blowing (usually nitrogen gas is used) at elevated temperatures, usually from 177 to 260°C. It removes any residual gas and polymerizes the asphalt.

Hydrocarbon and aerosols emitted from the air blowing processes are usually reduced by vapor scrubbing, vapor incineration, or by using a combination of both.

Catalyst regeneration. Fixed beds of catalysts are used in catalytic reforming, hydrocracking, and resulfurizing. In these processes, regeneration is relatively infrequent and the beds are purged of light hydrocarbons to a closed system before burning. Thus, emissions to the atmosphere are usually negligible.

Moving beds of catalysts are used in cracking by both the Fluid Catalytic Cracking Unit (FCCU) and Thermoform Catalytic cracking units (TCCU). In both types, the spent catalyst is removed continuously from the reactor, burned in a separate regenerator, and returned to the reactor with the fresh feed. While the concentration of unburned hydrocarbons in the waste gases are low, the quantities of waste gases are very large. CO waste heat boilers are commonly used to control hydrocarbon and CO emissions while recovering waste

heat. Hot regeneration operation is also commonly used to control CO emissions.

Pumps and compressors. Commonly used refinery pumps are centrifugal and reciprocating or positive displacement pumps. Leakage losses occur on these pumps where the driving shaft passes through the pump casing. These emissions include both the non-volatile and volatile products. In refinery applications, the pump shaft leakage is usually controlled with either a packed seal or a mechanical seal.

Further reductions in emissions from pumps and compressors are achieved by dual mechanical seals, secondary liquid seals or by using conventional vapor recovery systems.

Sources and Control of Carbon monoxide. Carbon monoxide originals originate primarily as a result of incomplete combustion . Major refinery sources of CO are Fluidized Catalytic Cracks (FCC) regenerator, steam boilers, process heaters, compressor engines, and gas turbines (87). Controls can be accomplished either by proper design and operation of equipment, or by providing a separate means for completing the conversion of carbon monoxide to carbon dioxide.

The best demonstrated controlled technology used for carbon monoxide in FCC regenerator is the carbon monoxide

incinerator-waste heat boiler. An alternative to the CO boiler is the use of new fluid catalytic crackers that use improved catalysts and high regeneration to limit CO generation. The catalyst is regenerated at a high temperature over 730°C or 620°C (with a promoter) and the CO is burned in the regenerator instead of being emitted to the atmosphere (73).

CO emissions from the process heaters and boilers are minimized by monitoring the combustion parameters, especially oxygen, to induce good combustion. The CO emissions from gas turbines and compressor engines are also minimized by the same techniques used for process heaters.

Sources and Control of Sulfur Oxides. Sulfur dioxide (SO₂) is one of the most common air pollutants often produced when a sulfur containing fuel is burned. Major sources of SO₂ emissions in a refinery are the boilers, process heaters, catalytic cracker units, treating units, H₂S flares, and coking operations. Table 13 (6) shows a list of potential sources of refinery emissions of sulfur compounds. In any specific refinery, the sources that must be controlled will vary with the sulfur content of the crude oil, the allowable sulfur content of the product and the refining processes employed (6).

Gases containing H_2S are usually first sent to an amine unit which recovers most of the H_2S from the gases. The H_2S gases are then sent to Sulfur Recovery Unit, substantially reducing the H_2S/SO_2 emissions to the atmosphere. Unfortunately, mercaptans and organic sulfides remain in the products.

The major source of emissions in refinery fuel combustion can be controlled either by restricting the sulfur level in the fuel or by scrubbing the stack gases prior to discharge into the atmosphere. Sulfur levels can be reduced first by using hydrodesulfurization process. Hydrodesulfurization is a catalytic process whereby a crude oil fraction is passed with hydrogen over a catalyst bed at elevated temperatures and pressures. The basic chemical concept of the process is to convert the organic sulfur in the feed stock to hydrogen sulfide. Hydrodesulfurization process is often referred to as hydrogenation process (93).

The process is next followed by sulfur recovery processes. Since installing stack gas scrubbing to control SO_x involves a heavy capital investment, it is sparingly used.

Sulfur dioxide emissions from FCC regeneration unit are generally controlled by desulfurizing the hydrocarbon feed to the unit or by scrubbing the regenerator stack gas prior

to discharge. Desulfurizing is often employed as its relatively much cheaper, but if a high degree of feed desulfurization is required to meet a stringent emission limit, then the feed desulfurization in combination with a sulfur oxide control catalyst or scrubbers are used.

Emissions from the Sulfur Recovery Unit, for example, the Claus unit are controlled both by increasing the level of sulfur recovery or by stock gas scrubbing. Besides these, as mentioned in the major equipment section of the chapter, alternative method such as tail-gas treatment method is often used.

Other less significant emissions that normally accompany SO_2 are some sulfur trioxide (SO_3), sulfuric acid, and other inorganic sulfur oxides (1). These are believed to increase with excess air in combustion process. Flue gas desulfurization (FGD) and electrostatic precipitation used to control such emissions. Unfortunately as stated in Manual on Acidic and Total Primary Sulfates (1), both of the methods are not that efficient in controlling acids and sulfates of sulfur compounds.

Sources and Control of Nitrogen Oxides. The major sources of NO_x emissions are combustion processes including

process heaters, boilers, compressor engines, and catalyst regenerators.

Oxides of nitrogen formed in combustion processes are usually due either to thermal fixation of atmospheric nitrogen in the combustion air, leading to 'thermal NOx' or to the chemically bound nitrogen in the fuel, leading to 'fuel NOx'.

The fixation of a small fraction of the molecular nitrogen in the combustion air results in the formation of thermal NOx. The main factors in thermal NO and NO₂ formation are flame temperature and length of time. The combustion gases are maintained at high temperature, combustion pressure, and the amount of excess oxygen present. Fuel NOx on the other hand, is due to the oxidation of a portion of the nitrogen combined with the fuel. Bound nitrogen is emitted preferentially as molecular nitrogen and only partly as NOx emission. The specific sources of NOx in a refinery together with the type of NOx are further illustrated in Table 14 (6).

Generally NOx formation can be reduced by lowering nitrogen level at peak temperature, decreasing oxygen availability at peak temperature, or by reducing peak temperature and residence time in the combustion zone. Control methods that can be used for NOx are basically grouped into two cat-

egories namely the control methods used to reduce the nitrogen oxides formation and control methods used to remove nitrogen oxides from flue-gas.

Both are often called flue gas treating process (FGT). Control methods used in reduction of NO_x formation include combustion modification and the use of flow nitrogen fluid. Control methods used in FGT include both the dry and wet processes.

Combustion modification. It is the most cost effective and energy efficient technology used to control combustion generated oxides of nitrogen and has been successfully implemented on existing gas and oil fired boilers to comply with emission standards. This technique often results in up to 60 percent reduction in NO_x emissions. The commonly used control techniques include the following processes:

a. Low excess air combustion. It involves reducing the total amount of excess air supplied for combustion in boilers and process heaters to decrease both thermal and fuel NO_x formation. Such a technique has been widely used.

b. Flue-gas recirculation (FGR). It consists of extracting a portion of flue gas and returning it to the furnace into the primary combustion zone. FGR lowers the peak

flame temperature and therefore reduces the oxygen concentration in the furnace. FGR has been found to be effective in reducing thermal NOx

c. Staged combustion. It is based on operation with a rich primary combustion zone in the furnace to reduce oxygen availability and peak temperature, followed by secondary air injection to achieve carbon burn out. The reduced oxygen availability in the primary combustion zone reduces the combustion of fuel nitrogen to nitrogen monoxide (NO) and the reduced peak temperature and subsequent heat removal prior to secondary air addition reduces thermal NOx

d. Low nitrogen oxides burner. They are generally designed to reduce flame turbulence, delay fuel air mixing and establishing fuel rich zones where combustion initially takes place. Such burners produce longer and less intense flames which result in lower flame temperatures and reduced thermal NOx generation. In addition, the reduced availability of oxygen in the initial combustion zone inhibits fuel NOx conversion.

e. Catalytic combustion. It uses a catalyst to promote the rate of the chemical reaction so that the rate of burning is achieved at a lower temperature, avoiding the formation of NOx.

Low nitrogen fuel use. It involves NO_x formation through modification of the fuel. Substitution of natural gas acts as a good alternative as it contains a much lower content of nitrogen.

Flue-gas treating process (FGT). As mentioned earlier, FGT comprises both the wet or dry processes. Dry processes usually utilize catalytic decomposition or absorption whereas the wet process utilizes absorption technology. High temperatures ranging from 320 to 980°C are often used prior to the boiler or process heaters. Wet processes, on the other hand are usually installed downstream of all equipment prior to entering the stack.

If both processes are compared, dry processes are much more cost-effective, simple to operate, and therefore are more commonly used.

Sources and Control of Total Suspended Particulates. The primary sources of particulates are the process heaters and boilers, the FCC regenerator, gas turbines, and the solid-waste incinerator.

The principal process unit subjected to control of particulates is the Fluid bed Catalytic Cracker. Particulates are controlled by an electrostatic process gen-

erator (ESP), high efficiency cyclones, dry scrubbers, wet scrubbers, or baghouses (fabric filters); but the most commonly used equipment is the ESP.

ESP removes particulates from gas streams by discharging the gas between a pair of electrodes namely a discharge electrode at a high potential and an electrically grounded collecting electrode (106). With a large potential difference created, a corona discharge (electron discharge due to high voltage) surrounds the discharged electrode. Due to the action of the electrical field gas ions formed move rapidly towards the collecting electrode and transfer their charge to the surface particles of the suspension. The charged particles are then forced to the grounded collection plates where they transfer their charges to the grounded electrode.

The dust layer that forms on the collecting electrode is removed by intermittent rapping causing the deposit to break loose from the electrode. Dust in agglomerated form under the effect of gravity then fall into dust hoppers (collectors) below the electrodes ESP functions both as an efficient particle agglomerator and as a gravity settling chamber.

Sources and Control of Odorous Emissions. The products, by-products, and wastes from petroleum operations represent

a long list of organic compounds having some odor potential. The main offenders producing obnoxious odors are sulfur compounds such as H_2S , mercaptans (organic compounds with a garlic odor and having a general formula $R-SH$, thiol group $-SH$ often attached to radicals such as CH_3 , C_2HS , etc.), and disulfides. Others include phenolic compounds, aldehydes, ketones, and ammonia. Tables 15 and 16 (87) provide some properties associated with the chemicals that produce odors. These compounds with offensive smell and low olfactory levels often give rise to the majority of complaints from the public.

The most economical methods used to control the refinery odors include eliminating them by modifying some operating procedures, avoiding accidental releases by proper maintenance. If they cannot be eliminated by such processes, then the following methods can be used :

Incineration. Organic vapor producing the odors can be oxidized to carbon dioxide and water in the incinerators. The operation of incineration can normally be accomplished without the production of odors. When odors are produced, it frequently indicates low incinerator temperatures. Usually, the addition of fuel gas can correct the situation by increasing the temperature. Commonly used incinerators in refinery are the catalytic and thermal incinerators, and

process boilers. Catalytic incinerator achieves a complete combustion at a much lower temperature as compared to thermal incinerators. As mentioned earlier, incinerators also serve to control CO emissions (44).

Adsorption. Several materials are often used effectively as adsorbing reagents. These include activated carbon, silica gel, activated alumina (alumina oxide), and zeolites (44). Of the above, activated carbon is the most commonly used adsorbent. It is so because of its high regeneration ability and easy recovery of odorous compounds.

Absorption. Absorption is among one of the most common methods in odor control. This include aldehyde absorption in bisulfite solutions; thiols absorption in sodium hydroxide solutions; hydrogen sulfide absorption in amine solutions, activated carbon, active manganese dioxide, and on sawdust; and hydrogen sulfide absorption followed by incineration or oxidation.

Neutralization. It is used to neutralize acidic or alkaline gases (e.g. ammonia used to neutralize some acids) by using scrubbing techniques such as lime scrubbing, and double alkali scrubbing. Detailed information on this topic is available in the following references (6, 44). Disposal of the aqueous wastes then becomes a water pollution problem.

Chemical oxidation. It can be achieved by using oxidizing materials such as calcium hypochlorite or potassium permanganate

Condensation. Condensation is a process of reducing a gas or vapor to its liquid state. Odor emitting gases such as ammonia can be reduced to liquid state by lowering temperature. Condensers generally use water or air to cool and condense vapor streams since they are typically used as pre-treatment devices. They are often used ahead of incinerators, absorbers, or adsorbers (43).

Hazardous Pollutants. Among the organic compounds occurring in small amounts, benzene is one of the more prevalent and it has been identified as a hazardous carcinogenic pollutant that can cause leukemia. Potential sources of benzene in the refineries are vapor losses from storage tanks. Stringent emission controls such as use of fixed roofs in conjunction with internal floating roofs to seal the storage vessels are being proposed to reduce the emissions effectively (20).

Strict maintenance measures requiring leak detection and repair programs for pipeline valves and existing pumps and compressors are also being considered to reduce benzene emissions (53).

Other Controls. Other control systems applied in a refinery include systems available to combat emergencies such as fires or explosions. Since a refinery processes large volumes of VOCs, volatile gases especially pentane, benzene, naphtha, etc. can be accidentally released to the atmosphere as a result of leaks, pressure changes or even abrupt temperature changes of the system. Such gases form vapor clouds, ignite and lead to explosions. Due to this, fire fighting capability is necessary in a refinery (72).

Refinery fire control system. Most refineries are well equipped with facilities to fight a fire if one should one occur. The refinery fire water system is a separate system with designated storage, pumps, and piping. Process areas maintain permanently installed water spray devices called monitors. Sewer systems, particularly those in process areas, are designed with seals, covers, traps, fire baffles, etc. to prevent the spread of fire between areas. Refineries also maintain a good foam system (often checked), fire trucks, and other fire fighting equipment. Appropriate training of the personnel is important in controlling spread of fires as it can lead to serious pollution of the air.

Summary of Controls and Design Parameters for Air Pollutants. A long list of control methods for various types of pollutants were discussed earlier. A summary illustrating

the methods together with the design parameters used are illustrated in a tabular form as shown in Table 17 (6, 87).

Management Guidelines for Air Pollution Control

Management responsibilities begin with a long range planning, selection of site and locating various units with a facility. Proper engineering, design and specifications of pollution control equipment used are also regarded as important responsibilities (101). A few of the parameters such as site selection and design of a refinery have already been discussed in the earlier sections of the Chapter. Other management guidelines include industrial hygiene concerns, explosive control technology and practice, personnel and fire safety, etc. Since the focus of the thesis is managing the air quality of the refineries, only the operating guidelines are discussed as follows (6, 73, 87, 101):

Operational Guidelines. The guidelines for general operation of a refinery can be viewed from three aspects which relate to each other. These areas are operating procedures and housekeeping, inspection, and maintenance. Guidelines that can be used to control air emissions are as follows:

Operating Procedures and Housekeeping. It is important to train the employees in the methods to be used in controlling air emissions. Some of the areas that should be included are:

1. The practices of open stirring, venting, and flaring be minimized.
2. Opening of tanks in relation to tank gauging and sampling be done only at the time of the day when the temperature and pressure is at a minimum merely to minimize vapor losses.
3. Operating practices should minimize spillages and insure that vapor collection and recovery equipment will control vapor loss to the atmosphere from transfer operations such as loading into trucks from storage tanks.
4. Masking agents or odor counteractants be used to cover up odors.
5. Pressure settings on storage tanks should be set to limit the release of hydrocarbon vapors.
6. Odors from incineration processes may be minimized by raising the combustion temperature.
7. If it is necessary to flare H_2S , the fuel gas feed to the flare should be increased and steam flow increased to improve combustion of H_2S and minimizing the odor emissions.

Inspection. Inspection programs are necessary to insure that all processes and pollution control equipment are operating properly and to detect any faulty equipment. Items typically inspected are pumps, compressors, valves, relief valves, combustion processes, seal systems, vents, gauge covers, etc.

Maintenance. Faulty equipment should be repaired as soon as it is practical both to eliminate emissions and to prevent failures of the equipment. Surface coating on storage tanks should be checked to reduce breathing emissions.

VI. MONITORING, MODELING, AND INSTRUMENTATION AT REFINERIES

OVERVIEW

In the process of selecting a refinery site, several assessments and evaluations relating to the air quality relative to site must be made. Factors to be assessed include:

1. Status of the air quality in the region around the site.
2. Type of terrain.
3. Background ambient air quality.
4. Air pollution sources which have impact on the site air quality.

Background ambient air quality plus the change in ambient air quality due to existing sources combined with the ambient air quality impact due to the projected emissions from the proposed refinery establish the projected air quality. This air quality level is a factor used in making a decision on whether or not to issue a construction permit for the proposed refinery by the regulatory agencies i.e. EPA or SAPCB. Even after the refinery is constructed, an oper-

ating permit must be acquired. Modeling and monitoring are both required in the permit acquisition process. In the Chapter, air quality monitoring and modeling are reviewed as they apply to both the pre-construction and post-construction phases of either a new refinery or a significant modification or expansion of an existing refinery.

OBJECTIVES OF MONITORING AND NETWORK DESIGN

Monitoring serves to (6):

1. Maintain historical records of air quality and establish air quality trends which might be necessary for future expansions.
2. To assess the effectiveness of the air pollution equipment being used.
3. To deal effectively with citizen complaints.
4. To evaluate existing control practices to insure compliance with regulations such as NAAQS and emission standards such as NSPS.

Before initiating monitoring at a site, the investigation showed, determine if Local Air Monitoring Stations

(SLAMS) or National Air Monitoring Stations (NAMS) (45) are operating in the vicinity. Data from SLAMS is used primarily for documenting air quality levels (attainment or non-attainment) in the geographical area of the proposed site. The data obtained from NAMS is used for National policy analyses and for reporting to the public on major metropolitan areas.

The decision on whether to permit construction of a refinery from an air quality standpoint rests on what current air quality levels are as measured by either a SLAMS monitoring stations or ones established privately. The network of stations comprising SLAMS are designed to meet a minimum of four basic monitoring objectives. The are (45):

1. To determine the highest concentrations expected to occur in the area covered by the network.
2. To determine representative concentrations in areas of high population density.
3. To determine the impact on ambient pollution levels of significant sources or source categories.
4. To determine general background concentration levels.

Private monitoring stations of large refineries would have a few other objectives in addition to the list as above. Some of these are discussed in the section on ambient air surveys in the Chapter. Important objectives of such stations include checking compliance with existing air pollution regulations, detecting any leakage of pollutants such as hydrocarbons, etc. Large operating refineries carry on continuous monitoring as required in the operating permit.

The design of an ambient air monitoring network for criteria and non-criteria pollutants should take into account factors such as topography, climatology, population, and existing emission sources.

SPATIAL SCALE OF REPRESENTATIVENESS

A physical entity called spatial scale of representativeness links up the general monitoring objectives specified earlier with the physical location of a particular monitoring station. The scale can be described in terms of the physical dimensions of the air parcel nearest to a monitoring station throughout which actual pollutant concentrations are reasonably similar. The scale of representativeness often employed are (45):

1. Microscale - The concentrations in air volumes associated with area dimensions ranging from several meters (m) up to about 100 m.
2. Middlescale - The concentration typical of areas up to several city blocks in size with dimensions ranging from about 100 m to 0.5 km.
3. Neighborhood scale - Concentrations within some extended area of the city that has relatively uniform land use with dimensions in the 0.5 to 4 km range.
4. Urban scale - The overall city wide conditions with dimensions on the order of 4 to 50 km and usually requires more than one site for definition.
5. Regional scale - A rural area of reasonably homogenous geography and extends from tens to hundreds of kms.
6. National and Global scale - These measurement scales represent concentrations characterizing the nation and the globe as a whole.

These scales can play important roles in locating the monitors. For example, to determine CO concentration emitted from a refinery over a broad geographical area having rela-

tively high CO concentrations, a neighborhood scale is most appropriate. Such a station would be located in a residential or commercial area having a high overall CO emission density but not in the immediate vicinity of any single roadway which is usually the case as CO concentrations are high there due to automobile emissions.

AIR MODELING

An air quality model is a logical analytical methodology for making predictions about air quality based on a knowledge of emission characteristics and atmospheric dilution, dispersion, and reaction mechanisms. Different type of models exist and can be intuitive such as proportional models, empirical such as Gaussian model, or can even be those based on numerical methods (54).

Formulas by Pearson, Pasquill, Karl Gauss, Turner, Gifford are used in air quality modeling analysis. Of particular interest because of their widespread use are Gaussian dispersion models, Pasquill-Gifford's dispersion modes, and Climatological Dispersion Model (CDM) which make use of computer applications.

A Gaussian dispersion model which is largely empirical in nature has been found to be applicable under many condi-

tions for the determination of downwind atmospheric concentrations resulting from a stack plume. This dispersion equation is an important consideration as the stack plume from refineries generally follows a predictable trajectory and moves in rather steady flow both downwind and vertically upwind (6). Since it is subjected to various turbulent wind forces, it results in being dispersed, diffuses, and then spreading of the contaminants occur. Dispersion can therefore be defined as the scattering of values of a frequency distribution (i.e. pollutant concentration) with a normal distribution shape (6).

The air quality modeling of plumes or contaminants is generally carried out prior to locating air quality monitors since the modeling results provide data for monitor siting. Previously, general air quality modeling depended on bulky mainframe computers. Due to the advancement of technology, personal computers are currently in widespread use for modeling purposes. Calculations using these models are not discussed here. Modeling has been addressed mainly to indicate the importance and significance of using it in relation to emissions from refineries. Reference to detailed modeling procedures and calculations is given by the references (6, 19, 33, 67, 77, 102-103).

LOCATION OF MONITORS AND PROBE HEIGHTS

The number and location of monitoring sites are determined by the operator and reviewed by the regulatory authority (45). Factors governing the location of monitors include the effects of existing sources, terrain, meteorological conditions, existence of fugitive or reentrained dusts, averaging time for the pollutant, etc. These factors may be taken into account during air quality modeling.

The monitors are sited to fulfill either of the monitoring objectives:

1. Locating monitors to determine the maximum concentration from the proposed source and/or existing sources.
2. Locating monitors to determine where the combined impact of the proposed source and existing sources would be expected to exhibit the highest concentrations for NAAQS averaging times.

To meet the first objective, the monitor is sited to measure the maximum impact from the proposed source. Emissions from elevated stacks depict the refinery case (not ground level emissions). In this case, mixing occurs during the transport of the emissions from the stack to the ground level resulting in small vertical gradients near the ground level, thus, a wide range of probe heights, from 3 to 15 m

for gases and from 2 to 15 m for particulates are used (45). Modeling as discussed previously is used to locate the monitors.

To monitor the maximum impact area with both the proposed source and existing sources in operation, the monitor site must be positioned at the location where ambient air quality is lowest due to the combined effects of all sources influencing the site. The location of a monitor to achieve the objective can vary considerably depending upon which source is the predominant influence on the maximum impact area. For example, in a situation where a proposed elevated stack of a refinery emitting CO into an urban area, the maximum combined CO impact would be an area adjacent to the heavily traveled corridor.

As the traffic along the corridors emit CO, the placement of the probe to measure the areas of highest CO concentration can vary significantly with probe height as well as distance from the corridor. As the traffic corridor is the major influence on the combined impact, it therefore controls the probe placement. In such microscale cases, the desired probe height is usually $3 \pm 1/2$ m while the distance of the probe from the roadway would be between 2 and 10 m (45).

Other desired probe heights and scales of measurements are cited in Title 40 Part 58 of the Code of Federal Regulations.

PRE-CONSTRUCTION PHASE

Objective

Monitoring and modeling to determine the ambient air quality distribution in the pre-construction phase of a refinery are essential for establishing the air quality of the proposed site. If its an attainment area, model impacts and PSD increments would be considered to apply for PSD application permit. In an non-attainment area, offsets in form of emissions trading would be necessary before a construction permit is required.

Site Location

Usually, more than one site is proposed for a refinery. This is done so that if the air quality assessment of a particular locality is poor, the operator still has other alternative sites. The location of monitoring sites for a refinery are initially determined by the operators or consultants responsible in the operation which are later reviewed by the permit granting authority such as EPA or SAPCB.

A screening procedure or refined model estimates are first used to determine the locations for the maximum air quality concentrations from the proposed source or modification. Secondly, modeling techniques as discussed earlier, are used to determine locations possibly having maximum air quality levels from the existing sources. Thirdly, modeled pollutant contribution of the proposed source or expansion is analyzed in conjunction with the modeled results from existing sources to determine possible impact areas.

Monitors

The number of monitors is often higher in areas where the spatial variability of the pollutant in the areas of investigation is higher (45). In remote areas, where the permit granting authority has determined that there are no

significant existing sources, a minimum number of monitors would be needed, i.e. one or probably two at the most. For new sources, in such remote areas, the monitors may even be located on convenient and accessible areas rather than the proposed sites since the air quality would essentially be the same for both areas.

Monitoring

On-site monitoring at pre-construction phase is necessary to determine the ambient air quality levels for compliance with NAAQS and for PSD increments if the site is in an attainment area. PSD increments are determined for the SO₂ and TSP increment levels depending upon the class designation of the site under the PSD classification, such as Class I, II, or III (82). TSP and SO₂ can be measured using the period of measurement as illustrated in Table 6 (Chapter IV). The ambient levels to satisfy NAAQS are determined for the criteria pollutants such as CO, NO₂, TSP, HC, O₃, and lead (Pb). Again, the period of measurement (averaging time) for the pollutants as indicated in Table 7 (Chapter IV) can be used.

Measurement of the ambient air for non-criteria pollutants, hazardous, and toxic emissions (gases) is not mandatory under the regulations of the 1977 CAAA (64). Such monitoring is done only if complaints from the public are

received. At present, according to Jewell (64) of SAPCB (Virginia), EPA is currently developing a program to handle hazardous pollutants.

Although monitoring of non-criteria pollutants such as trace elements, odorous gases such as H_2S , NH_3 , etc. and hazardous pollutants such as benzene and toluene are not mandatory, monitoring to some extent is often carried out by the operators (82). It is merely done for future preparedness to public criticisms of such pollutants. In preparing the document to apply for the PSD permit, Portsmouth refinery (82) carried out monitoring of non-criteria pollutants and hazardous gases such as benzene to some degree (82).

Ambient air quality information for the criteria pollutants for the site or for its vicinity may be available from the local SAPCB. If so, the data obtained can be agglomerated into the study of the monitoring carried out.

Ambient Air Quality Surveys. A report prepared by the Conservation of Clean Air and Water of Europe (CONCAWE) Committee (34) outlined the following guidelines that are important in planning and carrying out sampling, testing, and surveys when performing on-site monitoring at a refinery:

1. Type and use of information to be obtained.
2. Pollutants sampled, sampling, and testing procedures used.
3. Sampling points.
4. Meteorological data.
5. Data acquisition, reduction, and interpretation.

These five guidelines are briefly discussed below.

Information required. In planning ambient air quality surveys, the number and the location of sites, sampling methods, frequency of sampling, and all cost factors are important considerations (6). At the outset, the objectives of the survey often include (6):

1. Checking compliance with air pollution regulations in the area surrounding the refinery.
2. Obtaining background data on areas not affected by the refinery and where expansion or construction is proposed. Such information is usually collected prior to construction as indicated earlier.

3. Developing and testing diffusion models.
4. Setting emission standards such as NSPS or NESHAPS for Post-Construction Phase.
5. Estimating from emission factors. Such estimation is important in establishing what additional analytical work is required to accurately determine the emission rates.

Pollutants sampled, sampling, and testing procedures.

The pollutants sampled in the ambient air survey include SOX, Often, non-criteria pollutants such as H₂S, mercaptans, ammonia, fluorides, and hazardous emissions such as benzene are surveyed.

The samples collected are then tested using different reference or equivalent methods (see Table 19). A reference method is defined as a method for sampling and analyzing ambient air for a criteria air pollutant as specified in Title 40 Part 50 of the Code of Federal Regulations (32). Equivalent method namely the manual or automated method as designated in accordance with Title 40 Part 53 of the Code of Federal Regulations can also be used (44).

A quality assurance program to evaluate the precision and accuracy of the analytical results is necessary and

should be carried out by people not routinely involved in sampling and analysis process. Quality assurance audits are often made quarterly and should be conducted randomly and under normal operating procedures and conditions (46).

Three major methods of collecting samples and testing in a survey are:

a. Manual. Manual sampling methods are employed either at permanent locations or with mobile equipment at a variety of sites. The samples are usually analyzed at a central laboratory. They are more suited for preliminary surveys and to provide data for designing a long-range program and for intensive investigation (6).

b. Fixed instrument stations. The method employs continuous sampling and analysis by recording instruments at fixed sites. Such monitors are housed in buildings or in trailers provided with necessary means of protection from weather. They provide a continuous record of ambient air quality that can be correlated with meteorological conditions.

The method of sampling and testing is necessary for the long-term analysis and control of complicated situations in which many sources emit a variety of pollutants.

c. Mobile laboratories. Mobile laboratories provide a continuous analysis. It is useful and convenient especially for scattered refineries and has high demands from large oil companies in U.S. (6). The advantage of such units is that they can cover large areas and are very accessible to sites of pollutants. Meteorological facilities such as instruments for measuring wind direction, speed, turbulence, temperature, humidity, rainfall, and others are available on such units.

Sampling points. Sampling points are usually located in areas that are expected to be polluted from emissions, neighborhood areas not affected by refineries but affected by pollution from other sources, and areas not significantly affected by industrial pollution at all. Location of the monitors and the probes has been viewed in the earlier sections.

Tall structures and rough ground can also influence the dispersion of gases by inducing turbulence. In such cases, wind tunnel studies may be used for locating sampling stations. Wind tunnels, too, are, useful for investigating emissions from multiple stacks (representative of a typical refinery) (6).

An important consideration in sampling is determining the frequency of it. This can be done by applying statistical methods.

Meteorological data. The diffusion of emissions from the source to the point of impact largely depends upon meteorological factors such as wind speed and direction, atmospheric stability, relative humidity, precipitation, etc.

The monitoring network stations such as SLAMS collect and keep the meteorological data and records which are essential in dispersion modeling.

Data acquisition, reduction, and interpretation. Since the data involved is often voluminous and furthermore continuous recording is often necessary, computers are often employed to handle the data. Once data has been collected, other steps that follow are such as recording, validation, storage, and finally interpretation of data. In data interpretation, an important tool, pollution roses-indicating the direction of pollution is often employed.

POST-CONSTRUCTION PHASE

Objective

The post-construction phase occurs after further expansion and modification of a refinery. After construction, in order to acquire an operating permit, both monitoring and modeling are required.

Monitors

Usually, the location of monitor sites are maintained for the post-construction phase. However, the location of the sites can vary from those sites for the pre-construction phase due to other new sources or modifications in the area (45).

Monitoring

After construction and while operating the refinery, both the ambient air quality levels and stack emissions rates are measured.

Generally, the purpose of modeling done for post-construction phase is to represent actual emissions as measured by stack testing. Up-dating input data would be necessary if measured emission rates differ from those estimated before construction. Emission standards such as NSPS and NESHAPS are applied during this stage.

Ambient Air Quality Surveys. The methods specified in the Pre-Construction Phase are also used for the Post-Construction Phases. The objectives of surveying the air quality then are slightly different as compared to Pre-Construction. They are:

1. Checking compliance with recent air pollution regulations or amendments (may be different as revisions may have taken place).
2. Detecting pollution sources in an existing refinery which might be caused by leaks from storage tanks, valves, etc.
3. Detecting pollution of nearby plants.
4. Measuring the ambient air for hazardous gases in case of accidents at the refinery which is the responsibility of the Office of Emergency Services. In Virginia, this office is under the supervision of the Secretary of Transportation (64).

Stack Emissions. As illustrated in Table 9 (Chapter V), the pollutants emitted from refineries have been grouped into four categories namely hydrocarbons, malodorous materials, total suspended particulates, and oxides of sulfur and nitrogen.

Stack emissions measurement. Table 8 (Chapter 4) illustrates the NSPS for petroleum refineries. Federal regulations under the designation Title 40 Part 60 of the Code of Federal regulations (40 CFR 60) (31) establish the allowable emission rates of TSP, SO₂, CO from new and modified sources in petroleum refineries and of hydrocarbons from storage vessels. Those regulations also specify the methods of monitoring (e.g. if continuous monitoring is required), sampling, and analysis.

Sampling and analysis methods. Regulations require that items such as sampling points, platforms, safe means of access, utilities for sampling and testing equipment should be available at the stack sites (89). A sampling train as illustrated in Fig. 34 (44) is employed. Polluted air is drawn into the sampling train and passes through a sample collection device. The device either physically or chemically removes the pollutant from the air stream or collects the air for analysis later. Various modifications of the sampling train are used for measurement of various stack gases and particulates.

Stack sampling and analysis methodology employed at petroleum refineries is briefly stated below:

Manual procedures. Manual procedures have been specified for both the reference sampling and testing of sources of pollution under the Federal regulation as designated in Title 40 Part 60 of the Code of Federal Regulations. Methods were updated and are indicated in Table 18 (92). The Code of Federal Regulations details the measurements of sampling as:

1. The total flow of gases in a stack, the gas velocity distribution, and volumetric flow rate are measured by making a traverse across the stack with an S-type pitot tube.
2. A representative sample of particulates is obtained by sampling isokinetically at a number of locations across the stack (6).
3. Samples of SO₂ and other gases taken across the stack are relatively constant and therefore a straight probe fitted with an integral filter is used to remove the particulates.

Automatic procedures. Continuous monitoring as designated in NSPS (31) for several pollutants has been provided by automatic instruments. A continuous written record of emissions is available and alarms are incorporated to enable prompt corrective action in case of process upsets or emis-

sion control equipment failure. Two common and important approaches used for continuous monitoring are extractive and in situ approaches (36). The extractive approach is used for gas analysis whereas in situ approach is used to determine particulates.

a. Extractive. A continuous sample is drawn from a probe traversed in the stack and transported to an analyzer mounted in a convenient location. Interface systems to remove particulates and moisture are also available. Gas chromatographic sampling systems are used to monitor SO₂ in sulfur plant incinerator stack whereas continuous analysis systems use ultraviolet infrared spectrometric analyzers to monitor carbon dioxide, hydrocarbons, hydrogen sulfide, nitrous oxide, and sulfur dioxide (6).

b. In situ. In this approach, the instruments are mounted inside the stack or immediately outside (6). They consist of in-stack correlation spectrometer that measures SO₂ and a fast response continuous boiler system that monitors CO₂, NO₂, CO, SO₂, and the opacity of the plumes. Opacity is defined as the percentage of visible light attenuated due to the absorption and scattering of light by particulate matter in flue gas (44). Optical windows required in such approaches are also kept free of particulate

deposition, usually done by flushing with a stream of clean air.

VII. ENVIRONMENTAL ISSUES OF 1980S RELATED TO PETROLEUM REFINERIES

OVERVIEW

Important factors often considered in petroleum refining practices are the capital costs and regular maintenance costs with air quality management of refining practices. Other costs to which the refineries are subjected are environmental costs i.e. those costs associated with controlling and regulating the emissions emitted from the refineries. Such costs are steadily increasing as the standards and regulations set by 1977 CAAA are quite stringent as compared to the previous ones.

Such factors, dealing with environmental expenditures focusing on air quality as a result of refining activity, are discussed in this Chapter. Other economic related issues such as the economy of scale with respect to the age of refinery, closing down of refineries, delays in granting of permits, and etc. are discussed to a considerable depth.

Important issues like regulations on lead content in gasoline, acid rains and CO₂ 'greenhouse effect,' together with 'Ice-box effect' which can generally be referred to as issues

of the 1980s and are of great concern to both regulatory and public sectors, are also briefly presented in this Chapter.

ENVIRONMENTAL EXPENDITURES OF U.S. PETROLEUM INDUSTRY

A survey carried out by American Petroleum Institute's Environmental Affairs Department in 1983, as shown in Fig. 35 (4), showed that the petroleum industry spent over U.S. \$28 billion in environmental protection over the decade i.e. from 1973 to 1982 (4, 23). Of the \$28 billion spent in that period, air programs accounted for 53.3 percent while the water programs commanded only 35.3 percent of the amount.

Interestingly, as illustrated in Fig. 35, the expenditures of the oil industries totalled about \$4.8 billion in 1982 up from \$4.6 billion the year before. Infact the largest part of industry's total environmental expenditures, \$2.5 billion, was spent on air pollution programs. Table 20 (4) further illustrates the environmental expenditures of air management with the emphasis on manufacturing operations of the U.S. Petroleum Industry. As defined and listed in Environmental Expenditures of the U.S. Petroleum Industry, the U.S. Petroleum Industry manufacturing expenditures include the processing practices together with control technology expenditures (4). Included within the list are operation of bag filters, use of cyclones, electrostatic precipitators,

flare gas recovery systems, floating roof tanks, hydro desulfurizers, sulfur recovery plants, and etc. The manufacturing costs more or less give an insight of the amount that was spent in controlling the air quality at the refineries.

For the 10 year period, from 1973 to 1982, about \$4.1 billion, \$7.8 billion, and half a billion dollars were spent on capital expenditures, and administrative, operating and maintenance expenditures, and research and development expenditures respectively for manufacturing expenditures. This accounted for about 82 percent of the total expenditure spent on air quality by the petroleum industry.

Over the years, the expenditures involved in manufacturing practices have increased steadily. A closer look into Table 20 shows that an increase in costs, independent of the category of expenditure, reveals a demarcative increase after 1977. Such a phenomenal increase could only possibly be due to stringent standards and regulations set by 1977 CAAA.

According to the Battelle Report of 1980 (10), it was anticipated that by 1990 the cumulative capital investment expenditures on Environmental Regulations for managing the air quality of refineries by petroleum industry would be about \$19 billion. Furthermore, about \$3 billion would be spent

for maintaining and manufacturing practices for the same purpose.

The information provided by Battelle Report and Table 20 clearly indicates that in future, much heavier costs would be associated with the air quality management of the refinery industry as the standards and regulations set by the regulatory agencies are constantly being reviewed and made more stringent.

ECONOMY OF SCALE, AGE, AND TECHNOLOGY

In 1974/75, the U.S. Refining Industry incurred a huge loss due to heavy product imports (55). Due to this, U.S. Entitlements program, and the 'small refiner's bias clause' were set up to encourage the construction of refining capacity. Small refineries proliferated to such an extent that, by 1980, they accounted for 40 percent of the total number of refineries in U.S.A. (55).

The surplus occurring around 1981 forced the decontrolling of the prices of crude oil and eliminated the legislation favoring small refiners. As a result, refineries began to shut down at such rate that a substantial decline in U.S. refining capacity followed. In 1981, 23 refineries which catering the production of 700,000 b/d were shut down (55).

In 1982, production of 1.2 Mn b/d was further reduced due to the shutdown of 63 refineries This included a few large ones such as the Dow Chemical U.S.A. refinery located at Freeport, Texas which had a crude distillation capacity of 190,000 b/d (68). In addition, another 23 refineries accounting for a crude distillation of about 900,000 Mn b/d were shutdown in 1983 (68).

The kinds of refineries that were closed were mainly those that were built in the period 1973 to 1980 together with other old refineries. Only a few young refineries were shut down. Some of possible economic reasons for the closing down of refineries include :

1. Small refineries unable to cope with the cost associated with installing control technology as demanded by 1977 CAAA.
2. Old refineries unable to cope up with the final products produced by larger refineries with much better control technology. Also, the older refineries had much poorer and inefficient refinery control installations.
3. Concentration of refineries in form of modification or expansion of the facilities rather than having separate

individual refineries which have much higher associated costs.

4. Larger refineries such as the GHR refinery (Louisiana) were closed mainly because of financial difficulties that incurred during a major expansion (55).

CONSTRUCTION AND SITING OF REFINERIES

Siting refineries, monitoring, modeling, and other data gathering regulatory requirements are often excessive, costly and time consuming. The stringent standards and regulations set by 1977 CAAA, can often lead to delays and costly restrictions on new and modified sources. At times, it may not even be necessary to protect air quality or achieve environmental benefits.

As shown in Fig. 26 (Chapter V), obtaining a permit for the construction of a large 'grassroots' (new refinery) can take as much as approximately five years due to the preparation of environmental assessment etc. in the engineering phase. During this period, management decisions will comprise as to how further to proceed with land purchase, site preparation, and design engineering. Such steps usually involve multimillion dollar investments. Usually, after a year of engineering phase, purchase contracts are executed for

prefabrication of major refinery components, such as pressure vessels, piping, and etc. Such purchases can involve huge costs and losses would incur if a permit is not granted finally.

Such costs can eventually lead to the abandonment of the project. For example, in the case of the Portsmouth Oil Refinery, an eight year delay was caused in large part by the needed EPA approval of the SIP under the Clean Air Act and needed dredge and fill permit from the Corps. of Engineers (73). The project was finally cancelled, although construction permit was granted because (29) :

1. There was a decreased need for refinery capacity by the time the permit was obtained.
2. The initial anticipated cost of \$350 million rose to a final cost slightly more than \$550 million.

EMISSIONS TRADING ECONOMICS

Emissions trading, as discussed in Chapter 4, amounts to an invitation for firms to reduce their current obligations and serves as an incentive for participation and trading together and sells discharge reductions to firms that face higher marginal costs of control. Market based approaches

take advantage of the 'enterprise' incentive to 'truck' and 'barter' (17).

An example of the use of emissions trading in the form of offset price is that of Wickland Oil Company which paid a price of \$25,000 to set up a 40,000 b/d oil terminal, that had earlier been shut down, to the Virginia Chemical plant in Selby, California(66). The offset consisted of \$150 per ton per year of hydrocarbons. As a result an estimated capital cost of \$167 per ton per year was paid (66). The use of emissions reduction credits enables an emission emitting facility to operate in a non-attainment area although it might be non-attainable in a particular kind of pollutant.

SALEABLE BY-PRODUCTS

As illustrated in Chapter V, various control technologies are applied in reducing the pollutants from being emitted to the atmosphere. The pollutants stripped off the crude oil can be further treated and sold by the refineries. Such products would save the refineries some revenue that can be used for other operational practices.

An important product collected and sold is sulfur obtained from sulfur recovery process such as 'Claus' or FGD process. NOx. obtained from wet processes such as flue gas treating

(FGT) is usually treated to nitric acid (HNO_3) form and sold. Among some of the VOCs emitted from storage tanks include benzene, toluene, and even xylene. These are often derived from extraction processes of lubricating oils. These VOCs are common marketable industrial solvents.

Other useful by products include asphalts which are selected heavy fractions from crude oils. They are largely sold for use in road surfacing, roofing, manufacturing, and battery cases (90).

LEAD CONTROL

The ability of a fuel to resist 'knock' (detonate) is measured by its octane number or rating. Isooctane is defined as having an 'anti-knock' rating of 100 with zero normal heptane. Thus, a gasoline with antiknock properties similar to a blend of 97 percent isooctane and three percent normal heptane would have an octane number of 97 (90).

High octane numbers are often desirable in gasoline and this high octane value in gasoline can be achieved either by:

1. Using antiknock compounds such as tetraethyl lead after refining or blending processes or

2. Increasing the amount of reforming and alkylation processing in refineries (15).

EPA has proposed a lead content standard of 0.10 gram lead per gallon (gplg) effective from Jan 1, 1986; totally ban lead in gasoline by about 1995 by regulation or impose no additional regulatory action beyond the 0.10 gplg (25). The phased down standards proposed are 0.30 gplg on Jan 1, 1986, 0.20 gplg on Jan 1, 1987, and 0.10 gplg in 1988. The annualized costs associated to refiners for the standards proposed above are \$575 million in 1986, \$532 million in 1987, and \$503 million in 1988.

Large refineries will not be affected as they are often flexible in their operations and the octane numbers can be increased by an increased amount of reforming and alkylation processing. About 271 small refineries would be affected as heavy costs would incur to modify refineries into low pressure continuous catalytic reforming, isomerization, and recycling operations such as catalytic reforming of catalytically cracked naphtha (25). Such steps taken by EPA could threaten U.S. refining industry as the refineries would be forced to shut down due to their inability to adhere to the regulations and this might possibly lead to U.S. dependence on imported oil.

ACID RAINS

Acid rain is the the common term for the more general phenomenon of acid deposition. Acidic deposition includes acidic snow, sleet, fog, and particular matters, and acid rains. Pure water saturated with carbon dioxide (CO₂) yields a pH of 5.6, but both natural processes and man's activities can change it. Acid rain commonly refers to even lower pH values. Usually, the acid content of rain is about 60 percent sulfuric acid, 30 percent nitric acid, and 10 percent hydrochloric acid (73). There may be other organic acids associated with it in varying proportions depending upon the region and time.

The acidity of rainfall is influenced by the amount and kind of gases dissolved in it. These include SO₂, NO_x, hydrogen chloride, and ammonia. Particulate matter and heavy metals may also influence rainfall acidity by catalyzing the formation of stronger acids in rain.

A growing body of evidence suggests that acid rain is responsible for substantial adverse effects on public welfare. Such effects include the acidification of lakes and rivers with resultant damage to fish and other components of aquatic ecosystems, acidification, and demineralization of soils, possible reduction in crop and forest productivity, and the

deterioration of man made materials (56). There is an increasing evidence that SO₂ and NO_x emissions that come primarily from the burning of fossil fuels cause acid rain.

At present, there is no literature documenting that acid rains can be attributed to emissions such as SO₂ and NO_x from refineries. Some predictions have suggested that NO_x from refineries does contribute to the overall effects, but at a much similar and lesser scale as that of NO_x control technology applied at the refineries.

However, a study carried by National Oceanic and Atmospheric Administration (NOAA) in 1979 (22) indicated that the oil refinery emissions released into polluted air of Los Angeles, California may offset some negative effects of urban air pollution. Large cloud droplets form as a result of particles, especially sulfates, picked up by the clouds. These particles can then serve as condensed nuclei and restore the clouds ability to produce rain. Some form of acid rain can be associated in this manner.

At present Clean Air Act contains no statutory provisions dealing with acid rain (73). However in future, more stringent emission standards (e.g. NSPS may be set by EPA to further reduce the emission of such pollutants) might be set. If this occurs refineries, too, would be affected to a cer-

tain degree. An increased level of LAER technology might have to be applied then.

CARBON DIOXIDE 'GREENHOUSE EFFECT'

The CO₂ 'greenhouse effect' is a postulated global climate change resulting from higher atmospheric CO₂ concentration. The universal problem is associated with several industries including the oil and gas industries (73). It is based upon the fact that CO₂ in the atmosphere is transparent to ultraviolet rays in sunlight, but is opaque to some of the infrared (heat) radiation to which a portion of the ultraviolet light from the Sun is converted when it strikes the earth. This means that if the CO₂ content of the atmosphere increases, it will tend to prevent the reradiation to space of some of the energy of the Sun which can possibly lead to a profound change in climate, including an increase in the average global temperature (71).

Refining activities tend to produce a considerable amount of CO₂, especially as a result of fuel combustion. Research is still in progress to determine the possible global warming phenomenon. If proved to have profound effects, standards of CO₂ emissions might possibly be coined into both the NAAQS and emission standards such as NSPS. If so, refineries would

then have to use additional control technology equipment which means much heavier costs incurrences.

'ICE-BOX EFFECT'

Another phenomena somewhat alike the 'green-house effect' is the 'Ice-box' effect which occurs as a result of heavy industrialization. Its occurrence is due to the increase in particulates emitted to the atmosphere (106).

Particulates in the atmosphere tend to block the passage of solar radiation towards the earth's surface. Such blocking effect which is the reverse of the 'green-house effect' is believed to cause a drop in the average atmospheric temperature. Such considerations are important as the petroleum refineries contribute almost 0.5 percent of the total suspended particulates of the total atmospheric emissions from all anthropogenic sources.

VIII. DISCUSSION

Obtaining a construction permit for a refinery often takes a long time as several requirements, such as standards and regulations pertinent to the 1977 CAAA, have to be fulfilled. The scenario in Fig. 36 illustrates the steps involved in requesting an operating permit for air quality control for a typical refinery in the U.S.

Before a proposed refinery project construction permit can be issued, several tasks must be carried out. The first task is to designate one or more sites for the refinery, with two or more tentative sites designated as alternatives, in case of any disapprovals of permits by the regulatory authorities such as the EPA or SAPCBs. If an expansion or modification is proposed, which is often the case currently due to the plummeting cost, proper engineering designs would have to be planned.

In selecting a site several measures, which have been explained in Chapter VI (section on monitoring), are considered. They include modeling and monitoring to determine areas of maximum impact of the emissions from the refinery, etc. Estimation of emissions using projected emission fac-

tors are prepared. By preparing model impacts, sampling monitors are located at the particular sites to determine the background and projected ambient air quality levels. Such procedures are depicted in the EIA/EIS prepared for the particular kind of facility.

Here after, different steps are involved for both the attainment and non-attainment areas. For an attainment area, PSD permit application is applied either to the EPA or SAPCB. Usually, copies are sent to both the agencies as was noted in the case of Portsmouth refinery (82). Model impacts and PSD increments (i.e. for SO₂ and TSP) are considered in the application. If the PSD permit is refused, relocation and/or redesigning of the facility may be necessary. If approved, construction of the facility may be carried out. In some instances, due to the time involved in obtaining the permit and the cost associated building it that time, the construction project of the facility may be totally abandoned. Infact, this was the main cause for the abandonment of the Portsmouth Oil Refinery project. After construction, in order to acquire an operating permit, both monitoring and modeling with a calibrated model are required. LAER measures will be employed if the request of the operating permit is refused.

For a non-attainment area, offsets in the form of emissions trading would be necessary before a construction permit is requested. Emissions reduction credits, at times can be sought and then bought from other inactive facilities in the area (see Emissions trading, Chapter IV). As in the case of the attainment area, if the permit is refused, relocation and redesigning may be necessary. If granted, monitoring and modeling with a calibrated model would be necessary to further acquire an operating permit.

The EIS of the Portsmouth Refinery and the EIS of PETRONAS Refinery were compared to examine the different approaches used in a developing country like Malaysia and a developed country like U.S. It is imperative to state that a draft version of the EIS of PETRONAS Refinery was examined as compared to a final version of the EIS of Portsmouth Refinery. The draft version of PETRONAS Refinery might not have illustrated much of the control technology applied together with other investigations actually done in preparing the EIS. Comparison was made contingent upon the information contained in the draft EIS.

The proposed Portsmouth Refinery can be classified as a complex refinery having a crude oil processing capacity of 175,000 b/d. As mentioned in Chapter IV, its products would

have included gasoline, jet-fuel, fuel oil, and liquefied petroleum gas.

The preparation of the EIS was essential as deterioration of the air quality was apparent. The preparation of the EIS together with the issuance of other essential permits took almost eight years to complete (29). Determination of the meteorological observations itself took about five years. A lot of considerations went into the preparation of the EIS. It covered a broad range from meteorological studies such as atmospheric stability, wind speed, and health concerns up to considerations such as estimating construction emissions due to earth moving activities. A great deal of monitoring and modeling using computer technology were carried out to obtain data in relation to environmental impact concerns.

As pointed out by Choi, Y.H. (29), several public organizations formed against the construction of the refinery. These included Tidewater Refinery Opposition Fund (TROF), Ghent Neighborhood League and the Ecological Society (ECOS), Citizens Against Refinery Effect (CARE), and etc. Besides the delay caused by the permit granting authorities, criticisms from such organizations, too, were partly responsible for it.

The PETRONAS Refinery has a capacity of processing 30,000 b/d of crude oil. The crude processed contains almost negligible amount of sulfur as compared to the crude supposed to be processed by Portsmouth Refinery. As a result, practically, no equipment is necessary to control the emissions from the crude processing. The draft EIS indicated relatively very little (if any) monitoring and modeling of the air quality. It might possibly be due to the less stringent regulations set by the Division of Environment (Malaysia). In Malaysia, the air quality is regulated under the Environmental Quality (Clean Air) Regulations of 1978 which are Amendments to the Environmental Quality Act (EQA) of 1974 (40).

It is imperative to point out that as yet, preparation of an EIS is not mandatory in Malaysia (80). The statement was prepared on the basis that a degradation of the environment due to the setting up of the refinery was quite evident and apparent.

Although emission standards are outlined for facilities, they are less stringent as compared to those set by EPA or SAPCB in the U.S. Petroleum refineries are included within the same group as other emission emitting sources.

The EQA has prescribed three standards for each type of discharge of air impurities. Every facility set up on or after the date of enactment of the regulations has to comply with Standard C, which is the most stringent. Facilities existing before such date were given a maximum of two years to comply with Standard A and a maximum of three years to comply with Standard B, from that date. Thus, two levels of discharges are permitted: a stricter one for facilities established on or after October 1, 1978 and a more lenient one for those set up before that date (28).

A general classification of the the emissions have been set for emissions from all the industrial sources (40). For example, for the oxides of nitrogen, the standards set are 3.0 grams of sulfur trioxide (SO_3) normal cubic meters (Nm^3) for Standard A ,2.5 grams of SO_3/Nm^3 for Standard B, and 2.0 grams of SO_3/Nm^3 for Standard C. These set of standards are different when compared to those of U.S. in that a specific set of standards have been promulgated for the refineries in U.S.

Practically no public representation was indicated in the EIS of PETRONAS Refinery as compared to that of the Portsmouth Refinery. According to Chee, Y.L., (28), the Environmental Quality Council (EQC) body advising the Minister on matters pertaining to the EQA consists of civil servants

who are likely to operate under a compromise in favor of industrialization. As it may have included a little or practically no public participation at all, this may also be the one of the reasons for the quick approval of the permit for the construction of the refinery as compared to the Portsmouth refinery.

Although, monitoring and modeling on a wide scale were not carried out in preparing the draft EIS, the EIA prepared for Trengganu Crude Oil Terminal (TCOT) 1981 when examined indicated the application and the usage of the sophisticated technology. Since the discussion is on only the refinery, such document is of little significance.

As mentioned previously, EIS was not mandatory in Malaysia at the time the EIS was prepared and practically no public representation was indicated. However, the attitude and the concern of the public has changed over the years as the people have realized the probable degradation of the environment which can jeopardize health. Due to the complaints received from the public, PETRONAS undertook an air quality survey within the oil complex zone including the refinery on December 8 and 9, 1984. The main objectives as outlined were to identify the air pollution sources from operating plants in the industrial zone (i.e. including the refinery, Carigali Gas Terminal, Gas Processing Plant, TCOT), establish air

quality data from emission sources at the plants, and to refute the complaints from the public (79).

In the monitoring practices, equipment used were such as Interscan 4000 Series compact portable analyzer, Teledyne Analytical Equipment 900, and GASTEC Gas Sampler with detector tubes (79). The GASTEC Sampler used is not a sensitive instrument for detecting lower limits of the pollutants. For example, the primary NAAQS standards in the U.S. for an averaging time of 8-hour(hr) for CO is 9 ppm whereas for the 1-hr averaging time, it is 35 ppm. Since its lower measuring limit is 25 ppm, it is not sensitive enough to detect the low ambient pollutant levels. Sulfur dioxide, an irritant pollutant has a primary NAAQS standard of 0.03 ppm for an annual averaging time, 0.14 ppm for a 24-hr averaging time, etc. (see Table 7). The minimum detecting limit for SO₂ for GASTEC as indicated is 2 ppm and its far off the range of detection. Thus, it can be said that the sampler is useless for ambient standards detection if U.S. NAAQS were to be considered.

Such detector tubes are not suitable for such levels and therefore other sensitive equipment as discussed next should be utilized. Furthermore, being a grab sampler, it is not ideal for any continuous monitoring of the pollutants

The air quality data when examined indicates zero level pollutants from point source such as boiler stack. Usually, such values can never be attained from that point source. The use of insensitive equipment could be one of the reasons for the low levels of pollutants registered. Very sensitive equipment ought to be used for continuous monitoring practices in future. A few of which are commonly used in U.S. are (61):

1. Flame Photometric Analyzer (Melo Laboratory Inc. Model SA 285) It is used to detect SO_2 and has a lower limit capability of 0.5 ppb with a limit of detectability of one percent.
2. Chemiluminescence Analyzer (Monitor Labs. Nitrogen Oxides Analyzer Model 8440E) is used for continuous analysis of NO , NO_2 , and NO_x It has a four selectable ranges from 0.2 to 10.0 ppm.
3. Ozone Analyzer (Dasibi Env. Corp. Model 1003-AAS) has sensitivity ranges from 0.002 to 20 ppm with an incremental sensitivity of 0.001 ppm.

Although, EIS serves to foster good environmental quality, they do not help the public to understand the 'truth', but create a great deal of confusion and alien-

ation (6). Large numbers of literate people still hardly understand the enormous and vague technical issues and terms in an EIS. Confusion can arise due to the following (6, 58):

- a. Lack of fundamental knowledge of the existing environmental factors.
- b. Weaknesses in the techniques of assessment.
- c. Inability to identify and evaluate secondary and tertiary effects.
- d. Lack of an accepted basis for comparing the value of lost or degraded amenities with measurable economic effects.
- e. Lack of 'good' governmental guidelines.

In Chapter IV, summaries of both the PSDs of Portsmouth and Kenai Refineries were presented. PSD application for Portsmouth Refinery was essential as the proposed refinery was considered a major new source of pollutants i.e. emitting more than 100 tons of pollutants per year whereas the PSD of the Kenai Refinery was prepared because of its modification to increase refining

capacity from 48,500 to 80,000 b/d and to process 'sour' crude. Just as Portsmouth refinery it, too, was considered as a major modified source by emitting greater than 40 tons of pollutants per year.

In preparing the PSD permit, a great deal of monitoring and modeling were carried out for the Portsmouth refinery. This was so because it was subjected to stringent regulations under the 1977 CAAA. Ambient air quality levels together with PSD increments were investigated. Even the assessment of hazardous emissions such as benzene were investigated. Other areas of investigation included impact analysis of soil and vegetation. Kenai Refinery was also subjected to the 1977 CAAA. Modeling of stacks combined with monitored air quality levels to estimate total impacts on air quality, too, was investigated. PSD increments were also carried out.

To an extent, if viewed closely, procedures involved in monitoring, modeling, and assessment practices for both the refineries were very similar. This is so as both of them were subjected to the same stringent rules of the 1977 CAAA.

The practice of monitoring and modeling done as a requirement under the 1977 CAAA to gather data can be often

excessive, costly, and time consuming. It can cause delays in construction and expansion of refineries to such an extent that the project eventually might even be abandoned due to the cost factor shift as compared to when the permit was requested. Very few 'grassroots' (new) refineries are built due to the heavy subjection of such practices under the 1977 CAAA and further increasing revisions. The benefits of such practices can be subjective. It is good as further air quality degradation can be controlled. Disadvantage includes the suppression of the construction or expansion of the refinery which can be an economic loss. If approval for construction or expansion is granted, it can help to alleviate the local energy supply which otherwise can incur heavy cost due to foreign imports.

In Chapter IV, several alternative control policies in emission reductions such as the emissions trading in form of ERC were discussed. Emissions trading provides the opportunity to improve the air quality while reducing the costs of bringing about such improvements. For the refineries, as illustrated in Chapter IV, it can provide more cost-effective environmental quality management programs. On the contrary, as indicated by Liroff, R.A. (70), the bubble policy (a component of emissions trading) approved by EPA for a few cases were later disap-

proved after environmental groups revealed flaws in data and computer modeling. In such cases, it serves its function only on paper.

Among some of the proposed changes in the NAAQS are changes in a reduction of the CO concentration from 35 ppm (40 micrograms per cubic meter) to 25 ppm (29 micrograms per cubic meter) for both the primary and secondary standard levels (17). Another proposed rule is the classification of another Particulate-PM10 to the Primary NAAQS (50). EPA has proposed revisions on March 20, 1984 which would regulate particles less than 10 microns in diameter. The proposed NAAQS for PM10 would be an annual mean concentration of 50 micrograms per cubic meter which is approximately 43 ppm (100). The proposed standards will be in addition to the standards already set for TSP.

On the whole, the NAAQS should be reviewed and revised both to reflect sound, up-to-date scientific evidence and to provide a balance with other national goals. The standards should also take into account the important goals of producing sufficient energy (e.g. fuel and other products from refineries) and maintaining a sound economy (73). A few of the changes that should be considered are:

- a. Set primary standards based on relevant factors such as attainability and incremental costs and benefits.
- b. Make sure that the proposed NAAQS and exceedances of the NAAQS allow for the uncertainty in such factors as unique meteorological conditions, air quality monitoring, and air quality computer modeling. Proposed NAAQS should allow more flexibility in determining exceedances.
- c. Analyze additional costs and benefits, and consider regional differences into account in setting the standards.

New standards have also been proposed for new, modified, and reconstructed FCCU regenerators of the petroleum refineries. The proposed standards would require 90 percent SO_x (reported as SO₂) emissions reduction or 50 percent vppm SO_x in the flue gas, whichever is less stringent (23). However, if the emissions with no add-on control are less than 9.8 kg of SO_x/1,000 kg of coke burn-off in the regenerator or the sulfur content of the fresh FCCU feed is less than 0.30 weight percent, the regenerator would be required to meet the limit of 90 percent emissions reduction or 50 vppm. Also, the 90

percent emissions reduction or 50 vppm requirement is based on the use of Flue Gas Desulfurizer (FGD).

Other proposed regulations have been set for VOC leaks (fugitive emissions) from petroleum processing. The proposed rule states that in future, no detectable emissions will be allowed from pressure relief devices under normal operating conditions (20). By such enforcement, according to EPA, VOC leaks will decline from 49,000 megagrams (Mg) per year to 18,000 Mg per year (20).

A congressional survey carried out on toxic chemicals in the nation's air recently reported high levels of hazardous materials at high levels around large Chemical Companies (99). Many of the discharges occurred in areas of the country associated with refineries and petrochemicals such as Louisiana, Texas, New Jersey, Ohio, Kentucky, and West Virginia. Compounds such as benzene, xylene, toluene, and etc. were found around those areas. It means that more stringent measures are on the way for the hazardous pollutants. This might also lead to the necessity of monitoring of such pollutants around the refineries in the near future.

The proposed changes to the air quality regulations would incur a much higher cost for the refineries in fu-

ture for the trade-off for a slight improvement of the air quality. As a result, fewer refineries or expansions of refineries would be apparent in future due to high cost associated in managing the air quality. Currently, the cost involved in managing the air quality has grown to such an extent that small refineries that 'mushroomed' around the middle of 1970s have been made inoperational and were forced to shut down.

If such costs continue to plummet, there is a strong possibility that a shift in the location of refineries might occur from the U.S. to other third world countries where air quality regulations are less stringent. From air quality perspective, an economic gain would end up in significant deterioration of the air quality in such third world countries.

As discussed in Chapter VII, acid rain poses a serious threat to the environment. Damages to aquatic life, forests, farms, and buildings are imminent and evident. Such effects will probably lead to more stringent standards on the emissions such as SO_2 and NO_x which are the main contributors.

Some States such as New York for example, have passed legislation dealing with acid rain which is known as as

'State Acid Deposition Control Control Act' (60). The Act has set out a process and a schedule to curb the State's contribution to acid rain. By January 1, 1986, the Department of Environmental Conservation of the State must promulgate an interim control target for the control of sulfate deposition at each sensitive receptor sites.

A few of the controls for SO₂ and NO_x emissions suggested by the law include (20):

- a. The substitution of low sulfur levels.
- b. Use of one or more combinations of blending various sulfur content fossil fuels.
- c. Use of FGD equipment.

Such controls will lead to additional cost for the refineries.

Over the years, quite a lot of emphasis has been given to further improve the pollutant control technology at the refineries. It is mainly due to increasing stringent emission requirements that apply to the air quality control. An engineering feasibility study carried out for the Golden West Refining Company at Santa Fe Springs (Los

Angeles County) in 1984 proposed three new techniques for reducing SO₂ emissions from the FCCUs (12).

Modifications for the refinery is needed to comply with the South Coast Air Quality Management District (SCAQMD) Rule 1105 which states that after January 1987, SO₂ emissions from FCCUs shall not exceed 132 lbs. of SO₂ per 1,000 barrels of fresh FCCU feed (12). The design basis for modifications to the refinery process facilities considered in the investigation was to achieve a FCCU flue gas maximum SO₂ emission level of 110 lbs. of SO₂ per barrel of FCCU feed and a maximum sulfur content in FCCU gasoline blending stock of 250 weight parts per million (ppmw). The California sulfur limitation for unleaded gasoline is 300 ppmw whereas the normal industry standard in other areas of the U.S. is 1,000 ppmw. The three new modification techniques suggested are (12):

a. Gas Oil Hydrotreating

This process desulfurizes FCCU gas oil feed to the level sufficient to meet the sulfur limitations on both the FCCU flue gas and FCCU gasoline. The gas oils from the atmospheric and vacuum crude distillation units are hydrotreated in a new gas oil hydrotreating unit. About 90 weight percent sulfur

removal is anticipated which meets the sulfur limitations on FCCU regenerator flue gas and the FCCU gasoline product. In conventional processes, 45 to 55 percent is typically removed (26).

b. Stack Gas Treating

It includes scrubbing the stack gas to meet the FCCU flue gas SO₂ emissions limit and various desulfurization processes to reduce the sulfur content of the FCCU gasoline. The scrubbing process results in the removal of 75 percent of SO₂ and would meet the requirement of 110 lbs. per 1,000 barrels feed. Two flue gas treating processes considered were the Shell Flue Gas Treating (SEGT) Process which is a dry catalytic acceptor process and the Exxon Single Alkali Process which is a wet scrubbing process.

c. Sulfur Retention Catalyst

It uses sulfur retention catalyst in a high temperature CO-combustion regenerator to control SO₂ emissions in the FCCU regenerator Flue gas. The sulfur content of the FCCU gasoline will also be reduced by the same treating method used in case 2 .

An innovative change in the design and operation of existing sulfur recovery plants to produce large increases in capacity has been designed recently (69). Usually, a refinery has two Claus Sulfur Recovery trains, each capable of sustaining 60 percent of the normal refinery sulfur production. A technique was developed to modify the existing two 50 tons per day Claus plants such that normal high sulfur crude capacity can be sustained even if one sulfur train was taken off for repair. Its advantage would be that the refinery can still operate without flaring the H_2S in spite of taking off one of the lines.

Byrne et al. (26) developed a new FCCU about 45 to 55 percent of the feed sulfur is converted to H_2S in FCC reactor and about 35 to 45 percent remains in the liquid products. The catalyst when operated at high temperatures can reduce between 60 to 80 percent of sulfur emissions from the FCCU regenerator flue gas with no increase in NO_x emissions. It was developed for use by refineries in Southern California where the SCAQMD Board has proposed a standard of 132 lbs. of SO_x per 1,000 barrels of fresh FCCU feed.

Computers and microprocessors are finding ever wider application in refining operations. Earlier in the 1960s

and early 1970s, oil companies developed linear programs run on large main frame computers to simulate operational requirements (58,84).

The principle recent change has been the increasing use of on-line microprocessors/minicomputers to control individual refinery units. Oil companies with large chemical interests have tended to apply on line control and full digital instrumentation more quickly than smaller companies (58). Use of such processors are also growing in use in the monitoring of flue gases to minimize unburned hydrocarbons. Other advantages include improved monitoring, modeling, quality control, etc. The impact of computers, especially the microprocessors, on the whole refining process has become progressively more important with the rise in value of the products.

Currently, organizations such as the American Petroleum Institute (API), EPA, National Aeronautical and Space Administration (NASA), Research Laboratories such as Batelle Laboratories, and etc. have proposed and undertaken (in some cases) several projects pertaining to the maintenance of the air quality, directly or indirectly related to the refineries. A few of the current projects are (4):

- a. Investigation of atmospheric sulfates and the variables that affect sulfate formation

The focus of the project conducted by Environmental Research & Technology, Inc. is on acid precipitation and ways of further controlling sulfur oxides. Large gaps still remain about the understanding of the atmospheric reactions of SO_x

- b. Investigation of alternative forms of the NAAQS: Methodology assessment

The purpose of the study carried out by EPA is to produce more stable (robust) forms of the NAAQS, thus providing the petroleum industry (in particular the refineries) with greater confidence in the effective allocation of pollution control dollars in a timely manner. The research at present is focused on O₃ i.e. its standard-setting process.

- c. Determination of the Role of Petroleum Activities on acid deposition

Recent DOE and other reports have suggested that the combustion of petroleum products may create precursor pollutants that react more readily than coal

products to cause acid precipitation. If this is true, some of the regulatory burden could be shifted from the coal facilities to petroleum refineries.

d. Particulate Emissions from Delayed Cokes

The purpose of the study undertaken by Radian Corporation is to characterize particulate emissions from refinery coking operations by determining emission factors, size distribution, and chemical composition of particles from delayed cokers. In the study, NAAQS for particulates are being reviewed. According to API (5), the new standard may have some impact various refinery sources.

e. Removal of SO₂ from Stack Gases

The purpose of the research undertaken by Batelle Columbus Laboratories Stack Gas Coordination Center Program sponsored by API is to analyze and report on the many operational processes for for the removal of SO₂ from stack gases and to monitor new developments in the technology.

f. NOx Control Technology

API has sponsored the Batelle Laboratories in 1981 to further analyze and report on the various processes for control of NOx emissions from the petroleum industry and to monitor new technology developments. So far, no results have been published yet.

IX. CONCLUSION

From the study, it can be concluded that the pollutants emitted from the refineries in a descending scale of magnitude are HC, CO, SO_x, NO_x, TSP, and other odorous pollutants. Hydrocarbons, are often burned in flares, but those emitted from storage tanks, and other fugitive emissions such as benzene and toluene are hazardous.

Applicable technology for controlling pollutants were discussed in Chapter V. The most common and cost effective control technologies for the pollutants are briefly stated below.

- a. Hydrocarbons. Hydrocarbons can best be controlled by having a good maintenance of the flare burner system. For hydrocarbons such as VOCs, floating tanks are often employed.

- b. Sulfur oxides. The best measure for sulfur oxides is substituting fuel with lower sulfur content fuel. Desulfurization processes are very expensive for treatment of high sulfur residual stock. Other

methods often employed are scrubbing the stack gases prior to discharge to the atmosphere.

- c. Nitrogen oxides. Combustion modification techniques are good cost effective measures used for controlling nitrogen oxides. Such methods include the use of low excess air combustion, flue gas recirculation, and staged combustion.
- d. Particulates. The most common method employed is the Electrostatic precipitator. Electrostatic precipitators and Bag houses can produce satisfactory results if properly designed and maintained.
- e. Carbon monoxide. The use of incinerator-waste heat boiler has been demonstrated as the best control technology for carbon monoxide. An alternative method often used is the Fluid Catalytic Cracker with improved catalysts.

Some of the guidelines set for refineries or air quality as a whole are ambiguous and can lead to unnecessary investigations. Proper and clear cut set of guidelines stating exact investigations together with the methodology should be outlined by EPA. For example, the air quality part of the EIS fails to suggest and outline

the types of diffusion models ought to be used for monitoring purposes. Although EPA has published guideline document for the models, no exact reference to such documents is stated in the EIS. Misinterpretation of the rules can lead to excessive costs.

The procedures and approaches used in EIS preparation in Malaysia and U.S. are significantly different. In Malaysia, preparation of EIS for an oil refinery is not mandatory. A good set of guidelines and standards such as NAAQS, NSPS, and NESHAPS should be integrated into the existing standards there. Good monitoring and modeling practices, too, are essentially for continuous monitoring programs around the refineries.

The application of computers in refineries has increased over the years. This is important as the concentration records of the pollutants can be maintained. This is extremely necessary with the ever increasing stringent measures. Use of Personal computers have greatly eased modeling and monitoring practices.

More changes in NAAQS, NSPS, and NESHAPS are expected in the near future. This will further add more strict provisions into the existing 1977 CAAA. At present, 1977 CAAA does not contain any provisions explicitly dealing

with acid rain. With the tremendous amount of research being carried out, such provisions can be expected in the near future. If so, refineries will be affected as the NOx control technology is still inefficient.

Air pollution control technology for refineries needs to be improved to achieve higher efficiencies while becoming more cost effective. Control methods exist, but they are often too expensive to allow small refineries to be economically competitive. Larger refineries utilize the equipment in a more cost effective manner.

The U.S air quality regulations are very stringent as compared to other countries. Standards and regulations are continually assessed and they periodically become more stringent. Due to this, environmental cost of maintaining air quality around the refineries increases steadily with time.

Due to the more stringent environmental regulations and emission standards, and other cost factors, some U.S. refining companies are:

- a. Shifting from U.S. operation to third world countries where regulations are less stringent and other costs are lower.

- b. Closing down uncompetitive smaller refineries. This will eventually result in more expensive importation of refined oil.
- c. More expensive air quality control costs at the refineries.
- d. Finding that U.S. expansion and construction of refineries is not possible on a timely basis due to permit timing constraints.

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APPENDICES

Appendix A

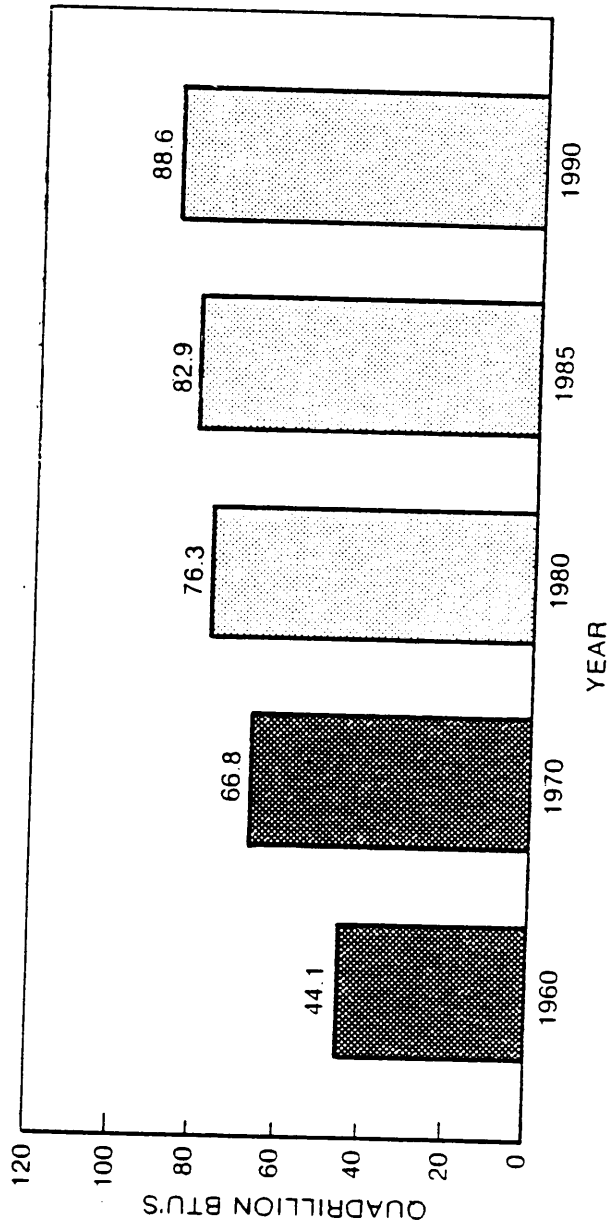


Figure 1. U.S. Energy Consumption Growth Pattern (37).

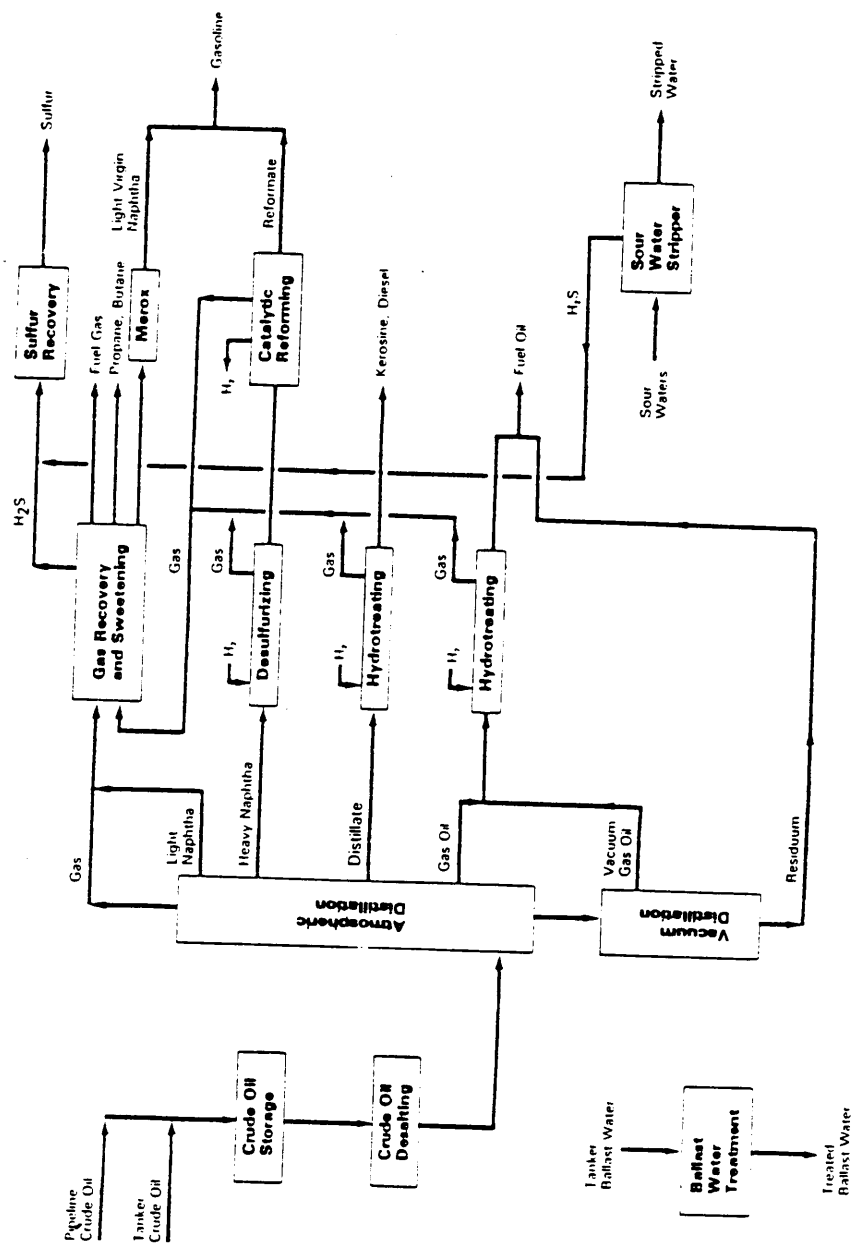


Figure 2. A Flow Chart of a Topping Refinery (87).

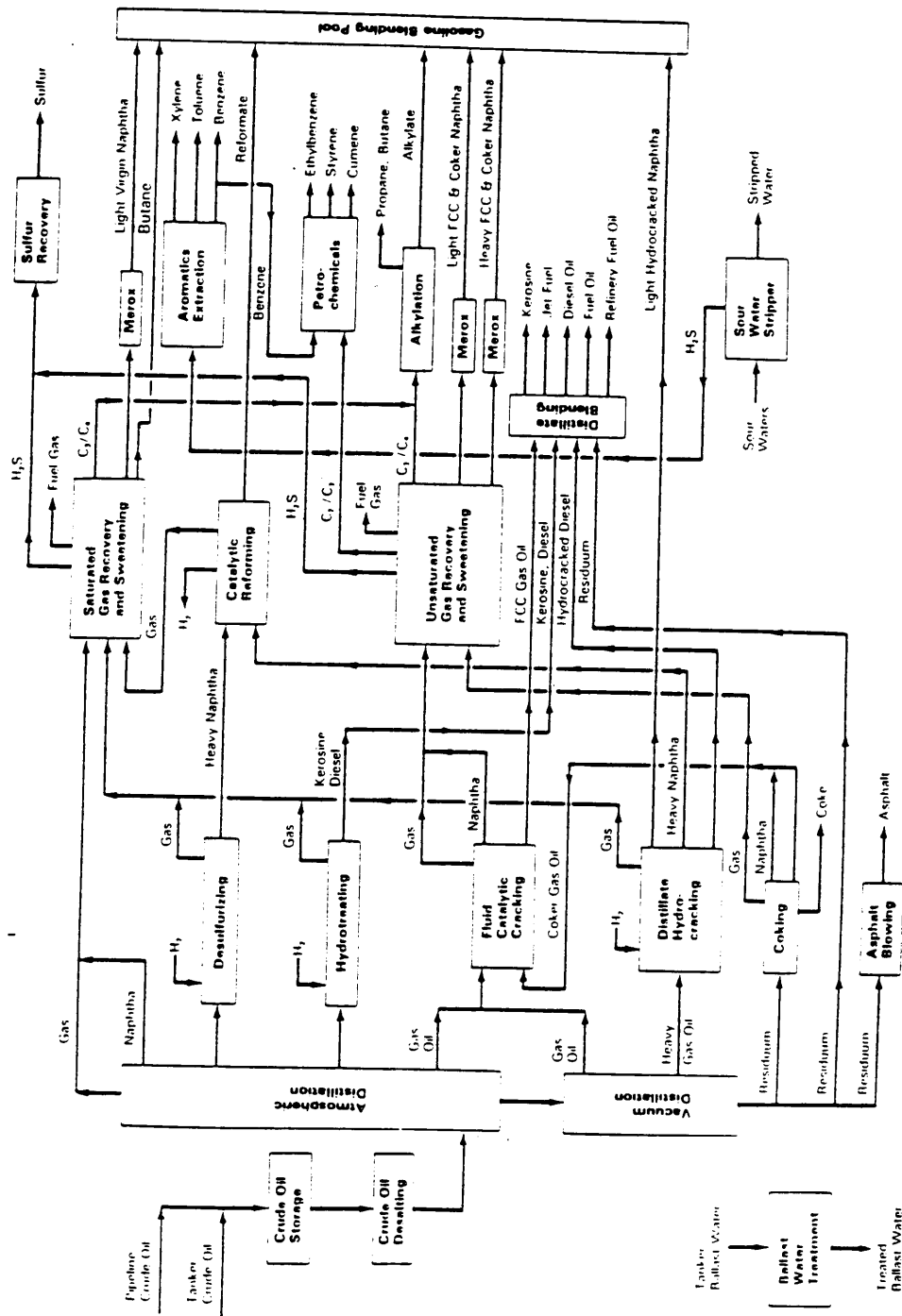


Figure 3. A Flow Chart of a Cracking Refinery (87).

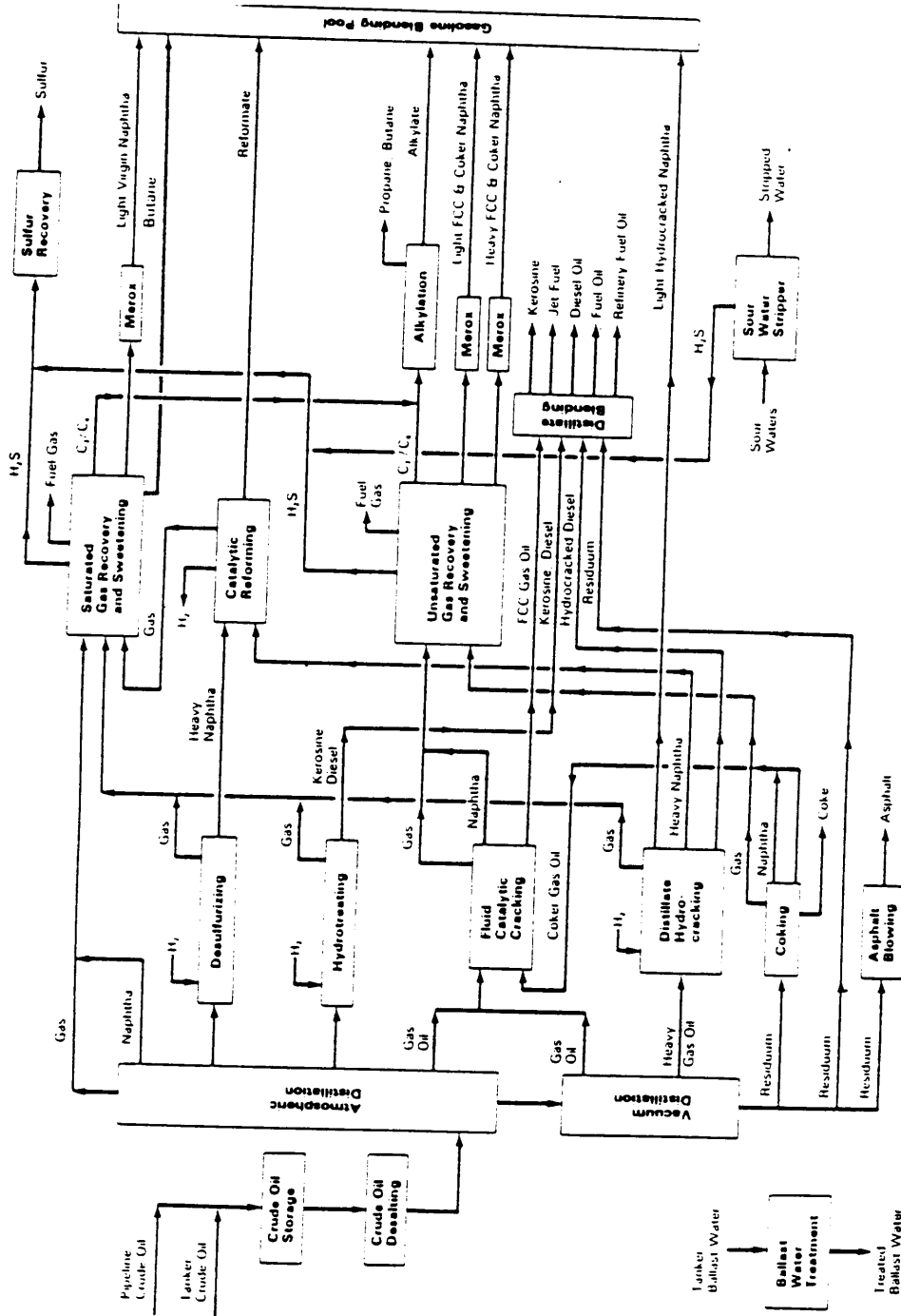


Figure 4. A Flow Chart of a Petrochemical Refinery (87).

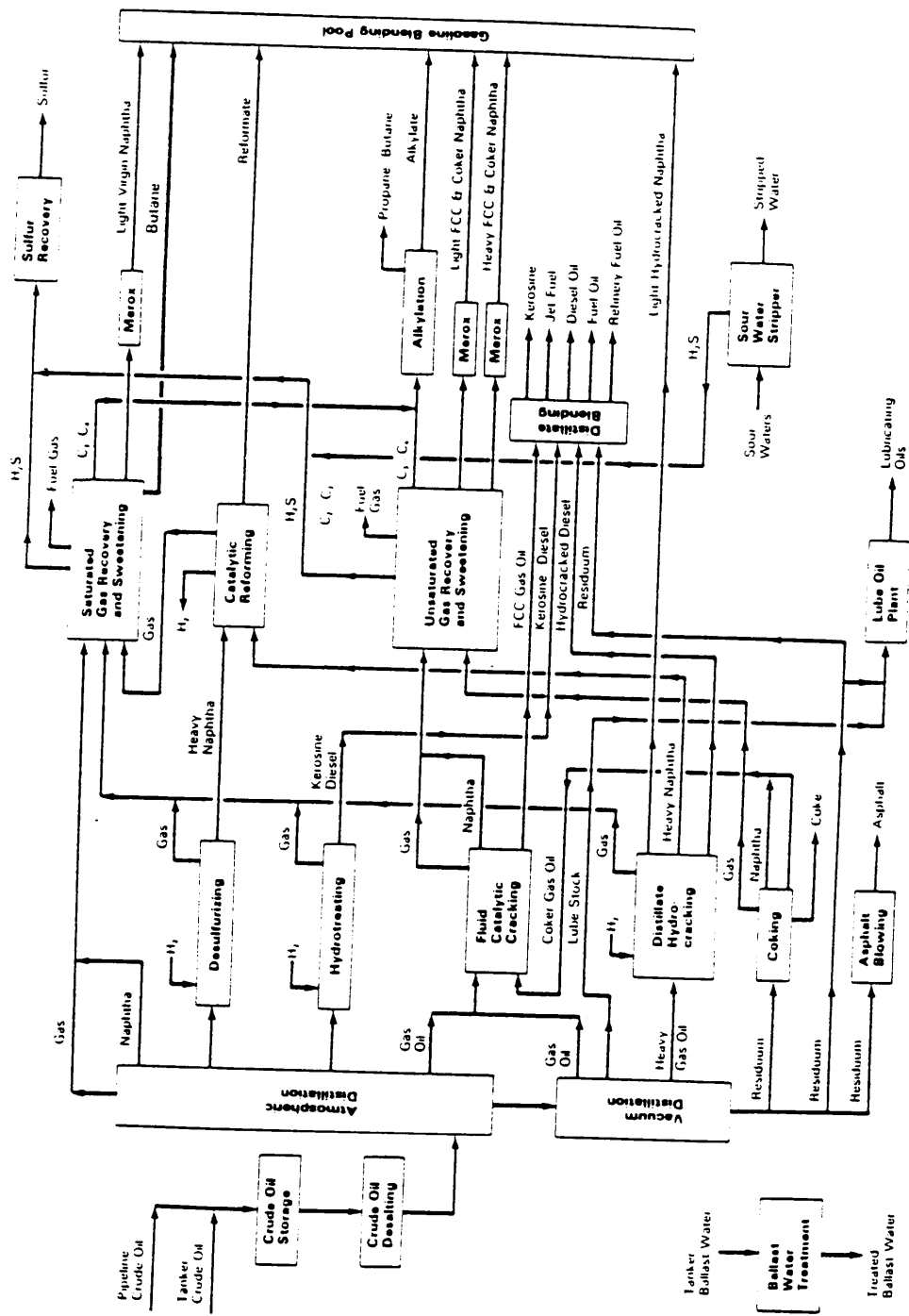


Figure 5. A Flow Chart of a Lube Oil Refinery (87).

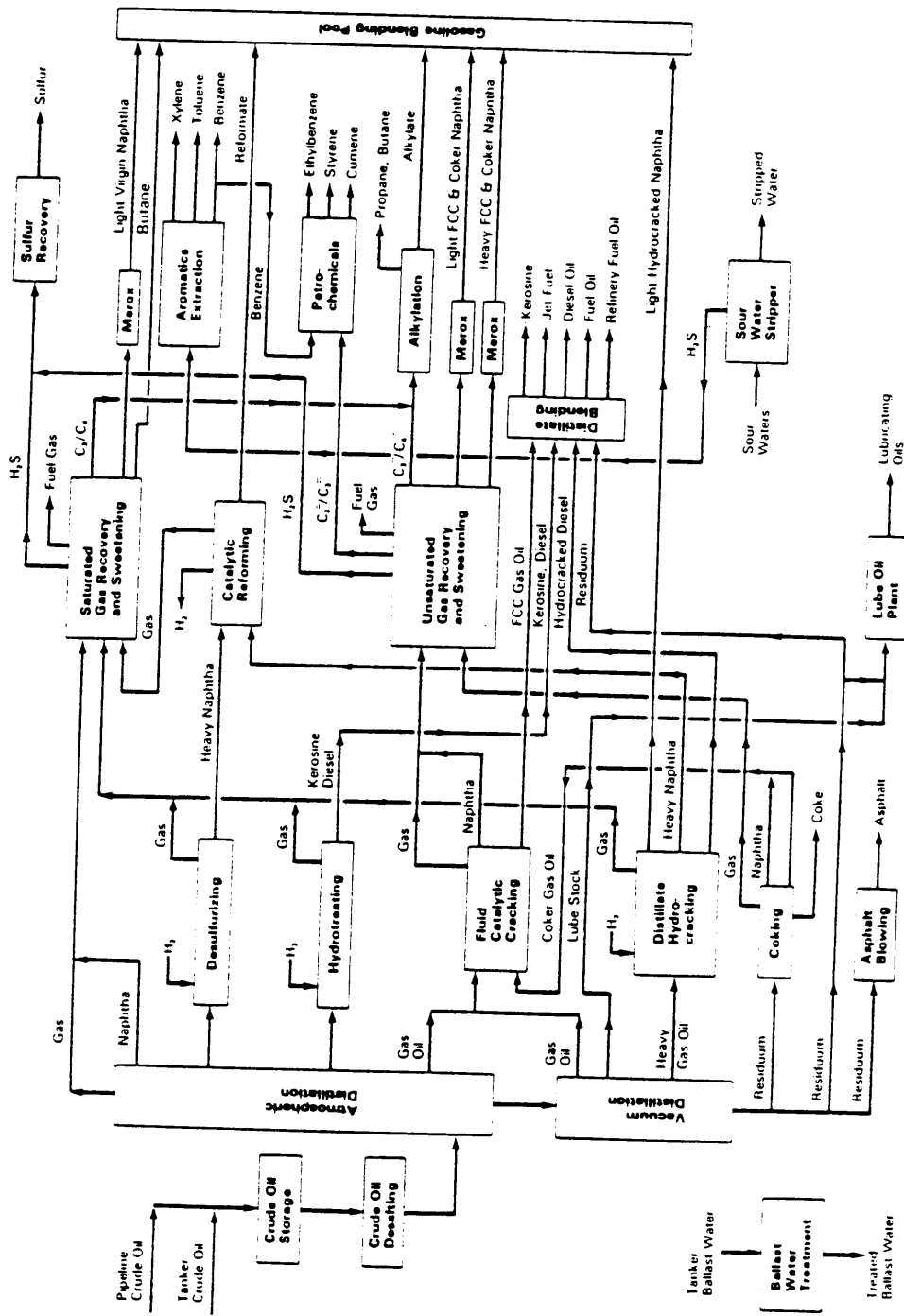
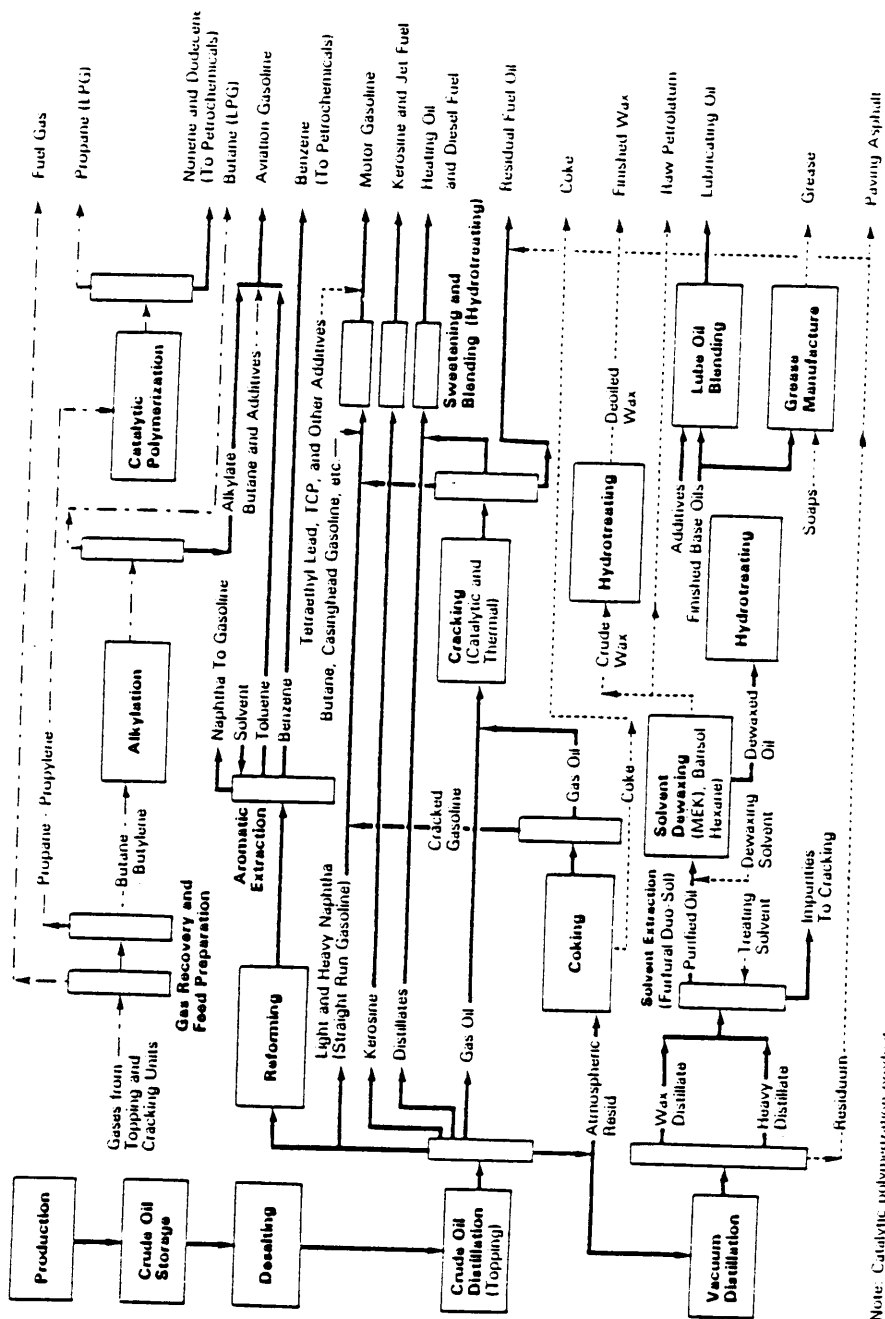


Figure 6. A Flow Chart of an Integrated Refinery (87).



Note: Catalytic polymerization product and alkylate may also be incorporated into gasoline blend stocks.

Figure 7. A Simplified Flow Chart of a Complex Refinery (87).

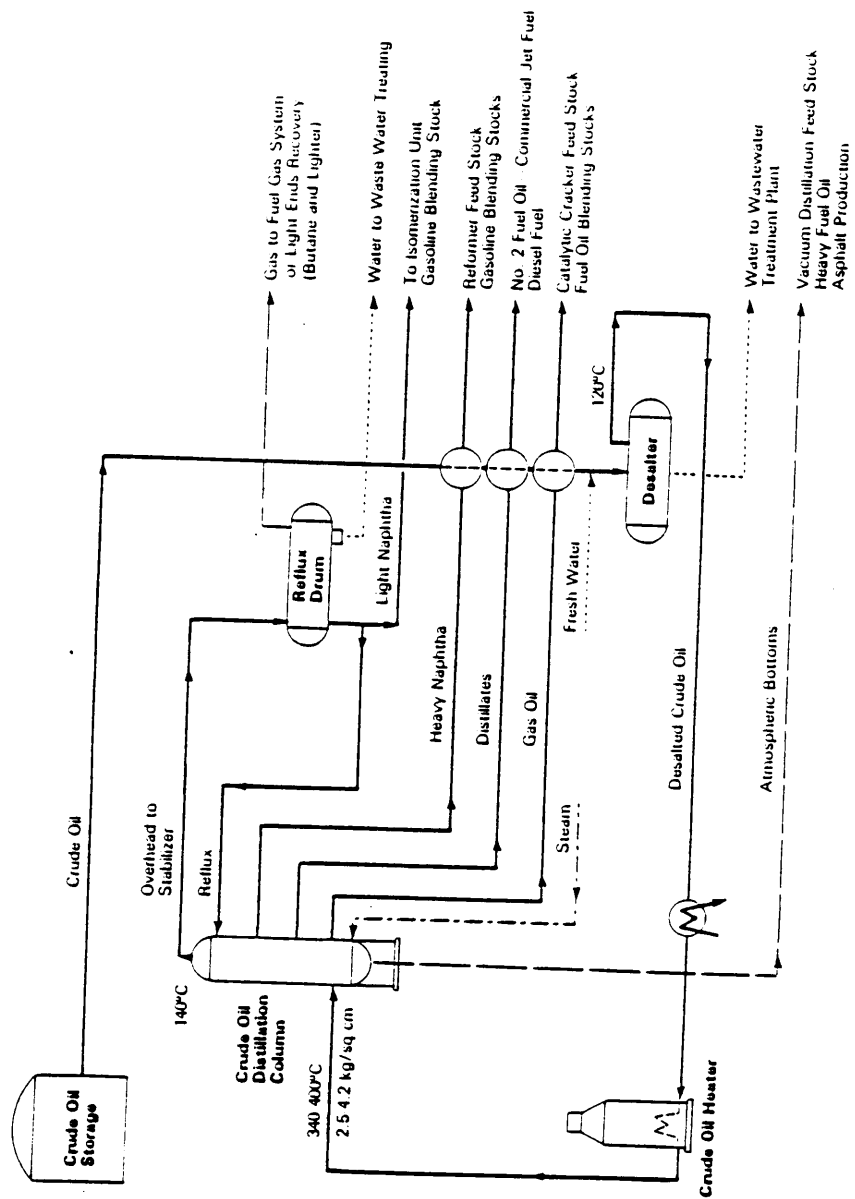


Figure 8. Crude Oil Distillation Unit (87).

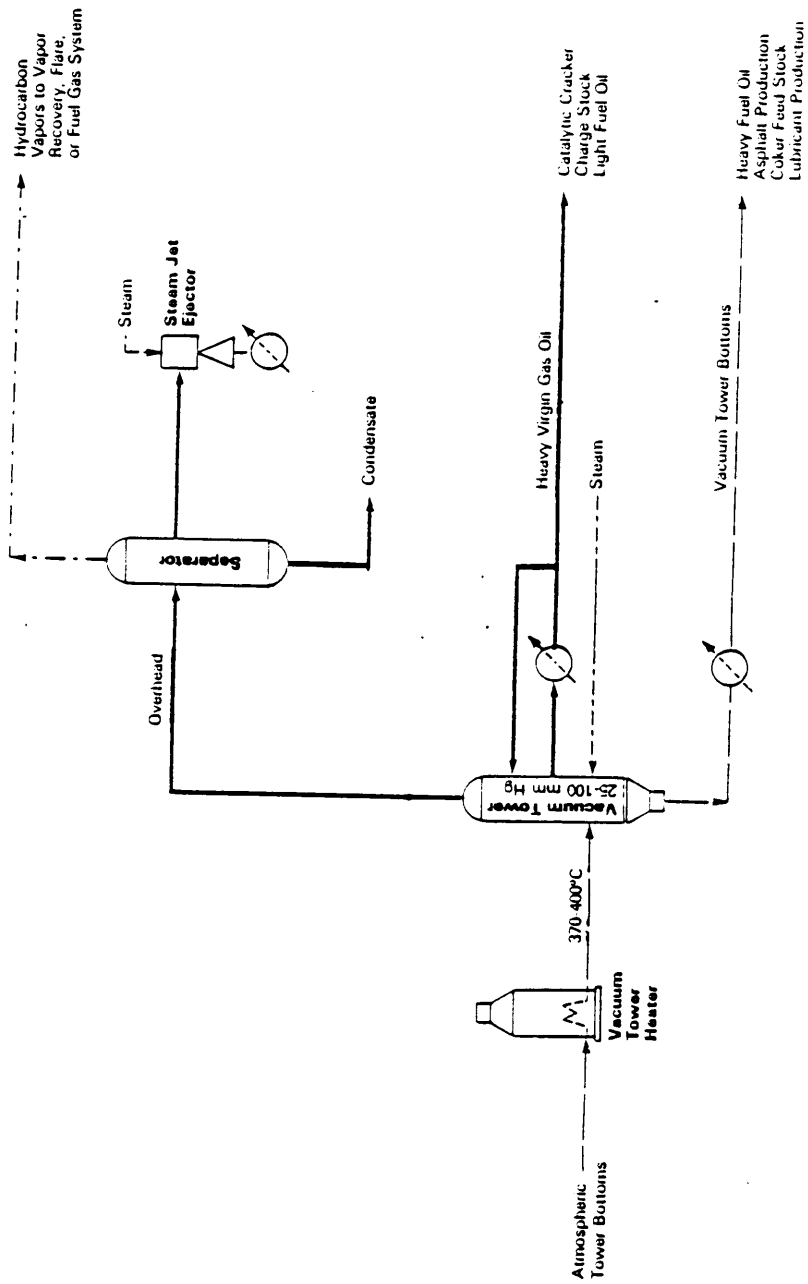


Figure 9. Vacuum Distillation Unit (87).

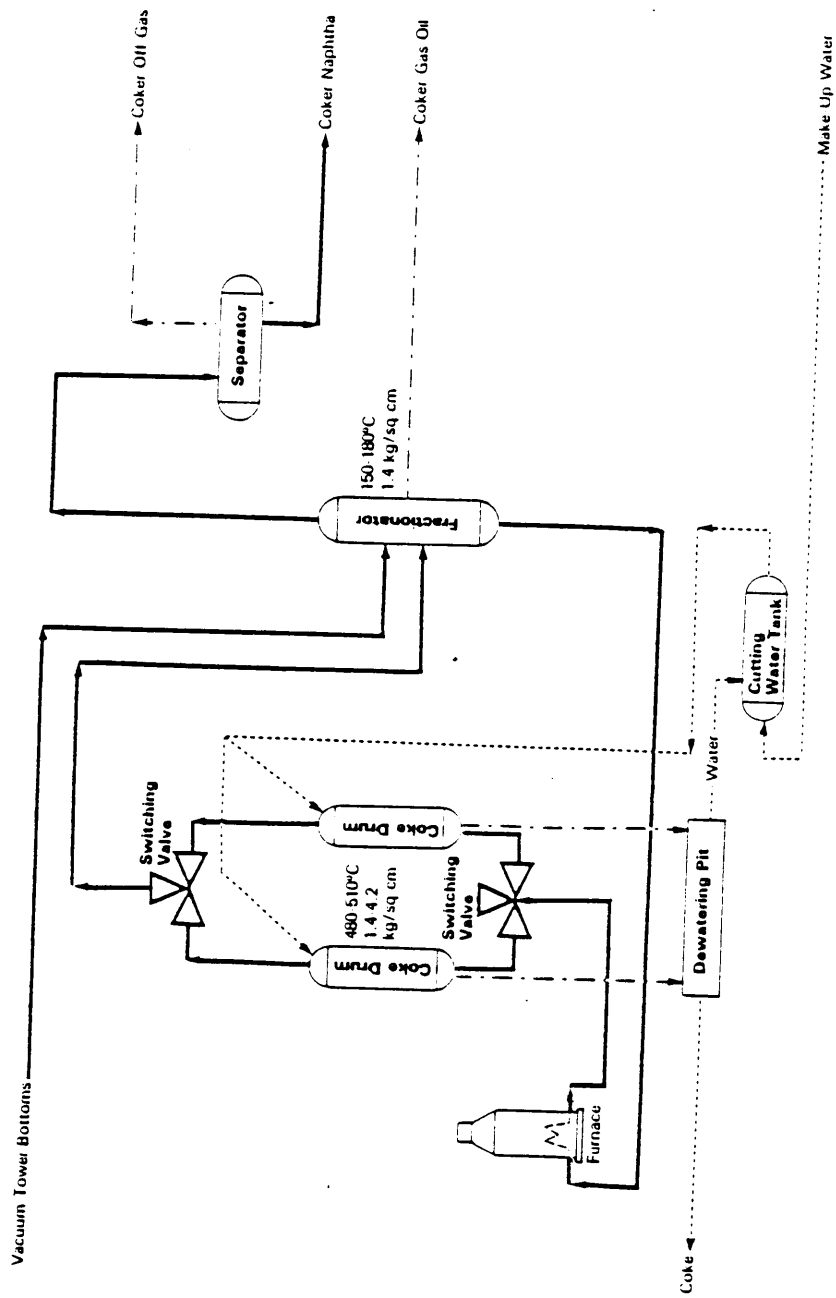


Figure 10. Delayed Coking Unit (87).

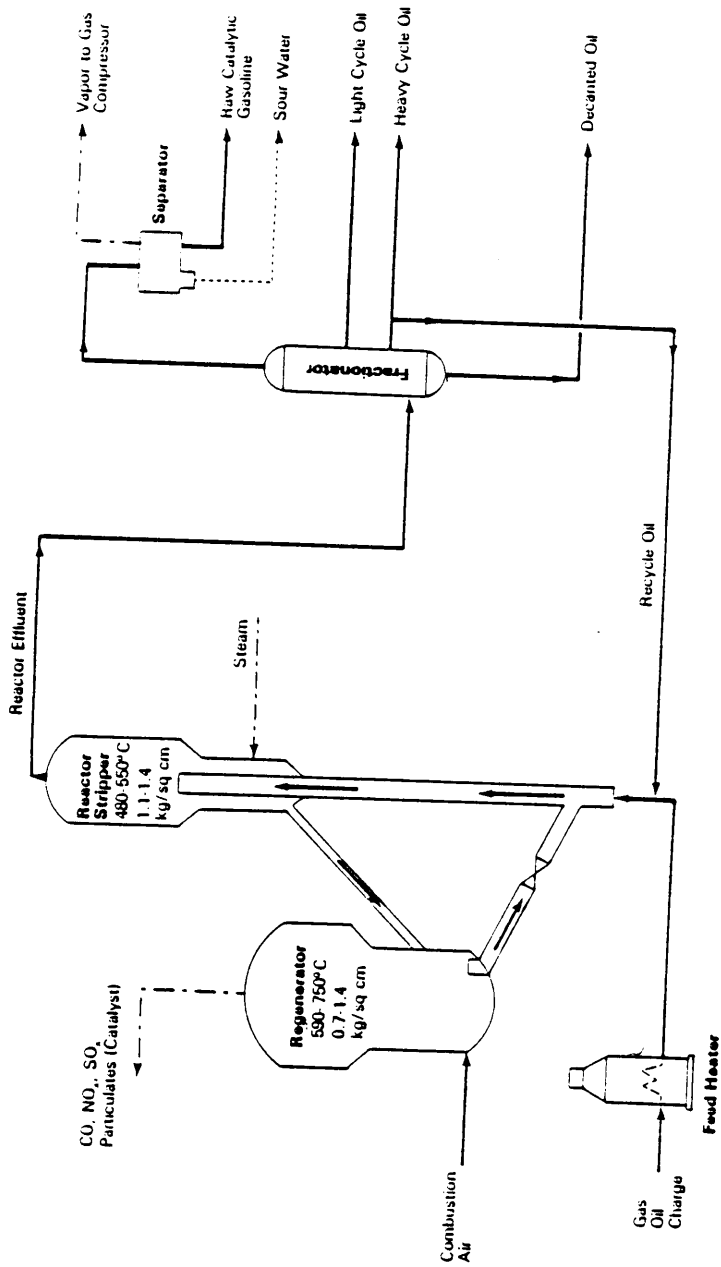


Figure 11. Fluid Catalytic Cracking Unit (87).

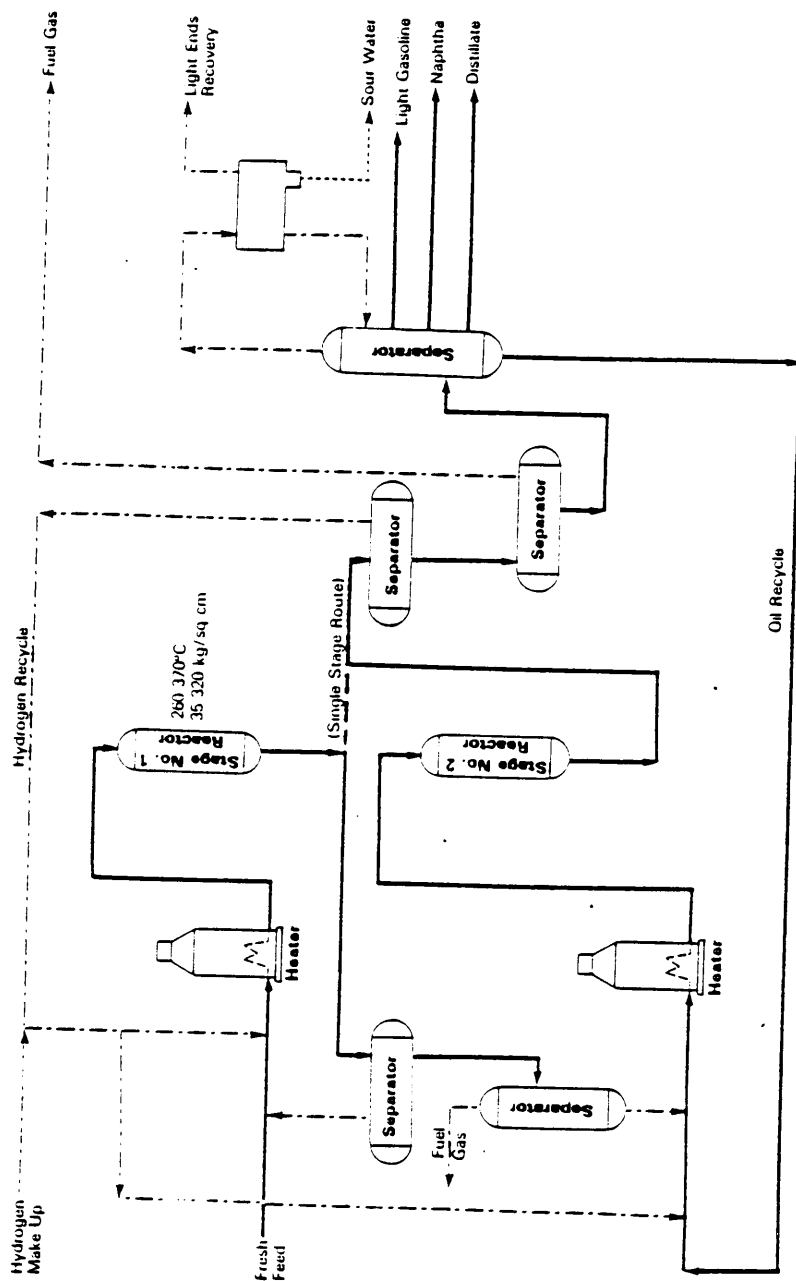


Figure 12. Typical Two-Stage Hydrocracker Unit (87).

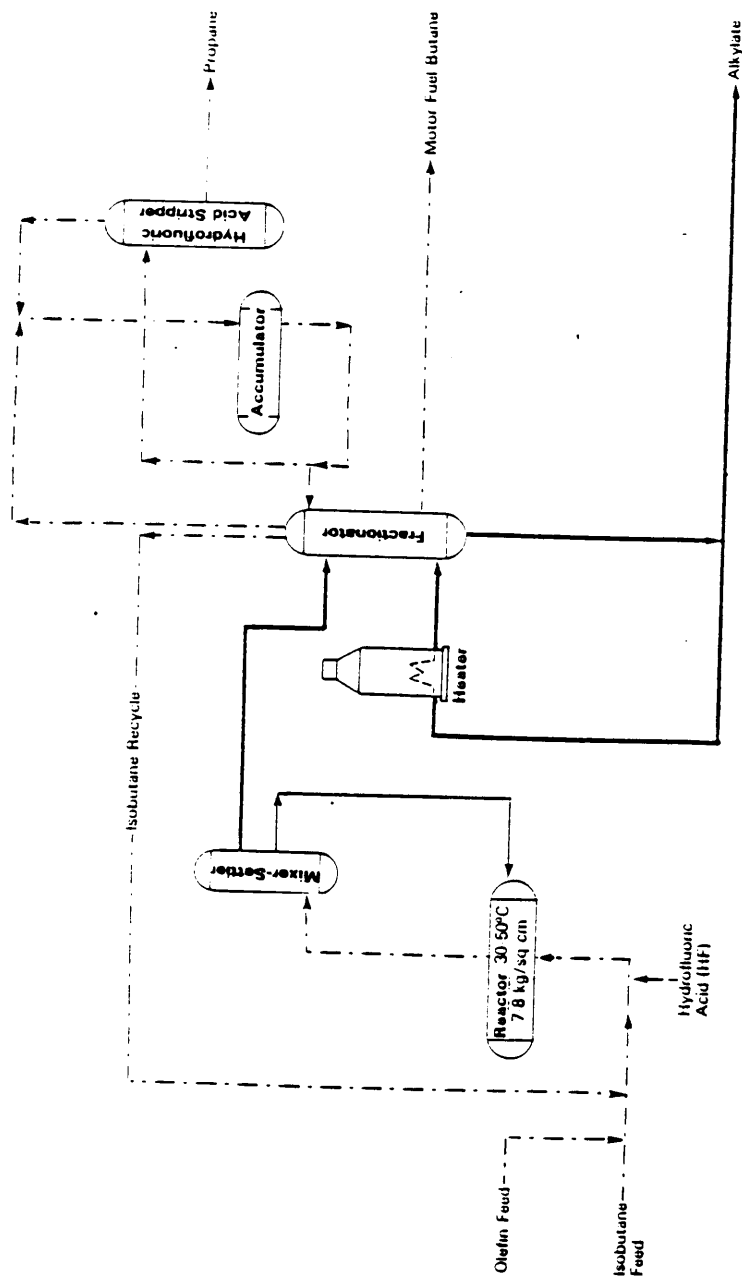


Figure 13. Hydrofluoric Acid Alkylation Unit (87).

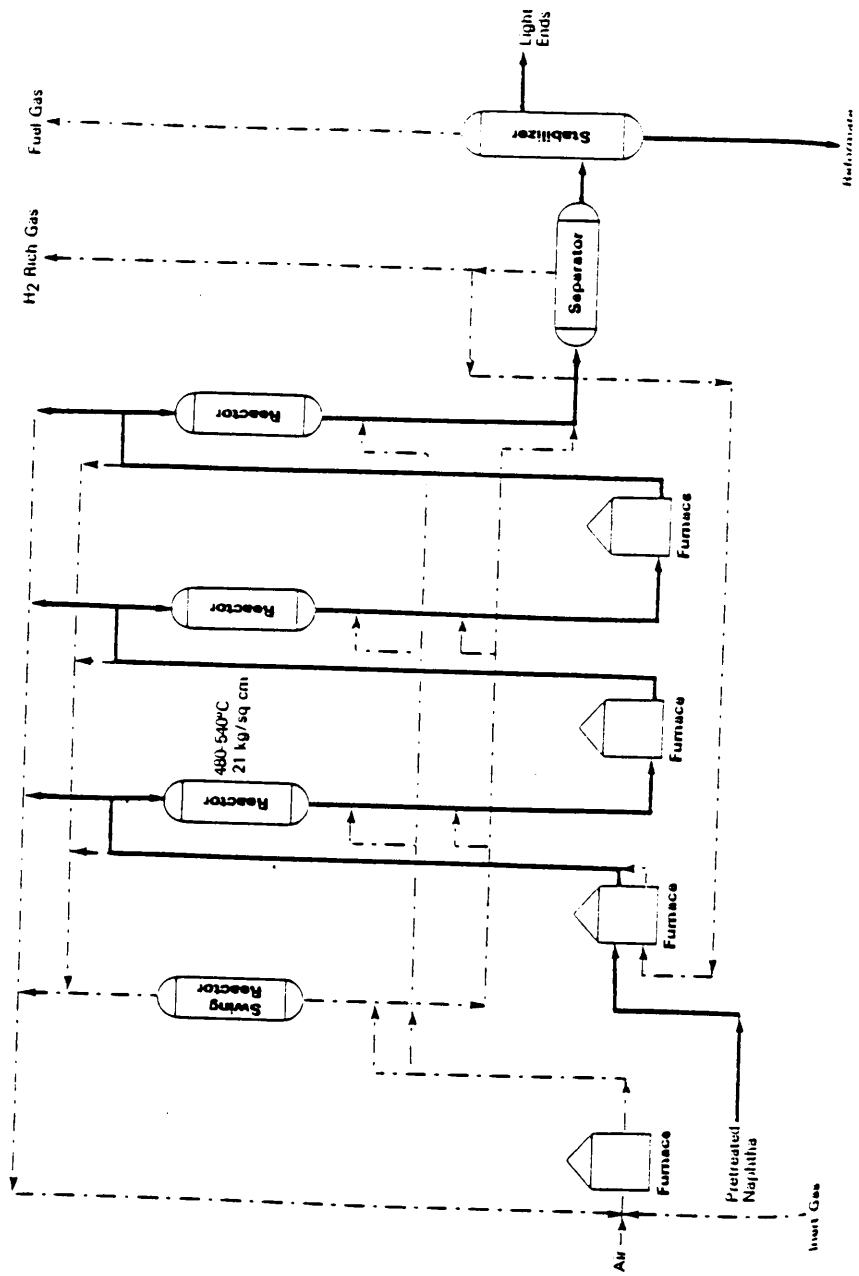


Figure 14. Catalytic Reforming Unit (87).

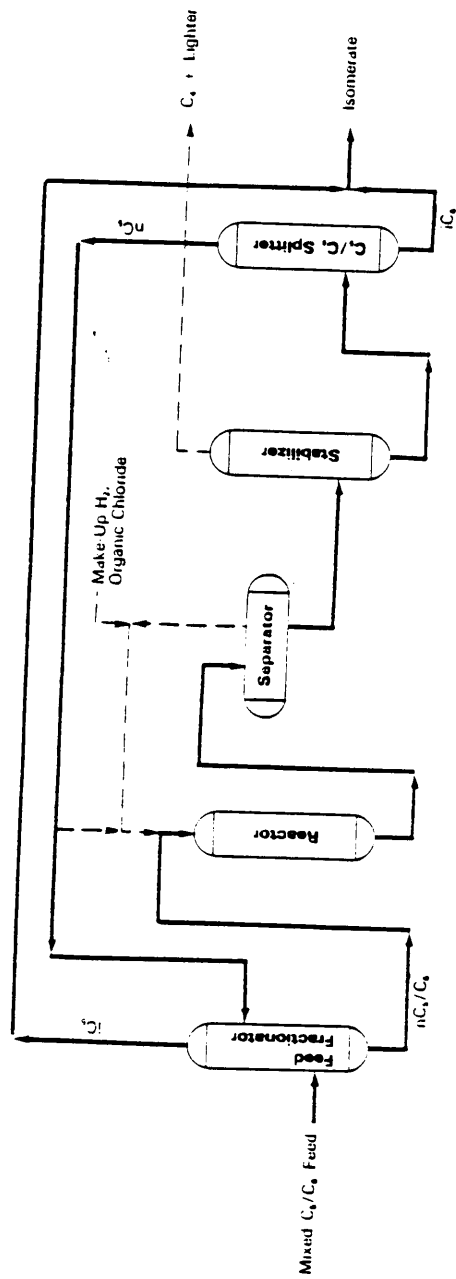


Figure 15. Pentane/Hexane (C₅/C₆) Isomerization Unit (87).

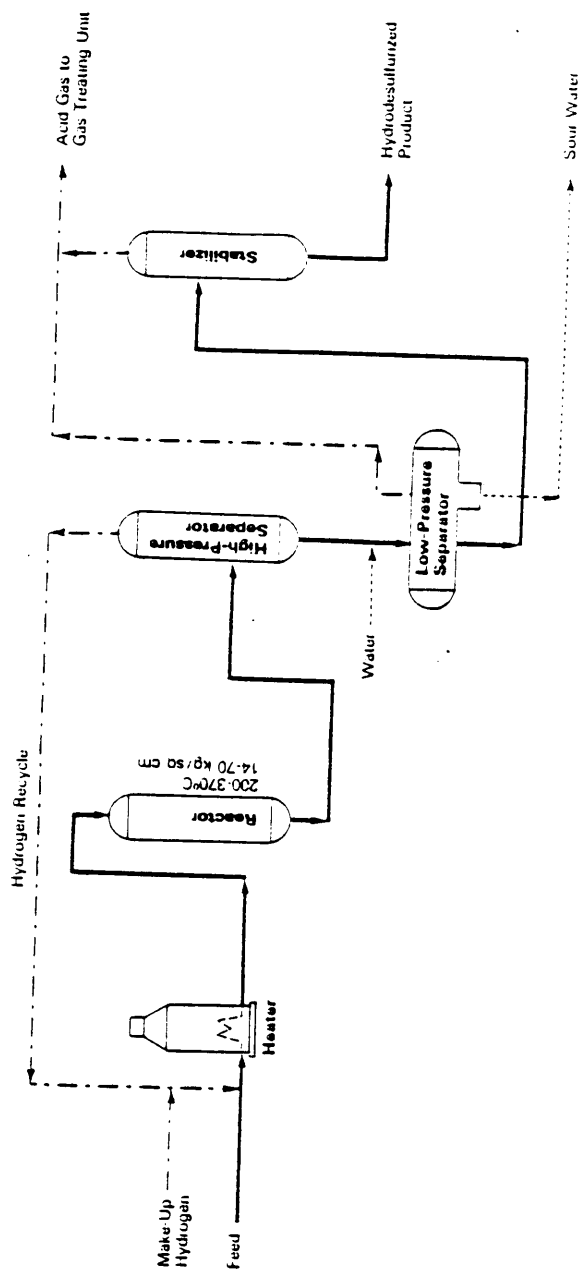


Figure 16. Hydrotreating Unit (87).

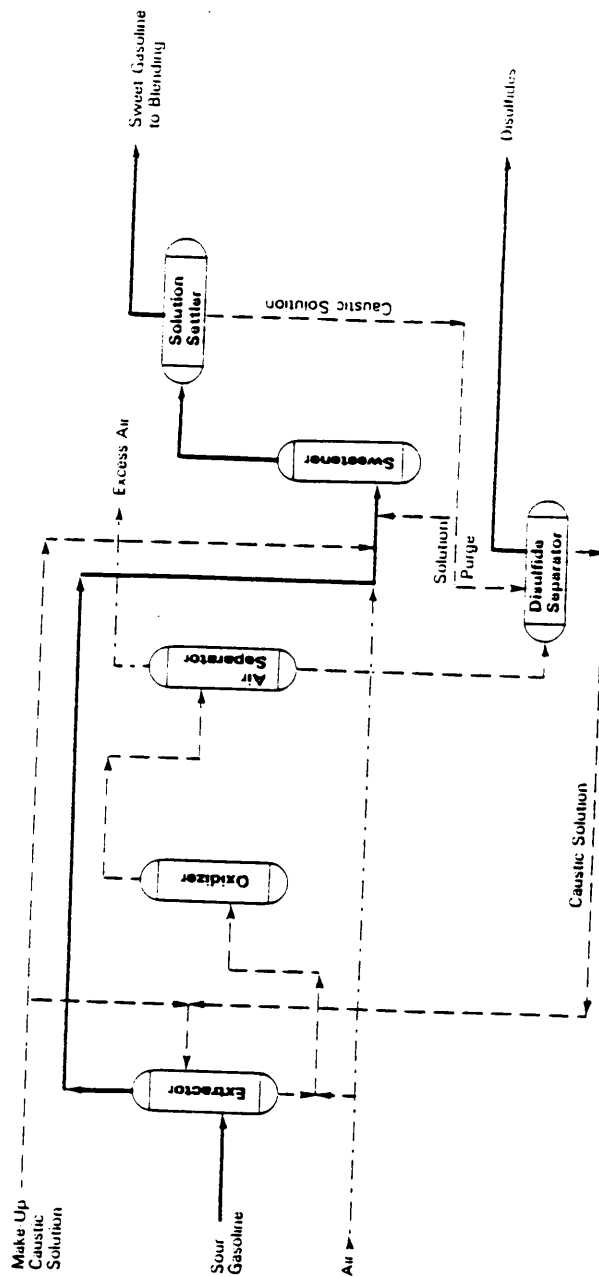


Figure 17. Gasoline Sweetening Unit (87).

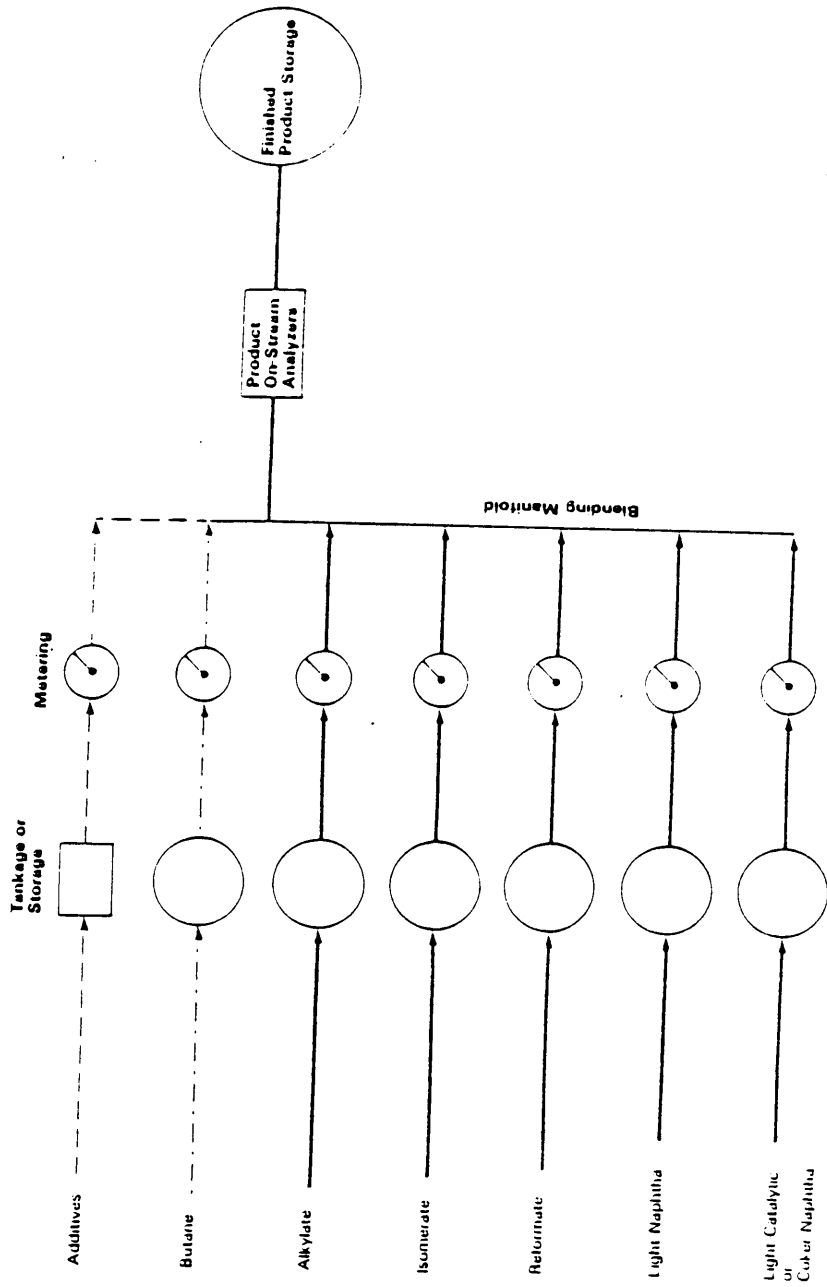


Figure 18. Gasoline In-Line Blending System (87).

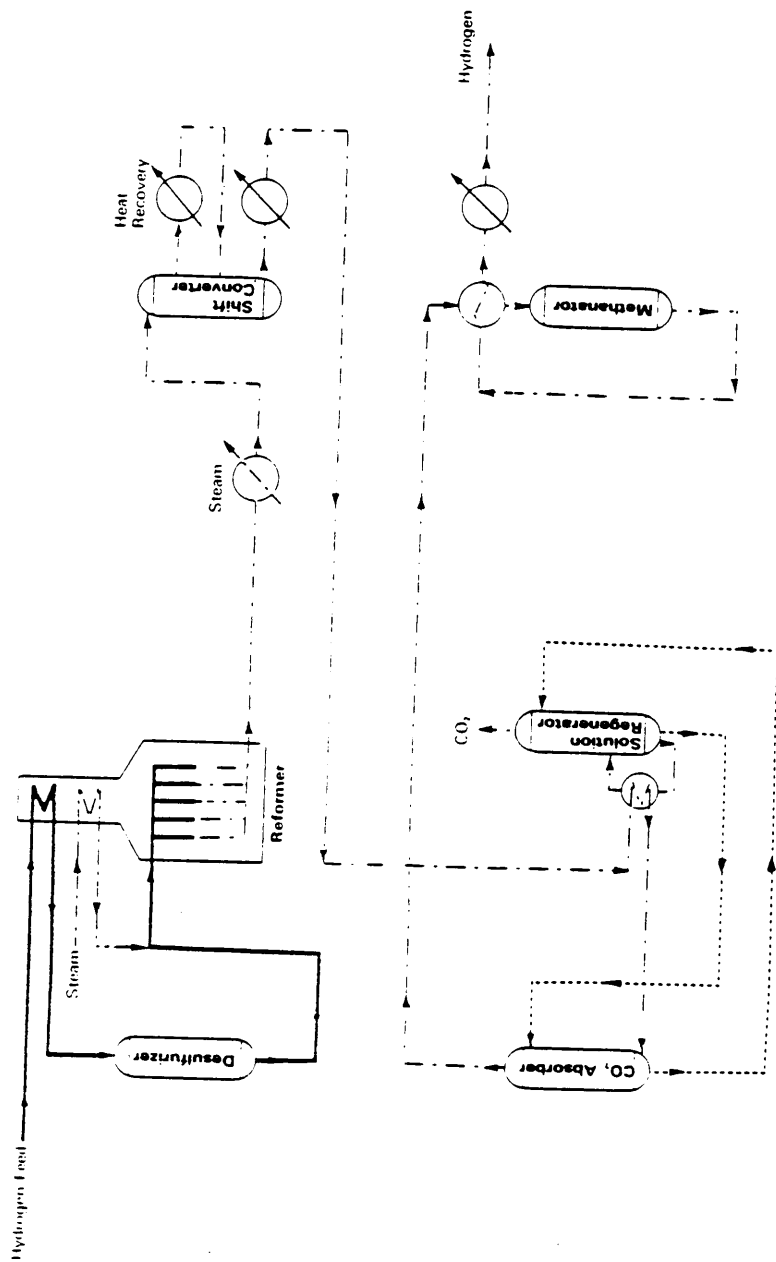


Figure 19. Hydrogen Production Unit (Steam-Reforming) (87).

California	New Jersey
Connecticut	New York
Hawaii	North Carolina
Indiana	South Dakota
Maryland	Texas
Massachusetts	Utah
Michigan	Virginia
Minnesota	Washington
Montana	Wisconsin

Figure 20. States with EIS Requirements (73).

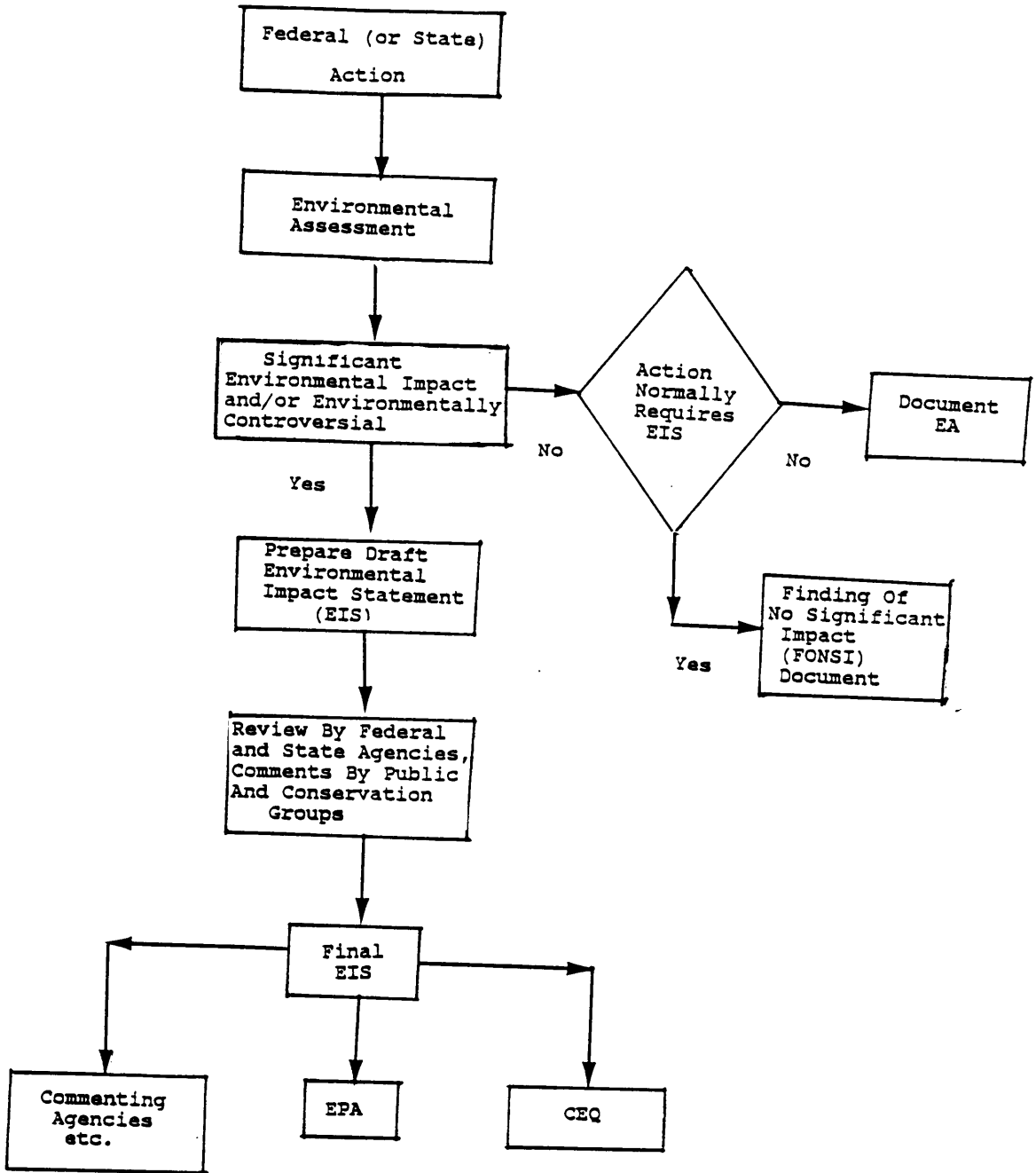


Figure 21. EIA/EIS and FONSI Relationship in U.S. (86).

Description of the Project

- A. Identify the project sponsor
- B. Explain the purpose of the proposed project which includes description of the products and services being provided and the extent of benefits being realized by the owner, the community within which the project is located, and the area being served.
- C. Locate the project in a regional, municipal, and neighborhood setting.
- D. Describe the project design and operational features :
 1. Include a site plan of the project.
 2. Describe the construction phase:
 - a. Identify development schedule and construction phasing.
 - b. Workforce required.
 - c. Construction traffic.
 - d. Site preparation, including clearing, excavating, filling, and cutting, burning and blasting.
 - e. Precautions taken (noise control, dust control, erosion, and sedimentation control, temporary sanitation.
 - f. Materials required (general).
 3. Describe the operational phase :
 - a. Output and capacity.
 - b. Work force.
 - c. Discharges and emissions (Both point sources and non point souces).
 - d. Traffic and access.
 - e. Use of resources.
- E. Include a listing of a listing of all licences, permits and certifications necessary for approval of the project - include status of each.

Figure 22. Guidelines for the Preparation of an EIS (88).

Description of the Air Section

1. Provide all data necessary to permit the State to perform diffusion modeling on the effect of the proposed action on the air quality of the area surrounding the project.

All the aspects of the project should be given consideration in terms of possible receptor sites of air pollutants directly or indirectly generated from the proposed project. Include a discussion of the cumulative aspects.

Discuss ambient air quality data present and projected so that direct comparisons may be made between present air quality, projected, and air quality standards.

2. Discuss if the project will meet applicable emission standards and regulations contained in the State implementation plan.
3. Discuss precautions taken to prevent odor problems from becoming a public nuisance and/ or being in violation of the State Air Pollution Control Act.
4. Discuss long-term considerations given to the relationship between nearby residences and businesses, the project and prevailing wind patterns on the seasonal and annual air quality in the area (give meteorological patterns, macro and micro where possible).
5. Discuss precautions taken to prevent the airborne transmission of pathogenic organisms, if applicable.
6. Discuss the possible influence of the proposed action on immediate area local receptors.
7. Base the evaluation of air quality on complete diffusion climatology providing adequate references.

Figure 23. Guidelines for Air Section of an EIS (88).

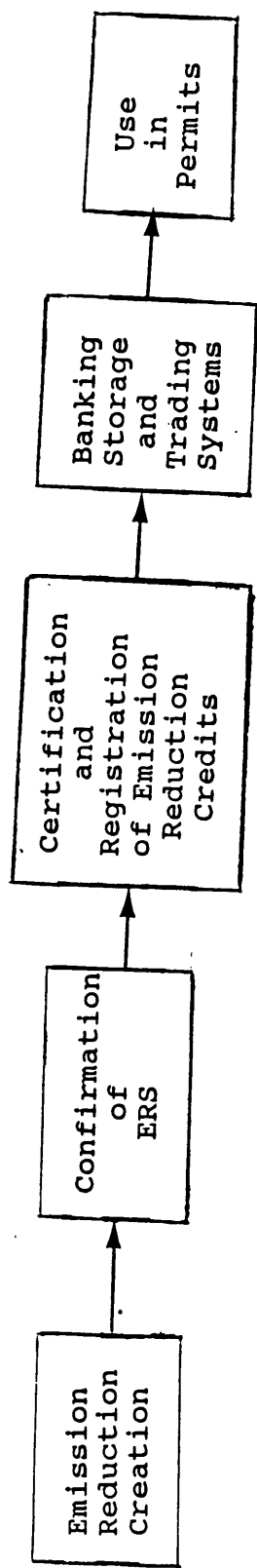


Figure 24. Overview of Components of Banking and Trading Systems (47).

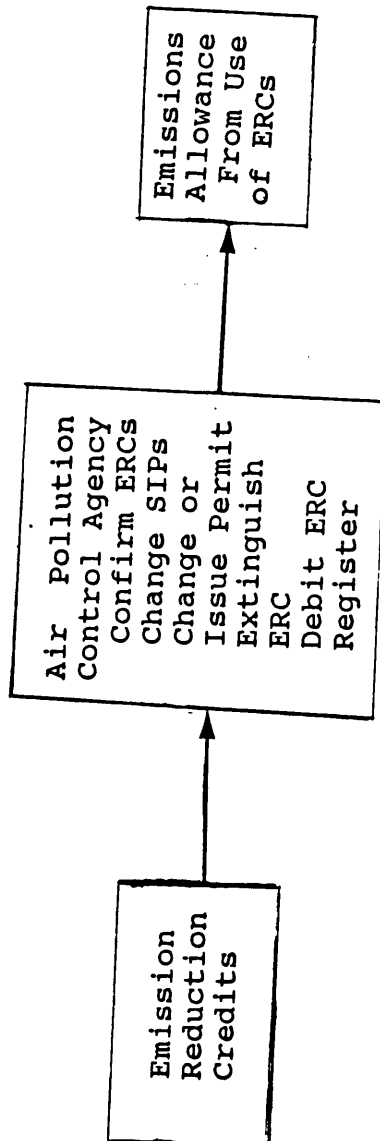


Figure 25. Conversion of Emission Reduction Credits Back Into Allowable Emissions (47).

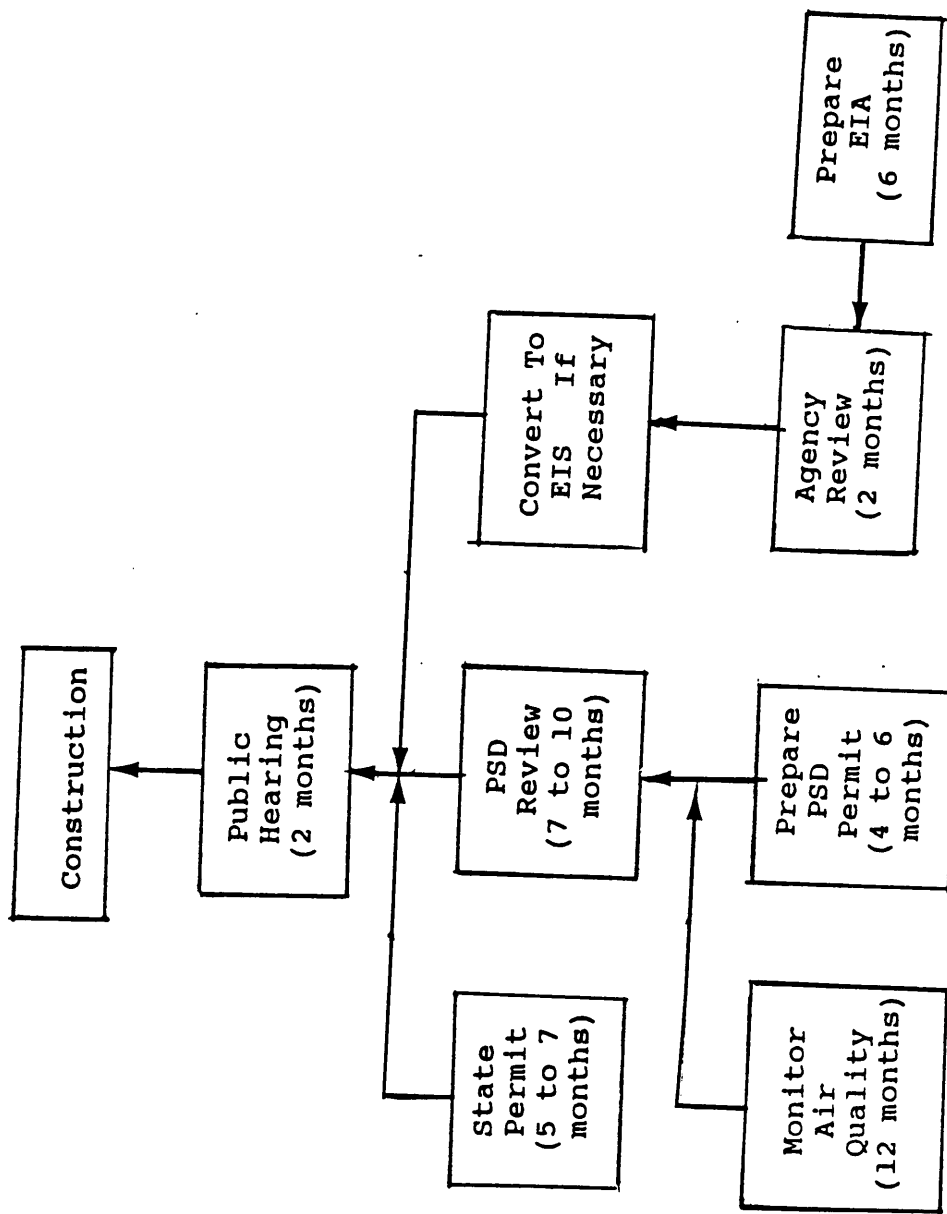


Figure 26. Refinery Construction and Permit Timing (73)*.

* With revisions.

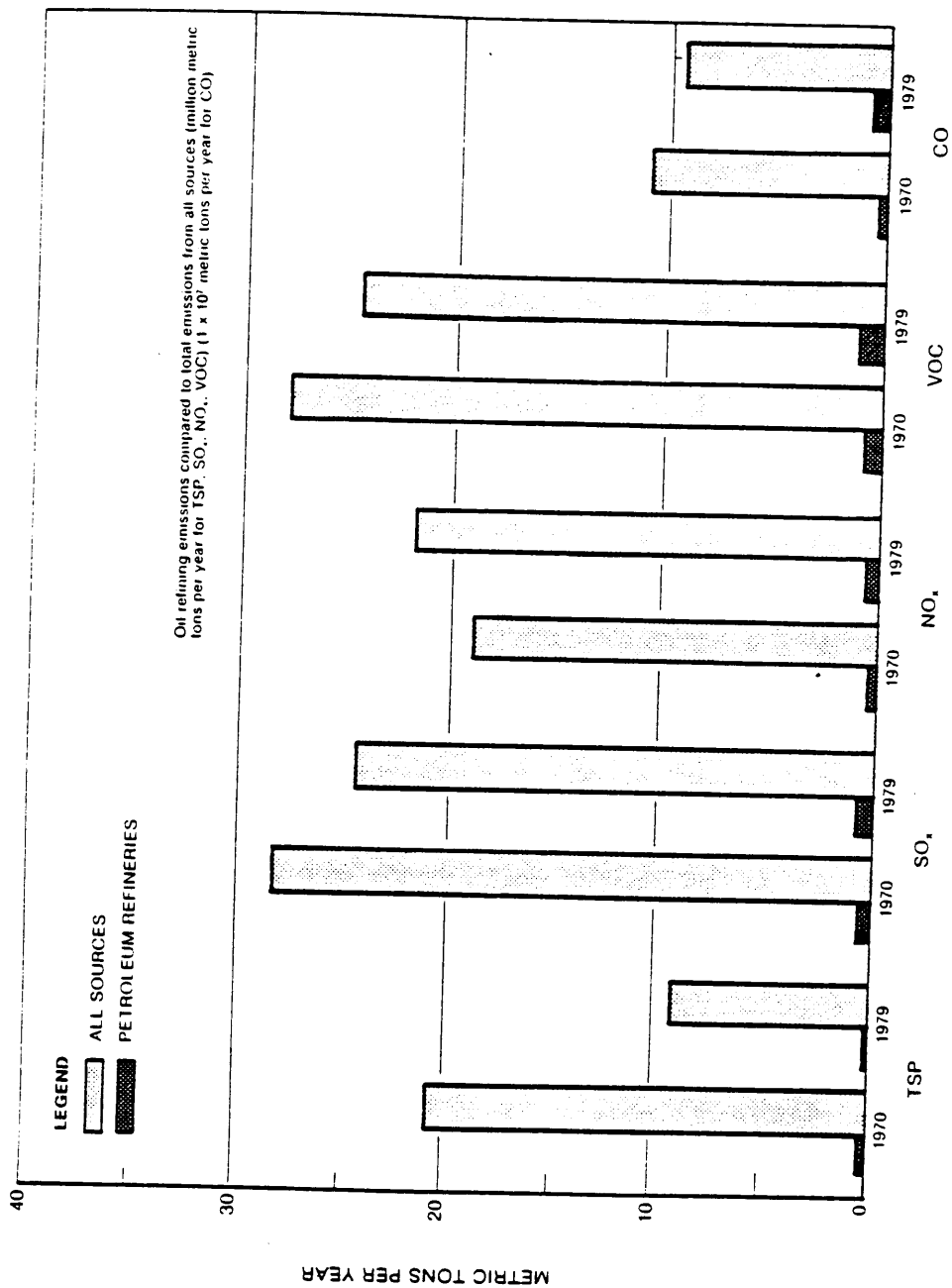


Figure 27. Emission Comparison Estimates in 1970 and 1979 (73).

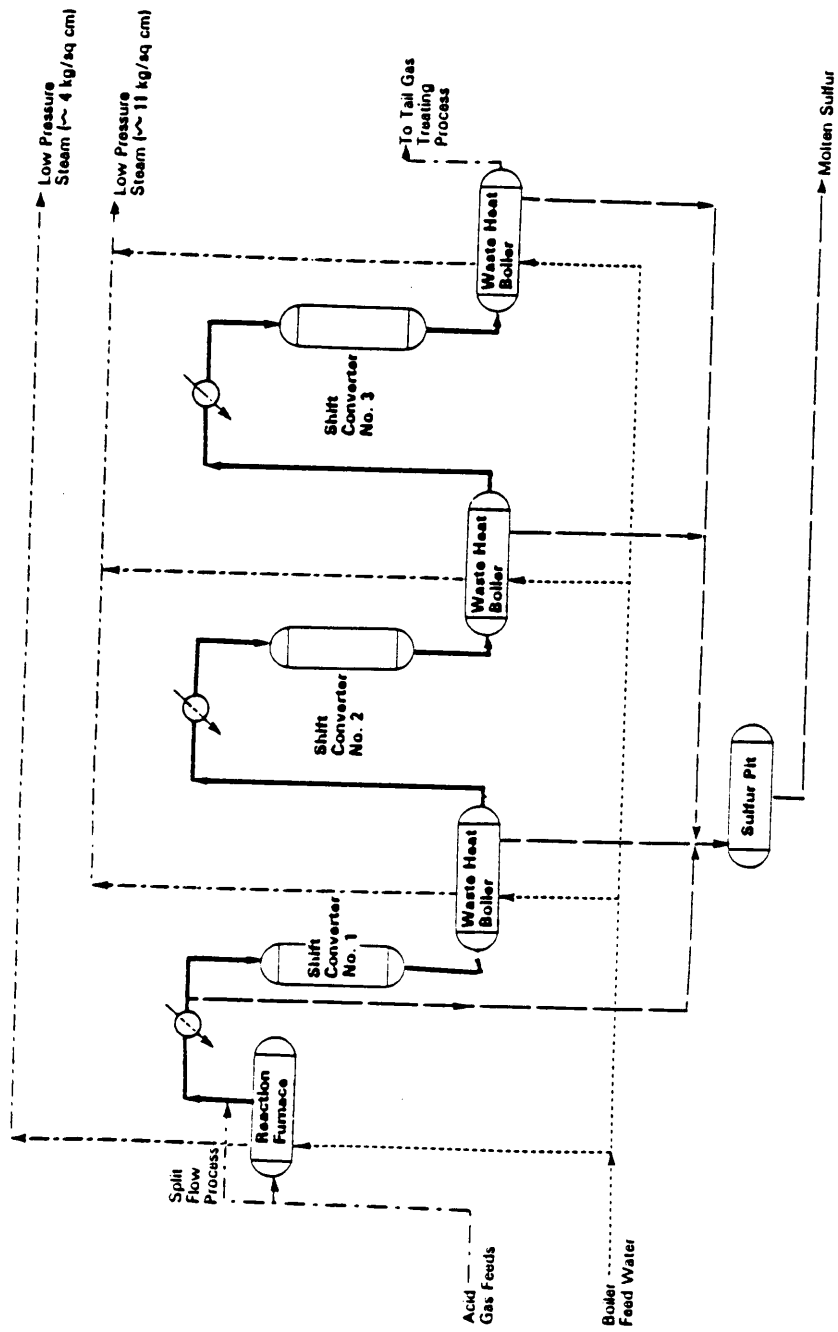


Figure 28. Claus Sulfur Recovery Unit (87).

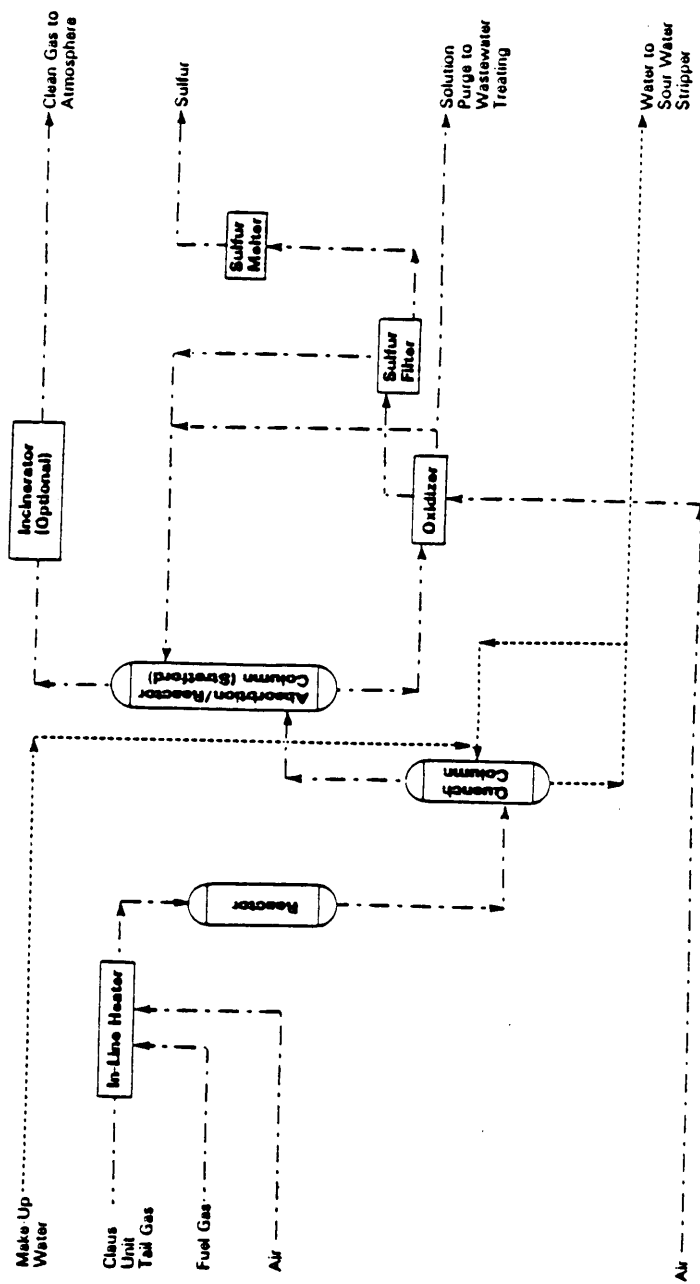


Figure 29. Beavon-Stretford Tail Gas Treating Unit (87).

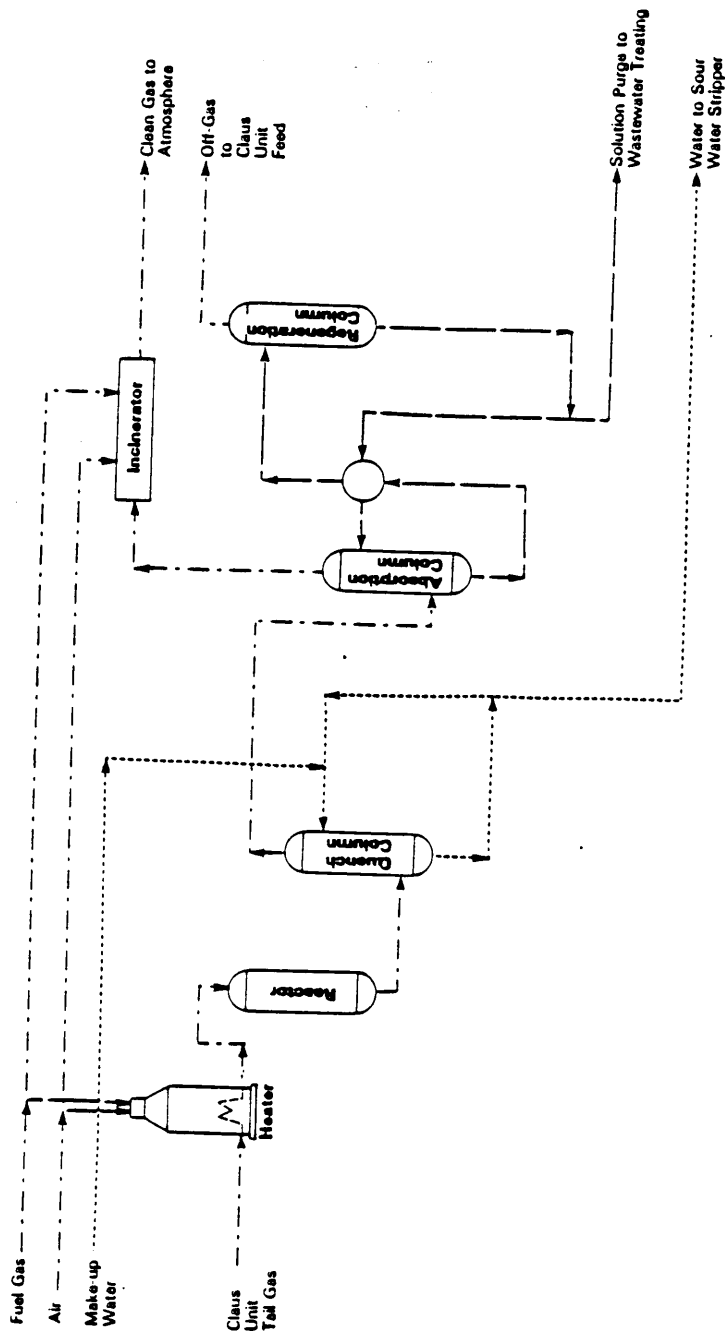


Figure 30. SCOT Tail Gas Treating Unit (88).

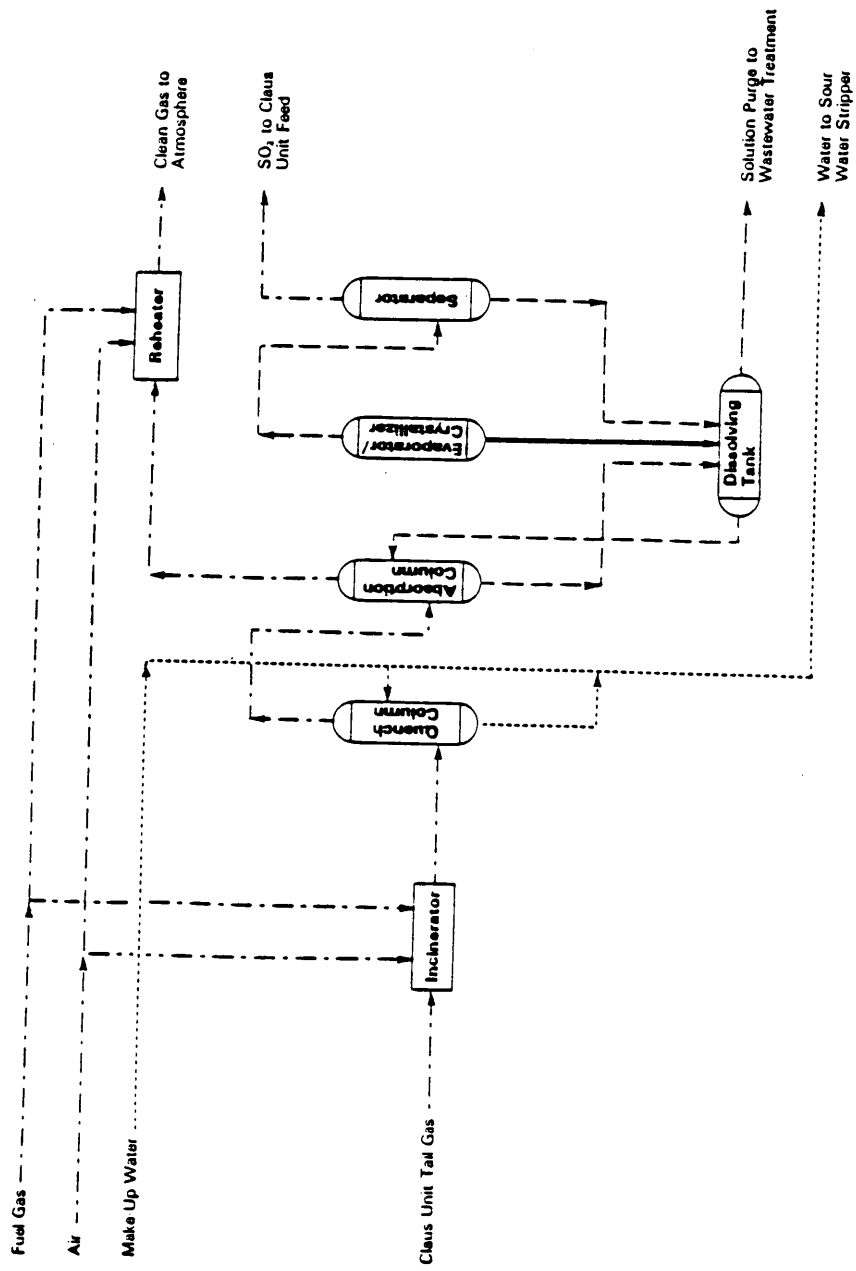


Figure 31. Wellman-Lord Tail Gas Treating Unit (87).

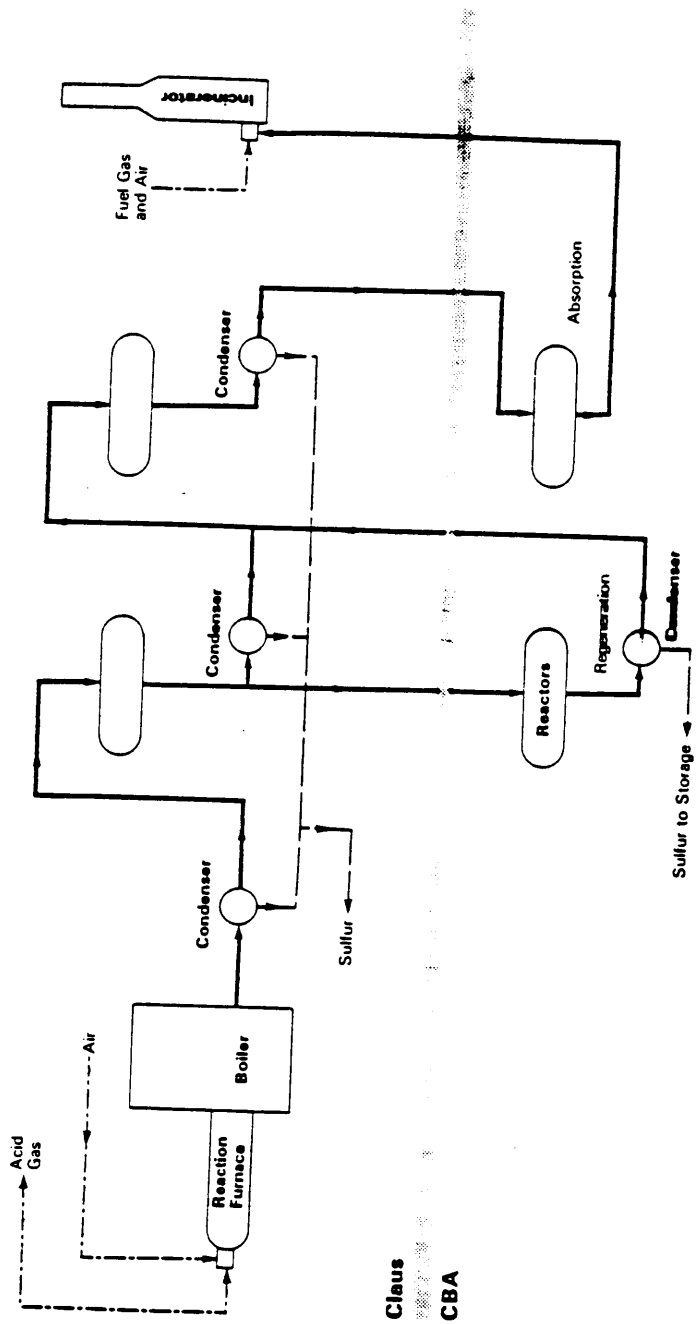


Figure 32. Cold Bed Absorption (CBA) Process (87).

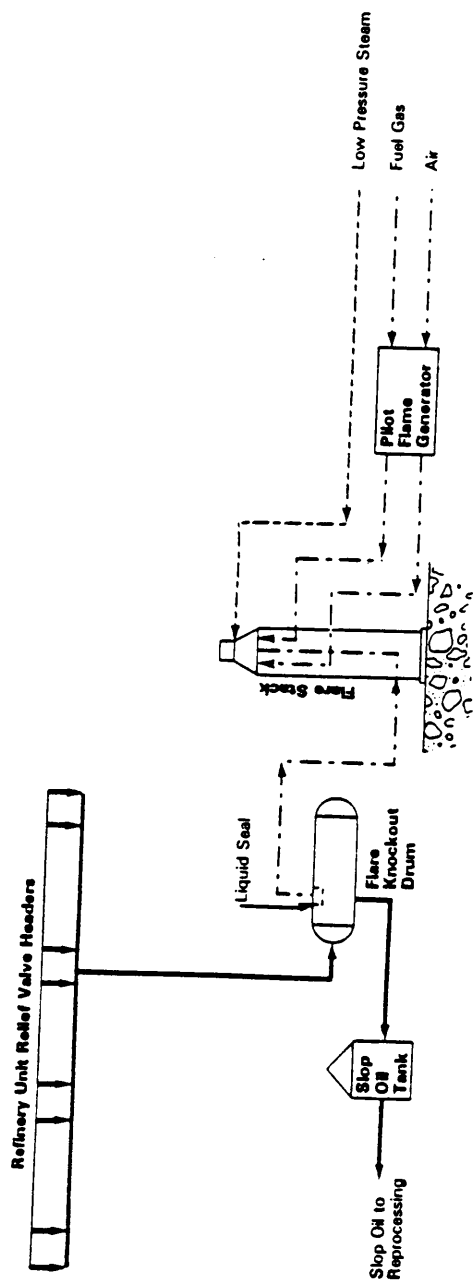


Figure 33. Refinery Flare System (87).

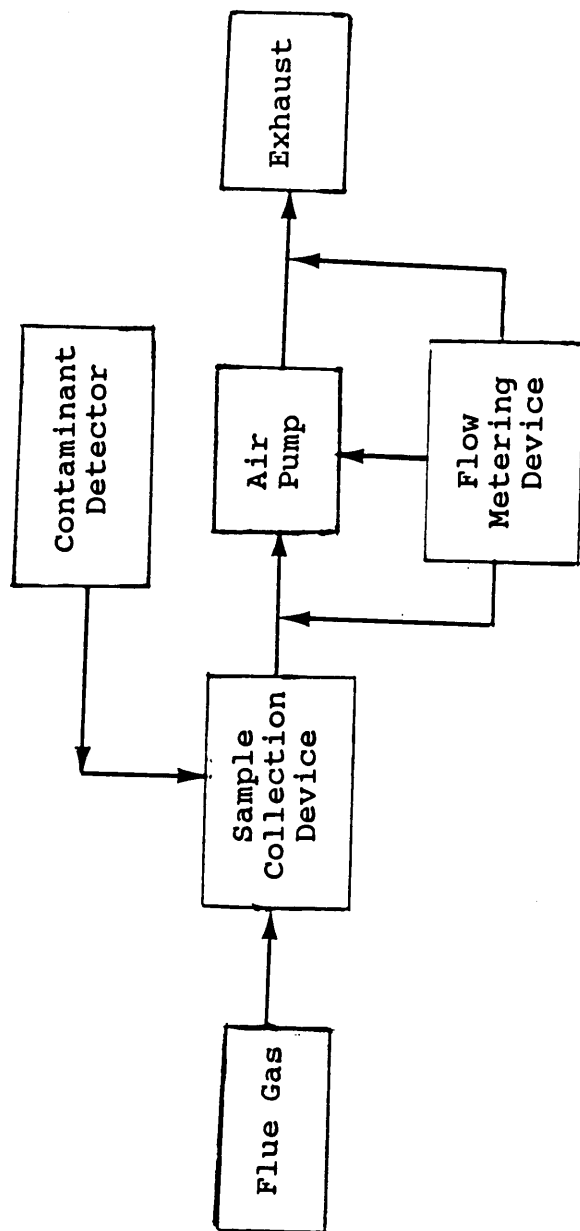


Figure 34. A Sampling Train (44).

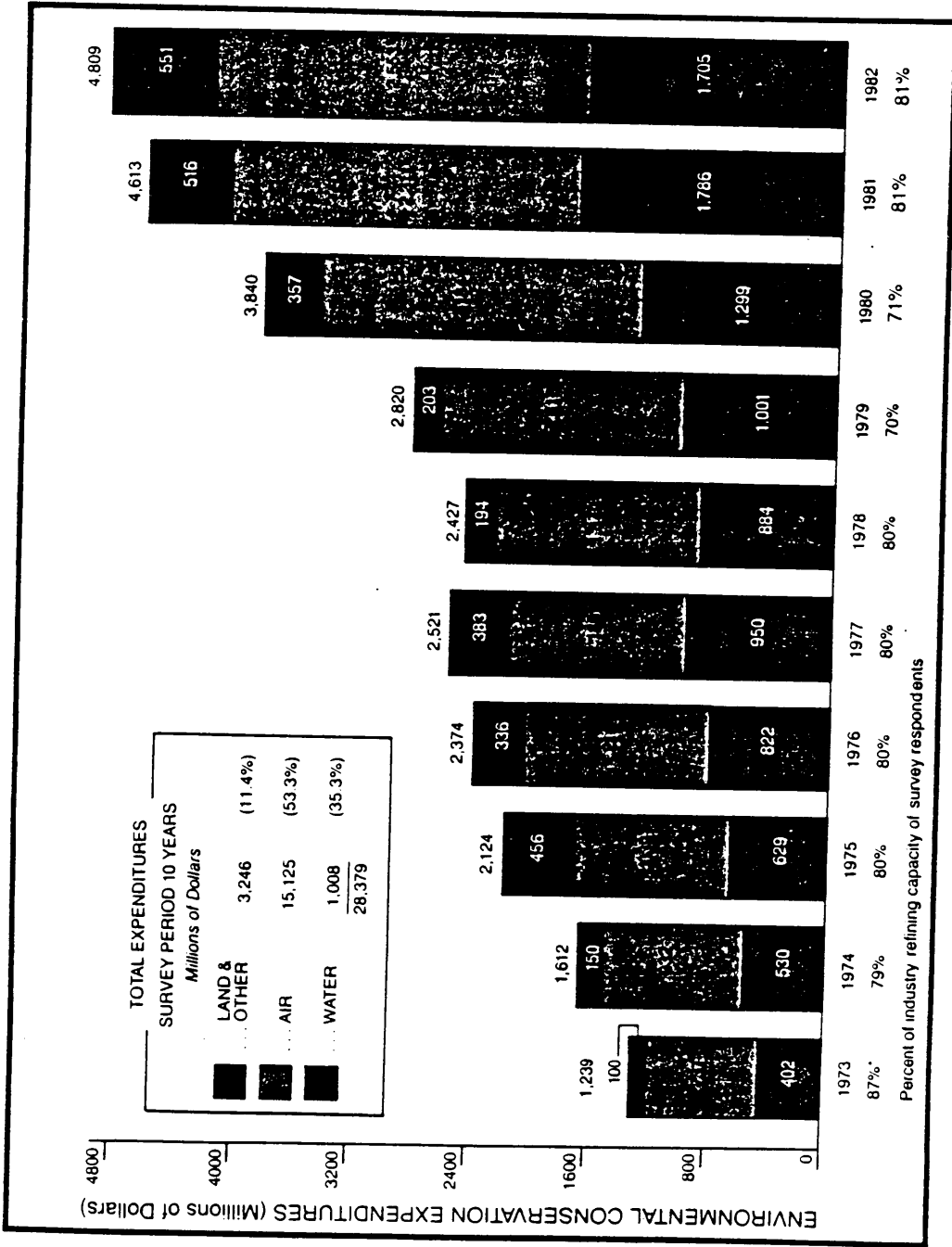


Figure 35. Total Environmental Expenditures- U.S. Petroleum Industry (1973 to 1982) (4).

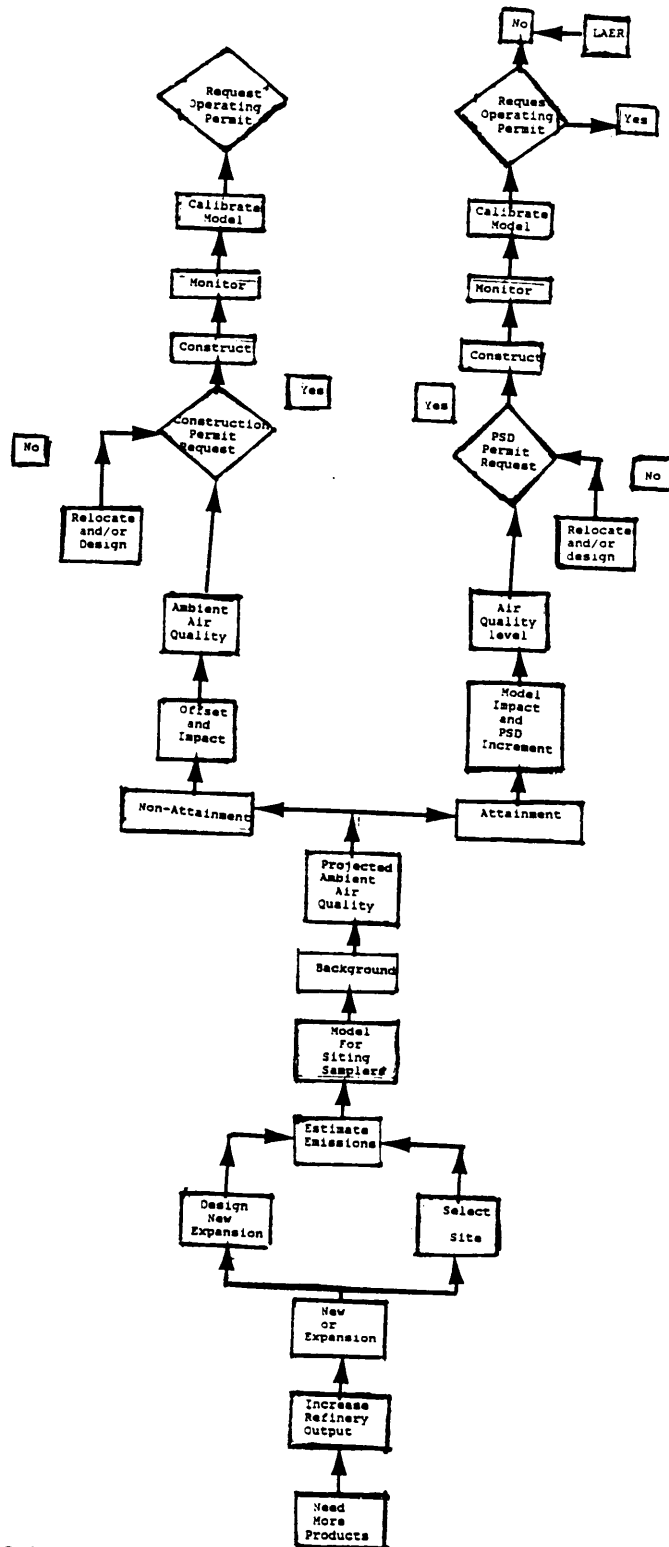


Figure 36. A Flow Chart of Steps Involved in Requesting Operating Permit (New and Expanded Refinery).

Appendix B

Table 1. U.S. Energy Consumption And Gross National Product
(1960-1990) (73).

	Total Energy (Quadrillion Btu's)	Gross National Product (Billion Dollars)
Actual 1960 Data	44.10	737
Actual 1970 Data	66.83	1,075
Actual 1980 Data	76.26	1,485
1985 Projection	82.92	1,630
1990 Projection	88.59	1,820
Annual Growth Rate (Percentage)		
Annual 1960-1970 Data	4.2	3.8
Annual 1970-1980 Data	1.3	3.3
1980-1985 Projection	1.6	1.9
1985-1990 Projection	1.3	2.2
1970-1990 Projection	1.4	2.7

Table 2. World Refining Capacity And Oil Product Consumption
(1940-1980) (55).

	1940	1960	1973	1980
Refining Capacity (Mn b/d)	6.87	24.47	60.21	81.92
Product Consumption (Mn b/d)	5.49	21.81	56.59	61.59
Consumption as % of Refining Capacity	80	89	94	75
Growth Rates (%)	<u>1940-1960</u>	<u>1960-1973</u>	<u>1973-1980</u>	
Refining Capacity	6.5	7.2	4.5	
Product Consumption	7.0	7.6	1.2	

Mn b/d - million barrels per day

Table 3. World Refineries in 1980 (107).

	Number of operating refineries	Refineries under construction	Proposed refineries
Western Europe	181	29	8
1) West Germany	37	6	
2) Italy	36	2	
3) France	23	2	1
4) United Kingdom	20	7	2
5) Others	65	12	5
Middle East	37	12	3
1) Iraq	7	1	1
2) Iran	7		
3) Egypt	4	2	
4) Kuwait	4	1	1
5) Others	15	8	1
Africa	31	5	3
1) South Africa	4		
2) Algeria	3	3	
3) Nigeria	2	1	1
4) Morocco	2		
5) Others	20	1	2
Far East and Australia	115	11	15
1) Japan	50	1	4
2) Australia	11	4	2
3) India	11		1
4) Indonesia	9		
5) Others	34	6	8
South America and Carribean	90	14	5
1) Argentina	14	2	1
2) Venezuala	14		2
3) Brazil	12	4	
4) Colombia	6	2	1
5) Others	44	6	1
North America	380	66	7
1) United States	330	64	4
2) Canada	41	1	3
3) Mexico	9	1	
TOTAL	834	137	41

Table 4. The Top American Refiners : Capacities based on U.S. Bureau of Mines Statistics (78).

Company	Capacity (b/d)	(%)
Exxon	1,243,000	8.46
Shell	1,150,000	7.83
Standard (Indiana)	1,115,000	7.59
Texaco	1,073,000	7.30
Standard (California)	952,000	6.47
Mobil	903,500	6.14
Gulf	866,400	5.89
Atlantic Richfield	724,600	4.92
Union Oil (California)	496,000	3.38
Sun	484,000	3.29
Standard (Ohio)	431,000	2.93
Phillips	408,000	2.78
Continental	377,000	2.57
Ashland	362,943	2.57
Marathon	324,000	2.20
	Total	74.32

Table 5. Petroleum Products of Refineries (40)*.

Sectors	Products
<u>Fuel Products</u>	
Industrial Sector	<ol style="list-style-type: none"> 1. Distillate Fuel Oil. 2. Residual Fuel Oil. 3. Liquefied Gases. 4. Motor Gasoline. 5. Kerosene.
Residential and Commercial Sector	<ol style="list-style-type: none"> 1. Distillate Fuel Oil. 2. Residual Fuel Oil. 3. Liquefied Gases. 4. Kerosene. 5. Motor Gasoline.
Transportation Sector	<ol style="list-style-type: none"> 1. Aviation Gasoline. 2. Distillate Fuel Oil. 3. Jet Fuel. 4. Motor Gasoline. 5. Liquefied Gases.
Electric Utility Sector	<ol style="list-style-type: none"> 1. Distillate Fuel Oil. 2. Jet Fuel. 3. Residual Fuel Oil.
<u>Nonfuel Products</u>	
Industrial Sector	<ol style="list-style-type: none"> 1. Ethane. 2. Liquefied Gases. 3. Lubricants. 4. Petroleum Coke. 5. Naphthas. 6. Wax.
Residential and Commercial Sector	<ol style="list-style-type: none"> 1. Asphalt and Road Oil.
Transportation	<ol style="list-style-type: none"> 1. Lubricants.

* With revisions (40).

Table 6. PSD Designations and Deterioration Increments (104).

Contaminant	Period of Measurement	Allowable increase over (Baseline Air Quality)		
		Class I Areas (ug/m ³)	Class II Areas (ug/m ³)	Class III Areas (ug/m ³)
1) Particulate matter	Annual geometric mean	5	19	37
	24-hr maximum	10	37	75
2) Sulfur dioxide	Annual arithmetic mean	2	20	40
	24-hr maximum	5	91	182
	5-hr maximum	25	512	900

* Note: Class III area is applicable to only a few states.

Table 7. National Ambient Air Quality Standards (17, 32)*.

Pollutant	Averaging time	Primary Standard (ug/m ³)	Secondary Standard
Carbon monoxide	8 hr	10,000 (9 ppm)	same
	1 hr	**40,000 (35 ppm)	*same
Nitrogen dioxide	Annual arithmetic mean	100 (0.005 ppm)	same
Sulfur dioxide	Annual arithmetic	80 (0.03 ppm)	-
	Mean 24-hr	365 (0.14 ppm)	-
	3-hr	-	1300 (0.5 ppm)
Suspended particulate matter	Annual geometric	75	60
	Mean 24-hr	260	150
Hydrocarbons (corrected for methane)	3-hr	160 (0.24 ppm)	same
Ozone	1-hr	240 (0.12 ppm)	same
Lead	3 months	1.5 (0.006 ppm)	same

* With revisions

** EPA has proposed a reduction of the standard to 29 ug/m³ (25ppm)
 ppm - parts per million
 ug/m³ - micrograms per cubic meter

Table 8. NSPS for Petroleum Refineries (31).

Affected facility	Pollutant	Maximum Allowable Emission Levels	Monitoring Requirement
Fluid Catalytic Cracking Unit	Particulates	1.0 lb/1000lbs of coke burn-off	None
Catalyst Regenerator	Opacity	30 % (6 minute exemption per hr)	Continuous
Fuel Gas Combustion Devices	CO	0.05 % by volume	Continuous
	SO ₂	Equivalent of 0.10 grains of H ₂ S per dscf in fuel	Continuous
	H ₂ S	230 mg/dscm**	Continuous
	SO ₂	0.025% (@ 0% oxygen)	Continuous
Claus Sulfur Recovery Plants (Plants greater than 20 long tons per day)	Reduced Sulfur compounds	0.030% (@ 0% oxygen)	Continuous
	H ₂ S	0.0010% (@ 0% oxygen)	Continuous

* dscf : dry standard cubic foot

** mg/dscm : milligrams per dry standard cubic meter

@ : at

Table 9. Potential Sources of Emission from Oil Refineries (6).

Emission	Source
Oxides of sulfur	Boilers, process heaters, catalytic units, regenerators, treating units, H ₂ S flares, decoking operations, fluid cokers, and sulfur recovery plants.
Oxides of nitrogen	Process heaters, boilers, compressors engines, catalyst regenerators, and flares.
Carbon monoxide	Catalyst regenerators, decoking, compressor engines, incinerators, and fluid coke burners.
Hydrocarbons	Loading facilities, turnabouts, sampling, storage tanks, wastewater separators, blowdown systems, catalyst regenerators, pumps, valves, blindcharging, cooling towers, vacuum jets, barometric condensers, air blowing, high pressure equipment handling volatile hydrocarbons, process heaters, boilers, compressor engines, flanged connections, distillation towers.
Particulates	Catalyst, regenerators, boilers, process heaters, decoking operations, flares.
Aldehydes	Catalyst regenerators.
Ammonia	Catalyst regenerators.
Odors (Hydrocarbons, aldehydes, ammonia, mercaptans, H ₂ S, sulfides.)	Heating units (air blowing, steam blowing drains, tank vents, barometric condenser sumps.

Table 10. Estimates of Total Emissions from Refineries
1970 and 1979 (73).

	1970	1979	Percentage change
Emission Estimates in Thousand Metric Tons per year.			
TSP	70	50	-29
SO _x	620	680	+10
NO _x	3100	340	+10
VOC	720	960	+33
CO	1990	850	-57

Emission Estimates in Metric Tons per Million Barrels
of Crude Oil run *

TSP	18	9	-50
SO _x	156	127	-19
NO _x	78	64	-18
VOC	181	180	0
CO	502	159	-68

* Emission estimates in metric tons per million barrels
of crude based on 1970 = 10,870 Mn b/d;
1979 = 14,648 Mn b/d.

Table 11. Emission Factors for Petroleum Refineries (41).

Type of Process	Parti- culates	Sulfur oxides	Carbon monoxide	Hydro- carbons	Nitrogen oxides	Alde- hydes
Boilers and Process Heaters						
lb/10 ³ bbl oil burned	840	NA ^b	Neg	140	29.00	25
kg/10 ³ liters oil burned	2.4	NA	Neg	0.4	8.3	0.071
lb/10 ³ ft ³ gas burned	0.02	NA	Neg	0.03	0.23	0.003
kg/10 ³ m ³ gas burned	0.32	NA	Neg	0.48	3.7	0.048
Fluid Catalytic Cracking Unit						
lb/10 ³ bbl fresh feed	61	525	13,700	220	63	19
kg/10 ³ liters fresh feed	0.175	1.5	39.2	0.630	0.180	0.054

Table 11. (continued)

Type of Processes	Parti- culates	Sulfur oxides	Carbon monoxide	Hydro- carbons	Nitrogen oxides	Alde- hydes
Moving-bed Catalytic Cracking Units						
lb/10 ³ bbl fresh feed	17	60	3,800	87	5	12
kg/10 ³ liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034
Compressor Internal Combustion Engines						
lb/10 ³ ft ³ gas burned	-	-	Neg	1.2	0.9	0.1
kg/10 ³ m ³ gas burned	-	-	Neg	19.3	14.4	1.61
Blowdown Systems						
lb/10 ³ bbl refinery capacity						
With control	-	-	-	5	-	-
Without control	-	-	-	300	-	-
kg/10 ³ liters refinery capacity						
With control	-	-	-	0.014	-	-
Without control	-	-	-	0.860	-	-

Table 11. (continued)

Type of Processes	Parti- culates	Sulfur oxides	Carbon monoxides	Hydro- carbons	Nitrogen oxides	Alde- hyde
Process Drains lb/10 ³ bbl waste water	-	-	-	8	-	-
With control	-	-	-	210	-	-
Without control	-	-	-	-	-	-
kg/10 ³ liters waste water	-	-	-	0.023	-	-
With control	-	-	-	0.600	-	-
Without control	-	-	-	-	-	-
Vacuum Jets lb/10 ³ bbl vacuum distillation	-	-	-	-	-	-
With control	-	-	-	-	-	-
Without control	-	-	-	-	-	-
kg/10 ³ liters vacuum distillation	-	-	-	Neg 130	-	-
With control	-	-	-	-	-	-
Without control	-	-	-	Neg 0.370	-	-

Table 12. Typical Range of Composition of Claus Plant Tail Gas (73).

Component	Composition Range (ppm) (Dry Basis)
Hydrogen sulfide	5,000 to 12,000
Sulfur dioxide	2,500 to 6,000
Carbon disulfide	300 to 5,000
Carbonyl sulfide	300 to 5,000
Sulfur (vapor)	100 to 200

Table 13. Potential Sources of Refinery Emissions of Sulfur Compounds (6).

<u>Refinery Source</u>	<u>Type of Sulfur Compound Emitted</u>		
	<u>Sulfur dioxide/trioxide</u>	<u>Hydrogen sulfide</u>	<u>Mercaptans/Organic sulfides</u>
Combustion			
Boilers and Process Heaters	X		
Flares	X		
Decoking	X	X	X
Incinerators	X		
Conversion Processes			
Distillation		X	X
Cracking			
Catalytic	X	X	X
Thermal		X	X
Coking			
Delayed Fluid	X	X	X
Fluid		X	X
Hydrocracking		X	
Hydrodesulfurization		X	
Catalytic Reforming		X	
Treating			
Sulfur Recovery	X	X	
Sour Gas Treating		X	X
Regenerating Spent Solutions		X	X
Stripping Sour Condensates		X	X
Sulfur Dioxide Extraction	X		
Sulfur Acid Alkylation	X		X
Treating Recovery	X		
Air Blowing		X	X
Anaerobic Digestion		X	
Miscellaneous			
Sour Crude and Product Purging		X	X
Leaks and Spills		X	X
Relief Valves		X	X
Pumps and Compressors		X	X

Table 14. Refinery Sources of NO_x from Combustion (6).

Classification	Source	Thermal NO _x	Fuel NO _x
High Temperature	Power Boilers-Gas	Present	Possible
	Power Boilers-Oil	Present	Present
	Power Boilers-Coal	Present	Strong
Internal Combustion	Engines	Strong	Unlikely
	Turbines	Strong	Possible
Moderate Temperature	Carbon Monoxide Boilers	Present	Present
	Coke and Residual Fuels	Present	Present
	Catalyst Regeneration	Unlikely	Present
	Incineration	Present	Present
	Process Heating		
	Gas Cracking	Present	Possible
	Oil Cracking	Unlikely	Possible
	Oil Heating	Unlikely	Possible

Table 15. Refinery Odors and Sources (87).

Type of Smell	Source	Odorous Compounds
Bad eggs	Crude storage Distillation of gases Sulfur removal Flare stacks (extinguished)	H ₂ S and trace of disulfides
Sewer smell	Effluent water Biological treatment plants LPG odorizing Spent caustic loading and transfer	dimethyl sulfide, mercaptans
Burnt oil	Catalytic cracking unit Coking Asphalt blowing Asphalt storage	unsaturated hydrocarbons
Gasoline	Product storage API separators	Hydrocarbons
Aromatics (benzene)	Aromatic plants naphtha reformers	benzene, toluene

Table 16. Odors in Refinery Emissions (87).

Chemical	Odor Threshold (ppb)*	Odor Description
Acetic acid	1,000	Sour
Acetone	1,000,000	Chemical, sweet
Amine, monomethy	21	Fishy, pungent
Amine, dimethyl	47	Fishy
Amine, trimethyl	0.2	Fishy, pungent
Ammonia	46,800	Pungent
Benzene	4,700	Solvent
Benzene sulfide	2	Sulfidy
Carbon disulfide	210	Vegetable-like, sulfidy
Chlorine	314	Bleach, pungent
Chlorophenol	0.03	Medicinal
Dimethyl sulfide	1-2	Vegetable-like, sulfidy
Diethyl sulfide	6	Garlic-like, foul
Diphenyl sulfide	5	Burnt, rubbery
Hydrogen sulfide	5	Rotten egg
Methyl ethyl kete	10,000	Sweet
Mercaptan, methy	1-2	Sulfidy, decayed cabbage
Mercaptan, ethyl	0.4-1	Sulfidy, decayed cabbage
Mercaptan, n-prol	0.7	Sulfidy
Mercaptan, n-but	0.7	Strong, sulfidy
Paracresol	1	Tarry, pungent
Paraxylene	470	Sweet
Phenol	47	Medicinal
Phosphine	21	Oniony, mustard
Sulfur dioxide	470	Sharp, pungent
Toluene	2,000-4,700	Solvent, moth balls
Butane	6,000	
Heptane	18,000	
Amylenes and pentenes	170-2,100	

* Units in parts per billion

Table 17. Summary of Control and Design of Parameters for Air Pollutants from Refineries (6, 87)*.

Air Pollutant	Control and Design Processes
Hydrocarbons	<ol style="list-style-type: none"> 1. Incinerate. 2. Flare. 3. Minimize losses. 4. Optimize operations.
Sulfur oxides	<ol style="list-style-type: none"> 1. Disperse. 2. Scrub flue gas. (e.g. from fluid catalytic cracker) 3. Blend high sulfur internal fuels with desulfurized distillates. 4. Steam stripping. 5. Use desulfurized fuels. 6. Increase stack heights to reduce ground levels of sulfur dioxide.
Nitrogen oxides	<ol style="list-style-type: none"> 1. Low excess air. 2. Flue gas recycle. 3. Two-stage combustion. 4. Steam or water injection. 5. No preheat. 6. Longer temperature operations. 7. Flue gas treatment.
Particulates (Smoke Process dusts mists)	<ol style="list-style-type: none"> 1. Control combustion. 2. Cyclones. 3. Electrostatic precipitators. 4. Filters. 5. Scrubbers. 6. Disperse. 7. Taking into account fugitive sources (e.g. roads, etc.) in site preparation.
Carbon monoxide	<ol style="list-style-type: none"> 1. Incinerate. 2. Flare. 3. Installation of carbon monoxide boilers.

Table 17. (continued)

Air Pollutant	Control and Design Processes
Odors (e.g. Hydrogen sulfide, mercaptans, organic sulfides, etc.)	<ol style="list-style-type: none"> 1. Disperse. 2. Incinerate. 3. Flare. 4. Adsorb. 5. Absorb. 6. Neutralize. 7. Condensation. 8. Check mechanical seals (e.g. of pumps and compressors). 9. Tie relief valves into vapor collection systems.
Others	
Inorganic Acids (e.g. hydrofluoric, hydrochloric acids)	<ol style="list-style-type: none"> 1. Usually Neutralization.
Asphyxiant Gases (Carbon dioxide, inert gases)	<ol style="list-style-type: none"> 1. Disperse. 2. Purge. 3. Ventilate. 4. Flare.

* With revisions

Table 18. Reference Methods for Testing Stack Emissions (92).

Source	Method
Stack gas characteristics	The dry molecular weight and the weight and density are determined by Orsat analysis and water content by condensation.
Benzene	Standard method 110 (April 18, 1980). A bag sample of stack gas containing benzene and other organics is subjected to gas chromatographic (GC) analysis using flame ionization detector (FID).
Carbon monoxide	Standard Method 10 (March 8, 1978). Analysed by the Non dispersive infra red method (NDIR) employing either a continuous or an integrated sample. CO absorbs energy and deflection of the diaphragm indicates concentration of CO.
Hydrogen sulfide	Standard Method 11 (Jan 1, 1978). H ₂ S is collected from a source and absorbed in pH 3.0 cadmium sulfate to form cadmium sulfide. Cadmium sulfide is then measured iodometrically.
Hydrocarbons	Standard Method 18. The method uses a gas chromatograph (GC) and separated components can be measured using suitable detector like FID.
Nitrogen dioxide	Standard Method 7A (Oct 7, 1982). A grab sample is collected in an evacuated flask containing dilute sulfuric acid - hydrogen peroxide absorbing solution. Nitrogen oxides, except nitrous oxide, are oxidized to nitrate and measured by ion chromatography.
Opacity	Standard Method 9 (Oct 28, 1981). Measure of emissions by a mobile lidar (base radar) unit.

Table 18. (continued).

Source	Method
Particulates matter	Standard Method 5 (Aug 18,1977). Collected on a dry glass fiber filter. The filter is later maintained above a temperature of 250°F to avoid condensation.
Sulfur dioxide	Standard Method 6B (Dec 1,1982). A grab sample is extracted over a 24 - hour period. SO ₂ fraction is measured by barium - thorium titration method.
Total Gaseous Non Methane Organic Emission (VOC - Methanes = NMHC)	Standard Method 25 (Oct 3,1980). Measurement of VOC as total gaseous non methane organics (TGNMO) as carbon in emissions is done.
Volatile Organic Compounds (VOC) Leaks	Standard Method 21 (Aug 18,1978). Uses a portable instrument to detect VOC leaks (Detector not specified).

Table 19. Reference Methods for Determining Pollutants in Ambient Air Quality Surveys (32, 43).

Pollutant	Method
Sulfur Dioxide	Pararosaniline method.
Suspended Particulate Matter	High Volume Sampler.
Carbon Monoxide	Non dispersion infra red spectrometry.
Ozone	Gas phase chemiluminiscent method with ethylene.
Hydrocarbons	Chromatography with flame ionization detector.
Nitrogen dioxide	Gas phase chemiluminiscence with ozone.
Lead	High volume sampling with atomic absorption analysis.

Table 20. Environmental Expenditures on Air Management
(Emphasizing Manufacturing) Activity of U.S.
Petroleum Industry (Millions of
Dollars) (4)*.

	Year										Total	
	'73	'74	'75	'76	'77	'78	'79	'80	'81	'82		
Air												
Capital Expenditures												
Manufac-												
-turing	369	373	450	385	230	332	448	498	403	631	4119	
Others**	67	154	151	151	109	97	113	230	308	301	1681	
Administrative Operating and Maintenance Expenditures												
Manufac-												
-turing	214	291	328	574	723	791	913	1262	1352	1373	7821	
Others**	37	61	61	61	69	73	84	130	186	181	943	
Research and Development												
Manufac-												
-turing	48	51	47	43	54	53	55	61	60	65	537	
Sampling & Testing	2	2	2	2	3	3	3	3	2	2	24	
TOTAL	737	932	1039	1216	1188	1349	1616	2184	2311	2553	15125	

* With revisions

Others** - includes exploration and production, transportation and marketing

Appendix C

APPENDIX C

API gravity as defined in Petroleum Processing Handbook (14) is an arbitrary scale expressing the gravity or density of liquid petroleum products.

The measuring scale is calibrated in terms of degrees API. It can be calculated in terms of the following formula:

$$\text{Degree API} = \frac{141.5}{\text{Sp. gr. } 60/60^{\circ}\text{F}} - 131.5$$

*Specific gravity for the equation is the ratio of a given volume of liquid at 60°F to the mass of an equal volume of pure water at the same temperature. Standard reference temperature is explicitly stated, as for example: specific gravity 60/60°F.

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