ANALYSIS OF WATER CHARACTERISTICS OF MANUFACTURING INDUSTRIES AND THEIR ADAPTABILITY TO SEMI-ARID REGIONS

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TECHNICAL COMPLETION REPORT

Project No. B-032-NMEX

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in cooperation with
Department of Chemical Engineering
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University of New Mexico, Albuquerque, New Mexico

June 1974

The work upon which this publication is based was supported in part by funds provided through the New Mexico Water Resources Research Institute by the United States Department of Interior, Office of Water Resources Research, as authorized under the Water Resources Research Act of 1964, Public Law 88-379, under project number A-032-NMEX.

ABSTRACT

Historically arid and semi-arid areas of the Southwest have exhibited a complete or almost complete dearth of manufacturing processes. In New Mexico's case this fact is emphatically underscored by the effective absence of any data on New Mexico in recent *Census of Manufactures* water use sections.

Because of its relatively limited water supply an area such as the Southwest must give more careful and considered thought to the water related impact of an industry than has generally been the case in other areas of the country. There are at least three significant categories into which an industrial water-using firm's impact on its surrounding water environment can be classified: 1) the polluting effect of its effluent, 2) its withdrawal demand for new water, and 3) its consumptive use of water. For informed planning more detailed information is required concerning the present operating characteristics of major water-using industries in each of these categories and their technological ability to adapt to the economic and environmental conditions of water use in the Southwest.

The industries chosen for detailed study are petroleum refining and coal gasification. Selection criteria were based on a high probability of the industry locating in New Mexico, a differing water use pattern, and process substitution possibilities. Of the industries chosen the petroleum refining industry currently has several facilities located within the state, and in the adjacent Southwestern area as well as one new refinery currently under construction. No commercial coal gasification facilities are in existence in the United States although several permit applications to build plants in New Mexico have been filed. Attention is given to process descriptions particularly in terms of wastewater generation, treatment process and process unit costs where available. Brief discussions are presented of the major New Mexico river and water basins, water quality measurement concepts, and wastewater treatment processes currently being used or having a high potential for use. An example of the application of a linear programming model predicting the response of a petroleum refinery to water costs is shown. The results of this work are felt to permit a ranking of other industries from a water-use viewpoint through the application of the concepts presented and to allow comparative evaluation of industries of interest to be made.

ACKNOWLEDGEMENTS

The authors would like to thank the personnel of the petroleum refining industry who responded to our questionnaire concerning their water-use patterns. We also are especially indebted to the following students who helped collect some of the information necessary to this report:

James Doty - Department of Economics
University of New Mexico

Wayne Dunlap - Department of Chemical Engineering
New Mexico State University

Leland Griffin - Department of Chemical Engineering
New Mexico State University

Naheed Hossein - Department of Industrial Engineering
New Mexico State University

Roger Melton - Department of Chemical Engineering
New Mexico State University

Judy Nelson - Department of Economics
University of New Mexico

Tsao Hsien-Yen - Department of Chemical Engineering
New Mexico State University

Special recognition is given to Judy Nelson who devoted much time and effort to the sections on Introduction to Petroleum Refining and Coal Gasification as well as the application of the model to petroleum refining.

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INTRODUCTION

Historically arid and semi-arid areas of the Southwest have exhibited a complete or almost complete dearth of water-using industrial manufacturing processes. This paucity of water-using manufacturing in such areas is not an especially surprising phenomenon since from an economic perspective it is to be expected that firms which are large water users will locate in areas where water is cheap and plentiful rather than where it is dear and scarce. However, in recent years a number of different factors have varied in such a way as to require a reexamination of the possibility of locating large water-using firms in semi-arid areas both with respect to the feasibility of such an occurrence and to its desirability from both the firm's and the area's point of view. A listing of these variable factors would include: 1) the increased demand for water in all uses which has occurred in the non-arid areas of the country as a result of their growth in population and industrial output, 2) the increased cost of preparing new water for use which has occurred as a result of the growing pollution of the water sources in these areas, 3) the growing outcry against pollution which has led to legislation and controls which either prevent a firm from emitting an effluent high in polluting character or impose a high cost for such an emission, and 4) numerous non-water related changes in labor costs, transportation costs, market for output, etc.

The first three of these changes have in combination essentially created a geographic cross-sectional structure for water costs which is much more favorably oriented toward areas such as the Southwest than previously existed. If the balance has not changed so dramatically as to make New Mexico absolutely advantageous with respect to water costs (and even this is not clear), then at least the balance may have been altered sufficiently so that water expense is no longer a deterrent to an industry's locating in the Southwest from the point of view of the firm. As evidence of this increased interest, one can point to the Kaiser-Fontana steel plant in a water scarce area of California, or locally, the recent interest of the Parsons & Whittemore Company in locating a pulp and paper plant near Albuquerque.

The associated question, however, is the desirability from the point of view of the state in having heavy water-using industry locate here. Obviously, the firm that simply wishes to move its sewer from New York to New Mexico is to be avoided. But does there not exist a course of careful and informed planning which can result in the locating of a large water-using industry in the Southwest which is acceptable to the people of the area with respect to its water-using characteristics? Because of its relatively limited water supply an area such as the Southwest must give more careful and considered thought to the water related impact of an industry than has generally been the case in other areas of the country.

There are at least three significant categories into which an industrial water-using firm's impact on its surrounding water environment can be classified: 1) the polluting effect of its effluent, 2) its withdrawal demand for new water, and 3) its consumptive use of water. For informed planning more detailed information is required concerning the present operating characteristics of major water-using industries in each of these categories and their technological ability to adapt to the economic and environmental conditions of water use in the Southwest.

It is the purpose of this report to isolate and separate the water connected characteristics of manufacturing firms from the overall question of the desirability of the firm's locating in a semi-arid region and seek to make operational judgments about the relative abilities of the various industries to adjust to the water use conditions of such a region. Also included is an example of the applicability of a linear programming model for describing the economic response of a petroleum refinery to the costs of water.

It must be recognized that the overall decision to attract heavy water-using industry to semi-arid areas requires information beyond the water-related effects of the industry in that other costs such as non-water environmental effects and the totality of benefits derived from the introduction of the industry must be weighed. Consequently a study of water characteristics alone is not a sufficient basis for providing an absolute ranking of industries as to their desirability. However, as noted previously, until recently the restrictions on industry created by the water environment of semi-arid areas have been a central factor in the lack of water-using industries in such areas. Now that there exists a realistic possibility that an industry of this type will move into a semi-arid region, the study of the water related effects of such movement becomes a subject of prime concern.

AN OVERVIEW OF THE PETROLEUM INDUSTRY

With the recent concentration of public attention on the petroleum industry, many conflicting explanations are being advanced concerning recent events in this industry and the circumstances that have given rise to them. It is not within the objective of the research reported here to attempt an unraveling of this confused tangle. Nevertheless, some perspective on existing market conditions in this industry was considered essential, and this section presents that perspective.

U. S. petroleum refining was carried out in 232 individual plants in 1971. For convenience, these are divided into three groups according to capacity; 100,000 barrels a day or over is described as large, 25,000-100,000 barrels a day is described as medium, and 25,000 barrels a day or less is described as small. The average size of a plant is approximately 54,000 b/cd and the median size is 25,000 b/cd. Sixty-three percent of the crude is processed in the 40 large refineries with the 75 medium-size refineries processing 30% of the crude, and the 117 small refineries processing the remaining 7%.

The trend in recent years has been for a growing proportion of the crude to be refined in large plants, while the smaller, older plants have gradually been eliminated from the market. From a 1947 total of 350 refineries, plant closings have accumulated at a rate of 2% per year with the trend accelerating in recent years. In previous years these closings have followed a natural economic evolutionary process due to changing technology which has lowered costs in large plants and lowered transportation costs. More detailed comment on this circumstance will be presented later. In recent years, however, controversy has surrounded many of the closings as charges have been leveled from many quarters that these recent closings are more the result of concerted efforts by the major companies to rid the market of the smaller independents than of changing economic circumstances. Although investigations of these charges have been undertaken by various official agencies, further comment on them is beyond the scope of this report.

Although the absolute number of plants has been declining, the additions to crude capacity have been increasing at approximately 1.5% per year since 1947. This trend has also been accelerating in recent years. The increases in capacity, however, have not been enough to keep up with current demand. This failure to maintain sufficient domestic refinery capacity is due to several factors that are summarized below: 1) Domestic production of crude oil has been declining since 1971. This circumstance, combined with a wide shortage in sweet crudes, has created a shortage in feed stock available domestically, even in the face of continued high demand for refinery production. In the face of this idle capacity, new refinery capacity has seemed superfluous. Sweet crudes are crudes with low sulfur content. Refineries are usually designed to accommodate one or two crude types. Most U. S. refineries were designed for sweet domestic crude. With domestic production declining, pressure was put on foreign sweet crudes creating a world wide shortage of sweet crudes. 2) The U. S. economy was in an unstable state generally as price controls, inflation, and dollar devaluation have created much economic uncertainty. The oil industry has expressed strong feelings that price controls have prevented effective competition for world oil supplies. 3) Although the U. S. Congress has passed a series of stringent clean air and water laws, much industry sentiment has supported a wait-and-see attitude in the hope that less costly modified regulations will eventually emerge. It should be noted that these regulations affect the processing industry directly in respect to the effluents that they are permitted to discharge, while at the same time changing the specifications of the finished products that they produce. These accumulating factors have led the industry to export most of their new capacity abroad, primarily to the Carribean. The question for New Mexico is the prospect for continuation of this trend and the possibility of a reversal. In order to provide some assessment of probable answers to this question, industry behavior must be examined more closely.

A common economic measure of monopoly power is the amount of capacity that is controlled by the largest companies. As portrayed by Table 1, the refining sector of the petroleum industry exhibits significant monopolistic conditions.

A similar conclusion can be documented in each of the other three sectors of industry operations--mining, transportation and marketing. When the international aspects of the major domestic oil companies' operations are included it becomes clear that the major companies do, in fact, dominate the industry. The question of whether this dominance has been used to non-competitively exclude the smaller independents is, once again, not pursued here. However, in assessing the prospects for introduction of additional refining capacity into New Mexico, judgement must be made as to the future viability of the smaller independents, since it is the smaller refining plants commonly operated by these independents that have the greatest probability of being constructed in this state. That assessment must inevitably be made in the face of the industry dominance by the major companies. Before exploring further the future of the independents, arguments must be presented which justify the low probability assigned to the construction in New Mexico of large refineries by the major companies.

Table 1. Percent Capacity Controlled by Largest Companies

	1972 refining
4 Largest	.33
8 Largest	.59
16 Largest	.77

Source: Oil and Gas Journal, April 2, 1973

One of the major factors influencing the oil companies are the numerous regulations that they face from all levels of government. Most of the regulations on a national scale come from the numerous quotas and tariffs imposed on foreign crude oil and various petroleum products. This system is important because of its effect on the demand for domestic crude. Crude oil is not a homogeneous product. Its price is primarily dependent upon its specific gravity of API measurement and its sulfur content. In the past, the average world price of crude was considerably below the average U. S. crude price. Increased world demand and pricing decisions of oil producing countries have in recent months reversed this disparity for sweet crudes. Although this reversal has tended to shift the pressure for increased production to the domestic markets, the past decline in domestic production plus increased U. S. demand for petroleum products has kept the demand for foreign oil high. Traditionally, crude production has been protected by only allowing a set amount of foreign crude to enter the U. S. With the relaxation of the import restrictions as a consequence of the severity of the shortage, the pricing mechanism would ordinarily tend to equilibrate foreign and domestic prices. However, embargo and pricing policies have prevented this convergence.

The beneficial effects of these policies are the increased demand for domestic crude with the resulting price rise stimulating new exploration and the development of additional supplies. For the short run, however, continued domestic shortages force a reliance on imported crude, thus placing a premium on ocean access for any major new refinery capacity. What remains of New Mexico prospects must rest instead on the need for relatively small amounts of additional refining capacity to support localized uses for finished petroleum products that are not adequately served by existing or planned major refining plants. But to satisfactorily understand those prospects, there must be some discussion of the markets for finished petroleum products with principal emphasis on U. S. import policy with respect to these commodities. It is the restrictions imposed by this policy that foster the development of domestic production of many of these finished commodities.

To understand the import policy on finished petroleum goods it is necessary to digress momentarily into a brief discussion of these refinery products. As the crude petroleum enters the plant it is broken down in a distillation unit into gasoline, naphtha, kerosene, fuel oil and heavy bottoms. These products, in turn, go through other production processes. Every downstream process from the distillation unit exists solely for the purpose of changing the initial product mix into something more profitable. The degree of mix alteration is dependent on the type of crude as well as economic and technological considerations. Economic theory teaches that the profitable product mix is determined by the product transformation curves and the marginal revenue of the various products. It is beyond the scope of this study to explain all of the technological considerations that are necessary to derive the transformation curves. The shape of the transformation curves, however, explains a product's sensitivity to changes in marginal revenue. Gasoline, the most important product for U. S. refiners, has increased from 33% to 60% yield per barrel crude possible. The marginal revenue is determined by the market structure existing for each product. The two main uses of petroleum products are in transportation and as heating or power sources. Currently no widely acceptable substitute exists in the transportation market. The value of petroleum products used for heat or power can be compared with other energy sources by measuring its value in terms of Btu (British thermal units) per dollar of cost. In the past, coal was the cheapest source of Btu's. Recently natural gas has replaced coal as the cheapest energy source in major regions of the country. But the price of natural gas has been kept artificially low creating the shortages that currently exist. As gas is deregulated, the price should increase. The only areas where fuel oil has been competitive as an energy source is on the Eastern seaboard, where large natural gas transmission costs and large quantities of cheap foreign residuals have given fuel oil the price advantage. The competitiveness of alternative fuel sources have kept the price of fuel oil at a low level.

The import quota system is justified by its proponents on the basis of security arguments. Its purpose is to protect and encourage U. S. production and refinery capacity. Fuel oil, however, is exempted from quota and tariff restrictions on the basis of a judgement that is a relatively unimportant determinant of U. S. refining capacity. The result of this exemption is that 70% of all residual oils used in the U. S. are imported, with 80% of the imports coming from U. S. owned companies in the Caribbean. Quotas on other finished products vary. Gasoline is only allowed into the country under special hardship clauses. These hardship clauses rest principally on a determination that U. S. refiners will be unable to meet the projected U. S. demand for these products. Canada and Mexico are exempted from the import quotas. Recently Canada has limited all exports to existing levels and Mexico has reserves.

In the presence of these conditions U. S. refiners have tended to optimize gasoline production with fuel oil assigned a secondary role. In most other countries of the world, fuel oil production is optimized with gasoline production playing a proportionately smaller role. Two current problems, the national concern with air pollution and what has been described as the "energy crisis", are changing this picture. As noted above, fuel oil is a potential competitor to both coal and gas in the production of heat and power. The natural gas moving in interstate commerce is highly regulated. Whereas oil industry regulation has been indirect, natural gas prices are directly regulated by the Federal Power Commission. The FPC has interpreted its court ordered role in the natural gas industry by holding prices down below a market equilibrating level. In recent years this policy has led to gas shortages, with the FPC forced into playing the role of a natural gas rationer, giving first priority to residential users. The courts also have ruled that gas companies engaging in interstate commerce must sell to all home owners first, including those residing out of state. Only the remaining natural gas can be sold to industrial customers. It should be noted that the price of gas is still cheap enough to encourage some industries to overcome restrictive capital costs and establish two alternative fuel systems (i.e., natural gas 3/4 of the year and coal the remaining 1/4 of the year). These natural gas curtailments to industrial uses have created a larger demand for alternative fuels.

From the industry standpoint the problem is exacerbated by the new clean air requirements. Natural gas is a clean fuel where oil and coal contain numerous impurities. For an industry under pressure to meet clean air standards, curtailment of gas means the industry must find an alternative clean fuel or be faced with large capital investment in pollution control equipment. By 1975 clean air standards will also effect coal consumers. Technologies which remove sulfur from coal before it is burned along with technologies for cleaning stack gases are still quite costly. Although the quantities of coal available remain plentiful, low sulfur coals are not as plentiful and are located in areas away from the centers of demand. Plants, primarily electrical utilities, that burn coal are often custom designed for one kind of coal and can only switch with losses in efficiency. The use of fuel oil is seen by most experts as the only way this energy demand will be met over the next five to ten years. The additional stress that clean air requirements will put on crude demand is shown in Table 2.

Table 2. Crude Oil Demand

Sources	1975 Volume barrels/day
Unsatisfied demand for gas (1)	1,750,000
Coal replacement (1)	3,700,000
For reduction of auto emissions	700,000
Total	6,150,000

(1) Btu equivalents

Source: Oil and Gas Journal, November 13, 1972.

The 6,150,000 barrels/day is out of a projected 25,000,000 barrels/day representing an additional demand of about 25%. It should be noted that most of the addition is for residual fuel oils. Sulfur is also a pollutant in fuel oil and to meet air standards, low sulfur fuel oil is required.

The resulting demand for low sulfur fuel has been great enough in recent years that the price of these fuels has risen to that of gasoline. This new pricing structure created largely by the market imbalance in the natural gas industry can be expected to shift some of the U. S. refinery capacity away from gasoline to fuel oil. The new refinery being built in New Mexico is an example of this phenomenon. Basically, the refinery is producing a high grade fuel oil that will meet all clean air standards. This will be sold exclusively to a gas company who will in turn sell it to the industrial customers that they were forced to curtail.

It is difficult to predict demand behavior for fuel oil and other finished petroleum products in the future. Industries can not afford to pay the current high price for fuel oil on a long term basis. It can only command the currently prevailing high prices since it is primarily used as a supplementary short term source. Several pressures exist to change this picture. The price of natural gas is expected to rise, bringing market forces into closer alignment, although it is still unknown how much of a price rise will be required to balance the market. The demand for fuel oil will depend on its competitiveness given the new market situation. The price of low sulfur fuel oil can also be expected to fall as refineries install desulfurizing equipment, making it more competitive with the higher priced natural gas. Measures designed to increase the available amount of gas exist through the importation of LNG, coal gasification, or pipeline gas from Alaska. Prices of these substitutes, however, are such that it is likely that it can be afforded on a short term supplementary basis only, and in the long run can't compete with fuel oil or natural gas. The demand for fuel oil will go up in the long run, and U. S. refiners can be expected to shift some of their capacity in this direction. However, if the current quota policy is maintained, foreign refineries will install desulfurizing equipment and the shift in demand should be dampened. In this event, the long run market situation will not change dramatically.

The relative degree of monopoly power in the industry has already been discussed. The giants that dominate the refining industry also dominate the mining and distribution ends. Vast financial resources are required for the exploration and production of new fields which eliminate all but a few "wildcatters." The distribution end is dominated by non-price competition between majors who sell "differentiated" productions. The independents who process oil seldom own their own oil fields or distribution systems. The ability of the independents to survive, and even slightly improve their position relative to the majors in recent years was due to the relatively competitive behavior of the whole crude oil and products markets.

A major factor behind this competitive behavior was the transportation system. Pipeline transportation of crude and finished products is the cheapest method available besides water transportation. Pipelines, however, require enormous capital investments ($1 million dollars/10 miles is a reasonable figure). Economies of scale exist, and operating costs are not related to capacity utilization. These circumstances have made joint construction ventures by the major firms profitable. The courts have ruled that these pipelines are "common carriers" thereby giving the independent the right to ship their products by these pipelines. Common carrier statutes also guarantee an equal price being offered to all buyers. In the past, this condition has assured the small company of crude transportation at the same price as the majors and a way of competing on an equal basis as far as transportation costs of its finished product. Consequently, buyers and sellers have largely ignored company lines and buy and sell solely on a short-term least cost basis. The situation has changed with current shortages. Company lines assumed a previously undefined importance as the majors tried to keep their facilities running at capacity. Independents had no problems selling their products but sources of crude became scarce. This has led to a system of semi-voluntary allocations in which suppliers of crude divide their supply among the refineries by a percentage of last year's demand. Congress has given the executive branch the power to make these controls mandatory in order to protect the competitive position of the independents.

The second factor important to the independents' survival is that a large percentage of the refiners' sales are made directly to customers. These products are produced to specification on contracts that are subject to competitive bidding. The demand for these products is, consequently, highly elastic as far as the individual refiners are concerned, thereby reinforcing competition. The servicing of specialized markets by the independents has also partially countered the trend to large coastal refineries.

Originally, refineries were built in oil fields. The atmospheric distillation unit was the only process used. The light upper fractions were marketed while the heavy bottoms were burned. The part of the crude used was less than 50% of the total volume. Although the cost of transporting the finished product was slightly higher, the reduced volume favored a refinery in close proximity to the oil field. A modern refinery, however, converts all of the crude into finished products. It has been estimated that the cost of transporting all of these products is twice the cost of transporting crude. Refineries have shifted so that most of the locational emphasis is now on market proximity. Small refineries are able to compete with larger refineries by servicing the special markets that are uneconomical for large refineries to service. These special markets include asphalt manufacture or jet fuel for an air base, or geographically isolated markets.

It is interesting to note that the average size of refinery built by a major in the 1964-72 period was 113,000 barrels of crude per day, while the average size built by an independent was 15,000. If the two types of refineries were competing for the same markets, only the larger refineries would remain. This is due to the considerable economies of scale that are associated with the capital and labor costs in refining. As the size of a process unit increases, both labor and capital costs increase less than proportionately. It has been estimated that a 30,000 barrels of crude per day refinery operates at a total 5% cost disadvantage when compared with a 100,000 barrel a day refinery. A refinery smaller than 30,000 barrels of crude per day would operate at an even greater cost disadvantage.

Assessment of the future prospects for additional refining capacity construction in New Mexico rests, then, jointly on the future viability of the independent producers and the development of significant local demand sufficient to justify the construction of a small refinery to serve this local need.

ANALYSIS OF REFINERY WATER REQUIREMENTS

Introduction

A general analysis is presented of the water requirements of the petroleum refining industry. Specific attention is devoted to the use of water in refining processes, the contaminants, their sources, and the treatment of such contaminated water either for reuse within the industry or prior to discharge to the surrounding environment. For background purposes and to provide a better understanding of areas of water use a brief description of the processes comprising the total refining operation is made. Similarly described are the treatment processes used to bring the refinery products within customer specifications.

It is the intention of this work to compile and interpret information which will be of use to the nontechnical person who is interested in the petroleum refining industry and its impact upon water in a water-deficient region. Any detailed feasibility study must be done by a team of technical specialists after management has defined the products, the precise process, and feed stock availability. However, the present generalized study should allow persons charged with the industrial development of an area to determine, if, from a water-use viewpoint, a refinery is desirable.

Two federally sponsored investigations of the water requirements of the petroleum refining industry have been documented--a U. S. Geological Survey water supply paper published in 1963 of a survey done in 1955-1956 [78] and a FWPCA survey in 1967 [107]. A number of reference books and periodicals exist which also give some insight into the water requirements and wastes of the refining industry [3, 10, 11, 38, 39, 76, 87, 88, 121, 123]. Typical gross water requirements--water intake plus water recirculated--are estimated to vary from 800-3,000 gallons per barrel of crude oil (gpbc) processed [3, 38, 39, 76, 78, 121]. The average fresh water requirement was estimated in 1950 to be 200-500 gpbc. Since 1950, these requirements have decreased to 30-100 gpbc with the use of newer technology. The wide ranges shown reflect differences in availability of water, in-plant reuse, and technologies. Approximately 21% of the total water requirements in a refinery is raw water, with the remaining 79% being supplied by reuse of in-plant water [121].

Petroleum refining operations use water both consumptively and nonconsumptively. The major consumptive uses are evaporation and wind blown losses from cooling towers and from the discharge of steam to the atmosphere. Water consumed averages 2-5% of the total water used or 30-60 gpbc. Discharge of cooling water blow-down and steam condensate are typical nonconsumptive uses. The extent of water reuse within a refinery is dependent upon the availability of a satisfactory quality water supply. However, with higher reuse the actual consumption of water usually increases. This is because of higher evaporative losses even though a decrease in refinery water intake and net effluent also occurs.

The largest water requirement in a refinery is for cooling purposes; this factor accounts for an average of 95% of the water demand. Most cooling water is used primarily for indirect cooling and does not come directly into contact with hydrocarbons and other process fluids. However, water used in washing petroleum products and the recovered steam condensate from stripping and vacuum operations have had contact with petroleum stocks and thus usually contain various dissolved or suspended contaminants.

The second major use of water in petroleum refineries is boiler feed water. Approximately 3% of the petroleum refinery water requirements are used in boiler feeds. Steam is used for stripping, heating, pumps, vacuum ejectors, and distillation. Because such uses of steam result in contact with petroleum products, the condensate is usually contaminated with petroleum or other wastes which decreases its reuse potential.

Petroleum Crude Material

The constituents of crude petroleum consist of hundreds of different individual chemicals ranging from methane to asphalt components. Most of these constituents are hydrocarbons but small quantities of nitrogen, sulfur, and oxygen may also be present. The hydrocarbons of crude petroleum may be separated into two chemical classes: aliphatic, or open-chain, compounds and ring compounds. Aliphatic compounds consist of the normal paraffin series, or saturated compounds such as methane, ethane, propane, butane; isoparaffin series, which are saturated compounds containing side groups or branched chains, such as isobutane; and the olefin series which are unsaturated compounds such as ethylene, propylene, and butylene. The paraffin series exist in crude petroleum in larger quantities than any other group while the olefins are not present or exist only in small quantities. The ring compounds may also be divided into several subgroups. Naphthene series are ring compounds corresponding to the olefin series of the aliphatic compounds but in the ring form are saturated, that is, all the chemical bonds are singly bonded rather than double or triple bonds. Naphthene series compounds are the second most occurring series in most crudes and consist of such chemicals as methylcyclopentane, cyclohexane, dimethyl cyclopentanes, and methylcyclohexane. The other ring series is the aromatic or benzene series which are the unsaturated ring compounds based on the benzene ring. Typical compounds are benzene, toluene, ethylbenzene and the xylenes. Only small amounts of the aromatic compounds are present in most sources of crude petroleum [40].

Petroleum Refinery Products

Some 2500 products may be derived from the petroleum refining of crude oil. The products from the crude petroleum may be essentially pure compounds such as acetylene, ethylene, propane, butane, benzene and toluene. Other products are mixtures of compounds which may be distilled off in a certain range of boiling temperatures such as the fuel oils and naphthas. Gasoline is a blend of petroleum based compounds while waxes are crystallized from the petroleum liquid. Some typical petroleum refining products are described as follows.

Gasoline--primarily composed of small-branched chain, cyclic, and aromatic hydrocarbons boiling in the range of 60-200°C. The natural material is only a small percentage of crude petroleum and the majority of the actual product sold must be produced by cracking, hydroforming and reforming of heavier hydrocarbons.

Naphtha--loosely defined petroleum fraction containing primarily aliphatic linear hydrocarbons with a boiling range from 125-240°C. It is recovered as a distillation fraction and is the intermediate between gasoline and kerosine containing compounds of both. It is used as a solvent, paint thinner, feed stock for gasoline production, and as a raw material for organic chemical preparation.

Kerosine--the fraction of petroleum boiling between 180-300°C. It contains hydrocarbons slightly heavier than those found in gasoline and naphtha. Its primary uses are fuels for jet engines and gas turbines. It may also be catalytically converted to gasoline and naphtha.

Diesel Oil--petroleum fraction consisting primarily of aliphatic linear hydrocarbons distilling in the range of 250-400°C. It is used in diesel engines and as a light fuel oil (No. 2).

Fuel Oils--the petroleum fractions having a higher boiling range than kerosine.

Residual Fuel Oil--high viscosity fuel oil collected after all lower boiling fractions have been distilled off.

Lubricants--oils obtained from residual fuel oil by solvent extraction.

Residues--material remaining after distillation of lighter hydrocarbons and contains asphalts, residual fuel oil, greases, coke and petrolatum. These are by-products of the refining process and may be separated and purified to produce valuable materials by proper techniques.

Petroleum Refining

The refining of crude oil is accomplished by a series of complex manufacturing processes involving both physical and chemical changes of the hydrocarbon mixture comprising the crude to create a variety of marketable products. The main processes by which crude oil is separated into its original component fractions are distillation and extraction. The yield of products having the specified desirable properties from these two operations is determined by the type of crude oil processed. Crude oils from various sources have much different properties.

Ideally, a refinery should be able to produce processed saleable products in the quantities demanded by its markets. If the yield is not in balance with the market requirements, other processes must be used to convert the excess products into different saleable products. Cracking, or chemical conversion by heating and/or catalysis, is the main process used to balance the product distribution. In the cracking process, surplus fuel oil may be converted into gasoline and gaseous petroleum products. Alkylation is used to synthesize larger molecules from gases, the gases mostly originating from the cracking process, thus increasing gasoline production and quality. Other conversion processes, isomerization and reforming, are used to improve the quality of gasoline fractions [40, 55, 73, 75, 101, 111].

Further refining of the products of these manufacturing methods is necessary since they are insufficiently pure for their ultimate application. In these processes, called treating, the small quantities of impurities are removed. Sulfur compounds contained in many products are odiferous and if not removed may be converted to non-odiferous compounds by a process generally referred to as sweetening; that is, the removal of the odor. The trend today is towards actual removal of the sulfur to meet the stringent quality standards placed on sulfur containing fuels.

No two petroleum refineries are identical. The varied properties of the crude oil along with the numerous possible products have resulted in diverse refinery processes, or treatment of the crude oil and resultant oil fractions, requiring different operations and equipment within each refinery. According to the processes used, refineries are normally classified by the complexities of their operations and finished products.

The simplest refining operation is called topping or skimming. In this type refinery the crude oil is distilled, or fractionated, by heating, usually at atmospheric pressure, and the petroleum fractions separated at various boiling ranges. Such refineries produce only a limited range of products. This operation alone is not considered a very economical process since principally low grade products result. A schematic of a topping process with typical products is shown in Figure 1.

The next level of refinery operation consists of topping and cracking. Cracking, or pyrolysis, is the conversion of long molecules into smaller molecules by the application of heat and/or catalysts to product hydrocarbons more suitable for gasoline. Catalytic cracking is preferred because of economic considerations since it produces larger yields of higher octane gasoline at lower unit costs than does thermal cracking. Alkylation units may be added for the production of premium automobile and aviation gasolines. Figure 2 shows a schematic of such a plant with products indicated.

The most complex refinery will consist of topping, cracking, and lube oil production. The bottoms from the crude fractionation tower are fractionated under vacuum and then further specifically treated to obtain the motor oils (wax-free) and the by-product, paraffin waxes and petrolatum. Figure 3 shows a schematic of a typical plant. These schematics are greatly simplified and do not show the interdependence of each unit on the others.

Some refineries also include asphalt plants and many refineries provide fuel oil and diesel fuel products as part of their regular production.

The distinctions among the various types of refineries is not clearly defined and there exist a number of borderline cases depending upon the crude oil supply and the readily available markets.

The present trend is towards integrated refineries, that is, refineries consisting of topping, cracking and lube oil production. It is this type of refinery which will be discussed in terms of its operations, water requirements, and aqueous waste streams.

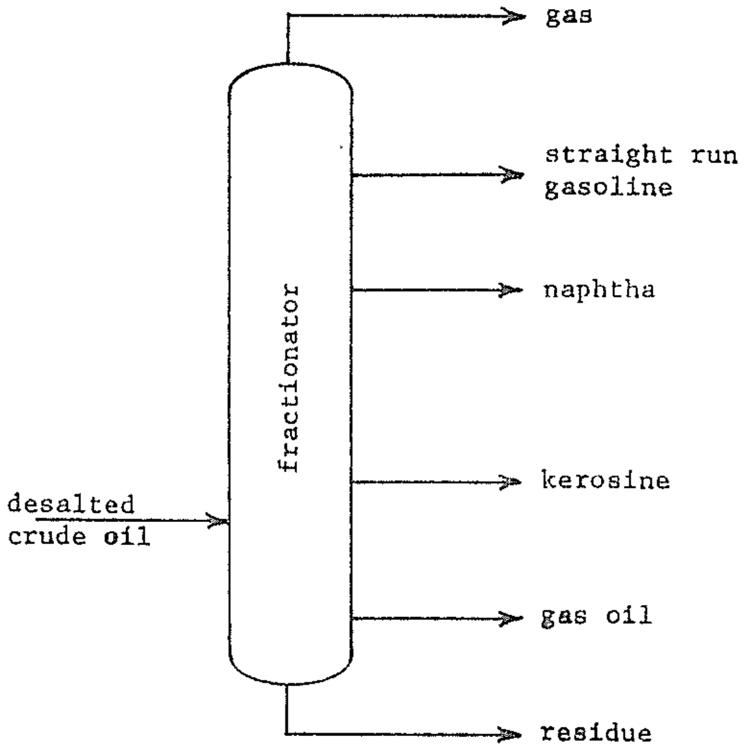

Figure 1. Representative Topping Refinery Flow Schematic

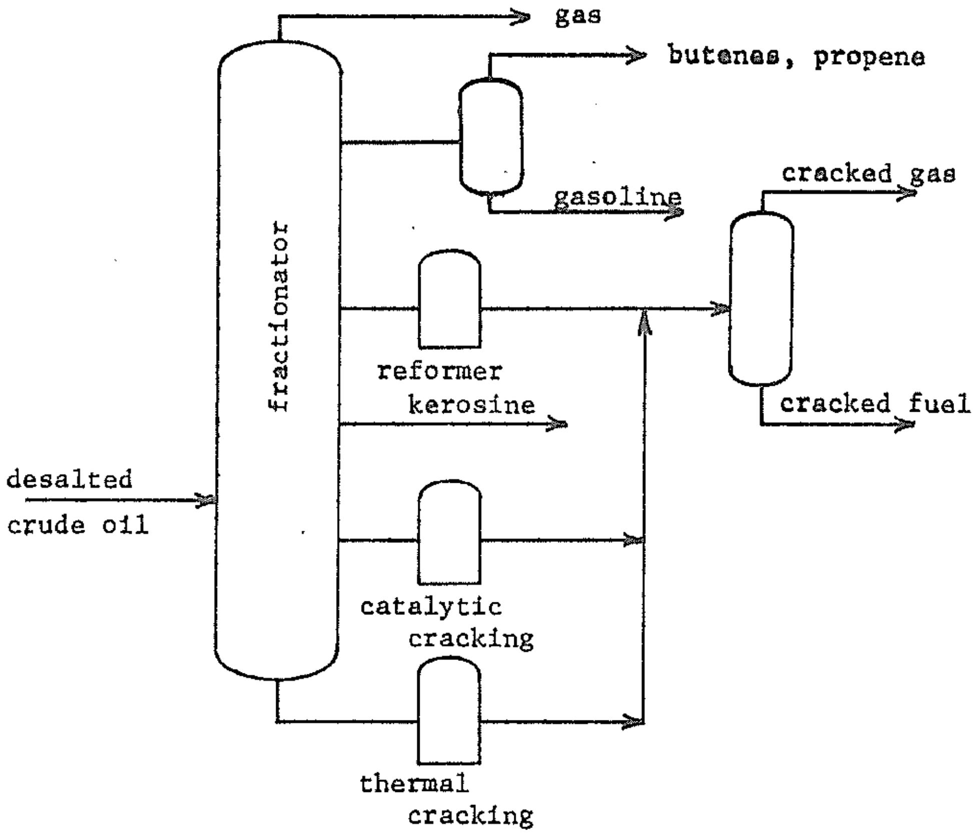

Figure 2. Representative Topping and Cracking Refinery Flow Schematic

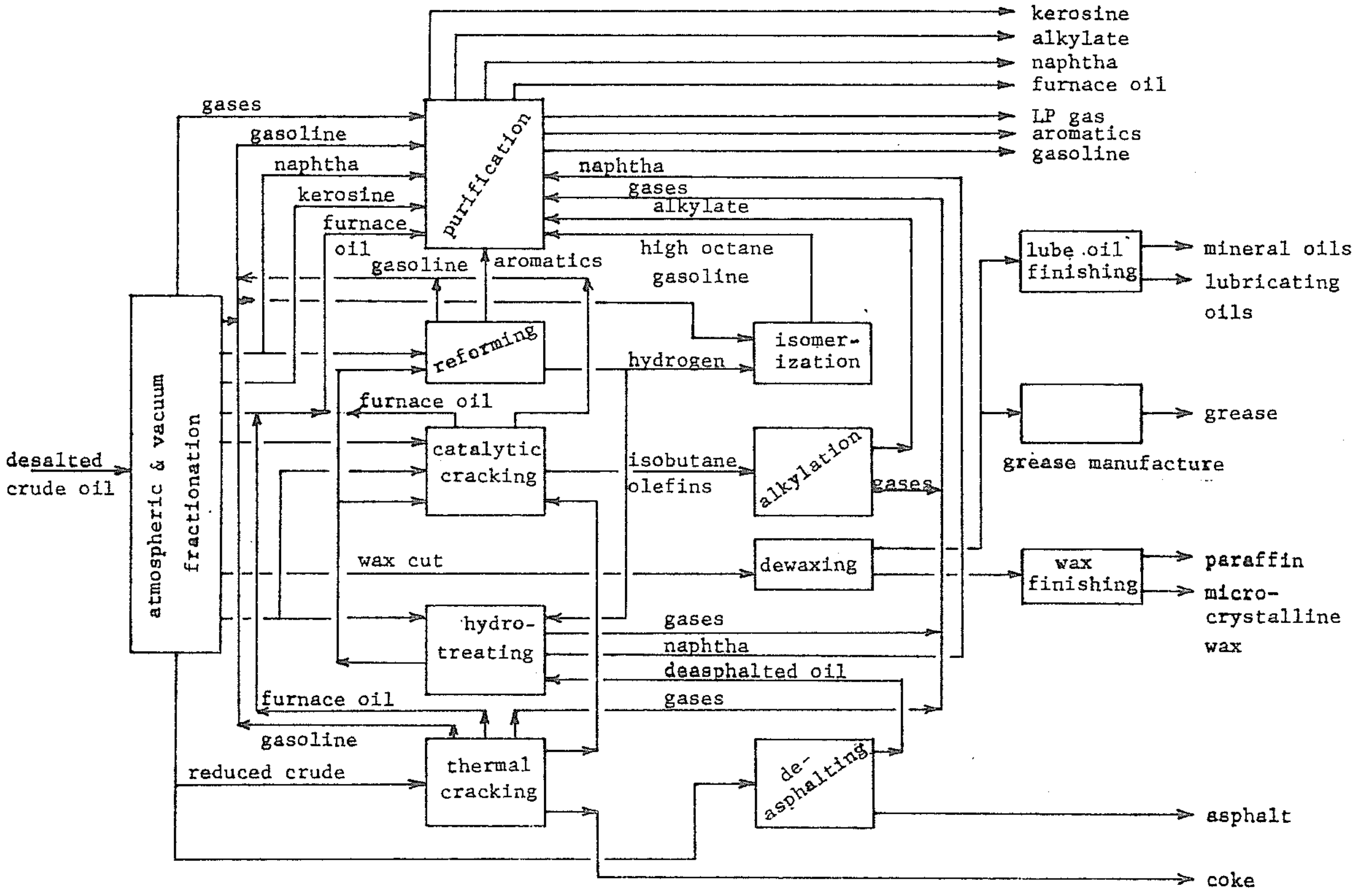

Figure 3. Representative Integrated Refinery Flow Schematic

Refinery Processes and Wastewater Generation

The generation and sources of aqueous wastes within a petroleum refinery operation can be shown by considering a typical fully integrated refinery, the schematic of which is shown in Figure 3. Typical aqueous wastes are shown in Figure 4 for the subprocesses within the refinery and Table 3 lists representative quantities of aqueous wastes according to source [11, 15, 38, 76]. For the major potential sources of aqueous pollutants, representative pollutant concentrations are listed in Table 4 [15]. It must be realized that these are a general approximation of the quantity and quality of refinery waters. Because of the efficiency of water reuse and waste control facilities, size of refinery, type of crude oil charged, and complexity of processing, it is impossible to give exact figures in a general discussion. However, it is felt these quantities are indicative of present aqueous streams discharged from the various processing units.

Principal operations used to produce the products within a petroleum refinery are: fractionation under pressure and vacuum distillations, thermal and catalytic cracking, reforming, polymerization and alkylation. Other operations such as acid treatment of lube stocks, sweetening of gasoline, extraction and stripping are used to make products meeting certain specifications and quality.

In addition to the equipment used directly to produce the petroleum products, other equipment and operations are required. Steam is used extensively for heating, stripping, and in vacuum systems, thus boilers are necessary. If the production capacity is sufficiently large and steam requirements are great, electrical generation equipment may be added to the facility.

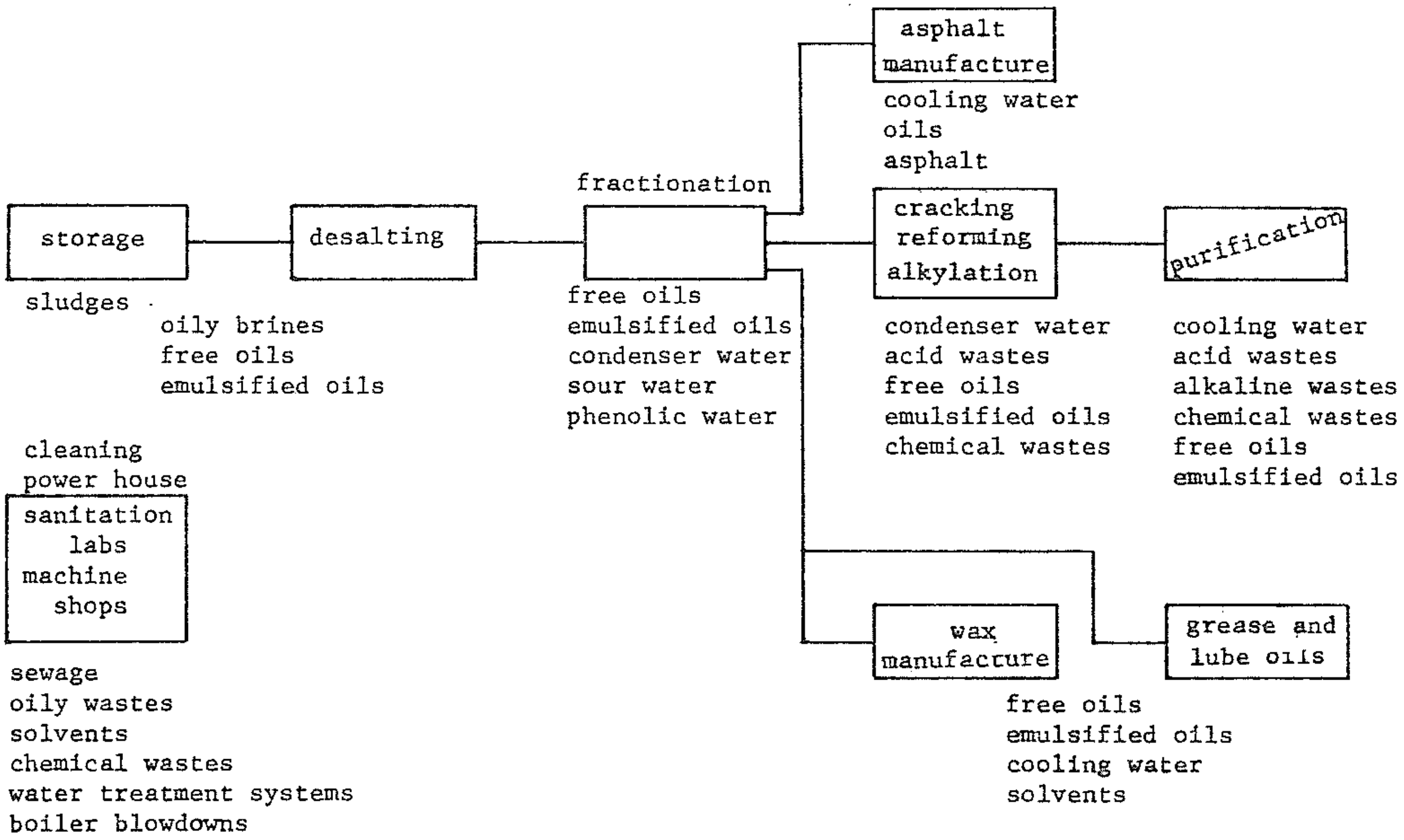

Figure 4. Typical Aqueous Waste Sources in Petroleum Refining

Table 3. Sources of Refinery Wastewater

	g/bbl
Crude oil storage	-
Crude oil desalting	3.5
Crude oil fractionation	4.1
Thermal catalytic cracking	6.0
Alkylation HF	nil
Sweetening and drying	2.0
Cooling tower blowdown	13.0
Boiler water blowdown	2.1
Caustic washes	4.0
	34.7 gal. per bbl.

Water evaporated from cooling towers 27 gal. per bbl.

Table 4. Representative Pollutant Concentrations

	Sulfides mg/l	Phenols mg/l	Oil mg/l	BOD mg/l	COD mg/l	pH	H_2S mg/l	NH_3 mg/l
Desalter Effluent Water	4.3	15	169	259	291	8.2	-	-
Sour Condensates (distillation & cracking)	-	420	-	-	-	8.5	4200	3100
Phenolic Condensates (cracking)	4500	350	3-100	120-3040	-	-	-	2000

Crude oil brought into a refinery contains salty water; the quantity of water depends upon the source of the crude and the transportation method used. Some of this water will settle out in the crude oil storage tanks and is withdrawn. The water is very oily, generally has a high salt content, and usually contains sulfides or other sulfur compounds.

In addition to water, all crude oils contain inorganic salts and suspended solids which must be removed prior to refining. Arsenic and other similar salts, in particular, are poisons for the cracking catalysts and must be removed. Desalters are used to remove these salts. Water is added to the crude oil and an emulsion formed by agitation. Water supplied is usually 3-10 volume percent of crude treated. The salts transfer to the aqueous phase and then the emulsion is broken by using a high voltage electrostatic field of 10,000-16,000 volts. The water and oil are separated by gravity in a settling tank. The salty water is withdrawn continuously and the desalted crude oil is sent on for refining. The aqueous waste stream contains free and emulsified oil, large quantities of dissolved inorganic solids, usually of high chloride content, and has a pH of about 8. The dissolved salts are the major waste problem since oil and sulfide levels are not extremely high.

Fractionation of the desalted crude oil is done to separate the crude into intermediate fractions of specified boiling point ranges. The overhead product is gasoline and sidestreams withdrawn may correspond to naphtha, kerosine, light diesel oil, and heavy diesel oil. The gasoline is debutanized, removal of butane, to raise its boiling point and stabilize it. Butane, propane, and methane are gaseous products of stabilization. The heavy crude leaving the bottom of the tower may be treated to produce gas oil, lube oil side streams, catalytic cracking feedstocks, and asphalt base stocks. Steam is used in the crude oil fractionator for stripping the low boiling components from the reduced crude and the sidestreams. The vacuum may be produced for vacuum fractionators by the use of steam ejectors. Aqueous waste streams from crude oil fractionators result from the condensed stripping steam in the accumulators and water not separated in the desalting operation which distills with the lower boiling crude oil components. Such water contains oil, large amounts of sulfides, chlorides, ammonia, mercaptans, and phenols. Large quantities of water are required to condense the overhead and sidestream product vapors but this water does not contact the products and is therefore not contaminated.

The heavy crude from the bottom of the crude oil fractionation tower is usually further separated in a vacuum fractionator and this residue thermally cracked to produce lighter fractions of more economic value. Steam ejectors produce the needed vacuum. The light fractions may be used for fuel oils or gasoline production. Again water is the major source of waste, it being recovered from the overheads and the ejectors. Cooling water is required for condensation of the vapors. The water may be high in ammonia, phenols, sulfides and usually contains various oil fractions. The waste is usually alkaline and may contain a high dissolved solids content.

Catalytic cracking of naphthas, gas oils and deasphalted oils is done to increase the yield and quality of gasoline and other desirable products. Catalytic cracking is similar to thermal cracking except that the cracking process is accomplished at lower temperatures and pressures due to the catalyst. Better yields of high octane gasoline are obtained as compared to thermal cracking. Steam is used to remove the products from the cracker and to seal the cracking vessel from the catalyst feed hopper and the kiln. Stripping steam is generally used to regenerate the spent catalyst. The steam condensates represent the major waste streams. Other aqueous streams are formed by condensation of the stripping steam in the fractionators which are used to separate the various hydrocarbon fractions produced in the catalytic crackers. The aqueous streams have high sulfide contents, are oily, contain phenols and ammonia, and are highly alkaline.

Hydrocracking is catalytic cracking in the presence of hydrogen, thus producing gasoline, high quality middle distillates, LPG or low sulfur residual fuels from distillates, gas-oils, heavy sour crudes, and crude fractionation residues. Steam is used for product removal and stripping in product separation fractionators. The aqueous wastes contain sulfides, phenols, ammonia, and oil. Most hydrogen sulfide will leave with gaseous products.

Reforming is used to convert naphthas to finished high octane gasoline and produces aromatics. Steam may be used for temperature control and regeneration of silica-alumina base catalyst. Aqueous waste materials from the reforming process are very small and contain sulfides, ammonia, mercaptans, and oil. The wastes are of an alkaline nature.

Conversion of isoparaffins, usually isobutane, into iso-octanes is accomplished in the alkylation process. These high octane alkylates are used as a gasoline blending component. The principal reaction occurs between an isoparaffin and an olefin to produce a larger isoparaffin and hydrogen in the presence of a catalyst under precisely controlled temperatures and pressures. Of the three major catalysts used, aluminum chloride, sulfuric acid, or hydrofluoric acid, the sulfuric acid process has most potential for wastewater production since it has a spent acid reactor waste having a pH of three or less and an acid content of about 85%. The overhead accumulations in the fractionators contribute small quantities of water containing oil and sulfides. Spent caustic washes are also released from the neutralization of the alkylation reactor hydrocarbon stream. If leaks or spills occur from hydrofluoric acid alkylation units, serious waste problems may arise; but, in normal operation, aqueous waste is negligible.

Processing to saturate olefins and to remove sulfur, nitrogen, and oxygen compounds from straight-run or cracked petroleum fractions is called hydroprocessing. The feed is combined with hydrogen, heated, and passed through a catalytic reactor. Aqueous waste streams have high sulfide and ammonia contents and are the result of stripping steam condensing in the overhead fractionator accumulators.

The deasphalting step is used to remove asphalt and resins from viscous hydrocarbon fractions by dissolving the desired hydrocarbons in the appropriate solvent, for example, propane, while leaving the asphalt and resins in the residues. Wastewater results from the steam stripping process used to separate the asphalt, solvent, and deasphalted oil. This water contains some ammonia, sulfides, and oil.

The remaining process operations used to produce petroleum products are relatively free of aqueous wastes.

Processes used for the purification of petroleum products contribute to the aqueous wastes and have high contaminant levels. Spent caustic solutions result from neutralization and extraction of the acidic materials present in the crude oil, from the acid reaction products of chemical treating processes, and from acidic materials formed during cracking. These solutions contain sulfides, mercaptans, sulfates, sulfonates, phenolates, naphthenates, and many other similar inorganic and organic compounds. Sulfuric acid is used frequently both as a treating agent and catalyst. The resulting acid sludges and spend acids may contain up to 60 percent hydrocarbon content with a titratable acid as high as 90 percent. Other wastewater streams are created by the regeneration of the treating materials used to purify the petroleum products. Steam heating and stripping is extensively used for regeneration of the absorbent chemical solutions and the steam condensates will contain sulfides, phenols, oils, etc.

Feed water for the boilers must be treated to lower its hardness, particularly in the Southwestern areas. The effluent from the back washing of the water softeners, although of an intermittent nature, is a source of very salty water. The blow-downs from the boilers, used to keep the dissolved solids from building up too high a level, are another small but highly salty stream.

The cooling water system also must be replenished frequently, especially if evaporative cooling is used to lower the temperature of the heated used cooling water. Blowdown of the cooling water system is necessary to prevent the buildup of dissolved solids and subsequent deposition of salts within the system. The amount of blowdown and its quality is determined by the quality of the replacement water, the evaporation level, and the corrosion and algae inhibitors used.

Water from sealing glands on pumps, water used to clean up spills and leaks, water from rains, water from laboratories, and water from sanitation facilities must also be considered.

If all of these sources of water were disposed of with no treatment, problems would arise. However, the petroleum refining industry has been among the leaders in waste water pollution abatement particularly in water scarce regions. Treatment and reuse of the water has been very common. With many refining operations in the Southwest any effluent water is sent to oxidation ponds, settling ponds, and evaporation lagoons. If there is discharge from the facilities, it is usually by percolation through the soil around the ponds. Normally this causes no problems unless the water table is quite near the ponds and the local geological structure permits seepage into the water.

Treatment of Wastewater

Treatment of aqueous streams within the petroleum refining industry can be classified as: physical, chemical, and biological. Physical methods involve the use of gravity separators, air flotation, or evaporation. Ten to eighty-five percent of the suspended solids and 50-99% of the free oil may be removed by gravity separation-air flotation. Chemical methods include coagulation-sedimentation, and chemically assisted air flotation. These methods are more effective for removal of emulsified oil than simple physical methods. Biological methods, such as activated sludge, trickling filters, aerated lagoons, and oxidation ponds are effective for removal of organic materials, thus lowering BOD and COD levels, but usually require pretreatment to remove oily or toxic materials. Physical-chemical treatment has been used for final clean-up of waters to produce a high quality effluent. Apparently only activated carbon and ozonation have been commercially used for final treatment to any appreciable extent.

Present disposal of waste water effluents in Southwestern petroleum refineries appears to be lagooning, with subsequent biological oxidation of biodegradable materials followed by solar evaporation of the water. Sour waters or water containing hydrogen sulfide, mercaptans and other odoriferous compounds are previously steam stripped of the odor forming materials. If the salt content is not too large, the stripped water is then either used in the desalters or as make-up water feed in the cooling system. Salty water is sent to the lagoons. All refineries use separators to remove suspended or free oil from the waste water prior to reuse or discharge. Segregation of water according to the type of treatment required for reuse of the water or removal of contaminants prior to discharge is common practice.

Treatment necessary for refinery waters depends upon the source of the water and its ultimate use or disposal. Waters are classified as sour if sulfur compounds are largely present, phenolic if phenols comprise the bulk of the contaminants, salty if high dissolved salt levels exist, and oily if free or dissolved oil is present. Water may also be caustic or acidic. Combinations of these conditions may exist.

Separation of free oil and suspended oil is accomplished in an API separator. Advantage is taken of the density differences between the oil and water and sediment present. Gravity separation is used in the slowly moving liquid with the oil rising to the surface where it is skimmed off and heavy sediment settling to the bottom to be dragged off and the water passing through. Efficiencies of such separators are highly dependent on oil golbule size, rate of flow through separator, water temperature, and design. Fifty-eighty percent free oil removal is normal.

For improving the quality of water leaving the API separators, filtration, chemical flocculation and sedimentation, and air flotation may be used. These methods further reduce the oil and suspended solids content and result in a greatly lowered BOD, as well as improving color.

Emulsified and dissolved oils are not separated from water in gravity separators. Emulsified water oil mixtures can be broken but the treatment depends upon the type of emulsification, water-in-oil, or oil-in-water, and the other molecular species present. Most emulsifications of interest are water-in-oil which can be broken by heating, centrifuging, filtration, use of chemicals, electrical fields, or combinations of these methods. Usually emulsion breaking is done in a series of batch operations and the separated oil returned to the appropriate processing unit.

To remove volatile impurities such as hydrogen sulfide or ammonia, stripping processes are used in which the solution is heated and the more volatile components separated. Stripping operations are highly effective for volatile components but for less volatile materials, such as phenolics, heating and equipment costs become prohibitive.

Extraction techniques may be used for removal of low volatility materials. A solvent, immiscible in water, is used to remove the contaminant from the water phase by dissolution. Phenolics can be removed by these techniques using benzene or light petroleum fractions. Extractive techniques are not commonly used in the treatment of refinery wastes unless the material being recovered has a high economic value.

Adsorption techniques, removal of dissolved materials by contact with a porous solid, has not been used extensively in refinery waste treatment. The undesired materials become attached to the surface of the solid either by physical or chemical means in this technique. After the solids become saturated, they are either disposed of or regenerated for further use. Activated carbons may be used for removal of dissolved organic materials and some metal ions. Adsorption processes are more commonly used in fresh water purification but if good quality effluent or water for reuse is required, adsorption offers a potential treatment method.

Ion exchange processes have been used extensively to replace ions in solution with ions from a solid phase, for example, softening of water by replacing the calcium ions with sodium ions. Ion exchange techniques, although extensively used for water conditioning, have been little used for refinery waste water treatment. A few special applications have been developed but ion exhange resins are expensive and unless the cost of such treatment can be justified, immediate use is not anticipated except on a small scale.

Reverse osmosis in which high pressure and specific membranes are used to produce low salt content water from salty or brackish water offers possibilities for clean up of water from the desalters and water conditioning units. However, reverse osmosis operations are quite expensive and are still in the application development stage as far as refinery effluent waste treatment is concerned. They do offer an exciting potential for reclaiming high quality water from aqueous waste streams. For example, Westinghouse has recently announced the availability of reverse osmosis units which can treat waters containing up to 5,000 ppm of dissolved solids and have capacities ranging from 10,000 to more than one million gallons per day.

Oxidation processes have been used to lower the oxygen demand of refinery wastes, particularly the removal or reduction of phenolics.

Chemical oxidants, such as chlorine, chlorine dioxide, peroxides, and ozone, have been effectively used. For easily oxidized wastes, air may be used, for example, the oxidation of sulfides to thiosulfates and the treatment of sulfates in caustic mediums. For highly concentrated, low flow rate streams, oxidation by incineration may be used. This latter method is particularly applicable for toxic materials.

Since many waste streams contain oxygen consuming materials which are biodegradable, biological treatment is necessary. Activated sludge processes, trickling filters, oxidation and stabilization ponds, and anaerobic treatment methods more commonly associated with treatment of municipal wastes may be required. In any biological process the organic materials are converted to cellular products which if decomposed would constitute a source of high oxygen demand. Deposition of these cellular products must be considered. The stabilized sludges from activated sludge treatment are dewatered and may be used as soil conditioners.

Newly constructed refineries have been designed and built to treat all potential waste waters. Existing refineries are making the necessary modifications and adding treatment facilities. A treatment scheme which would produce usable water is presented in Figure 5. Such a facility would be expensive; however, future requirements to protect the environment may demand such treatment. At this level of treatment much of the water may be reused with fresh water required only to make up for losses.

Water Economy

Water economies within the petroleum refining processes can be practiced by some revisions of the processing techniques. Although older refineries will be slow to change equipment because of the large investments required,

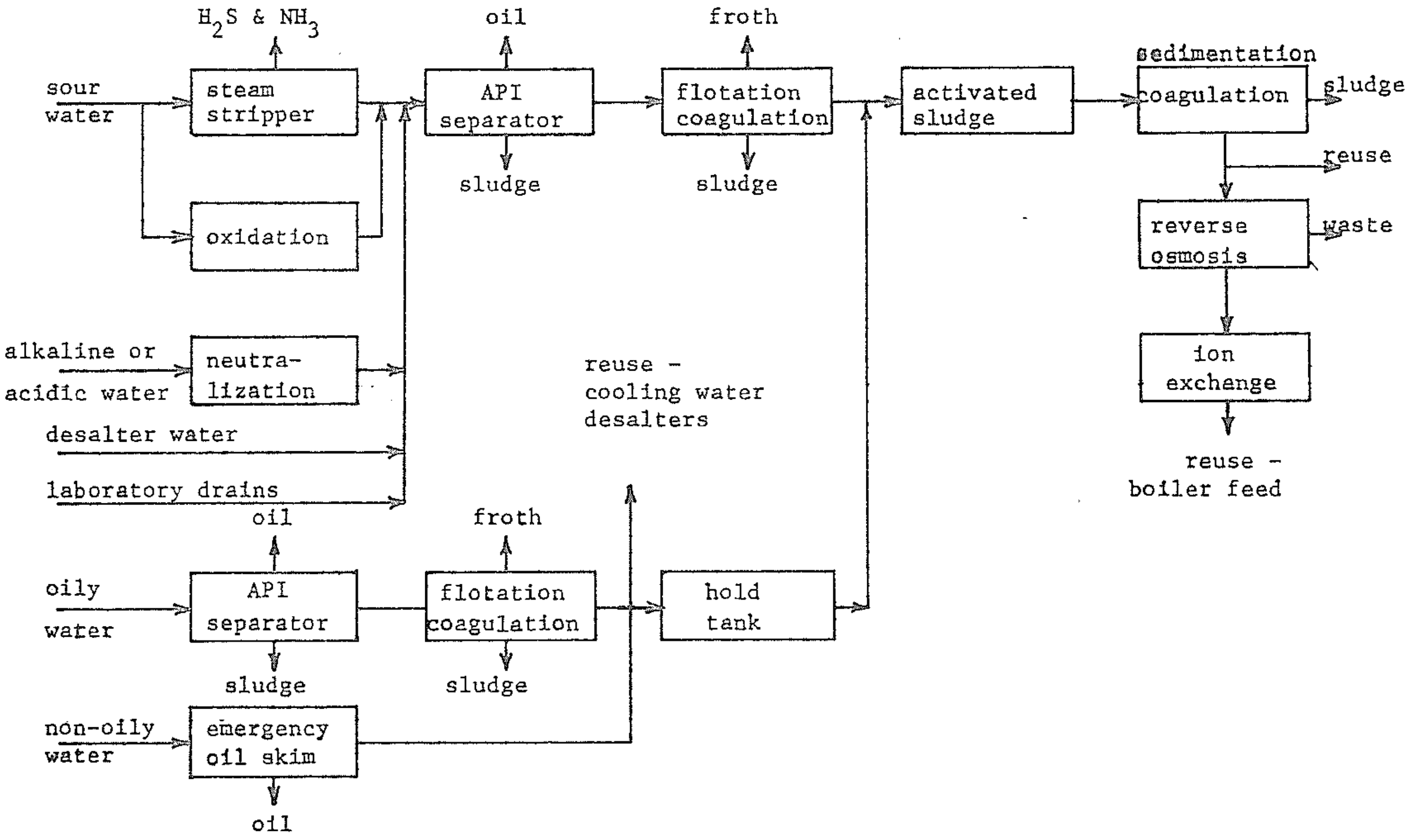

Figure 5. Aqueous Effluent Treatment Scheme

newer refineries are incorporating processes designed to reduce water usage, to reduce process contamination of water, or to clean up contaminated waters. The replacement of barometric condensers and steam ejectors with surface condensers and vacuum pumps for vacuum distillations will eliminate the oily waters generated in the barometric condensers. Elimination of the steam ejectors would greatly diminish steam demand.

A source of large quantities of oily and sour waters results from the use of stripping steam to stabilize petroleum fractions by removal of lower boiling components. The use of steam for stripping purposes is likely to continue since there are many economic advantages with its use. The stripping steam condenses with the hydrocarbon vapors resulting in much smaller sized condensers being required as compared with stripping by non-condensible gases. However, much more cooling and condenser water is required to condense the vapors and stripping steam than if non-condensible gases were used. The use of such an inert gas for stripping purposes would greatly reduce the water requirements but would increase costs of condenser, compressors, and vacuum producing equipment.

Facilities using cooling towers to lower the temperature of the circulated cooling water lose water to the atmosphere by evaporation and windblown losses. The evaporation losses are directly proportional to the temperature change achieved. These water losses could be reduced by using air cooling in closed cooling water exchangers. Such cooling water could be used for higher temperature range cooling. Where cooling is necessary near ambient temperatures, cooling towers or refrigerated cooling could be used. Reductions in the use of cooling water could further be accomplished by using air cooled condensers on some of the higher temperature boiling fractions rather than water cooled condensers as is presently done.

Permitted Effluent Levels

The Environmental Protection Agency has been working on a set of effluent guidelines for the petroleum industry. The tentative acceptable levels are shown in Table 5 [68]. These recommendations were based on activated sludge facilities being used to treat the aqueous effluents. Further reductions in effluent levels can be reached if necessary but the cost increases rapidly as the complexity of treatment facilities becomes greater.

Costs

The determination of the construction costs of a new refinery entails the design of a plant, its layout, and detailed itemizations of the units of equipment to be purchased. The geographic area needs to be considered also. An estimation of $1,025 per barrel of crude processed daily based on 1973 Nelson Cost Indexes will be used for the cost of a newly constructed integrated refinery [74]. Operating costs of $1.47 per barrel of crude are estimated as shown in Table 6 [74, 80]. The costs of effluent treatment for discharge or treatment of effluents for reuse are not included in the above estimations. For effluent treatment facilities, it is assumed 50 gallons of aqueous material will need to be treated for every barrel of crude processed. Thus, for a 50,000 barrel per day refinery 2.5 million gallons of effluent need to be treated. This effluent will be treated so as to produce reusable water and will assume no discharge of aqueous material from the facilities.

Table 5. Refining Industry Effluent Level Guidelines

lbs/1000 barrel of crude oil processed

	Ammonia as N	Chromium	BOD_5	COD	Total Oil	Phenol	Sulfide	Suspended Solids	Total Dissolved Solids
Topping Plants	10	0.04	9	52	1.0	0.1	0.1	22	4500
Topping and Cracking Plants	10	0.05	12	73	8.0	0.5	0.1	35	450
Integrated Plants	31	0.10	24	76	17.0	0.3	0.4	17	550

Table 6. Typical Operating Costs of U. S. Refineries

	cents per barrel
Purchased Fuel	18.0
Total Labor	50.0
Purchased Power	3.5
Chemicals and Supplies	30.6
Maintenance Materials	8.1
Insurance and Taxes	5.9
Royalties or Research	5.7
Obsolescence and Improvements	13.0
Interest on Capitalization	12.4
Total	147.2

At this point in time the purchased fuel costs are changing rapidly.

The estimated construction and operating costs for such a treatment system is tabulated in Table 7.

Table 7. Treatment Costs

	Construction* $1000	Treatment ¢/1000 gal.
Activated Sludge	1370	18.8
Coagulation-Sedimentation	130	4.1
Activated Carbon	950	16.0
Reverse Osmosis	1540	22.0
Total	3990	60.9

*50,000 barrel per day refinery treating 2.5 million gallons of aqueous waste.

Source:

It is felt that although the petroleum refining industry might be considered a major user of water, its wastes are amenable to treatment producing a water of high quality which may be reused. As has been demonstrated in the Southwest, most refineries do not ordinarily contribute to aqueous pollution; nevertheless improved water economies can be effected. It might be noted that some of the smaller, 4,000 or less barrel per day of crude processed, topping plants which produce straight run gasoline, diesel fuel, and residue use no water in the process except for sanitation and laboratory purposes.

Two hundred forty-seven refineries have an average capacity of 53,000 barrels per day exist today in the United States. Projections for energy requirements in 1980 will require 58 new refineries with an average capacity of 160,000 barrels per day [99].

INTRODUCTION TO COAL GASIFICATION

The gasification of coal is an old process, first used in the eighteenth century. In the late nineteenth century most of the gas used was manufactured or synthetic gas. Natural gas did not become widely used until the 1920's and national markets for natural gas were not fully developed until the late 30's when major transportation problems were overcome. Because of the large reserves of natural gas and the development of cheap transportation, the use of manufactured gas has declined in the United States, as a percentage of total gas used since 1935, and in actual volume since the early 50's. Table 8 illustrates this trend.

The manufactured gas produced ranges widely in Btu values, but is, in general, significantly lower than natural gas. Production of manufactured gas costs more than the wellhead price of natural gas. During the 30's this price differential was as high as five to one. However, the major natural gas producing areas of the United States were in the Southwest, creating a large divergence between production and market areas. The advent of the seamless pipe made possible the development of a nationwide pipeline network which was not completed until the late 30's. Because of the competitive advantage of natural gas, the use of manufactured gas has been generally reserved for emergencies, and facilities for producing this gas have not been replaced as they deteriorated.

In Europe, where supplies of natural gas and oil were not as plentiful, the technological development of manufactured gas continued. During the late 30's three German processes were developed that permitted the continuous gasification of coal. Of these processes, the Lurgi process continues to have wide commercial application in many areas of the world. The Btu value

Table 8. Total Gas Customers* of Utilities 1932-1966
(thousands)

		Type of Gas			
Year	Total	Natural	Manufactured	Mixed	Liquidified Petroleum**
1932	15,532	5,499	8,476	1,557	
1935	15,819	5,556	8,352	1,911	
1938	16,876	6,742	8,097	2,037	
1940	17,600	7,257	8,221	2,122	
1943	19,064	8,381	8,365	2,318	
1945	19,977	8,914	8,582	2,400	81
1948	22,246	11,466	8,503	1,962	315
1950	24,001	14,267	7,618	1,789	327
1953	26,708	19,960	2,795	3,653	300
1955	28,479	22,864	1,296	4,078	240
1958	31,242	28,023	401	2,643	175
1960	33,054	30,554	176	2,198	125
1963	35,551	33,940	140	1,399	72
1965	37,338	36,537	128	617	55
1966	38,228	37,513	99	573	43

*Gas customers were compared because of the difficulty in converting gas to Btu values.

**Liquidified Petroleum gases are tabulated with manufactured gas before 1945.

of the gas derived from this process is 450-500 Btu per standard cubic foot, about half the Btu value of natural gas in the United States.

The resurgence of interest in manufactured gas in the United States has paralleled the decline in our natural gas reserves. Manufactured gas can be made from a variety of feedstocks through many different processes. In terms of construction time and capital costs, gas from oil and oil products has a definite advantage. One plant is on stream currently that converts oil products to manufactured gas, seven others are under construction, and 28 additional plants are either in the planning or engineering state. The Famariss Oil and Refining Company facility under construction in southeastern New Mexico will produce naphtha and fuel oil. A unit to convert the naphtha into manufactured gas is planned for the future. The largest disadvantage of this process is its primary dependence upon oil. Over 80% of the cost of the finished gas is due to the costs of feedstocks. The current oil shortage, and the subsequent higher prices for oil products will affect the commercial feasibility of these plants.

Synthetic natural gas from coal has higher initial capital costs and a longer time from conception to completion of a plant. As the costs of other fuels raise, however, the relative position of coal improves. A complete description of the various processes that can be used to convert coal to SNG are included in the engineering section. These break down into two main types, a direct conversion process that is still being researched, and the indirect processes used in Europe. Both of the companies that are building plants in northern New Mexico use the German developed, Lurgi process. The low Btu valued gas will then be subject to a methanation process which will upgrade the Btu value to make it comparable with natural gas.

In the past, the major advantage of manufactured gas has been that it could be created close to population centers. Because of clean air legislation and the location of large coal deposits in less developed areas, the newest emphasis is the creation of coal gasification plants outside the major population centers, primarily in the western states. The gas produced is then easily transported in existing natural gas pipelines. This is a major benefit to the pipeline companies who now face the existence of a large fixed capital investment in terms of existing pipelines and dwindling gas supplies to fill them. Both gasification plants in northern New Mexico are being built primarily for pipeline companies.

The equipment to consume gas in the United States is so specifically designed around the high Btu value of natural gas that any use of another fuel of a lower Btu value would require modification of existing equipment. This, and the higher transportation costs implied in a lower valued Btu gas has caused major importance to be attached to the manufacturing of a gas with sufficient Btu value, i.e. at least 950 Btu/feet^3.

Once manufactured gas is converted to the comparable Btu value of natural gas, these fuels become natural gas substitutes. In order to examine the potential market for manufactured gas it is necessary to examine the market for natural gas. The position that manufactured gas will occupy in the future will depend upon its price in relationship to the price of natural gas, and the relative position of gas as compared to other fuels. These will be discussed below.

One of the major influences in determining the relationship of natural gas to other fuels has been the regulation of the gas industry. Gas sales to consumers were regulated by individual cities and states very early because they were deemed to be affected with the "public interest".

The Natural Gas Act of 1938 extended the regulation, and gave the Federal Power Commission the responsibility of regulating gas transmission in interstate commerce and its sale for resale. The act required pipeline companies to file, publish, and adhere to their rate structures, and gave the commission the right to suspend price changes except to industrial consumers. It also gave the commission the right to approve changes in the transportation system (i.e. pipelines) and order the extension or prohibit the contraction of services. Although the act specifically exempted the production and gathering of natural gas, it has since been broadly interpreted to give the commission the power to regulate the wellhead price of gas that will be sold in interstate commerce.

The power to regulate the wellhead price of gas moving in interstate commerce, in effect gave the commission the control over the pricing structure of the major sectors of the industry. Several methods of regulating the wellhead price, all of which have had major flaws have been used by the commission. The regulation of wellhead prices has followed the usual utility practice of trying to price on some form of a cost plus basis, either for the individual well or the general area. Lately demand for natural gas has been exceeding the discovery of new resources. Many experts believe that part of this deficiency should be attributed to the artifically low price of natural gas which has been encouraged by regulation. The current feeling by the commission and other supporters is that this area of regulation should be abandoned, and expectations are high for the deregulation of natural gas at the wellhead. Even if this move fails, the current commission is moving away from cost as a determinant of gas pricing, and using a more demand oriented approach.

Besides the power over the pricing structure of natural gas, the act firmly established the right of the commission to regulate natural gas in the public interest. This gives them the implied powers to determine the distribution of gas between consumers. The commission has done this by establishing as the most important use of natural gas, the right of every consumer to have gas available for home heating. Commercial establishments have secondary priority, and industrial establishments are given last priority.

The regulation of the natural gas industry has had major effects on the industry. As mentioned previously, regulation has been blamed for the decline in exploration of natural gas. Because of the low price to consumers, regulation has encouraged the large expansion in the demand for natural gas. It has affected the structure of the industry by discouraging vertical integration. And, finally it has affected the distribution of final users of natural gas.

The increase in production and the corresponding decline in reserves of natural gas for the United States is shown graphically in Figure 6. Because the reserves committed to natural gas pipelines are considered critical to all interstate markets, the trends of these reserves are shown in Figures 7 and 8.

As the price of natural gas has increased in the last few years, the total number of wells drilled have also increased. There is a definite lag time between the discovery of new gas reserve and the ability to bring it into full production, often as long as five years. The full effects of the current price increases on the supply of natural gas will not be known for a number of years. If the move to deregulate the wellhead price continues,

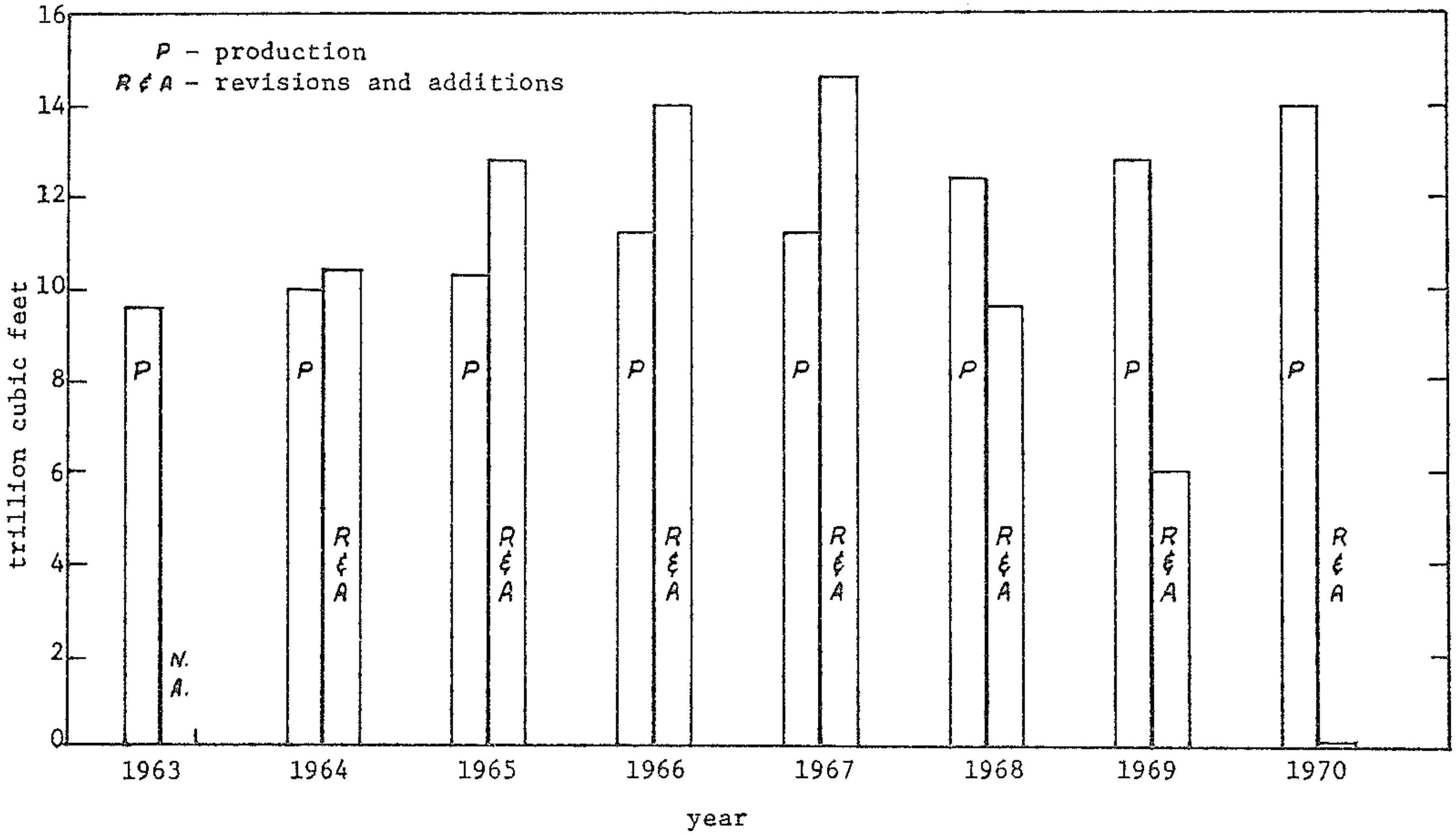

Figure 6. Production and Revisions and Additions to Reserves

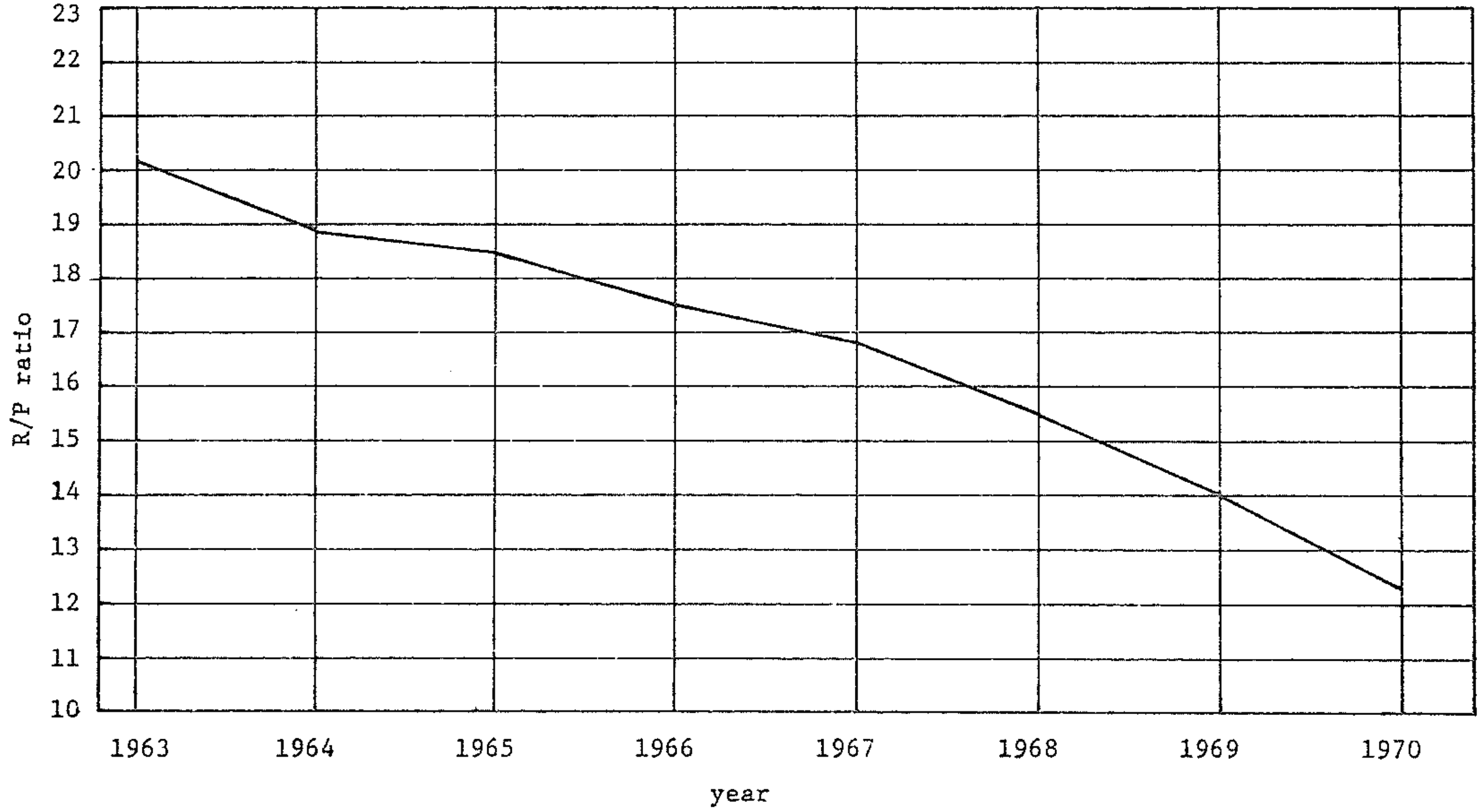

Figure 7. R/P Ratio, All Interstate Natural Gas Pipeline Companies

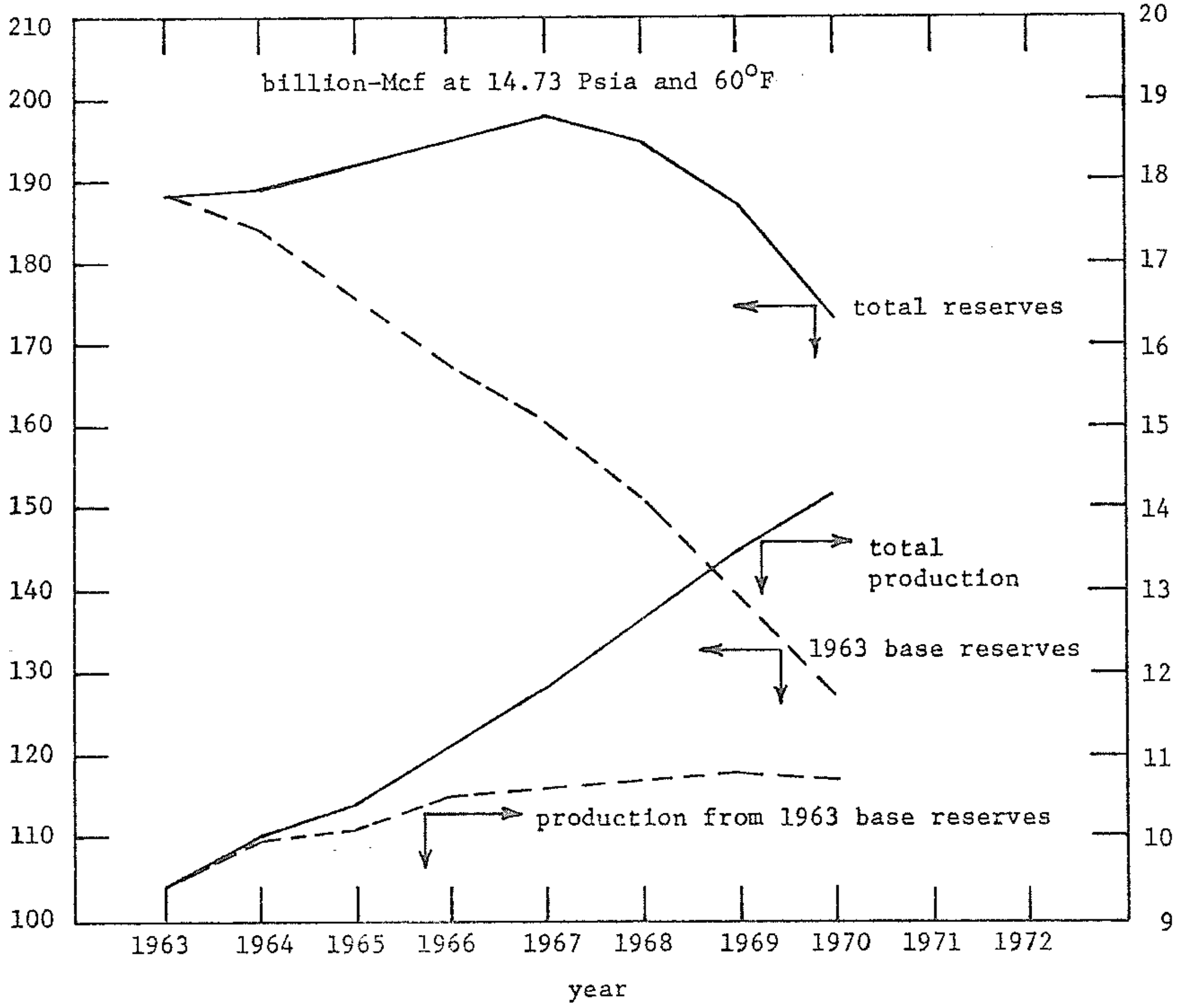

Figure 8. Domestic Reserves and Production Trends

future price increases will occur. As this stimulates exploration, and more gas is produced, and as the raise in price decreases consumption, a new equilibrium will occur. There are no good estimates on the price that this will occur at. It is this equilibrium price that is critical to the long run profit ability of any manufactured gas.

There are several factors that will probably reinforce each other to keep this price fairly high. New sources of natural gas are becoming increasingly harder to find, and more expensive to recover as the drilling depth becomes deeper. Other energy substitutes for natural gas prices have been rapidly increasing. The price of foreign oil, which had accounted for a full 35% of domestic consumption, has increased sharply, in some cases more than quadrupled. Domestic oil prices which are controlled have also increased more than 25% in the last year with future increases likely. Finally, natural or synthetic gas has the advantage of being the cleanest fossil fuel energy source. With clean air legislation, and the imposition of standards, natural gas will maintain a competitive advantage even if its price/Btu is slightly higher than alternative fuels.

The future demand for natural gas has been estimated, on the assumption that its relative price remains constant. One such estimate is shown in Table 9 and Figure 9. This also shows the relative position that alternative sources of gas are expected to occupy. According to this estimate, demand for gas will grow at a steady rate, while domestic production of natural gas declines. Liquid natural gas (LNG) imports, natural gas from Alaska, and synethic natural gas from coal are expected to make up some of the deficit, but a net deficit of approximately 18 trillion cubic feet is predicted for 1990. Recently the ability to import LNG in the

Table 9. United States Gas Supply-Demand Balance

Actual 1966-1970; Projected 1971-1990
(All Volumes in Trillions of Cubic Feet @ 14.73 Psia and 60° Fahrenheit)

Year	Annual 1/ Demand	Net Pipeline Imports	LNG Imports	Gas From Coal	Gas From Alaska	Gas From Liquid Hydrocarbons	Domestic Production	Annual Consumption	Un-Satisfied Demand	Reserve Additions	Year-end Reserves	R/P Ratio
1966	17.9	0.4	-	-	-	-	17.5	17.9	0.0	19.2	286.4	16.4
1967	18.8	0.5	-	-	-	-	18.4	18.8	0.0	21.1	289.3	15.8
1968	19.9	0.6	*	-	-	-	19.3	19.9	0.0	12.0	282.1	14.6
1969	21.3	0.7	*	-	-	-	20.6	21.3	0.0	8.3	269.9	13.1
1970	22.6	0.8	*	-	-	-	21.8	22.6	0.0	11.1	259.6	11.9
1971	24.6	0.9	*	-	-	-	22.8	23.7	0.9	12.0	248.8	10.9
1972	26.1	1.0	*	-	-	**	23.8	24.8	1.3	13.0	238.0	10.0
1973	27.7	1.1	*	-	-	**	24.7	25.8	1.9	14.0	227.3	9.2
1974	28.8	1.1	*	-	-	**	24.8	25.9	2.9	15.0	217.4	8.8
1975	29.8	1.2	0.3	-	-	**	24.7	26.2	3.6	16.0	208.7	8.4
1980	34.5	1.6	2.0	0.3	0.7	**	20.4	25.0	9.5	17.0	186.1	9.1
1985	39.8	1.9	3.0	1.4	1.3	**	18.5	26.1	13.7	17.0	175.4	9.5
1990	46.4	1.9	4.0	3.3	2.3	**	17.8	29.3	17.1	17.0	170.4	9.6
1971-1990 Totals	707.6	31.1	38.0	17.3	20.6	**	414.2	521.2	186.4	325.0	-	-

* Very small volume

** Insufficient data for quantitative projection: unsatisfied demand will be reduced by the amount of SNG actually produced

1/ Contiguous 48 states

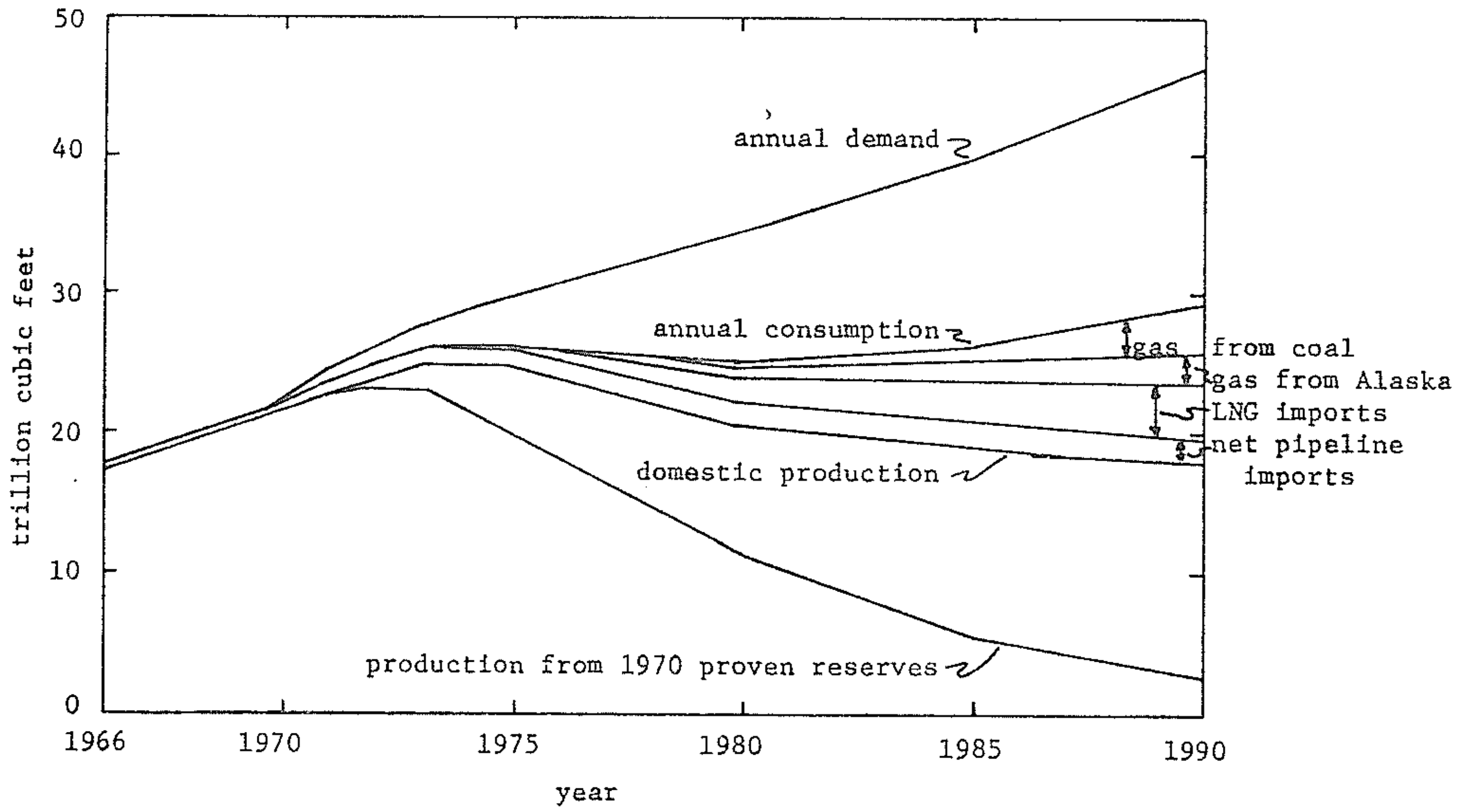

Figure 9. U. S. Gas Supply Balance

quantities originally planned have been questioned making the predicted deficit worse.

The supply and demand will have to be brought into balance by a decrease in demand, either by an increase in the price of gas or a rationing system. Currently a form of rationing exists, as mentioned previously, where preference is given in descending order to residential, commercial, and industrial users. During the 1971-72 heating seasons, curtailments to industrial users amounted to 500 billion cubic feet. During the 1972-73 season curtailments amounted to over a trillion cubic feet, which represented a 10% deficiency in demand. The FPC estimates that curtailments by 1975 will amount to 3.6 trillion cubic feet, with curtailments of 9.5, 13.7, and 17.1 trillion cubic feet in 1980, 1985, and 1990 respectively. Whether the industrial sector will continue to absorb all of the curtailments will become a very sensitive political question. The 1972 breakdown of final consumption of gas was: [125]

Residential and commercial	32.6%
Industrial	46.5%
Electrical Power	17.9%
Transportation	3.0%

In the short run, a higher price of gas is unlikely to have much influence on the demand for gas due to the difficulties in finding ways to reduce consumption and converting to alternative fuels. Demand will equal what is available at even very high prices. In the long run, substitution will occur both in terms of energy saving capital and other fuels. If the price increases in other fuels are maintained, the relative position of gas will not shift that drastically and most savings will have to come from reduced consumption.

It is difficult to compare coal gasification costs with alternative sources of gas because of the unstable nature of the energy market. Even if coal gasification costs more it might be preferred because of its riskless nature. One method of comparing alternative sources used in National Gas Supply and Demand 1971-1990 is to compare estimated capital costs required to develop equivalent volumes of natural and synthetic gas. Capital costs of the mine and gasification plants required to produce one trillion cubic feet for 20 years of synthetic gas are estimated at 2.4 billion dollars. To produce one trillion cubic feet of natural gas yearly and insure deliverability would entail the discovery and development of 30 trillion feet of reserves at a cost of $2.8 billion. The exact cost of using nuclear devices to stimulate production of equivalent reserves in gas is unknown due to the difficulty in estimating the increase in gas production. The gas in nuclear projects has the additional problem of being radioactively contaminated. Tables 10-13 show the status of various natural gas augmenting projects.

Table 10. Proposed[1] Contiguous United States LNG Import Projects

	Company	Source	Destination	Daily Volume (MM c.f.)	Year
1.	Distrigas Corp.	Algeria	US east coast	120[2]	1975
2.	El Paso Natural Gas Co.	domestic	domestic	500	-
3.	Phillips Petroleum Co.	Nigeria or North Sea	domestic	1,000	-
4.	Shell International Oil Co.	Nigeria	domestic	650	1978
5.	Standard Oil Co. (Indiana)	Trinidad	domestic	450	-
6.	Venezuelan Government	Venezuela	domestic	1,000	1975
7.	Pacific Lighting Corp.	Alaska	US west coast	400	1975

[1] Publicized in the trade press and having at least announced volumes and sources; for long-term projects which have been filed with the FPC see Nos. 14 and 15.

[2] Converted from 45,000,000,000 cubic feet per year based on a 365-day year; rounded to 10,000,000 cubic feet.

Table 11. Proposed Projects for Production of Synthetic Pipeline Quality Gas From Coal

Company	Location	Process	Plant capacity (MM c.f. per day)	Anticipated cost of gas (dollars/ M c.f.)	Project status
Announced projects:					
El Paso Natural Gas Co.	Northwestern New Mexico	Lurgi	250	0.88-1.08	Sponsor states first deliveries could begin in 1976.
Texas Eastern Pacific, Lighting-Utah International	Northwestern New Mexico	Lurgi	250	(1)	Sponsor hopes for initial operation in 1975.
FMC Corp.	(2)	Cocas	250	0.75-0.90	Sponsor states could begin operation in 1976. Process produces synthetic crude oil as byproduct.
Active pilot plant projects:					
Institute of Gas Technology.	Chicago Illinois	Hygas	1.5	0.50-0.85	Pilot plant in operation
Consolidation Coal Co.	Rapid City S. Dak.	CO_2-acceptor	(2)	0.50-0.60	Pilot plant under construction.
Bituminous Coal Research, Inc.	Homer City Penn.	BI-GAS	2.0-3.0	0.60-0.90	Pilot plant in design stage. Could be ready in 1973.
US Bureau of Mines	(2)	Synthane	2.0	0.55	Pilot plant in design stage.

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[1] Not available, not announced.

[2] Not available.

Table 12. Proposed[1] Facilities to Produce Synthetic Gas From Light Liquid Hydrocarbons

Company	Plant Location	Capacity (M c.f. per day)	Anticipated cost of gas (dollar/ M c.f.)	Source of feedstock	Completion date
Columbia LNG Corp. (FPC Docket No. CP72-8)	Green Springs, OH	250	1.12	Imported	1973
Algonquin SNG, Inc. (FPC Docket No. CP72-35)	Freetown, MA	120	1.41	Domestic	1973
Tecon Gasification Co. (FPC Docket No. CP72-100)	South Plainfield, NJ	500	1.23	Domestic and imported	1974
Consumers Power Co.	Marysville, MI	200	(2)	Imported	1973
Brooklyn Union Gas Co.	Brooklyn, NY	50	(3)	Domestic	1973
Public Service Electric & Gas Co.	Newark, NJ	125	(3)	Imported	1973
Boston Gas Co.	Everett, MA	40	(3)	(3)	1972
Transcontinental Gas Pipe Line Corp.	New York, NY	250	(3)	(3)	(3)
Panhandle Eastern Pipe Line Co.	IL	250	(3)	Imported	(3)
Continental Oil Co.	(3)	125[4]	(3)	domestic	(3)
Northern Illinois Gas Co.	IL	150-250	(3)	Domestic	(3)

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[1] Publicized in the trade press.

[2] Not available, not announced.

[3] Not available.

[4] Proposes 2 plants.

Table 13. Nuclear Gas Stimulation Projects[1]

Name and location	Industrial Sponsor	Firing date	Depth and size of service	Result	Present status	Est. cost (mil.)
Gasbuggy, northwest New Mexico	El Paso Natural Gas Co.	Dec. 10, 1967	4,240' 26 kilotons	5-8 fold increase in gas production.	Shut-in additional testing scheduled for 1972.	$ 4.7
Rulison, northwest Colorado	Austral Oil Co.	Sept. 10, 1969	8,426' 40 kilotons	5-10 fold increase in gas production.	Shut-in.	8.3
Dragon Trail, northwest Colorado	Continental Oil Co.				Canceled.	
Rio Blanco, northwest Colorado	Equity Oil Co. and CER Geonuclear Corp.	Fall of 1972 (tentative)	5,000-7,000' simultaneous detonations of 2 or 3 devices totaling about 90 kilotons.		Project definition work in progress.	3.52
Wagon Wheel, southwest Wyoming	El Paso Natural Gas Co.	1973 (tentative)	9,000-12,000' sequential detonation of 5 devices each with a yield of about 100 kilotons.		Project definition work in progress.	14.5
Wasp, southwest Wyoming	Oil & Gas Futures, Inc.				Potentially suitable areas are being surveyed.	

Note: 1 kiloton (kt) is equivalent to 1,000 tons of TNT.

[1] Joint industry-Government projects being conducted under the Atomic Energy Commission's Plowshare program.

[2] Cost of first well. 2d phase would consist of 4 to 6 well stimulations at cost of $5 to $10 million.

ANALYSIS OF COAL GASIFICATION WATER REQUIREMENTS

Introduction

Coal gasification to produce synthetic natural gas has gained considerable attention in the past several years. A shortage of natural gas supplies coupled with the demand for clean energy has created ever expanding activity in the technology of conversion of coal to a gaseous fuel. Impetus was added in June, 1971, when President Nixon singled out coal gasification and nuclear breeder reactors for greatly increased federal funding. The proposed 1973 federal budget called for $31 million for work on gasification projects to produce high-Btu pipeline gas. Coal gasification has attracted much interest because it promises to ease long range gaseous fuel supply problems while at the same time not contributing greatly to the degradation of the environment.

Gasification of coal to produce low-Btu gas is a well-known process. European cities and many United States cities have used the process to produce city gas or town gas, a gaseous fuel having a heating value of about 450 Btu/cubic foot. In the 1950's new pipeline networks brought inexpensive natural gas to the cities and changed the economy of the country to a higher heating value gas around 900-1,000 Btu/cubic foot. With the increased use of natural gas, research on better gasification technology diminished to a very low level. Suddenly the shortage of natural gas has caused coal gasification to again become important.

The major technical problems are the upgrading of the gas from 450 to 1,000 Btu/cubic foot, the enormous size of the plants being planned, and lack of experience with such processes. Most proposals presented will use a methanation step to upgrade the gas heating value while pilot plants are being built to study operational and scale-up problems. Coal gasification is a complex process with the sometimes unpredictable and difficult handling characteristics of the coal contributing greatly to the problems.

The Department of Interior through the Bureau of Mines Office of Coal Research has strongly urged and vigorously supported the development of new coal gasification processes as evidenced by the work either being done or supported by them. Of the federally supported technologies, the Hygas process of the Institute of Gas Technology is expected to go on line in 1977 producing 250 million standard cubic feet of gas per day (SCFD). Private commercial ventures are also being rapidly developed but rather than waiting for more-advanced gasification processes, private industries expect to use the commercially proven Lurgi technology followed by upgrading of the gas to the required heating value. At the present time El Paso Natural Gas has plans to have a 250 million SCFD coal gasification plant operating in northwestern New Mexico by mid-1976. WESCO, a joint venture by Pacific Coal Gasification Company and Transwestern Coal Gasification Company, expects to construct a 250 million SCFD plant also in northwestern New Mexico. This latter plant should become operational in 1977. Table 14 lists a number of the coal gasification projects presently under development in the United States [17, 20, 65, 118].

Water requirements for coal gasification processes have been determined primarily from the results of pilot plant studies, detailed process analysis, and feasibility studies. At the 65th Annual Meeting of the American Institute of Chemical Engineers held in New York City, November 26-30, 1972, it was stated that a coal gasification process producing 250 million SCFD would require a minimum of 6,000 acre-feet of water per year. This figure

Table 14. United States Coal Gasification Development Projects

Process	Developer	SNG Production MM SFD	Cost MM	Status	Service Year
Hygas	Institute of Gas Technology	1.5	9.0	compl. Pilot Plant	1971
CO_2 acceptor	Consolidated Coal Company	-	8.5	conctr. Pilot Plant	1972
Bi Gas	Bituminous Coal Research	2	-	Engr. Pilot Plant	1973
Synthane	U. S. Bureau of Mines	-	-	Engr. Pilot Plant	1973
Lurgi	Pacific Lighting Service Company/ TETCO	250	350	Plan.	1975-6
Lurgi	El Paso Natural Gas Company	250	250	Engr.	1976
-	Panhandle Eastern Pipeline Company, Peabody Coal	250	-	Plan.	Before 1980
-	Colorado Interstate Gas Company	-	-	Study	-
-	Garrett Research and Development Company	-	-	Develop.	-
-	Stone and Webster	-	-	Develop.	-
Kellogg	M. W. Kellogg Company	-	-	Bench Scale	-
COED*	FMC Corporation	-	-	Pilot Plant	-

*Produces fuel oil as well as gas

was based on water available, not on process balances. Since this time detailed feasibility studies of Lurgi type processes have indicated 6,000 acre-feet per year to be a slightly low estimate since the demands ranged from 6,500-8,200 acre-feet per year [79, 97]. Water requirements for the process are approximately 10% for process consumption, 70% returned to atmosphere, 9% to mine reclamation and 11% for other uses [79]. In areas where water is plentiful, 18,000 acre-feet per year might be used for the same size plant since water economy would not be practiced as rigidly as in water scarce localities.

Coal Gasification

Two general catagories of processes are being planned: indirect and direct. The indirect processes convert the coal into a synthetic gas by completely gasifying the coal in the presence of steam and oxygen. The gases produced, a mixture of carbon oxides and hydrogen, are then catalytically converted at moderate pressure and temperature to methane. The direct processes react coal and hydrogen, hydrogasification, at high temperatures and pressures to form methane. No catalysts are required with this method. Presently there is no demonstrated superiority for either the direct or indirect processes but then neither has yet to be fully evaluated on a large commercial scale. Both methods are in the development plans of commercial ventures. Several gasification processes are incorporating both methods and producing a large portion of the methane without a catalyst by hydrogasification of the coal while forming the remaining portion of the methane by the catalytic reaction of the carbon monoxide and hydrogen.

There exist a large number of proposed gasification projects which have been sufficiently studied that estimates of production costs and selling prices are now available as shown in Table 15 [26, 43, 54, 60, 98, 100, 127]. The costs of coal gasification plants are great and the economic risks are immense. It should be noted that the Kellogg and Bi-Gas economic evaluations are based on purchased coal resulting in lower capital investments as compared to the other processes which include costs of coal mines.

Coal Gasification Process

Coal gasification processes consist of a sequence of operations to gasify the coal and to convert gasification products into methane with removal of all impurities. Variations within the overall process will exist depending upon the particular coal gasification process being used and the technologies used to upgrade the raw coal gases. Some processes will use catalysts not susceptible to sulfur poisoning and therefore may not remove the sulfur until the methanation step while other processes may remove the sulfur earlier in the process.

Figure 10 shows a typical process which may be used to produce synthetic natural gas from coal. In the gasifier coal reacts at high temperatures with steam and oxygen to form hydrogen, carbon monoxide, methane, and carbon dioxide. The hot reaction gases are quenched with water to halt the reactions and then sent to a gas cleaning unit. This unit contacts the gases with hot water to separate any entrained solids or heavy oily liquids from the gases. Heat is recovered from the hot gases by passing them through a boiler to produce low pressure steam. The gases are next cooled to condense out volatile organic vapors and water vapor prior to the shift conversion units. If the catalyst in the shift converters is sulfur sensitive, the sulfur, usually in the form of sulfides, is removed from the gas by contacting with a solution which will remove the sulfides.

Table 15. Estimated Coal Gasification Project Costs

Process	Capacity 10^6 SCFD	Fixed Capital Investment	Working Capital	Operating Expense $/year	Gas Selling Price ¢/10^6 Btu
Kellogg	264	$155,500,000	$ 7,800,000	41,000,000	66.1*
Bi-Gas	250	147,800,000	7,000,000	39,800,000	54.9
COED	250 (+27,000 bbl/day crude oil)	439,000,000	17,000,000	134,860,000	108.8
COG	332 (+ other petroleum products)	757,300,000	28,400,000	131,600,000	75.0
El Paso (Lurgi)	250	338,000,000	-	-	-
WESCO (Lurgi)	250	380,000,000	-	-	-
Hygas	250	87,000,000	6,300,000	38,400,000	59.0

*20 year average gas selling price $4/ton coal

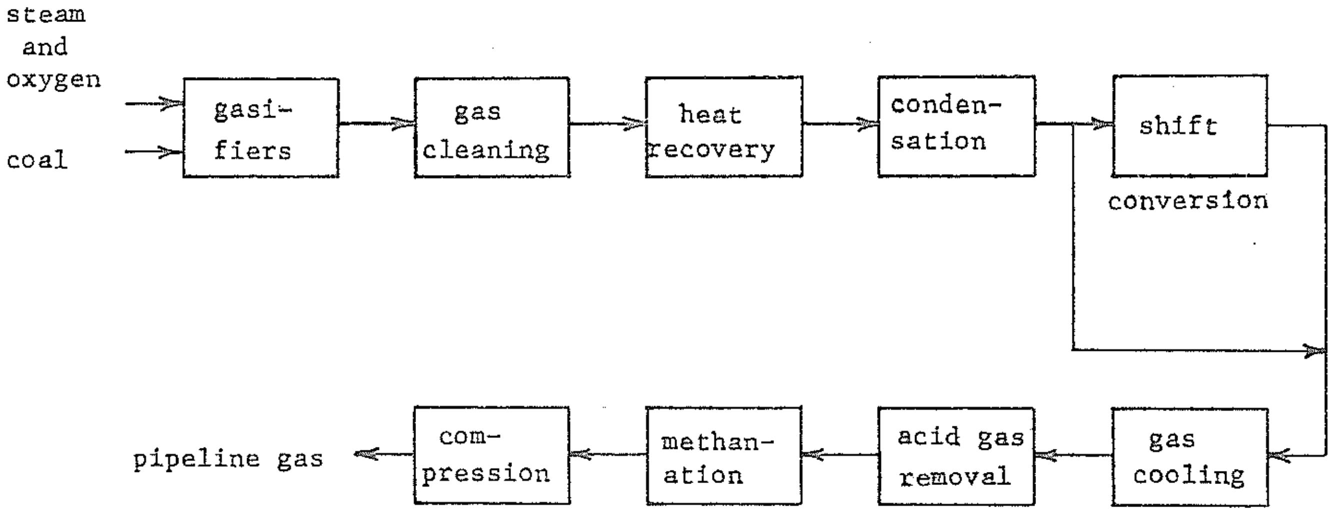

Figure 10. Typical Coal Gasification Flow Schematic

In the shift converters a catalyzed reaction occurs between carbon monoxide and steam producing the hydrogen necessary for the methane production. Not all the gas is passed through the shift converters, only that amount needed to produce sufficient hydrogen for the methane production. The remainder of the gas is bypassed and is recombined with the converted gas to be compressed to a higher pressure. Acid gases, carbon dioxide and hydrogen sulfide, are removed by an appropriate liquid solvent and then the pure gases sent to the methanation unit. In the methanation unit carbon monoxide and hydrogen are catalytically reacted to form methane and water. The product gas, primarily methane, is dried and sent out to the consumer.

Indirect Processes

Most indirect processes are based upon the production of water gas as an intermediate product which is subsequently upgraded in heating value by a methanation process. Water gas is any gas produced by any process involving the reduction of water by carbon and consist primarily of carbon monoxide and hydrogen. The mixture has a relatively low heating value. Processes producing water gas require large amounts of heat to sustain them since the reactions are endothermic with high temperatures between 1,700 to 2,500°F being required to obtain favorable rates of conversion. Pressures may vary from slightly above atmospheric to elevated pressures of 500 psig or more. Advantages are to be found with higher pressure operation since the formation of methane is favored, smaller size equipment can be used for gas production, and high pressures mean that gas can be transported long distances without the addition of numerous pumping stations being necessitated. Economic transmission of gases over long distances requires high heating value gas thus the need for methanation of the water gas.

Water Gas Based Processes

American developed processes for producing water gas from coal are two step processes. The coal bed is first heated by partial combustion of the coal with air and then steam is admitted to the heated coal bed resulting in the production of gas. This is an intermittent process with the usable gas being produced only on the steam cycle. Only more expensive fuels, such as anthracite or coke could be used.

Continuous processes were developed by the Germans using oxygen rather than air. Oxygen eliminated the large volumes of nitrogen introduced when air was used, thus allowing steam to be used simultaneously with the oxygen and producing gas continuously. Gas yields are much higher than the yields from the intermittent processes. The German processes use low-cost fuels. A number of German gasification processes exist and presently the Lurgi process appears to be the least expensive for production of a gas suitable for direct transmission and fuel uses. Descriptions of several of the processes being considered follow.

Lurgi Process

The Lurgi process is a high pressure operation of about 20 atmospheres pressure employing a fixed bed with dry ash removal [17, 79, 97]. Gas generation is continuous, the heat being supplied by the combustion with 95 percent pure oxygen. Superheated steam of approximately 900°F is mixed with the oxygen and the carbon-steam-oxygen reaction produces a gas with a heating value of approximately 450 Btu/cu.ft. One advantage of this process is high pressure operation which favors the production of methane. The additional heat produced by the formation of methane in the exothermic reaction aids the carbon-water reaction. A disadvantage exists in that noncaking coals must be used since a fixed bed is used. But low grade coals may be used offsetting the disadvantage of the noncaking coals requirement. Presently the Lurgi process is the only commercially available high pressure method for producing gas from coal, it being used in a number of foreign countries. The process uses many small gasifiers, rather than a single large unit, combining the gas produced.

Koppers Process

The Koppers process, another German process, can gasify any type of fuel and has low oxygen and labor requirements [17]. It uses pulverized coal which is suspended in the gasification unit. The fuel is picked up by the oxygen, enters the combustion chamber via a nozzle, and steam is directed into the mixture from an annulus surrounding the nozzle. Although operated at atmospheric pressures, there is belief that the Koppers process could be successfully operated at 20 atmospheres pressure. This process has not been commercially proven but is attractive because of its ability to handle caking coals.

Kellogg

Gasification of coal at 1,200 psig in a bath of molten sodium carbonate through which steam and oxygen passes is in the development stages and is being evaluated [26]. The molten salt serves to supply heat to the coal, disperses the coal and steam permitting use of caking coals, and catalyzes the basic steam-coal reaction permitting essentially complete gasification of coal. Further advantages are found in the methane formation at the comparatively low temperatures of the molten salt bath.

CO_2 Acceptor

The CO_2 Acceptor process uses two reactors in series, a devolatilizer and a gasifier [17]. In the devolatilizer ground, dried coal and dolomite are fluidized with steam and gas from the gasifier. Partially consumed char from the devolatilizer is fed to the gasifier where it is fluidized with steam in the presence of calcined dolomite. Product gases from the devolatilizer containing methane, carbon monoxide, hydrogen and impurities are purified, catalytically methanated, and compressed to form pipeline gas. As of 1974, the reactors have been pilot plant tested. Advantages of the process are: (1) no coal pretreatment step is necessary, (2) no oxygen or externally produced hydrogen are used, and (3) product gas is free of carbon dioxide and nitrogen. The operation of the reactors does pose an operating problem since a dynamic balance of the fluidized beds must be maintained.

COED

Another concept of interest is the COED process in which coal is converted to fuel gas, refinery products, and char as well as producing hydrogen [37, 98, 104]. Coal is heated to successively high temperatures in several stages of fluidized beds with products withdrawn at each stage. By manipulation of the subprocesses within the overall process, the ratio of products may be varied to satisfy the market demands.

Many other gasification processes are presently being developed utilizing the production of water gas as the intermediate gaseous product with some process modifications permitting the simultaneous formation of some methane. Ultimately, the gases produced in these processes must be subjected to a methanation step so as to upgrade the heating value of the gas.

Methanation Step

Methanation is the process whereby carbon monoxide and hydrogen gases are reacted catalytically to form methane [67]. The reaction is exothermic but occurs at a lower temperature than the gasification reactions thus making the energy released not too useful in supplying heat to the endothermic gasification reactions. However, the heat generated can be used to form steam for use in the gasifiers. Since the hydrogen-carbon ratio of coal is insufficient for methane formation, additional hydrogen must be supplied and is usually formed by the catalytic reaction of carbon monoxide with steam or steam with char. The major difficulty foreseen in the methanation step is the removal of the large amount of heat released so as to keep the reaction temperature sufficiently low as not to harm the catalyst and also to maintain favorable equilibrium conditions. Methanation is a well-known process but has not yet been used commercially at the capacities envisioned in the coal gasification processes.

Direct Processes

Direct processes combine hydrogen and coal to produce methane directly in addition to other gaseous products which are separated. One advantage to such processes is the elimination of the methanation step. However, many of the direct processes still incorporate a methanation reactor so as to increase the methane content of the final product.

BCR Bi-Gas

A super-pressure, entrained, slagging two stage gasifier is used with pulverized coal fed to the top stage [53, 54]. Devolatilization of the coal occurs producing methane and a reactive char. The char reacts with hydrogen to produce more methane and with steam to produce carbon monoxide and hydrogen. The unreacted char drops into the bottom stage where it reacts with steam and oxygen forming carbon monoxide and hydrogen. These gases pass upward to the top stage where they react with the feed coal. Temperatures are maintained at 2,700 and 1,700°F in the bottom and top stages respectively. The hydrogen to carbon monoxide ratio is shifted with steam catalytically to three to one and this gas, after purification, is converted catalytically to methane. The technology of the Bi-Gas process appears sound but the gasifiers have yet to be tested. Single stage entrained slagging gasifiers, similar to the bottom stage, operating at atmospheric pressure have been successfully operated on a commercial level. Before such a process becomes available much more development work needs to be done.

HYGAS

This process presently in pilot plant operation produces two-thirds of the methane by hydrogasification and one-third by catalytic reaction of carbon oxides and hydrogen [17]. Ground coal is pretreated to reduce its caking tendencies, mixed with light oil, a gasification by-product, and pumped to a three-stage hydrogasifier operating at 1,000 to 1,500 psi. In the top section the oil is evaporated by hot product gases rising from the middle section while the coal is heated. In the middle section the coal contacts the gases from the bottom stage reacting with the hydrogen to produce methane. In the bottom stage partially converted coal reacts with fresh hydrogen and steam feed forming methane and carbon oxides. The methane formation in the bottom two stages is about equal and comprises two-thirds of the total methane production. Gases leaving the top of the reactor are purified and the carbon monoxide and hydrogen methanated catalytically. Fresh hydrogen is made from the unreacted char leaving the bottom stage and steam.

Water Requirements

Although many different physical configurations are being proposed for coal gasification developments, the basic processes may be subdivided into gasification, shift gas reactions, methanation, and gas purification. For direct processes the methanation process does not comprise a large section of the overall process but is still important.

The gasification step is a reaction between steam, oxygen, and coal producing carbon oxides, hydrogen, and methane. The relative amounts of the component gases depend upon the operating conditions of the gasifier. Low temperatures and high pressures favor methane production if sufficient hydrogen is present while high temperatures push the equilibrium towards carbon oxide and hydrogen formation. The reactions involved are shown in Table 16.

Table 16. Principal Gasification Reactions

$$\text{coal volatile matter} \longrightarrow CH_4 + C \text{ (1100-1500°F)} \tag{1}$$

$$C + H_2O \longrightarrow CO + H_2 \text{ (1700-2500°F)} \tag{2}$$

$$2C + O_2 \longrightarrow 2CO \tag{3}$$

$$C + O_2 \longrightarrow CO_2 \tag{4}$$

$$C + 2H_2 \longrightarrow CH_4 \text{ (1700°F)} \tag{5}$$

$$CO + H_2O \longrightarrow H_2 + CO_2 \text{ (1700°F)} \tag{6}$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \text{ (700°F)} \tag{7}$$

$$2C + 2H_2O \longrightarrow CH_4 + CO_2 \text{ (overall)} \tag{8}$$

Reaction (2) is endothermic while the remaining reactions are exothermic. Reactions (3) and (4) are essentially used to supply heat to the gasifier permitting reaction (2) to proceed. Reaction (6), although occurring to some extent in the gasifier, is usually conducted at a much lower temperature as a catalyzed reaction to produce hydrogen necessary for the methanation reaction.

Reactions (2) and (6) are the major water-using reactions while reaction (7) produces water. Each pound of carbon reacted in each of these first two reactions requires 1.5 pounds of water. Although reaction (7) produces water as a product, the bulk of the hydrogen used in the reaction comes from water so this reaction should not be considered to create new water but only to reduce the net total water requirement. In gasification projects using the Lurgi process, it is expected that approximately forty percent of the methane will be produced in the gasifiers while the methanators will account for the remainder of the methane production.

The amount of hydrogen present in coal is insufficient to supply all of the hydrogen required for reaction with carbon to form methane. In most coals, on an ash and moisture free basis, the carbon to hydrogen weight ratio is about sixteen to one, that is, about eighty weight percent carbon and five weight percent hydrogen. Thus the production of further hydrogen is necessitated. This hydrogen is obtained from two sources: the partial combustion of the coal with steam and the shift conversion of carbon monoxide with steam. If all the hydrogen requirements had to be supplied from carbon-steam reactions, less than fifty percent of the carbon would be available for methane production. In actual practice, however, only about forty percent of the carbon is converted to methane as a result of inefficiencies, hydrogen production, and unavoidable combustion of carbon directly to carbon dioxide.

Water requirements for coal gasification facilities will vary considerably depending upon the water economies practiced. In the Four Corners area of New Mexico, the scarcity of water has forced the designers of coal gasification plants to be quite water conscious [78, 97]. A typical design water balance for a coal gasification facility is given in Table 17 for a 250 million cubic foot per day operation [97].

Wastewater Sources

Excess steam used in the gasifiers along with the quench water is recovered during the gas cleaning process and gas cooling step when the steam condenses. This water amounting to about one pound of water per pound of moisture and ash free coal processed contains phenols, sulfides, ammonia, naphtha, and tars.

Approximately half of the gas produced in the gasifiers is passed through the shift converters to convert the carbon monoxide and steam to hydrogen and carbon dioxide. Prior to shift converting steam must be supplied to these gases. The quantity of steam used is in excess of that needed for the reaction, and the unreacted steam condenses out during the gas cooling phase prior to acid gas removal. These waste waters contain sulfides, large quantities of carbon dioxide, naphtha, and tars.

Depending on the system used for acid gas removal, such as hydrogen sulfide and carbon dioxide, wastewater may or may not be generated. Most designs are utilizing systems which do not use water based absorbents and have wastewater only as a result of condensation of water vapors.

Table 17. Coal Gasification Water Balance

Water Uses

	GPM
Gas production gasifiers	1380
Shift Conversion	267
Sulfur recovery vent gases	60
Sulfur recovery incineration	2
Degasser vent (CH_4 synthesis water)	30
Ammonia Solution	142
Fuel gas to production	3
Cooling water system evaporation	2435
Cooling water system drift	140
Fuel gas production	237
Raw water storage evaporation	126
Medium and hi-pressure boiler dearator vents	81
Low pressure boiler dearator vents	19
Low pressure boiler losses	240
Ash dewatering and transportation evaporation	131
Evaporation ponds	782
Water in wet ash	165
Mine and offsite uses	1119
TOTAL	7359

Water Sources

	GPM
Moisture in coal	664
Moisture in air	4
Raw water	6125
Moisture in air to sulfur recovery	2
Water produced by methanation	548
Water produced by sulfur recovery reaction	16
TOTAL	7359

Based on 250 cubic feet per day plant capacity and El Paso Natural Gas Company Plant Design Calculations.

The methanation process generates water as one of the reaction products but this water is fairly high quality water and may be used for boiler feed water.

Steam generation is another source of wastewater since the water must be treated to lower its hardness. Effluent from back-washing of water softeners is a source of salty water. Boiler blow down water also contains a high dissolved solids content. Both of these sources of wastewater are of an intermittent nature.

The cooling water system must have make-up water supplied to replenish the evaporation losses and the blow down water losses used to keep the dissolved solids content from becoming too high with the resultant deposition of salt. This cooling water blow down contains high dissolved solids, algae inhibitors, and corrosion inhibitors.

Other wastewater sources include sanitary water discharges and pump sealing gland leaks.

The waters containing phenols, naphthas, and tars are collected and treated to separate these oily materials prior to reuse of the water within the plant. The acidic waters containing primarily hydrogen sulfide and carbon dioxide are further treated to strip the sulfides from the water before the water is recirculated for reuse.

None of the water brought into the coal gasification facilities leaves the process as wastewater. All water is consumed either directly in the process, is used to agglomerate the fine ash leaving the gasifiers, or evaporates in the cooling towers or from the tailings pond. About 70% of the fresh water supplied eventually leaves by evaporation. The only areas in which water economies could be further practiced are in changing the evaporative cooling water system or in treating the water sent to the tailings pond so that it could be reused. Although air coolers could be used in some applications for cooling of high temperature process streams, the use of refrigerative cooling for lower temperature streams could prove to be prohibitive.

ECONOMIC MODEL APPLIED TO PETROLEUM REFINING

An economic model of the petroleum refining industry was developed to illustrate a method for choosing among alternative production processes to adapt to various water and air quality criteria.

A petroleum refinery with a crude input capacity of 50,000 barrels a day was modeled. The 50,000 barrels per day size represents a medium size refinery that exists in New Mexico. This size refinery was selected as being representative of refinery capacities in New Mexico. There seems also to be a trend toward extremely small refineries in New Mexico which are fractionation plants only (capacity 6,000 barrels per day). These are relatively inexpensive and require unskilled labor.

The coefficients that were used are from a model of the refining industry developed by Russell [93]. They are based on a refinery size of 150,000 barrels a day. The existence of economies to scale in refining leads to a downward bias of the cost estimates. As in Russell's model, we also assumed an input of East Texas Crude. To apply the model to a specific refinery, the coefficients would have to be adjusted for the particular crude used.

The refining process converts crude oil to final petroleum products and residuals. The final products can be sold directly or further refined to change the final product mix. The residuals can be recycled or disposed of through alternative processes to meet environmental standards.

The model describes the refining process and includes alternative activities for each process step. The activities are incorporated in a Linear Programming (LP) model. The LP model takes the traditional form of maximizing a net revenue function (the objective function) subject to production and environmental constraints.

Production Alternatives

All 50,000 barrels of crude have to be routed initially through the desalter and then through the atmospheric distillation units. The heavier residue is then sent to the vacuum distillation unit. Because no substitution is allowed, these activities are all condensed in the model into one activity. The heat input into the fractional distillation units, and hence the waste heat that must be disposed of can be reduced by additional capital investment in the form of heat exchangers. These alternatives were included in the model. The products, inputs and residuals for the above processes are described in Table 18.

The products from the fractional distillation unit can either be sold directly, processed further to form alternative products, or burned to supply the refinery heat input. The alternatives open to each fraction will be followed individually. It was assumed that the gasoline was sold directly. A more complex model would allow for the possibility that the gasoline might be scrubbed, to remove impurities and tetraethyl lead (TEL) added to improve the octane rating.

Naphtha can either be sold directly, or subject to hydrogen treating to remove sulfur, and then processed through the catalytic reformer. The hydrogen treating and catalytic reforming of naphtha was combined into one activity. The primary product of this activity is a high octane gasoline referred to as reformate. The butane produced can either be sold or routed to the alkylation unit which combines butane and isobutane to produce gasoline. Older refineries have an isomerization unit that can convert

Table 18. Desalting and Fractional Distillation

Products (as a percent of volume)	
Gasoline	26.0
Naphtha	10.0
Raw Kerosene	10.0
Gas Oil	39.0
Reduced Crude	15.0

Utilities and Residuals

	Desalting	Distillation	
		High Capital	Low Capital
Fresh Heat input (10^6 Btu)		0.1107	0.1274
Water input (gal)	2.4		
Steam (lbs)		45.0	45.0
Waste heat (10^6 Btu)		0.0791	0.0845
Condensate (gal)	2.5	11.7	11.7
Cost per barrel* ($)		0.080	0.076

Residual Characteristics of Process Condensate (lbs/1000 gal)

	Desalting	Fractional Distillation
H_2S	0.12	1.02
NH_3	0.09	0.76
Phenol	0.12	0.83
Oil	1.88	0.0
BOD	2.34	1.42

*Cost net of steam, heat, and cooling water butane into isobutane for the alkylation unit. This was eliminated from this model because technological changes have made other sources of isobutane cheaper. Both the refinery gases (C_3 and lighter) and the reformate can either be sold as petrochemical feedstock or burned to meet refinery heat requirements. These products, plus the utility requirements and residuals generated are described in Table 19. The catalytic reforming process can be run under more or less "severe" conditions. Low severity was assumed, but a more complex model might include both. Two relative capital levels were allowed to provide for substitutability between capital and heat.

The straight run kerosene can either be sold directly or hydrotreated. The hydrotreating removes sulfur and the product can be sold as jet fuel. Table 20 describes this process.

The gas oil fraction can be further refined by being sent to the catalytic cracking unit. The products and costs are summarized in Table 21. The cat gasoline must be caustically scrubbed before it is sold as gasoline. The cycle stock, the uncracked portion of the input gas oil can be recycled to achieve higher conversion rates. The cycle stock may be sold as distillate fuel oil, or mixed with reduced crude and sold as residual fuel oil. The gas can be burned for heat or desulfurized and sold with the reformer gases as petrochemical feedstock. The removal of coke from the catalyst generates large quantities of heat, some of which are captured for heat input into this process and other processes. Only the net heat is recorded in the model.

The bottom fraction, the reduced crude may be sold as residual fuel oil, burned or further refined by coking. The coking process, described

Table 19. Hydrotreating and Catalytic Reforming of Naphtha

Products (per barrel of feed - low severity process)	
Hydrogen (lb)	4.65
C_3 and lighter (lb)	25.3
C_4-butane, butene (lb)	16.0
Reformate (bbl)	0.80
Polymer (bbl)	0.035

Utilities and Residuals

	Hydrotreater	Catalytic Reformer	
		High Capital	Low Capital
Fresh heat (10^6 Btu)	0.04	0.304	0.350
Steam (lb)	5.5	60.0	60.0
Waste heat (10^6 Btu)	0.046	0.241	0.263
Condensate (gal)	.66	*	*
Off-Gases** - (25% H_2S) (lb)	0.85		
Cost per barrel ($)	0.259	.485	.510

Residual Characteristics of Process Condensate - Hydrotreating

Stream (lbs/1000 gal)	
H_2S	96.30
NH_3	72.10
Phenol	0
Oil	0
BOD	1.00

*Catalytic reformer condensate is assumed to be free of residuals

**Off-Gases can either be flared or subject to treatment - air quality parameters were not kept track of in this model.

Table 20. Hydrotreating of Kerosene

Product (yield per barrel of feed)	
Jet fuel (bbl)	1.0
Utilities and Residuals	
Hydrogen (lb)	1.16
Fresh heat (10^6 Btu)	0.08
Steam (lb)	10.0
Waste heat (10^6 Btu)	0.086
Condensate (gal)	1.2
Off-gases-25% H_2S (lb)	0.09
Cost per barrel ($)	0.271
Residual Characteristics of Process Condensate (lbs/1000 gal)	
H_2S	289.0
NH_3	226.0
Phenol	0.0
Oil	0.1
BOD	10.0

Table 21. Fluid Catalytic Cracking of Virgin Gas Oil

Products (yield per barrel of fresh feed)	Low conversion	High conversion
Gases: C_1 - C_3 (lb)	19.1	30.5
C_4 Butane, butene (lb)	17.2	25.9
Isobutane (lb)	8.6	15.2
Cat Gasoline (bbl)	0.532	0.545
Cycle Stock (bbl)	0.331	0.165
Coke (lb)	18.0	26.0
Utilities and Residuals		
Fresh heat input (10^6 Btu)	0.0985	0.160
Steam (lb)	39.0	56.0
Residual heat (10^6 Btu)	0.155	0.258
Condensate (gal)	4.2	9.0
Flue gas* (10^3 acf)	4.18	6.04
Cost per barrel ($)	0.2920	0.4047
Residual Characteristic of Process Condensate (lbs/1000 gal)		
H_2S	22.68	14.84
NH_3	17.0	11.13
Phenol	4.59	4.59
Oil	0.42	0.42
BOD	7.67	7.67

*Air parameters were not included in the model in Table 22, produces refinery gases, coker gasoline, coker gas oil and coke. Before it is sold the coker gasoline must be subject to hydrotreating and catalytic reforming, described in Table 23. The coker gas oil must be subject to catalytic cracking, described in Table 24. Although these are entered as separate activities, the model is set up so that both processes must be carried out for coking to enter. Choices of high and low capital are included for the coker and catalytic reformer. A choice of high or low conversion is included for the catalytic cracker.

The alkylation unit combines butane and isobutane to produce alkylate, a high octane gasoline blending stock. The reaction is summarized in Table 25.

Products

No constraints on the products were assumed in the model. Instead the model was free to choose the optimum product mix to maximize profits. This makes the model very sensitive to product prices, which often display wide regional variations. To apply the model to a real case exact information on product prices would have to be available. The product prices that the model was based on are shown in Table 26. These prices should be considered to be representative of relative differences between prices of different streams and not absolute. Many of the products in the model are actually combinations of several product streams. For example gasoline is a combination of regular and premium gasoline. The price selected represents some kind of average of the prices of the different streams. An alternative way to make the refinery yield fit a specific case would be to constrain the output of the model to approximate the yield of the refinery studied. This approach would be of particular use in cases where the refinery output is

Table 22. Coking of Reduced Crude

Products (yield per barrel of fresh feed)

Gases C_1-C_3 (lbs)	23.7
Coker Gasoline (bbl)	0.253
Coker gas oil (bbl)	0.557
Coke (lb)	70.3

Utilities and Residuals

	Low Capital	High Capital
Fresh heat (10^6 Btu)	0.279	0.242
Steam (lb)	20.0	20.0
Waste heat (10^6 Btu)	0.269	0.251
Condensate (gal)	15.0	15.0
Cost per barrel ($)	0.264	0.298

Residual Characteristic of Process Condensate (lbs/1000 gal)

N_2S	35.53
NH_3	26.60
Phenol	3.34
Oil	1.25
BOD	5.59

Table 23. Hydrotreating and Catalytic Reforming of Coker Gasoline

Products (per barrel of feed - low severity process)

Hydrogen (lb)	3.86
Refinery Gases (lb)	25.3
Butane-Butene (lb)	16.0
Cat Gasoline (bbl)	0.80
Polymer (bbl)	0.035

Utilities and Residuals

	Hydrotreating	High Capital	Low Capital
Fresh Heat (10^6 Btu)	0.04	0.304	0.350
Residual Heat (10^6 Btu)	0.046	0.241	0.263
Steam (lb)	5.5	60.0	60.0
Condensate (gal)	0.66	*	0
Cost per barrel	0.311	0.485	0.510

Residual Characteristics of Process Condensate (lb/1000 gal)

H_2S	174.0
NH_3	130.5
Phenol	0.0
Oil	0.3
BOD	30.0

Table 24. Catalytic Cracking of Coker Gas Oil

Products (yield per barrel fresh feed)	Low Conversion	High Conversion
Gases: C_1-C_3 (lb)	20.1	32.2
C_4: Butane, butene (lb)	18.0	27.2
Isobutane (lb)	9.1	16.0
Cat gasoline (bbl)	0.528	0.584
Cycle stock (bbl)	0.331	0.165
Coke (lb)	19.2	28.0
Utilities and Residuals		
Fresh heat (10^6 Btu)	0.0985	0.160
Steam production (lb)	41.0	60.0
Residual heat (10^6 Btu)	0.155	0.258
Condensate (gal)	4.2	9.0
Flue gas* (10^3 acf)	4.47	6.60
Hydrocarbons (lb)	0.218	0.338
Cost per barrel feed ($)	0.2920	0.4047
Residual Characteristic of Process Condensate (lb/1000 gal)		
H_2S	72.60	51.00
NH_3	54.50	38.20
Phenol	8.34	8.34
Oil	0.83	0.83
BOD	13.93	13.93

*Air parameters were not included in the model.

Table 25. Alkylation

Inputs	
Isobutane (lb)	57
Butane-butene (lb)	215
Output	
Alkylate (bbl)	1
Utilities and Residuals	
Steam (lb)	290
Spent acid (lb)	15.01
Waste heat (10^6 Btu)	0.6
Cost per barrel alkylate ($)	1.50

Condensate is assumed to be free of any contamination.

Table 26. Product and Input Prices

Products	
Gasoline (bbl)	$ 6.22
Kerosene (bbl)	4.96
Jet Fuel (bbl)	5.12
Naphtha (bbl)	2.00
Gas Oils (bbl)	4.60
Reduced Crude (bbl)	3.10
Cycle Stock (bbl)	3.10
Refinery Gases (lb)	0.022
Butane (lb)	0.0185
Isobutane (lb)	0.0168
Coke (ton)	8.00
Polymer (bbl)	5.00
Hydrogen (lb)	0.022
Inputs	
Fresh Heat (10^6 Btu)*	0.30
Isobutane (lb)	0.0168
Water*	
Cooling (10^3 gal)	0.015
Desalter (10^3 gal)	0.075
Boiler (10^3 gal)	0.15

*These prices will be varied to examine the changes in residual generation that is affected by region variation.

significantly different from national output. The new Famariss Oil and Refining Company facility in southern New Mexico that will primarily produce naphtha and fuel oil is an example of where this approach would have particular validity.

The products were not constrained to meet any quality standards. The most normal constraint of this type would be a constraint on the octane level of the final gasoline stocks. This constraint has been met by refiners in part by the addition of tetraethyl lead (TEL). Clean air standards that have been passed by Congress require the reduction of the TEL level, and the eventual removal of TEL from gasoline stocks. If the octane level and the amount of gasoline produced remain at present levels, this law will require the more intensive use of refinery units that produce high octane gas, and the subsequent increase in residuals from these processes. Because the law makes gasoline more expensive to produce, another alternative is to produce less gasoline and instead to concentrate on production of distillate and residual fuels. A more complete model could be constructed to allow for these alternatives. The octane levels of the gas produced by the different production units are:

Fractional Distillation	70
Catalytic Cracking of Virgin Gas Oil	97
Catalytic Cracking of Coker Gas Oil	90
Alkylation	99

The untreated octane number of the gasoline in the model's solution was 84.

Refinery gases is another stream which is subject to variation depending on the process unit in which it originates. To deal with refinery gases in a complete model, the hydrotreating necessary to make the gases conform to a standard would have to be included as a separate activity vector for each product stream.

An implied quality standard was imposed on jet fuel by forcing kerosene to be hydrotreated before it could be sold as jet fuel. The model could be expanded to include the hydrotreating to remove sulfur of several streams in a similar manner. This removal of sulfur from fuel oil might be given importance in an expanded model.

Inputs

A major portion of the heat input into refineries in the Southwest is supplied by natural gas. This is because of the relative cheapness of natural gas due to the close proximity of natural gas fields. The model assumes that natural gas can be purchased at a cost of $\$.30/10^6$ Btu. An alternative source of heat can be obtained by burning some of the refinery products. It was assumed that there was no cost of burning the by-products. The refinery would burn these products when the cost of purchased fuel was more than the loss in revenue from selling the products. This approach is a little misleading because the substitution between different fuels implies large differences in the gross air pollutants generated. The costs associated with treating the air pollutants to meet any air quality standards would have to be included in a more complex model. To give the reader a feel for this change the gross emissions in Table 27 shows the heat value and the air parameters of the by-products.

The water used is broken down into three different price ranges to reflect the different treatment levels necessary for the different water uses. The initial prices used reflect national prices but are substantially

Table 27. Sources of Refinery Heat

Source	Heat Value 10^6 Btu	SO_2 emissions lb/10^6 Btu	Particulate lb/10^6 Btu
Natural gas (MCF)	1.0	0.0	0.0
Hydrogen (lb)	0.0331	0.0	0.0
Refinery Gases (lb)	0.025	0.08	0.0
Coke (lb)	0.015	2.10	2.0
Polymer (bbl)	6.45	0.0	0.0
Reduced Crude (bbl)	6.20	1.40	0.0545

lower than prices that exist in the Southwest. These prices will be varied to examine the effects of location in the Southwest on the model.

Isobutane is included both as a product and as an input that can be purchased to supplement the refineries production. The cost is considered the same in both instances.

Water Treatment

There are two main wastewater streams, the cooling water stream that removes the residual heat, and the condensate stream. The cooling water is assumed to be recirculated in cooling towers. A once through cooling system was not considered because of the scarcity of water in New Mexico. The cooling water was assumed to remove 0.292×10^6 Btu/1,000 gallons. Make-up water has to be provided to the cooling towers because of losses due to evaporation, windage, and blowdown. Make-up water is assumed to amount to 5% of total cooling water. The make-up can either be purchased or obtained from treated condensate at an additional cost of $.04/1,000 gallons. The cooling tower is assumed to cost $.0356/1,000 gallons. Air cooling is also included as an alternative.

The refinery was forced to treat all waste streams except the cooling tower blowdown. This stream is very high in dissolved solids and treatment would be very expensive. Instead of treatment it was assumed that the water would be evaporated at a cost of $.10/1,000 gallons.

All of the condensate streams were initially sent to a sour water stripper and an API separator. Because of the heavy waste load associated with the desalter, it was assumed that this stream would have to be separated from the other condensate streams and treated at a higher cost

The treatment costs used were \$.322/1,000 gallons for the condensate stream and \$.555/1,000 gallons for the desalter stream.

The treated wastewater could then be sent to the cooling towers for use as makeup, or be further treated in a biological treatment unit. The cost of biological treatment was assumed to be \$.236/1,000 gallons. Additional treatment at a cost of \$.04/1,000 gallons makes this water of sufficient quality to be used in the desalter.

If the water is not diverted to the desalter, it can be subject to an additional treatment step that makes it reusable as boiler water. This is assumed to cost an additional \$.43/1,000 gallons.

Results

The refinery modeled converted about 60% of the crude input into gasoline. It used all of the major processes available except the alkylation unit. Out of the processes with high and low capital investment alternatives only the fractional distillation process appeared at the high capital level in the initial solution. The refinery failed to convert kerosene into jet fuel, either because the price of jet fuel was too low or the price of the hydrogen was too high.

The refinery burned coke as its major heat source. Purchased natural gas provided the rest of the heat. The effect of changing the price of heat was not studied in the model. As the price of heat increases the more capital intensive units will be chosen over the less capital intensive units. If the price of just one heat source is varied, for example natural gas, the modeled refinery will also adjust by burning other refinery by-products. It should be noted that any change in the price of heat that causes a shift to more capital intensive units will reduce the amount of water required for cooling.

The only water the refinery was permitted to discharge was blowdown from the cooling tower. It was also assumed that there was not enough water available for a once through cooling. Initially, the refinery withdrew 1,194,000 gallons a day for cooling. Because of the price structure the model would have used once through cooling water if it was available, amounting to over 24 million gallons a day. The price of water was varied at increments of ten cents per 1,000 gallons to all three water catagories. Some of the results are shown in Table 28. The use of higher capital option on the reformer did not come in until the price of cooling water was over $.80/1,000 gallons, considerably above the price of water in New Mexico.

All of the processing water was used as cooling tower makeup. This reduced withdrawal demands by over 40% of what it would have been if the refinery was permitted to discharge condensate. The model could permit the recycling of cooling tower blowdown, by including a reverse osmosis or ion exchange unit. This would have the effect of reducing the refinery intake by the amount of cooling tower discharge, or by an additional 80%. This recycling activity could only be added at substantially higher cost. It should be noted that the additional cost per barrel of crude processed of increasing the cost of water $.10/1,000 gallons amounts to less than 0.4 cents. This additional cost is still below the cost of transporting the oil from East Texas.

Because of the zero discharge constraint imposed on the model, the model did not keep track of residual discharge levels. Total discharge levels were calculated and are as follows:

Table 28. Refinery Response to Changes in the Price of Water

		Price Alternatives		
		1	2	3
Cost of Water:	Cooling	.015	.315	.815
($/1000 gal)	Desalter	.07	.37	.87
	Boiler	.15	.45	.95
Additional Cost/barrel of crude		-	.0035	.0178
Capital Intensity:				
Fractional Distillation		High	High	High
Reformer		Low	Low	High
Coker		Low	Low	Low
Purchased Heat (10^6 Btu)		986.2	986.2	756.2
Water volume (10^3 gal)				
Cooling water withdrawal		1193.7	1193.7	1174.9
Recir. to cooling tower		946.5	946.5	946.5
Desalter withdrawal		120.0	120.0	120.0
Recir. to desalter		-	-	-
Boiler water withdrawal		465.4	465.4	465.4
Recir. to boiler		-	-	-
Cooling tower discharge		1498.2	1498.2	1485.0

Sulfide (lb)	8771.3
Phenols (lb)	1439.3
Oil (lb)	441.8
BOD (lb)	2123.0
NH_3 (lb)	6483.5

Possibilities exist for the recovery of some of these residuals as useful by-products. Eighty percent of the oil is normally recovered and burned as part of the refinery heat input. Possibilities also exist for the recovery of sulfur from the sulfide, if the scale of the plant is large enough to justify the capital expenditure. Oil is recovered in the refinery modeled, but no use is made of it.

SUMMARY

Analysis of the water requirements of two industries, petroleum refining and coal gasification, have been presented along with descriptions of the processes involved in these industries. The petroleum refining industry, which is well established has been found to be practicing water economies both in process design and reuse of water by reclamation of aqueous streams which normally would be discharged. Coal gasification to produce high Btu pipeline quality gas is a new process in the United States and has yet to be operated on a commercial sized basis. Design considerations for coal gasification plants have given much attention to the water requirements particularly as related to the Four Corners area of New Mexico.

An economic model of the petroleum refining industry was developed to illustrate a method for choosing among alternative production processes to adapt to various water and air quality criteria. In this model the net revenue function was maximized subject to production and environmental constraints. The model showed that until the cost of water becomes considerably greater than the present price of water in New Mexico, major process revisions would not be observed if only the economic factor were considered.

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APPENDICES

APPENDIX A

WATER USE REGIONS

Introduction

New Mexico is a semi-arid state with precipitation ranging from 8" in the deserts to 30" in the high mountains, with a state average of 13". The precipitation is highly variable, both on a seasonal and yearly basis. Summer is the rainy season and New Mexico receives the majority of its precipitation from May to September. Locally, rainfall may exhibit wide differences on a yearly basis. Roswell averages 13.5" of precipitation, but recorded 4.35" in 1956 and 32.92" in 1941. The variability of the water supply can present as much of a problem as its relative scarcity.

There are six major river basins in the state and three closed drainage basins. These are the San Juan (Upper Colorado), Rio Grande, Arkansas-White-Red, Lower Colorado, Pecos, and Southern High Plains (Texas-Gulf) River Basins; and the Central, Western, and Southwestern Closed Basins. The locations and boundaries of these basins are shown in Figure A-1. Current water use and availability of water in these basins are presented in Table A-1. In general the water in the basins is dependent upon the water resources with all good quality water having been allocated. Any further water usage must come from more efficient use of currently available water or from the recovery of marketable water from the brackish water found in the basins, which is not currently being allocated. The United States Geological Survey estimates that there are 20 million acre-feet of ground water under New Mexico, 3/4 of which is high in salts. Not all of this water is economically recoverable, but desalting offers an alternative source of

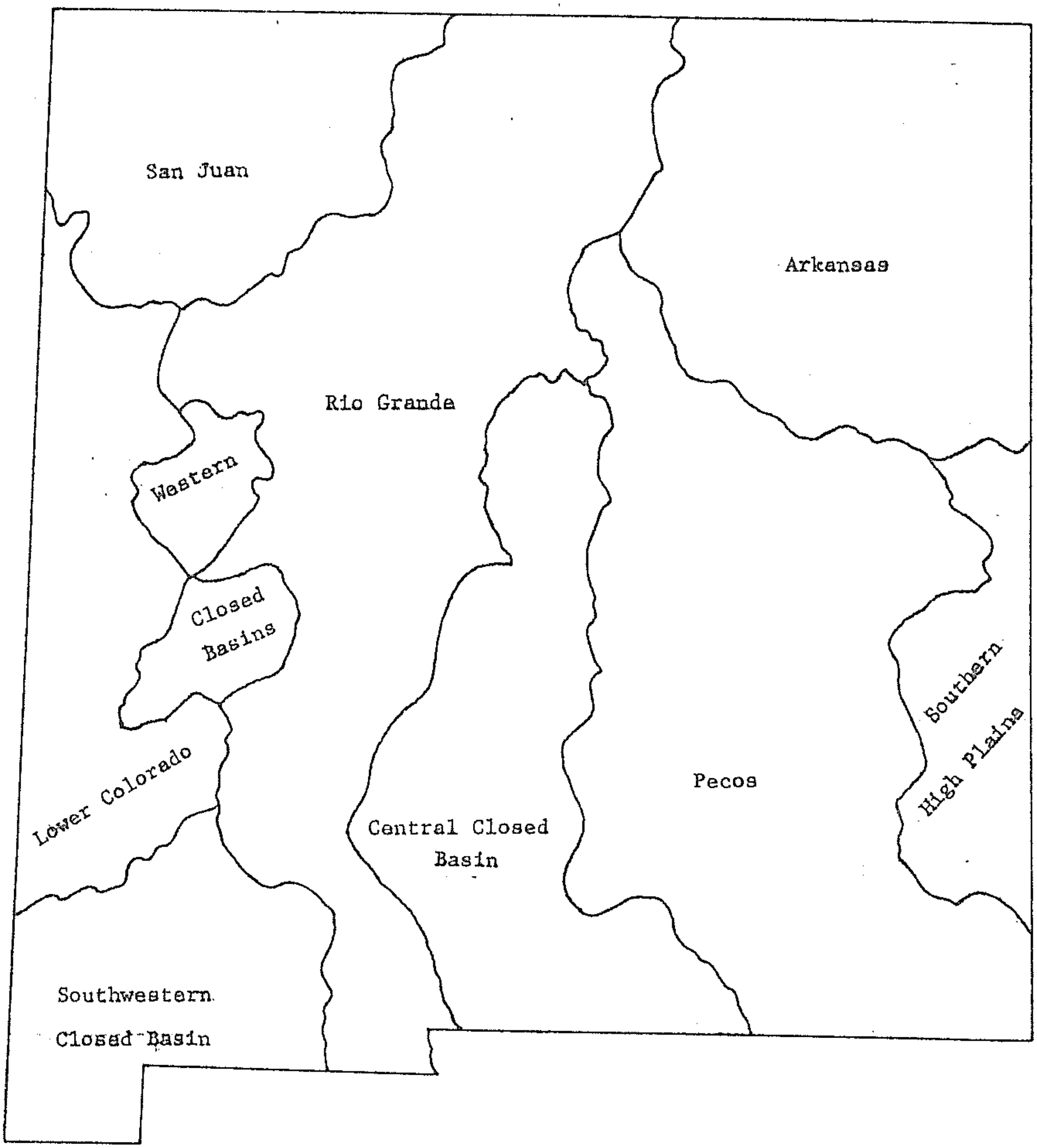

Figure A-1. Major River Basins in New Mexico

Table A-1. Current Water Use and Availability in New Mexico--1965

Basins	Urban	Rural	Irrigation	Manufacturing	Minerals	Military	Livestock	Stockpond Evaporation	Power	Fish & Wildlife	Reservoir Evaporation	Total	Surface Water	Ground Water	1965 surplus or deficit
Rio Grande & Closed Basins	40.5	4.1	651.8	3.6	10.4	5.0	6.0	6.2	6.4	9.3	179.4	922.7	619.8	303.0	*
Pecos River	12.3	2.2	418.9	0.5	10.5	1.1	5.2	5.2	0.8	11.4	66.7	534.8	214.6	320.2	*
Texas-Gulf Basin	8.0	0.7	313.7	0.3	0.3	0.6	2.0	0.5	2.3	0.1	18.1	346.6	19.7	326.9	*
Upper Colorado	2.4	0.8	80.4	0.1	1.4	0.0	0.8	1.7	9.9	1.4	33.7	132.6	131.5	1.1	572.0
Lower Colorado	1.1	0.3	55.3	0.1	0.6	0.0	1.2	2.4	0.3	0.4	6.1	67.8	23.7	44.1	65.0
Arkansas-White-Red	1.6	0.6	186.6	0.2	0.2	0.0	3.6	7.6	0.1	19.2	69.1	288.8	215.8	73.0	112.2
State Total	65.9	8.7	1706.7	4.8	23.4	6.7	18.8	23.6	19.8	41.8	373.1	2293.3			

All Values shown are thousands of acre-feet.
* Underground water is being mined (withdrawals exceed recharge) in these basins
Source: State Water Plan (Preliminary Draft), U. S. Bureau of Reclamation, April 20, 1972.

water. The prospects of desalting such brackish water become imminent as the demand for water increases and the desalting technologies become better developed. The U. S. Office of Saline Water has been supporting water desalting and has recently issued some guidelines matching proven technologies to water source conditions and water use requirements. It is felt that by 1980, desalting techniques may be supplementing some of the water supplies of these basins to meet the demands for water.

Possibilities also exist for one basin to augment its water supplies by transferring water from another basin. Only one water transfer project currently exists in New Mexico, the San Juan-Chama project, which when fully completed will bring 50,000 acre-feet a year from the San Juan to the Rio Grande basin. A similar project, but one that involves greater distances is under consideration by the Corps of Engineers and the Bureau of Reclamation. Their proposal would bring water from the Mississippi River Basin to Western Texas and Eastern New Mexico (affecting the Southern High Plains and the Pecos River Basins). Current estimates of the cost of this water are $\$1.50/10^3$ gallons. Projects of this magnitude not only involve engineering and economic considerations but political ramifications which may be more difficult to overcome than the former two considerations. Diversion projects such as these require 10 to 25 years to complete so can not be considered as immediately available water sources.

A brief discussion of the individual river basins in New Mexico follows.

San Juan. The San Juan Basin is part of the Upper Colorado River Basin system. The basin covers approximately 9,740 square miles. The average annual surface water supply in the San Juan is estimated at 2,250,000 acre-feet. Of this supply, New Mexico's share is about 704,000 acre-feet/year.

The principal means of regulating stream flow in the basin is the Navajo Dam, a unit of the Colorado River Storage Project, which provides storage for about 1.7 million acre-feet of water.

The surface water quality in the San Juan basin is generally good. During periods of low water flow, however, high levels of dissolved solids have been reported. Tables on average TDS (tons and concentration) for reporting stations are available.

Ground water in the San Juan basin has been used only on a limited scale, for agriculture. Estimated depletions are 1,100 acre-feet annually. No large supplies of good quality ground water have been found. The depths that water is found at is around 1,000 feet in the western portion, becoming shallower in the east. Water quality is poor in the western region with dissolved solids at more than 1,000 ppm. Good quality water is available in the eastern portions in the San Jose formation. The eastern portions of the basin are the only areas that have the potential of producing water in large volumes. The ground water is not declared basin.

Present use of water in the San Juan basin amounts to approximately 131,500 acre-feet. However, most of the surplus, 572,900 acre-feet has been allocated to proposed projects.

Rio Grande. The Rio Grande River Basin runs from Colorado to Texas down the middle of the state. The usable supply is estimated to be 619,800 acre-feet which is fully appropriated and utilized. Two dams are currently located along the Rio Grande, Elephant Butte and El Caballo, for water storage purposes.

Water entering the state is of generally good quality, with average concentrations of dissolved solids of 220 ppm. Various tributaries of the

Rio Grande are higher in dissolved solids. This, plus the agricultural use made of the water, contributes to the 823 ppm dissolved solids in the water leaving New Mexico. The average concentration at the Bernalillo recording station is 264 ppm.

Heavy use is made of the ground water in the Rio Grande Basin and most of the ground water is in declared underground water basins. There are two types of underground aquifers, valley fill and bed rock. The valley fill aquifers are primarily recharged from streamflow. Some of the bed rock aquifers are also recharged from stream flow. The wells drilled in bed rock formations generally yield only small to moderate amounts of water.

Pecos River Basin. The usable average annual water supply in the basin is around 214,600 acre-feet. Streamflow through this region is highly erratic, being largely influenced by heavy runoff, 60% of which occurs from May to September. The quality of surface water is poor throughout most of the Pecos Basin. The quality generally deteriorates in the downstream reaches, due primarily to the soluble material that underlies the basin. Dissolved solids of over 1,000 ppm are a rule in the lower reaches.

The alluvial aquifers in the Pecos Basin are generally stream connected. The exception is the Roswell aquifer that is recharged upward from the underlying artesian aquifer. In the northern part of the basin groundwater is used primarily for public water and livestock. In the southern part the groundwater is also used for irrigation. In this part of the basin water is being mined, and the water level has, in parts, declined by as much as 85 feet. Water pumpage and discharge to the Pecos is estimated to exceed recharge by more than 120,000 acre-feet annually. Total ground water use is about 320,000 acre-feet annually.

The quality of the ground water in the north is good. In the south, the heavy use of irrigation and the mining of the water is causing the water to become more saline.

Southern High Plains. The Southern High Plains Basin of New Mexico is part of the Texas-Gulf Basin. There are no permanent streams in the area. Some use is made of surface water for livestock feeding when the runoff is trapped in ponds or surface depressions. The average annual supply is estimated at 19,700 acre-feet.

The area uses about 326,800 acre-feet of ground water annually, for irrigation, industrial, municipal, and recreation uses. This has resulted in the mining of the water, and in areas of the Portales Valley, ground water is about depleted. The quality of this water is generally good.

Remaining Basins. The Lower Colorado contains about 88,700 acre-feet of water, of which 23,700 acre-feet are currently being used. The water quality is very good except in the Puerco River.

Ground water of limited quantity is available throughout most of the basin. Its quality is considered good although some of it ranges high in dissolved solids. Current depletions are about 44,100 acre-feet annually.

The Arkansas-White-Red Basin's only perennial stream is the Canadian. Current available surface supply is 328,000 acre-feet, in which 215,800 are currently used. Water quality is good at the upper reaches of the Canadian River but deteriorates downstream. Dissolved solid concentrations are particularly bad in periods of low flow and have reached 4,000 ppm at the state line.

Ground water has not been developed extensively, and information on the total quantity is unknown. Recharge is local, and large amounts are not thought to be available. Quality varies widely throughout the basin. Ground water depletion is estimated at 73,000 acre-feet.

None of the closed basins have any perennial streams and no large uses are made of any of the surface water. The areas are mainly dependent on ground water. Wells in the Central basin yield only small to moderate amounts and are used domestically or for livestock. The Western Closed Basin is sparsely populated and present ground water usage is low. It is believed that large quantities of water might be available in this region. In the Southwestern Closed Basin the ground water is more widely developed for irrigation, municipal and industrial uses and withdrawals exceed recharge.

APPENDIX B

POLLUTION PARAMETERS

Since it is nearly impossible to characterize the waste characteristics of an industry in terms of the quantities of pollutant produced per unit of product produced, it is customary to utilize pollutional parameters as a measure of the characteristics of an effluent stream and its effect upon the receiving waters. Some of these parameters are discussed.

Total organic carbon (TOC) is a measure of all organic carbon present in a wastewater and may be determined by the use of one of the commercial instruments available. Its value lies in the ability to measure completely all the organic constituents in terms of their carbon content.

Biological oxygen demand (BOD) is one the oldest and most commonly used measurements to determine the organic strength of sewage. Usually the five day BOD test is made which specifically is a measurement of the oxygen utilized by microorganisms in the stabilization of the organic matter in the wastewater during the five day period. With municipal sewage the BOD test is fairly consistent and may be used to determine the total biologically oxidizable organic matter. The difficulty with its usage in industrial wastewater measurements in many cases is the lack of the specific microorganisms for the dissolved organic materials present or the existence of chemicals which are toxic to the microorganisms. Unless the proper microorganisms are present and active, the BOD test will result in low oxygen demands indicating less polluting characteristics than are actually present.

Chemical oxidation demand (COD) is the measurement of the quantity of oxygen required to chemically oxidize the organic compounds in wastewater. Many of the organic materials present in petroleum or oily wastes are chemically oxidizable.

The immediate oxygen demand (IOD) is the dissolved oxygen consumed in the first fifteen minutes of reaction time by compounds introduced into oxygen containing solutions. The importance of the IOD measurement is the information obtained about the rapidity with which dissolved oxygen levels may decrease when the wastewater is discharged into waterways. Knowledge of the rate of dissolved oxygen removal is important since some materials with slow biodegradable rates may be safely disposed of in waterways without upsetting the aquatic life by greatly lowering the oxygen level. However, rapidly biodegraded materials could cause great harm to aquatic life by using all the available oxygen, thus greatly diminishing or killing off the aquatic life.

The theoretical oxygen demand (TOD) is a measure of the amount of oxygen required to completely oxidize waste materials. It is largely a theoretical device with little practical significance.

pH is a measurement of the degree of acid or alkaline content of the wastewater. Industrial wastes which are highly acidic or highly alkaline, as measured on the pH scale of 0 to 14, must be treated before discharge since most aquatic life cannot tolerate pH levels outside the range of 5 to 9 pH units with the optimum range being 6.5 to 8.5. Acidic water is a major cause of metal corrosion while highly alkaline waters may also cause deterioration of materials, particularly concrete.

Both turbidity and color are measurements of the optical quality of the water. Turbidity is the result of particles suspended in the water. It is commonly measured in either turbidity units or mg/l of the particles suspended. The suspended material can be inert matter, clay, silt, or sand, or organic matter including algae and bacteria. Man contributes to the turbidity of water through agricultural and mining runoff and industrial wastes.

The color of the water is measured after the coarse suspended matter has been removed through centrifuging. Its measurement involves the comparison of the sample to chemical mixtures using a standard platinum cobalt method; the results are described in units of color. The color that occurs in nature can be organic, the results of "vegetable dyes", or fine bacteria, or inorganic matter primarily the result of dissolved metallic ions (especially iron and manganese). Industrial wastes can contribute substantially to the color of water. Especially critical in this category are the wastes contributed by textile plants, certain chemical plants and processes where dyeing is involved.

Both color and turbidity affects the degree to which sunlight can penetrate the aquatic environment. Sunlight in turn is an element necessary for the growth of plants, a necessary link in aquatic food chains. Because of the contribution to dissolved oxygen made by the plants, sunlight penetration is also a factor in preventing water bodies from becoming anaerobic.

Solids, both suspended (SS) and dissolved, are measurements used in the determination of wastewater characteristics. Suspended solids are objectional since they may cause turbid conditions or settle out, silting the waterway channels. Such a covering may interfere with the reproductive cycles of aquatic life as well as become resuspended again upon being disturbed by changes in flow rates. Dissolved solids may cause odor, color, taste, or toxicity problems. High dissolved solids contents are harmful to fresh water aquatic life and is undesirable for human consumption, some industrial purposes, and irrigation water. Water containing in excess of 1,000 ppm dissolved solids is considered brackish. Certain dissolved solids are present in sufficient quantity or cause such problems that they have been specifically identified.

Hardness is generally a natural phenomenon and is caused primarily by the presence of magnesium and calcium. Other metals which contribute to hardness are strontium, barium, aluminum, manganese, iron, copper, zinc, and lead; but these are important only at certain geographic locations. To a certain extent hardness of water is a desirable quality of water used for irrigation, but it has problems associated with industrial use. Hardness results in scaling, the coating of exposed surfaces with the minerals that were in solution. Eventually the scale can cause the clogging of the equipment, in addition to changing the heat transfer characteristics of the surface. Another problem associated with hardness is the necessity to use more detergents for the same cleaning power as soft water. Hardness, like alkalinity and acidity is measured in terms of $CaCO_3$.

Alkalinity is a measure of the bicarbonate, HCO_3^-, carbonate $CO_3^=$, or the hydroxide present in water. In nature alkalinity is produced by the action of water running through limestone or chalk beds.

The toxicity of a substance in water is a relative concept because of the necessity of specifying both what the substance is toxic to and the background conditions in the water. A test for toxicity, the TL_m, is the concentration necessary to kill 50% of the test organism in a specified time lingth. The subscript m stands for the length of time used in the test, commonly 24, 48 or 96 hours. This is alternatively referred to as the 50%-lethal dose, or the LD_{50}. For the results of the tests to be comparable both the test organisms and the physical and chemical condition of the water have to be specified. Mercury, which is highly toxic to man, is generally less toxic to lower life forms; whereas DDT, which has no immediate effect on man, is highly toxic to lower life forms. Among the most important background variables affecting toxicity are DO, temperature, pH, and the level of dissolved solids. The effects of these background variables can be highly significant, a 10°C rise in the temperature alone can decrease the LD_{50} concentration by half, and a decrease in the level of DO is toxic in itself.

An important consideration, along with the immediate toxicity of the substance, is its long range toxicity. If a substance is immediately toxic but breaks down quickly, its effects will be more limited than a non-degradable or refractory substance. The chlorinated hydrocarbons, DDT, Aldrin, Eldrin and Toxaphene, are chemicals that are refractory and cumulative so the original toxic effects are passed along the food chain. These pesticides have been replaced by organo-phosphates, Parathion and Malathion, which are more toxic to higher forms but break down quickly (24 Hours). Although radioactive wastes are in the process of decaying, the half-lives of most components therein are long enough for them to be considered refractory.

Taste and odor problems occur in nature, with objectionable algae growths and high concentrations of dissolved solids. Industrial wastes that are particularly objectionable are phenolic compounds, sulfur compounds, and ammonia compounds. Taste and odor problems are objectionable in drinking water, water used for recreation, and some industrial processes. There is no set measurement standard on tastes and odors, just the subjective test that it be "unobjectionable" to the people who use it.

An important category that affects health is the presence of pathogenic bacteria in the water. Because of difficulty in measuring pathogens, a measurement is made of coliform bacteria, a harmless bacteria that inhabits the intestines of warm blooded animals. It is assumed that the absence of coliform bacteria indicates an absence of pathogens. The presence of pathogenic bacteria is a concern of sewage treatment plants but is of little concern in the treatment of most industrial wastes. Animal wastes, especially runoff from feedlots, where large concentrations of animals accumulate, possess a potentially large amount of pathogenic organisms.

Because a large percentage of the industrial and utility water is used for cooling, heat is a major pollutant of water. Higher temperatures speed up the metabolism of plants and animals, increasing their rates of growth and their susceptibility to poisons and other factors. A rule of thumb is that a $10^{\circ}C$ rise in the temperature will double the rate of metabolism in lower life forms. A rise in temperature above a certain maximum will prove toxic. Temperature also affects the amount of DO the system can hold; the higher the less DO. Temperature is, therefore, a large factor in the ability of a water body to maintain aerobic conditions.

Fire and explosive hazards can result when volatile materials (oil and explosive chemicals) are dumped into waterways. A less obvious cause is from the anaerobic decomposition of organic wastes in closed systems (sewers) and the subsequent formation of methane (CH_4).

APPENDIX C

WASTEWATER TREATMENT TECHNOLOGY

The technology of wastewater treatment can be separated into several categories: biological and physical-chemical methods. Biological treatment of wastewater has been extensively used for wastes containing organic materials and municipal wastes. As it became necessary to treat industrial wastewaters biological treatment was found not to be adequate particularly for the treatment of inorganic contaminants and especially materials which were toxic to the microorganisms used in biological treatment processes. More advanced technologies were thus developed using physical-chemical processes which offer greater flexibility and efficiency as compared with biological processes.

Wastewater treatment facilities usually combine both physical-chemical and biological processes to effect adequate treatment of industrial wastes. Unlike municipal wastes, which are primarily organic in matter industrial wastes may contain many inorganic materials showing extreme ranges of potential polluting capabilities. Industrial wastewaters are of varied compositions depending not only upon the type of industry, but also upon the processes used within the same industry. Within some industries the quantity and composition of the wastewaters will fluctuate drastically over very short time spans as a result of the intermittent operation of some processes. Most industrial wastewaters will contain some materials that are considered determental to the environment if released and therefore wastewater treatment practices must be utilized.

The components of industrial wastewaters may be categorized into at least four classes:

1. Wastes in which organic compounds predominate.
2. Wastes in which toxic materials are present.
3. Wastes in which biologically inert materials are present but in such concentrations as to be undesirable.
4. Wastes which contain thermal energy.

Many industrial wastewaters will contain combinations of the above components. Industrial wastes could also be subdivided according to the physical state of the components, suspended solids, insoluble liquid films or globules, dissolved solids, or dissolved gases. This physical state of the wastewater component will greatly influence the type of treatment used.

In water scarce areas such as the Southwest, water economy has to be highly practiced usually in the form of a high degree of water reuse within the industry. Such a reuse of water places heavy demands on water treatment facilities to bring the water back to a quality sufficient for the use intended with minimum loss of water. It is quite common in the Southwest to find no aqueous effluent leaving the industrial site after multiple water reuse. Water is reused in the plant with the only losses being due to evaporation in cooling towers, consumptive process uses, spills, and evaporation from tailing ponds which are used to collect blow down waters and other wastewaters not considered economically worth recovering.

In the next two following sections, brief descriptions of biological and physical-chemical wastewater treatment processes are given.

Physical-Chemical Treatment Processes

The treatment of process waste streams to recover valuable components has always been practiced by industry when it was economically profitable. The bulk of these treatment methods were physical and/or chemical in nature. With stricter environmental regulations being enforced and newer technological developments in physical-chemical wastewater treatment processes, wastewater treatment is becoming more and more practiced by industry to produce higher quality aqueous effluents. Table C-1 lists some wastewater treatment processes that currently are being used by industry.

Table C-1. Physical-Chemical Wastewater Treatment Processes

Filtration
Screening
Sedimentation
Flotation
Coagulation
Centrifuging
Precipitation
Adsorption
Ion Exchange
Evaporation
Foam Fractionation
Stripping
Incineration
Reverse Osmosis
Electrodialysis
Ultrafiltration
Chemical Oxidation
Neutralization

Filtration processes may be used to remove suspended solids or oily globules from the wastewater. Commonly used filtering methods are beds of sand or other granular material through which the wastewater is allowed to percolate with the solids and/or globules being retained in the bed. Mechanical filters are also being used in which cloth or wire mesh serves to retain the solid material while the wastewater is passed through the filtering medium. Bed filters require rather large land areas and have high initial costs but operating costs are minimal. While mechanical filters require much less space, the initial costs and operating costs may be great.

Screening is generally done to protect other waste treatment equipment from damage due to large solid objects or to reduce the strength of the wastewater by removal of organic solids. Screens may be sloped, mechanically vibrated, or may be rotary.

Sedimentation is a separation of solids from wastewater by gravitational forces. It is an effective method for removal of settleable suspended solids. The wastewater is passed through a large chamber which holds the water for a sufficient length of time to allow the solids to settle. Some solids removal is accomplished by a scraper bar. Sedimentation processes are used in pretreatment of wastewaters containing large quantities of organic solids and for removal of any sludges or solid materials formed during the wastewater treatment process.

Buoyancy forces predominate in the separation of solids, or oil and fatty globules, lighter than wastewater in flotation processes. Sufficient time for the solids to rise to the surface is provided in a large chamber with the floating solid being removed from the surface either by screening or skimming. If small suspended solids heavier than water will adhere to air bubbles, small air bubbles are dispersed in the unit which will allow removal of the solids adhering to the air bubbles by flotation as well as enhancing the normal flotation process. If such a choice exists, flotation is preferred to sedimentation since the separation is more rapid, thus requiring the use of smaller equipment.

Coagulation refers to the overall process of particle agglomeration to increase the efficiency of either the sedimentation or the flotation process. Coagulation is depicted as a two-part process involving both physical and chemical phases in which destabilization of the particles must be achieved followed by transport of the particles into sufficiently close vicinities such that they adhere to one another. Coagulating agents such as alum may be required. Coagulation is used commonly for removal of turbidity and color. If treatment processes such as ion exchange, adsorption, or membrane separations are planned, then coagulation processes are used to remove colloidal materials which hinder these processes. The flocs or sludges created by the coagulation process must be further thickened by sedimentation, flotation, centrifuging, filtration, or by chemical processing.

Centrifuging is used to separate suspended solids from liquids by using the centrifugal forces imparted to fluids contained in a rapidly rotating vessel. Centrifuging finds its primary use in the dewatering of sludges.

The chemical reaction between a dissolved solid and another dissolved material added for the purpose of forming an insoluble compound with the dissolved solid is called precipitation. This process may be used to reduce the dissolved mineral content of wastewaters. Chemical sludges are formed as a result of precipitation. They may be removed by filtration and settling.

Liquid-liquid extraction is the process in which an immiscible liquid is added to the wastewater with the subsequent separation of particular components of the wastewater since they have a greater affinity for the added immiscible liquid. This process has not been widely practiced in wastewater treatment but does have potential use for oily water treatment.

Adsorption is the removal of dissolved gases or dissolved solids from solution by accumulation on solid phase surfaces in contact with the solution. Adherence to the solid surface is by either physical or chemical attraction. Not only must the solid used contain large surface areas per unit volume of solid, but the surface properties are equally important. Functional groups on the solid surface are responsible for surface property characteristics. Adsorption treatment techniques are of considerable industrial importance for the removal of odors and color reduction.

In ion exchange processes ions held by electrostatic forces to charged functional groups on the surface of a solid are exchanged for ions of similar charge in a solution into which the solid is immersed. Ion exchange has been used extensively for removal of hardness ions calcium and manganese. It may be used for removal of ionic forms of metals in solution.

Evaporation may be used to separate non-volatile dissolved solids from wastewaters. Unless the vapors are condensed, this method results in loss of water to the atmosphere. Evaporation processes are used in areas of low rainfall and hot weather. In these instances the wastewater is sent to collection ponds and solar evaporation allowed to occur. Air pollution (dusting) from dried material in such ponds can be a severe problem.

Foam fractionation is a process in which air is bubbled through the wastewater, and if necessary, a foaming agent added to cause a semistable foam to be formed. Soluble surfactant organic compounds will concentrate in the foam and may be separated from the wastewater. When suspended solids adhere to the air bubbles, foam fractionation will also separate these solids from solution. Foam fractionation holds some promise but has not been used much yet in wastewater treatment although it has been used for industrial purification processes.

Stripping is a process in which a gas or steam is used to remove dissolved gases or volatile materials from wastewaters. Stripping is essentially a distillation process in which steam or gas replaces the heating requirement to effect a separation. The steam or gas is contacted with the wastewater in packed bed columns, the dissolved gases come out of solution and are removed by the stripping gas. Reduction of dissolved hydrogen sulfide and ammonia in wastewaters has been accomplished using stripping processes. It is extensively used in industrial wastewater treatment.

Incineration is the combustion of the waste materials. It is not practiced on dilute wastewaters and is practical only for certain concentrated wastewaters.

Reverse osmosis is a process in which pressures higher than the osmotic pressure of the solution are used to cause water to pass through a membrane, concentrating the waste material while producing pure water. Initially, reverse osmosis techniques were confined to small scale purification systems but recent developments in membrane technology have led to its use in brackish water recovery. Pretreatment of the feed to reverse osmosis units is necessary to prevent damage or deterioration of the membranes. It offers some advantages over ion exchange units since it can remove dissolved organic compounds.

Electrodialysis is another membrane process in which electric current is used to induce partial separation of components in an ionic solution.

Membranes selective to cations are placed alternately with anion selective membranes across the current path with the ionic solution flowing through the partitions formed. As schematically shown in Figure C-1, the cations and anions pass through the appropriate membranes producing pure water in alternate partitions and a concentrated solution between the pure water partitions. Applications have been made in brackish water desalinization and wastewater demineralization. Industrial usage has been in the recovery

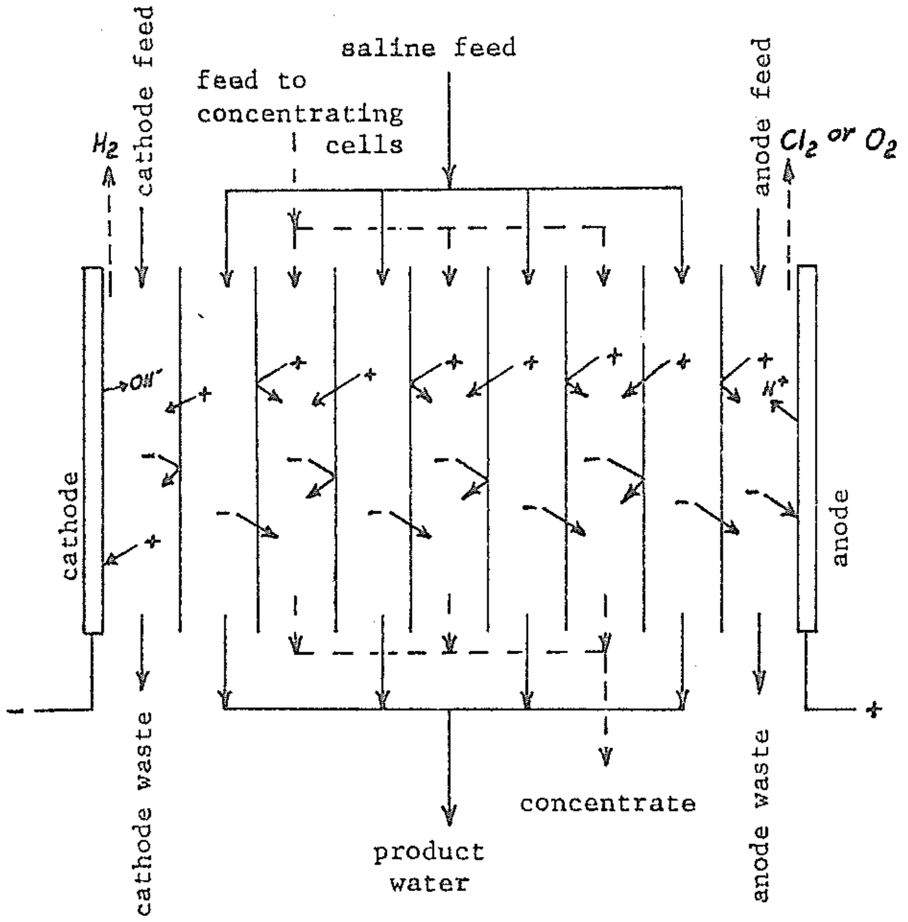

Figure C-1. Electrodialysis Cell

of chemicals from dilute waste streams, carboxylic acid recovery, and many other applications. Both the reverse osmosis process and the electrodialysis process have the disadvantage of producing a very concentrated reject stream which must be disposed of in some manner.

Ultrafiltration is the separation of dissolved solutes from solution using a selective membrane and pressure on one side of the membrane. It is similar to reverse osmosis except it uses much lower operating pressures and does not provide good separation of small solutes, those below a molecular weight of 500. Selective sieving of molecules through the membrane pores seems to be the predominant mechanism. Ultrafiltration has been used in the food and pharmaceutical industries quite extensively. In wastewater treatment it serves to remove clay, microorganisms, and vegetable matter from water and has sludge dewatering applications.

Chemical oxidation methods are used to treat both inorganic and organic constituents of wastewater using oxygen or other chemicals such as chlorine, ozone, hydrogen peroxide and ferrous salts.

Neutralization is used to adjust the pH level of wastewaters to meet pH ranges required for the treatment processes being used.

Biological Treatment Processes

The reduction of organic pollutants in wastewater streams may be accomplished in biological treatment processes where microorganisms convert the organic matter into relatively harmless material. In wastewater treatment the major concern, after solids separation, is removal of the dissolved biodegradable components. These dissolved organic materials are more easily treated by microorganism activity than the solid organics since the dissolved materials are in a form best assimilated by the microorganisms. In general most naturally occurring organic materials may be reduced biologically to harmless matter if sufficient time of exposure to the suitable microorganisms is provided.

Unlike municipal wastes in which all the necessary nutrients for microbial growth are usually present in sufficient quantities, industrial wastewaters are usually deficient in the nitrogen and phosphorous. These two nutrients must be added to the industrial wastewaters at the treatment plant if biological activity is to be maintained. Many industrial wastewaters are also either too acidic or too basic, thus pH levels must be adjusted to maintain a pH value in the optimum range of 6 to 8 for biological activity. Biological processes are also adversely affected by transient loading effects, thus fluctuations of flow and compositions need to be smoothed out by the use of surge tanks.

Biological treatment processes alone are not sufficient for effective wastewater treatment because solids, or undissolved liquid oily or fatty globules may be present. Sedimentation and flotation tanks may precede the biological treatment units in the more simple facilities. Sedimentation tanks usually are used after the biological treatment units to separate the sludges formed by the biological activity from the aqueous effluent. The major types of biological wastewater treatment processes are listed in Table C-2.

Table C-2. Basic Biological Wastewater Treatment Processes

1. Oxidation Ponds
2. Activated Sludge
3. Trickling Filters
4. Anaerobic Digestion

Variations of these basic processes exist and are being used to meet specific wastewater treatment requirements.

If sufficient land area is available, lagooning in oxidation ponds is an inexpensive method for removal and oxidation of organic matter in wastewaters. As the waste flows into the pond, solids settle around the inlet to the pond and decomposition of the sediment by microorganisms changes the sludge into inert residues and soluble organic materials. This decomposition may occur by either aerobic or anaerobic microorganisms, or both types depending upon the depth of the pond and the pollution loads. It is desirable to maintain aerobic conditions since aerobic microorganisms cause the most complete oxidation of organic matter. Anaerobic conditions lead to odiferous gases being formed which can be a nuisance. Further reduction of dissolved organic material may occur but this is not desirable since it may lead to an oxygen depletion and anaerobic conditions. Supplementary aeration may be supplied by mechanical means if necessary.

The activated sludge process is an aerobic biological treatment process in which high concentrations of newly-grown and recycled solid masses of microorganisms are suspended in a holding tank to which raw wastewater is added. The active masses of microorganisms stabilize the dissolved organic matter by forming simpler compounds such as carbon dioxide, water, nitrates, and sulfates. As the sludge settles from the aqueous waste, in a sedimentation basin, the clear liquid of low organic content is passed on for further treatment if necessary while a portion of the sludge is returned to the aeration tank to serve as seed microorganisms. The excess sludge is further treated by digestion. The activated sludge process is somewhat unstable particularly if the flow or organic loading varies widely. Oxygen must be supplied to the process at a rate which will maintain highly aerobic conditions since anaerobic, or low oxygen levels, do not result in the microorganisms developing fully and thus retard sludge formation. With industrial waste treatment, some nutrients usually have to be added such as nitrogen and phosphorous since these are usually missing. pH levels and temperature are activated-sludge environmental factors which must be maintained within certain levels. The activated sludge process is quite versatile, producing an effluent having any desired organic concentration ranging from very high to very low.

Trickling filters are aerobic biological treatment processes in which the aqueous waste is dispersed over a 3 to 14 foot deep bed of granular material such as gravel, rock, or other inert material on which is maintained a fixed growth of microorganisms. Sufficient void space must be maintained between the packing to allow oxygen to reach the microorganisms and to allow some of the growth to slough off and pass through the bed. The use of synthetic packings has allowed 40 foot trickling filters to be constructed. Wastewater is normally sprayed through a rotary distributor over the top of the bed and flows by gravity to an underdrain system which diverts the effluent to a sedimentation tank. Some of the effluent is recycled to improve the performance. Trickling filters have been used extensively although they occupy a large amount of space, have a tendency to become clogged with solids, exhibit pooling tendencies which decrease oxygen transfer, and have limits on the flow rates, organic loading and strength of waste applied.

Highly concentrated organic industrial wastes, organic solids removed from wastewaters in sedimentation tanks, and the biological solids from trickling filters and activated sludge units are often treated by anaerobic biological method. In this process the anaerobic bacteria break down the water binding organic solids and produce a reduced sludge mass which can easily be separated from the water to form a stable solid. Circulation and temperature control of the material is important to maintain high rates of microbial activity. pH control must also be exercised.

Costs of Wastewater Treatment

Major economic factors to be considered in wastewater treatment include:

1. Capital cost of treatment process required to produce a defined quality level of effluent and the operating costs associated with the treatment process selected.
2. Returns to the specific industry resulting from its wastewater treatment in terms of product recovery, new by-products, and water reuse.
3. In-plant modifications necessary to render a treatment process feasible or less costly.

One general approach to determine capital costs of wastewater treatment facilities would involve the estimation of the unit costs of each process within the treatment facility and to increase the unit cost by a fixed percentage to allow for piping, pumps, auxiliary equipment, engineering and equipment. Operating costs are calculated based upon the complexity of the process and the chemicals needed. Other factors which must be considered are geographical location, land cost, climatic conditions, area labor and materials cost fluctuations, and over-design considerations.

Such estimations of costs within the chemical industries have been shown to be adequate for preliminary design purposes.

For wastewater treatment unit costs of certain types of treatment processes have appeared in the literature. These costs are typical only and before being used consideration must be given to quantity and quality of feed, quality of effluent produced, geographic factors and disruptions in the existing process for installation. Typical capital costs and operating costs are shown in Table C-3. Treatment costs for wastewaters generated in the organic chemical industry are shown in Table C-4. Although not directly applicable to petroleum or synthetic natural gas facilities, Table C-4 does give some indication of the magnitude of the cost involved in wastewater treatment and the effect of effluent quality on cost. The cost figures shown in Table C-4 are for relatively simple waste treatment systems such as activated sludge process with the associated processes of neutralization for pH control, oil separation, sedimentation, filtration, carbon adsorption, and ion exchange. Where reverse osmosis, electrodialysis, or other more advanced technological processes are required costs will increase rapidly.

Table C-3 Unit Process Wastewater Treatment Costs

Unit	Capital Costs	Annual Operating Costs
Activated Sludge	1,500,000	190,000
Coagulation/Sedimentation	375,000	225,000
Dual Media Filtration	400,000	75,000
Chlorination	75,000	91,000
Reverse Osmosis (Demineralizing)	3,100,000	1,070,000
Activated Carbon Adsorption (Dissolved organic matter removal)	600,000	163,000
Electrodialysis (500 mg/l* TDS reduction)	1,000,000	150,000

*milligrams per liter
Based on 10 million gallons per day

Source: W.&S.W.-Reference Number-1968 R-222

Table C-4. Wastewater Treatment Cost for Organic Chemical Industry

Level of Treatment	Removal of Critical Pollutants BOD	COD	SS	Capital Costs	Operating Costs per year	Relative Costs
1	Removal of Gross Pollutants			470,400	22,400	1.0
2	10%	10%	65%	563,200	27,200	1.21
3	83	13	71	800,000	41,600	1.86
4	98	30	89	2,240,000	336,000	15.0
5	99	33	99	2,403,000	384,000	17.13
6	100	100	100	5,273,600	1,120,000	50.0

Based of treatment of an average of 3.2 million gallons per day

Source: Environmental Sci. & Tech. 3(4) 311(1969)