POLLUTION CONTROL IN THE ORGANIC CHEMICAL INDUSTRY

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FOREWORD

Waste products from organic chemical plants manufacturing identical compounds may be quite dissimilar because of the difference in processes and raw materials. Since the organic chemical industry is now largely petrochemical, preference has been given to waste treatment from such operations although basic coal tar processes have not been neglected. Detailed treatability evaluation of each waste stream has become a prerequisite for any profitable product.

Physical methods for waste and by-product removal include gravity separation, air flotation, filtration, evaporation and adsorption techniques. Chemical methods include precipitation, polyelectrolyte treatment, oxidation and other chemical conditioning such as neutralization. Biological treatments comprise activated sludge formation and its modifications, i.e., trickling filters, aerated lagoons and waste stabilization ponds.

This book intends to assist the chemical engineer in treating chemical waste products and effluents in conjunction with prudent raw material choices and methods, and thus bring about process economies. It presents condensed vital data from government and other sources of information that are scattered and difficult to pull together. Important pollution removal processes are interpreted and explained by examples from 72 U.S. patents. This condensed information will enable you to establish a sound background for action in combating pollution by the organic chemical industry.

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The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

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INTRODUCTION

The frontiers of the chemical industry which have produced most of the exciting new products of the past years in the forms of new drugs, plastics, fibers and pesticides are firmly based on industrial organic chemistry.

Organic chemicals were once almost wholly based on coal, and indeed much of the growth impetus for the early days of the industry was provided by the profits from coal tar dyes. Then as lower cost petroleum hydrocarbons became available in huge volumes, the term "petrochemical" became almost synonymous with "organic chemical." Now, with a new look at hydrocarbon sources spurred by energy shortages, a more balanced choice of coal and petroleum sources for organic chemicals is in evidence. In any event, this multibillion pound, multibillion dollar industry has its own pollution problems which must be addressed in consort with problems of raw material choices and process economics.

It is the purpose of this book to outline some of those pollution problems as well as some of the cures for those problems.

BACKGROUND AND ECONOMIC TRENDS

Synthetic organic chemicals are derivative products of naturally-occurring raw materials (petroleum, natural gas, and coal) which have undergone at least one chemical conversion. The organic chemicals industry was initially dependent upon coal as its sole source of raw materials. However, during the last two decades it has moved rapidly from coal to petroleum-based feedstocks. Although the cost of coal is less than half that of most liquid fuels, the handling and processing of liquids is much cheaper. In addition, the extraction of coal is much more labor-intensive than is the extraction of liquid fuels.

In recognition of the change in origin of raw materials, the term "petrochemical" has come into common usage. Although a precise definition of petrochemicals has yet to gain universal acceptance, it commonly refers to all organic chemical products derived from petroleum fractions and by-products or from natural gas constituents. From its modest beginnings in the 1920's with the manufacture of isopropanol from refinery off-gas propylene, petrochemistry has by now not only made possible the almost total elimination of coal and coal tar as sources of chemical raw materials, but has also gone a long way towards replacing such methods of obtaining organic chemicals as fermentation, extraction of compounds from materials occuring in nature, and chemical transformation of vegetable fats and oils.

Now in 1974, however, with the world energy crisis putting an entirely new perspective on hydrocarbon economics, coal chemicals may well be on the increase again. After having become accustomed to relatively cheap energy and plant feedstocks, chemical makers must now pay more for these materials as other demands crowd in on their traditional sources.

The alternate use for natural gas is as fuel. In the past, this alternate value as fuel set a base price of about 0.4¢/lb on chemical feedstocks such as ethane and propane. With chemical producers willing to pay 0.7¢/lb for these feedstocks, the natural gas industry found it advantageous to sell them for chemical usage.

However, recent drastic increases in demand for natural gas as a pollution-free fuel, coupled with a leveling off of gross gas production, have more than tripled the base fuel value for ethane and propane as chemical feedstocks. This has led most chemical producers to plan future production of chemicals such as ethylene on processes that use heavier feedstocks such as liquid crude oil distillates.

Light liquid distillates, however, have an alternate use and value as gasoline. A typical barrel of crude oil usually contains only about 20% light distillates in a boiling range suitable for use as gasoline. All of this must be processed at some expense, and in order to satisfy the automobile-oriented society in the United States, another 25% of the higher boiling crude oil distillates must be converted into the gasoline boiling range by cracking and other refinery processing.

With crude oil valued at 7.5¢/gal ($3.15/bbl), the final gasoline product, representing 45% of the barrel, must be valued at close to 12¢/gal. The light distillate fractions suitable either for manufacturing of chemicals or for processing into gasoline carry an intermediate value of 8.5¢/gal, or 1.4¢/lb.

This increasing cost for feedstock amounts to about 40% of the total 3¢/lb ethylene price prevailing for Gulf Coast markets during the past several years, as pointed out by the Environmental Protection Agency in *Report EPA 440/1-73/009* entitled, "Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category," Washington, D.C., EPA (Dec. 1973).

Increasing gasoline demands and a limited supply of available crude oil will only cause the shortage of chemical feedstocks to become more severe. In economic terms, the expected increase in energy costs between now and 1980 will bring some dramatic changes in the cost of key petrochemicals. The brief tabulation on the following page illustrates the theoretical effect of an increase of 50¢/bbl in the cost of crude oil.

Cost Increase Associated with 50¢/Bbl

Petrochemical	Current Cost	Increase in Crude Oil
Ethylene	3.0¢/lb	+0.3¢/lb
Butadiene	5.0¢/lb	+0.8¢/lb
Benzene	23.0¢/lb	+1.7¢/lb
p-Xylene	5.5¢/lb	+0.7¢/lb

The above price differentials, predicated on a 50¢/bbl increase in crude prices now seem like a ludicrously conservative projection at a time when in late 1973 crude oil prices increased by magnitudes ten times greater—of the order of $5.00 per barrel.

Costs must be developed for the pollution control systems which may be utilized to comply with the effluent limitations. The pollution control costs may be put on the same cents-per-pound basis and added to the required realization to provide a meaningful assessment of the economic impact on specified products. Performing this calculation for several of the products within a subcategory or between subcategories will provide a basis for general conclusions relating to the industry as a whole.

AIR POLLUTION

While air pollution in the sense of emission of hydrocarbons, H_2S, HCl, HF, and Cl_2 constitute something of a problem for manufacturers of organic chemicals, they do not seem to constitute a problem of the magnitude of the industry's water pollution problem.

The organic chemical industry must, however, be concerned with two aspects of the air pollution problem: 1. The effect of discharges on the public ranging from really toxic fumes to soot emissions on washdays. 2. The effect of discharges on the utility of air as a chemical raw material. This is essentially the problem of industry fouling its own nest.

As pointed out by M. Sittig in *Combining Oxygen and Hydrocarbons for Profit,* Houston, Texas, Gulf Publishing Co. (1962), the requirements of many organic chemicals manufacturing processes for reaction air are considerable indeed. Some examples are as follows:

Process	Tons Air Required/Ton Product
Synthesis Gas	4.0
Hydrogen Cyanide	10.0
Phthalic Anhydride	5.0
Carbon Black	22.0

The presence of dust, coke breeze, nitrogen oxides, sulfur oxides or carbon oxides in such air intakes may cause a variety of process problems such as system plugging and catalyst poisoning. A recent discussion of atmospheric emissions from the petroleum industry, while not wholly applicable, gives some guidance as to emissions which may be encountered in petrochemical manufacture and their control. The source is "Atmospheric Emissions from the Petroleum Refining Industry," *Report PB 225,040,* Springfield, Va., National Technical Information Service (Aug. 1973).

Now that the coking of coal may be growing in importance as a source of organic chemicals, the particular air pollution problems presented by coke ovens come into focus as a problem related to organic chemicals manufacture. Some control techniques associated with coke oven operations will be detailed later in this volume.

WATER POLLUTION

The 1972 amendments to the Federal Water Pollution Control Act impose much more severe and specific strictures on the organic chemicals manufacturing industry than did the Clean Air Act of 1970. Thus, a substantial part of this volume will be devoted to aqueous wastes from this industry and possible techniques for their treatment.

The sources of wastes emanating from refinery and petrochemical operations can be divided into five general categories as noted by W.L. Jewell and D.L. Ford of Engineering-Science, Inc. in *Report 12020 EID 03/71,* Washington, D.C., EPA (Mar. 1971):

1. Wastes containing a principal raw material or product resulting from the stripping of the product from solution.
2. By-products produced during reactions.
3. Spills, slab washdowns, vessel cleanouts, sample point overflows, etc.
4. Cooling tower and boiler blowdown, steam condensate, water-treatment wastes, and general washing water.
5. Storm waters, the degree of contamination depending on the nature of the drainage area.

The principal contaminants in the wastewaters include organics from residual products and by-products, oils, suspended solids, acidity, heavy metals and other toxic materials, color, and taste and odor-producing compounds. The concentration of BOD_5 and COD, respectively, in untreated refinery effluents has averaged 108 and 204 lb/1,000 bbl of crude oil refined. The pH of refinery wastewaters is normally alkaline, but may vary considerably depending on disposal of spent acids, acid washes, etc.

The large variety of compounds produced within the petrochemical and refinery industries makes the task of treating wastewaters difficult and complex. Wastewaters from plants manufacturing similar or even the same compounds usually display dissimilar characteristics. This can be ascribed to the use of different manufacturing processes coupled with the fact that the by-product disposal pattern may occur in a number of different ways. Thus, a wastewater treatability study should be undertaken when the treatment of petrochemical and refining wastes is considered.

A detailed treatability evaluation of each waste stream is a prerequisite to determining the proper integration of unit processes which constitute an optimum waste treatment system. The waste treatment methods applicable to the refining and petrochemical industries can be categorized as follows: physical, chemical, biological, special in-plant methods, and ultimate disposal.

Physical methods include gravity separation, air flotation, filtration, centrifugation, vacuum filtration, evaporation, and carbon adsorption. Gravity separators and air flotation units, which are used extensively throughout the industry, are designed primarily for removal of free-floating oil and settleable solids. Filtration is used primarily as a pretreatment for deep well injection; and centrifugation and vacuum filtration are used for sludge dewatering. Evaporation ponds are often efficient, but are limited to areas where land is available and climatic conditions are favorable. Carbon adsorption is used to remove refractory organic substances.

Chemical treatment methods include coagulation-precipitation, chemical oxidation, ion exchange, and chemical pretreatment or sludge conditioning. These methods enhance oil and solids removal, particularly with respect to oil emulsions.

The biological treatment methods include activated sludge and its modifications, trickling filters, aerated lagoons, and waste stabilization ponds. Usually some form of wastewater pretreatment is required to remove oils, suspended solids, and toxic substances, and to provide neutralization, equalization, and surge or holding capacity.

The activated sludge process is generally considered the most effective biological process for removing organic materials with removal efficiencies in the range of 70 to 95% for BOD_5, 30 to 70% for COD, and 65 to 99% for phenols and cyanides. The conventional activated sludge process is the most widely applied. Contact stabilization is most applicable when a large fraction of the organic constituents is in suspended or colloidal form. Extended aeration is particularly adaptable to industrial applications as the longer detention periods allow the microorganisms more time to degrade the complex organics and, more importantly, sludge production is minimized.

Deep well injection of petrochemical and refinery wastewaters is used primarily as an ultimate disposal method for low-flow, highly concentrated wastes. The efficacy of disposing of these streams by deep well injection depends on the extent of pre-injection treatment requirements, the receiving formation, and the risks involved in contaminating overlying or underlying aquifers.

The more important in-plant treatment control methods include stripping and recovery operations, neutralization and oxidation of spent caustics, ballast water treatment, slop oil recovery, and temperature control. The practice of such in-plant treatment methods not only reduces the waste loadings to the treatment facility, but also enhances its performance. In some cases, in-plant control will show a cost credit in the form of product recovery.

An integral part of in-plant treatment procedures is adequate in-plant waste control practices. In-plant control techniques include salvage of unreacted chemicals, recovery of by-products, multiple reuse of water, good housekeeping techniques to reduce leaks and spills, and curbing and diking of drainage areas.

These controls can reduce both the volume and concentration of pollutants requiring treatment.

New production methods are being directed toward increases in product yield, often resulting in reduced amounts of by-products and unused raw materials in waste streams. A more general indication of pollution reduction by in-plant processing practices is the much lower pollutant loadings per unit of throughput for "newer" refineries as compared to "older" refineries.

To date, biological treatment methods have afforded the most economical secondary treatment processes for pollution abatement. In order to minimize biological treatment costs, several pretreatment processes have been adopted, depending on the characteristics of the waste streams being treated. Design of biological treatment units must consider the possibility of spills, storm runoff, ballast water handling, variation in flow and contaminants, and toxic or inhibitory substances.

Completely mixed activated sludge units, therefore, are applicable to dampen these fluctuations and inhibitory effects. Aerated lagoons are often used where the waste has a large volume but relatively low concentration of dissolved organics. Anaerobic lagoons, anaerobic contact units and high rate trickling filters are used individually or conjunctively when high strength wastes are involved.

Facilities for handling the treatment of the accumulated primary and biologically synthesized sludges often represent a major portion of the treatment facility costs. One inexpensive method of disposing of sludges practiced in many parts of the country is lagooning. However, dewatering the sludge to reduce the volume or direct disposal at sea or in remote areas may be more favorable alternatives where land is unavailable. Aerobic digestion is presently favored over anaerobic treatment in industrial waste applications and is generally followed by thickening, vacuum filtration, filter pressing, or centrifugation and ultimate disposal by incineration or trucking.

The problem areas encountered in the treatment of wastes discharged from the refining and petrochemical industries are generally those associated with pretreatment and biological treatment systems. Problems may be attributed to process changes or modifications, accidental spills resulting in the discharge of slugs of contaminants, or poor in-plant management.

Problems related to pretreatment processes may be caused by excess concentrations of free and emulsified oils, high or widely fluctuating temperatures, acidity or alkalinity, or other contaminants which adversely affect process operation. Waste oil usually occurs from leaks, spills, washing operations, and rainfall runoff from oily areas. When oily wastes and water commingle, there is always a good chance for emulsification, which sometimes is difficult and costly to break.

Wastes affecting pH in the refinery and petrochemical industries include strong acids and alkalies as well as dissolved solids which often buffer their effects. Spills, leaks, scrubbing operations, and point discharges of spent acid are the main sources of acid wastes while the main contributor of acidity is sulfuric acid. However, HCl, H_2S, HF, and CO_2 contribute to a lesser extent to the acidity of the wastewater. Alkalies from process neutralization, process operations, and kettle washes are the main sources of alkalinity. The oxygen demand of refinery and chemical wastewaters is probably the most important factor to be considered. The most concentrated oxygen-demanding wastes discharged from a refinery usually occur in the crude and cracking units. Although much of this oxygen demand in terms of BOD, TOC, COD, etc., is attributable to the oily fraction, a significant portion results from the presence of lighter hydrocarbon contaminants. Moreover, substances such as sulfides and various nitrogen compounds are responsible for an additional oxygen demand.

Toxicity to living organisms is a critical factor in evaluating the treatability of chemical and refinery wastes. Ammonium salts, sulfides and polysulfides resulting as wastes from the use of ammonia as an anticorrosive agent, as well as other boiler and cooling tower inhibitors are toxic. Heavy metals used as catalysts or preparants in process operations are other sources of pollutants which may be toxic to living organisms.

The taste and odor-producing wastes resulting from washing high sulfur crude oil, or cracked distillate from high sulfur stocks, may have highly noticeable and persistent odors. The odor is attributable to complex organic sulfur compounds and alkylated substances.

Acid sludges are the next most important group responsible for taste and odor problems. Sludges from the acid treatment of light distillates have a much more pronounced odor than those from the treatment of lubricating stocks. Much of the odor from light oil sludges is due to mercaptans, which are disagreeable and can be detected at concentrations of a fraction of a part per trillion.

Large concentrations of sulfides in biological treatment units impair the treatment efficiency of these units because of the oxygen required to satisfy the chemical oxygen demand or the possible inhibitory or toxicological effects on the system bacteria. Preaeration of sulfide wastes results in stripping the sulfide from solution when the wastewater is acidic, or oxidizing the sulfides to thiosulfate or sulfate at high pH values.

Because of the diversity of products, it is difficult to generalize regarding the reuse of petrochemical wastewaters. The American Petroleum Institute's *Manual on Disposal of Refinery Wastes* (1969) summarizes the treatment processes presently used to treat 80 different organic chemicals, 20 inorganic chemicals, and 11 overall plant wastes. All of these chemical waste streams present serious problems whenever the COD exceeds 1,000 mg/l, or when phenols or heavy metals exceed toxic levels. The quality of wastewater from the petrochemical manufacturing processes depends on the type of petroleum feedstock, products manufactured, in-plant control, maintenance, and types of processing equipment.

A major source of contaminated water in petrochemical industries is the cooling water and steam equipment. The total volume of this water will amount to 10 to 80% of the total wastewater and its degree of contamination depends on the following factors:

1. Process leaks
2. Water treatment additives
3. Input from air scrubbing
4. Blowdown and condensates

These waste streams have a high potential for reuse, but their degree of contamination must be considered.

There are now three treatment levels designed to ultimately achieve the U.S. national goal of zero discharge of aqueous pollutants. Listed below are these levels of treatment, the first two to be applied to existing plants and the third to new plants.

Best Practicable Control Technology Currently Available (BPCTCA)
(by 7-1-77)
Best Available Technology Economically Achievable (BATEA)
(by 7-1-83)
Best Available Demonstrated Control Technology (BADCT)
(New Sources)

The EPA has formulated these as model systems which are considered capable of attaining the reduction factors associated with each technology. It should be noted and understood that these particular systems chosen for use in cost estimation and economic analysis are not the only systems which are capable of attaining the specified pollutant reductions. There exist many alternate systems which either taken singly or in combination are capable of attaining the recommended effluent limitations and standards. These alternate choices include:

1. Different types of end-of-pipe wastewater treatment.
2. Different in-process modifications and pollution control equipment.
3. Different integrated combinations of end-of-pipe and in-process technologies.

Some of the specifics of these various systems will be discussed later in this volume.

It is the intent of the EPA to allow the individual manufacturers within the organic chemicals industry to make the ultimate choice of what specific combination of pollution control measures is best suited to his situations in complying with the published limitations and standards presented.

SOLID WASTES

A historical survey of the trends in solids disposal at refineries and petrochemical plants indicated that this is a significant problem as reported by W. Jewell and D.L. Ford of Engineering-Science, Inc. in *Report 12020 EID 03/71,* Wash., D.C., EPA (March 1971). Landfill was found to be the most common method of disposal and was used primarily for separator and tank bottom sludges, sewer cleanings, water treating sludges, cooling tower bottoms, and biological treatment plant sludges. Incineration and open burning has been used for general refuse. Contract disposal services have been used for filter cakes, treating clays, and slop oil disposal.

Based on the results of this survey, it was decided that further information on the following areas would improve the disposal techniques available.

1. Determination of hydrocarbon content and calorific values of solid wastes.
2. Evaluation of incinerators to establish capabilities for handling different wastes.
3. Investigation of land spreading techniques to establish land and manpower requirements.
4. Identification of wastes that are amenable to de-oiling treatment, i.e., separation of solids and hydrocarbons.
5. Investigation of development of spent caustic disposal systems.

The topic of "Solid Wastes in the Petrochemical Industry" has also been addressed in a technical report to the U.S. Environmental Protection Agency by R.G. Makela and J.F. Malina, Jr. of the Center for Research in Water Resources, Austin, Univ. of Texas (Aug. 1972).

As discussed in that report, waste solids in the petrochemical industry occur in diverse forms, many of which would not be brought to mind by the term "solid wastes." These waste solids or solid wastes may occur as actual solids, such as scraps of wood, paper, or metal; as semi-solids, such as tars and resins; as suspended solids, such as monomers and polymers in a process waste stream; or as dissolved solids, such as inorganic or organic solids. These materials may be characterized by such terms as combustible or noncombustible, organic or inorganic, inert or biodegradable, dry or mixed with either aqueous or nonaqueous liquids, or as a combination of several of these terms.

Almost every plant in the petrochemical industry has some form of solid waste handling or disposal facility on the premises. Every plant with a liquid waste stream probably has a solids removal unit and some type of solids concentration unit. Most plants will have one or more disposal facilities or areas on the site. Many plants, however, find it more economical or expedient to contract for someone else to handle some or all of their solid wastes.

The solid wastes found in the petrochemical industry may be stored, handled, and disposed of by various combinations of many different methods. Materials may be stored in large open or closed bulk containers, in smaller bulk containers such as drums or barrels, or in open piles or pits. Plant personnel or private contractors collect and transport the wastes in flat bed trucks, stake-sided trucks, dump trucks, open or closed top vans, compacting trucks, tank trucks, or by pipeline to the disposal facility.

Unit processes for solids removal from liquid waste streams include sedimentation, flotation, coagulation, flocculation, precipitation, and filtration. Unit processes for concentration of solids include gravity and flotation thickening, centrifugation, vacuum and precoat filtration, filter press and heat treatment.

On-site disposal methods include incineration and land disposal. Incineration facilities include multiple hearth furnaces, rotary kilns, fluidized bed reactors, controlled air open-pit incinerators, and liquid burners. Land disposal methods include lagooning, spreading on land or "land-farming," and landfill.

Off-site disposal methods include land disposal by lagooning, land-farming, or landfill, incineration by various methods, and ocean disposal by pipeline to inshore waters, bulk dumping of barge transported wastes in offshore waters,