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*Development Document for Effluent Limitations Guidelines
and New Source Performance Standards for the*

MAJOR ORGANIC PRODUCTS

*Segment of the Organic
Chemicals Manufacturing*

Point Source Category

APRIL 1974



U.S. ENVIRONMENTAL PROTECTION AGENCY
Washington, D.C. 20460

DEVELOPMENT DOCUMENT
for
EFFLUENT LIMITATIONS GUIDELINES
and
NEW SOURCE PERFORMANCE STANDARDS
for the

MAJOR ORGANIC PRODUCTS SEGMENT OF THE
ORGANIC CHEMICALS MANUFACTURING
POINT SOURCE CATEGORY

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ABSTRACT

A study of the major organic chemicals segment of the organic chemicals manufacturing industry was conducted by Roy F. Weston Company for the Environmental Protection Agency. The purpose of this study was to establish effluent limitations guidelines for existing point source discharges and standards of performance and pretreatment standards for new sources. This study and subsequent proposed regulations were undertaken in fulfillment of Sections 304, 306, and 307 of the Federal Water Pollution Control Act Amendments of 1972.

For the purposes of this study, 41 major product-process segments of the industry were investigated. These product-processes and others significant segments to be covered in the second phase of this study were categorized into four subcategories based on process technology as related to process water requirements. Industry segments were further subcategorized wherever appropriate on the basis of raw waste loads. Effluent limitations guidelines and standards of performance were then developed for 7 subcategory groups which include 40 product-processes on the basis of treatment and control technologies. Supportive data and rationale for development of the proposed effluent limitations guidelines and standards of performance are contained in this report.

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SECTION I

CONCLUSIONS

The organic chemicals manufacturing industry is a complex one in which interrelated chemicals compete for raw materials and markets via increasingly complex technologies. The water usage and subsequent waste water discharges are closely related to this mix of products and processes. The effluent limitations guidelines and standards presented in this document were developed with full recognition of these complexities.

The industry is not readily defined in terms of the Standard Industrial Classification (SIC) system. However, commodities included under SIC 2815 (Cyclic Intermediates and Crudes) and SIC 2818 (Industrial Organic Chemicals) provide a reasonable approximation and have been used to define the limitations of the industry for the current study. Primary petrochemical processing, plastics, fibers, agricultural chemicals, pesticides, detergents, paints, and pharmaceuticals have been excluded. Lists of the specific products covered by SIC 2815 and 2818 are presented in Tables I-1 and I-2.

The diversity of products and manufacturing operations to be covered indicates the need for separate effluent limitations for different segments within the industry. To this end, process-oriented subcategories have been developed as follows:

Subcategory A Nonaqueous Processes

Contact between water and reactants or products is minimal. Water is not required as reactant or diluent, and is not formed as a reaction product. The only water usage stems from periodic washes or catalyst hydration.

Subcategory B: Process with Process Water Contact as Steam Diluent or Absorbent

Process water is in the form of dilution steam, direct product quench, or absorbent for effluent gases. Reactions are all vapor-phase over solid catalysts. Most processes have an absorber coupled with steam stripping of chemicals for purification and recycle.

Subcategory C: Aqueous Liquid-Phase Reaction Systems

Reactions are liquid-phase, with the catalyst in an aqueous medium. Continuous regeneration of the catalyst requires extensive water usage, and substantial removal of spent inorganic by-products may be required. Additional process water is involved in final purification or neutralization of products.

Subcategory D: Batch and Semicontinuous Processes

Many reactions are liquid-phase with aqueous catalyst systems. Requirements for very rapid process cooling necessitate provisions for the direct addition of contact quench water or ice. Reactants and products are transferred from one piece of equipment to another by gravity flow, pumping, or pressurization. Much of the materials handling is manual, and there is only limited use of automatic process control. Filter presses and centrifuges are commonly used for solid-liquid separations, and air or vacuum ovens are used for drying. Cleaning of noncontinuous production equipment constitutes a major source of waste water.

Sample flow diagrams illustrating typical unit operations and chemical conversions for a process in each subcategory are provided in Figures I-1, 2, 3, and 4. Table I-3 is a comprehensive listing of the chemicals and processes assigned to each subcategory. The products and processes covered in Phase I are listed, by subcategory, in Table I-4. The raw waste load (RWL) data obtained in the field surveys are summarized in Table I-5. Subcategories B and C were further subcategorized on the basis of raw waste loads. For subcategories B and C, product-processes were classified by subcategory groups: B1, B2, C1, C2, C3, and C4. The groups consist of product-process segment with similar raw waste load characteristics for the major pollutant parameter, BOD5. Effluent limitations and guidelines for Subcategory D have been deleted from Phase I regulations as a result of the limited available data base and will subsequently be covered in Phase II proposed regulations.

The effluent limitations proposed herein are based primarily on the dissolved organic pollutant contaminants in the process waste waters associated with the processes listed in the various subcategories. No specific limitations are proposed for pollutants associated with noncontact waste waters, such as boiler and cooling tower. These are primarily inorganic materials, and it is difficult to allocate such wastes among specific processes in many multi-product plants. Since raw waste loads are based on process waste waters, it is assumed that all noncontact waters be segregated from process waste waters. Otherwise, combined waste waters are subject to effluent limitations.

Separate limitations are presented for each of the seven subcategory groups. The parameters involved are: biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total suspended solids (TSS) and phenols.

Other possible RWL parameters were considered during the study: total organic carbon, ammonia, cyanide, extractable oils and various metals, but were found to be in concentrations substantially lower than those which would require specialized end-of-pipe for the entire industry. Effluent limitations are not established for cyanide and cadmium pollutants although these

have been designated as toxic substances. It is expected that the best practicable control technology currently available end-of-process treatment will substantially reduce these pollutants in the effluent stream. Effluent standards will be established for toxic pollutants wherever applicable.

Effluent Limitations for the Best Practicable Control Technology Currently Available and New Source Performance Standards (BADCT) were based upon three significant pollutant parameters: BOD₅, total suspended solids (TSS) and phenols. Effluent limitations guidelines for phenolic compounds applicable only to the cumene process, bisphenol A, and p-cresol manufacturing for BPCTCA, BATEA and BADCT. The application of alternate oxygen demand parameters such as COD or TOC in lieu of the BOD₅ parameter may be possible, in situations where a direct correlation with BOD₅ has been satisfactorily established. For Best Available Technology Economically Achievable, four significant pollutant parameters are specified: BOD₅, COD, TSS, and phenols.

End-of-process treatment for the 1977 standard is defined as biological treatment as typified by current exemplary processes: activated sludge, trickling filters, aerated lagoons, and anaerobic lagoons. These systems will be adequately equipped with pH control and equalization in order to control variable waste loads and clarification with the addition of chemicals to aid in removing suspended solids where this is required. These systems do not preclude the use of equivalent chemical-physical systems such as activated carbon in situations where necessary land area is not available. Additionally, suitable in-process controls are also applicable for the control of those pollutants which are inhibitory to the biological waste treatment system.

Best Available Technology Economically Achievable, BATEA, (1983 Standard) is based upon the addition of activated carbon to biological systems. This technology is based upon substantial reductions of dissolved organics compounds which are biorefractory as well as those which are biodegradable. Exemplary in-process systems are also applicable to this technology. End-of-process activated carbon treatment does not preclude the use of such treatment as an in-process technology. The following in-process controls are applicable to BATEA:

1. the substitution of noncontact heat exchangers for direct contact water cooling;
2. the use of nonaqueous quench media as a substitute for water where direct contact quench is required;
3. the recycle of process water, such as between absorber and stripper;
4. the reuse of process water (after treatment) as a make-up to evaporative cooling towers through which noncontact cooling water is circulated;
5. the use of process water to produce low pressure steam by non-contact heat exchangers in reflux condensers of distillation columns;

6. the recovery of spent acids or caustic solutions for reuse;
7. the recovery and reuse of spent catalyst solutions; and
8. the use of nonaqueous solvents for extraction of products.

End-of-process technology for new sources utilizing the best available demonstrated control technology (BADCT) is defined as biological treatment with suspended solids removal via clarification, sedimentation, sand, or dual-media filtration. In addition, exemplary in-process controls, as previously enumerated, are also assumed to be applicable, particularly where biotoxic pollutants must be controlled. This technology does not preclude the use of equivalent chemical-physical systems such as activated carbon as either an in-process or end-of-process treatment. This may be advantageous in areas where land availability is limited.

Effluent limitations for BPCTCA, BATEA, and New Sources (BADCT) were developed on the basis of mean subcategory group raw waste loads and the degree of reduction achievable by each level of technology. Performance of exemplary treatment plants were considered in deriving the BPCTCA limitations for each category. Performance of BATEA and BADCT systems, together with in-process controls were considered in determining effluent limitations for each level of technology. It was determined that Subcategories B and C would be further subcategorized on the basis of raw waste loads. In these cases, median raw waste loads for subcategory groups were determined for B1, B2, C1, C2, C3 and C4.

Finally, time based effluent limitations were derived on the basis of the maximum of any one day and the maximum average of daily values for a period of thirty consecutive days. The factors used in deriving these time based limitations were determined from long term performance (i.e. daily, weekly, monthly) from the best treatment systems evaluated. Time based limitations consider the normal variations of exemplary designed and operated waste treatment systems.

Table I-1
Chemicals Listed Under SIC Code 2815

Cyclic Intermediates, Dyes, Organic Pigments (Lakes and Toners), and Cyclic (Coal Tar) Crudes

Acid dyes, synthetic	Food dyes and colors, synthetic
Acids, coal tar: derived from coal tar distillation	Hydroquinone
Alkylated diphenylamines, mixed	Isocyanates
Alkylated phenol, mixed	Lake red C toners
Aminoanthraquinone	Lithol rubine lakes and toners
Aminoazobenzene	Maleic anhydride
Aminoazotoluene	Methyl violet toners
Aminophenol	Naphtha, solvent: product of coal tar distillation
Aniline	Naphthalene, product of coal tar distillation
Aniline oil	Naphthol, alpha and beta
Anthracene	Naphtholsulfonic acids
Anthraquinone dyes	Nitroaniline
Azine dyes	Nitrobenzene
Azobenzene	Nitro dyes
Azo dyes	Nitrophenol
Azoic dyes	Nitroso dyes
Benzaldehyde	Oils: light, medium, and heavy-- product of coal tar distillation
Benzene, product of coal tar distillation	Orthodichlorobenzene
Benzoic acid	Paint pigments, organic
Benzol, product of coal tar distillation	Peacock blue lake
Biological stains	Pentachlorophenol
Chemical indicators	Persian orange lake
Chips and flakes, naphthalene	Phenol
Chlorobenzene	Phloxine toners
Chloronaphthalene	Phosphomolybdic acid lakes and toners
Chlorophenol	Phosphotungstic acid lakes and toners
Chlorotoluene	Phthalic anhydride
Coal tar acids, derived from coal tar distillation	Phthalocyanine toners
Coal tar crudes, derived from coal tar distillation	Pigment scarlet lake
Coal tar distillates	Pigments, organic: except animal black and bone black
Coal tar intermediates	Pitch, product of coal tar distillation
Color lakes and toners	Pulp colors, organic
Color pigments, organic: except animal black and bone black	Quinoline dyes
Colors, dry: lakes, toners, or full strength organic colors	Resorcinol
Colors, extended (color lakes)	Scarlet 2 R lake
Cosmetic dyes, synthetic	Stilbene dyes
Cresols, product of coal tar distillation	Styrene
Creosote oil, product of coal tar distillation	Styrene monomer
Cresylic acid, product of coal tar distillation	Tar, product of coal tar distillation
Cyclic crudes, coal tar: product of coal tar distillation	Toluene, product of coal tar distillation
Cyclic intermediates	Toluol, product of coal tar distillation
Cyclohexane	Toluidines
Diphenylamine	Toners (reduced or full strength organic colors)
Drug dyes, synthetic	Vat dyes, synthetic
Dyes, synthetic organic	Xylene, product of coal tar distillation
Eosine toners	Xylol, product of coal tar distillation
Ethylbenzene	

Table 1-2
Chemicals Listed Under SIC Code 2818
Industrial Organic Chemicals, Not Elsewhere Classified

Accelerators, rubber processing: cyclic and acyclic	Citrates
Acetaldehyde	Citric acid
Acetates, except natural acetate of climate	Citronellol
Acetic acid, synthetic	Coumarin
Acetic anhydride	Cream of tartar
Acetin	Cyclopropane
Acetone, synthetic	DDT, technical
Acids, organic	Decahydronaphthalene
Acrolein	Dichlorodifluoromethane
Acrylonitrile	Diethylcyclohexane (mixed isomers)
Adipic acid	Diethylene glycol ether
Adiponitrile	Dimethyl divinyl acetylene (di- isopropenyl acetylene)
Alcohol, aromatic	Dimethylhydrazine, unsymmetrical
Alcohol, fatty: powdered	Enzymes
Alcohols, industrial: denatured (nonbeverage)	Esters of phthalic anhydride: and of phosphoric, adipic, lauric, oleic, sebacic, and stearic acids
Algin products	Esters of polyhydric alcohols
Amines of polyhydric alcohols, and of fatty and other acids	Ethanol, industrial
Amyl acetate and alcohol	Ether
Antioxidants, rubber processing: cyclic and acyclic	Ethyl acetate, synthetic
Bromochloromethane	Ethyl alcohol, industrial (non- beverage)
Butadiene, from alcohol	Ethyl butyrate
Butyl acetate, alcohol, and pro- pionate	Ethyl cellulose, unplasticized
Butyl ester solution of 2, 4-D	Ethyl chloride
Calcium oxalate	Ethyl ether
Camphor, synthetic	Ethyl formate
Carbon bisulfide (disulfide)	Ethyl nitrite
Carbon tetrachloride	Ethyl perhydrophenanthrene
Casing fluids, for curing fruits, spices, tobacco, etc.	Ethylene
Cellulose acetate, unplasticized	Ethylene glycol
Chemical warfare gases	Ethylene glycol ether
Chloral	Ethylene glycol, inhibited
Chlorinated solvents	Ethylene oxide
Chloroacetic acid and metallic salts	Ferric ammonium oxalate
Chloroform	Flavors and flavoring materials, synthetic
Chloropierin	Fluorinated hydrocarbon gases
Citral	Formaldehyde (formalin)
	Formic acid and metallic salts
	Freon

Table 1-2
(continued)

Fuel propellants, solid organic	Potassium bitartrate
Fuels, high energy, organic	Propellants for missiles, solid, organic
Gases, fluorinated hydrocarbon	Propylene
Geraniol, synthetic	Propylene glycol
Glycerin, except from fats (synthetic)	Quinuclidinol ester of benzylic acid
Grain alcohol, industrial	Reagent grade chemicals, organic: refined from technical grades
Hexamethylenediamine	Rocket engine fuel, organic
Hexamethylenetetramine	Rubber processing chemicals, organic: accelerators and antioxidants--cyclic and acyclic
High purity grade chemicals, organic: refined from technical grades	Saccharin
Hydraulic fluids, synthetic base	Sebacic acid
Hydrazine	Silicones
Industrial organic cyclic compounds	Soaps, naphthenic acid
Ionone	Sodium acetate
Isopropyl alcohol	Sodium alginate
Ketone, methyl ethyl	Sodium benzoate
Ketone, methyl isobutyl	Sodium glutamate
Laboratory chemicals, organic	Sodium pentachlorophenate
Lauric acid esters	Sodium sulfoxalate formaldehyde
Lime citrate	Solvents, organic
Malononitrile, technical grade	Sorbitol
Metallic salts of acyclic organic chemicals	Stearic acid esters
Metallic stearate	Stearic acid salts
Methanol, synthetic (methyl alcohol)	Sulfonated naphthalene
Methyl chloride	Tackifiers, organic
Methyl perhydrofluorine	Tannic acid
Methyl salicylate	Tanning agents, synthetic organic
Methylamine	Tartaric acid and metallic salts
Methylene chloride	Tartrates
Monochlorodifluoromethane	Tear gas
Monomethylparaminophenol sulfate	Terpineol
Monosodium glutamate	Tert-butylated bis (p-phenoxy-phenyl) ether fluid
Mustard gas	Tetrachloroethylene
Nitrous ether	Tetraethyl lead
Normal hexyl decalin	Thioglycolic acid, for permanent wave lotions
Nuclear fuels, organic	Trichloroethylene
Oleic acid esters	Trichloroethylene stabilized, degreasing
Organic acids, except cyclic	Trichlorophenoxyacetic acid
Organic chemicals, acyclic	Trichlorotrifluoroethane tetrachlorodifluoroethane isopropyl alcohol
Oxalates	Tricresyl phosphate
Oxalic acid and metallic salts	Tridecyl alcohol
Pentaerythritol	Trimethyltrithiophosphite (rocket propellants)
Perchloroethylene	Triphenyl phosphate
Perfume materials, synthetic	Urea
Phosgene	Vanillin, synthetic
Phthalates	Vinyl acetate
Plasticizers, organic: cyclic and acyclic	
Polyhydric alcohols	

Table 1-3

Products and Manufacturing Processes Listed by Subcategory

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory A (Continuous Non-Aqueous Processes)	
Mixed aromatics with saturates (reformate)	Hydrogenation of pyrolysis gasoline from ethylene manufacture Naphtha reforming
Mixed aromatics concentrate	Solvent extraction
Benzene	Fractional distillation Toluene disproportionation Toluene hydrodealkylation
Toluene	Fractional distillation
Mixed xylenes (o-X, m-X, p-X, EB)	Fractional distillation Toluene disproportionation
Ortho-xylene	Fractional distillation
Para-xylene	Fractional distillation Isomerization Crystallization and filtration
Petroleum naphthalene	Fractional distillation Hydrodealkylation of alkyl naphthalenes
Ethyl benzene	Alkylation of benzene with ethylene
Cumene	Alkylation of benzene with propylene
Cyclohexane	Hydrogenation of benzene
Phosgene	CO and chlorine synthesis
Ethyl chloride	Hydrochlorination of ethylene Chlorination of ethane
Cyclopropane	Extraction from LPG gas
Subcategory B (Continuous Vapor Phase Processes) WHERE WATER IS USED AS DILUENT OR ABSORBENT)	
Ethylene	Pyrolysis of hydrocarbons
Propylene	Pyrolysis of hydrocarbons
Butadiene	Pyrolysis of hydrocarbons Dehydrogenation of N-butane, N-butylene (catalytic with steam dilution) Catalytic oxidative dehydrogenation Purification by extractive distillation
Methanol	Steam reforming of natural gas--CO & CO ₂ synthesis
Ethanol	Catalytic hydration of ethylene
Isopropanol	Catalytic hydration of propylene
Acetone	Dehydrogenation of isopropanol
Maleic anhydride	Air oxidation of benzene or butene

Table 1-3
(Continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory B (continued)	
Phthalic anhydride	Air oxidation of ortho-xylene or naphthalene
Acetaldehyde	Oxidative-dehydration of ethanol
Acetylene	Calcium carbide process Wulff process (thermal cracking) BASF process (methane partial oxidation)
Acetic anhydride	Absorption of ketone (by cracking of acetic acid) in acetic acid
Ethylene oxide	Catalytic oxidation of ethylene
Acrylonitrile	Ammonoxidation of propylene
Formaldehyde	Oxidation of methanol
Acrylic acid	Catalytic oxidation of propylene
Ethylene dichloride	Oxychlorination of ethylene by HCl Direct chlorination of ethylene
Vinyl chloride	Thermal cracking of ethylene dichloride Acetylene and anhydrous HCl
Ethyl ether	By-product of ethanol production via catalytic hydration of ethylene
Isoprene	Propylene dimerization/isomerization/ cracking Dehydrogenation of iscamylene
Vinyl acetate	Acetylene and acetic acid process Vapor phase ethylene and acetic acid process
Mixed cresols and xlenols	Phenol and methanol synthesis
Methyl amines	Methanol and ammonia reacted over dehydration catalyst
Methyl halides	Gaseous methanol and halogen acid passed through thermal converter
Dichlorodifluoromethane	Reaction of hydrofluoric acid with chloroform
Fluorinated hydrocarbons	Reaction of hydrofluoric acid with carbon tetrachloride
Trichlorotrifluoroethane	Reaction of perchloroethylene and hydrofluoric acid
Phthalates	Reaction of phthalic anhydride and alcohol
Hexamethylenediamine	From adipic acid by reaction with NH ₃ followed by hydrogenation of adiponitrile From butadiene From acrylonitrile

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory B (Continued)	
Urea	NH_3 and CO_2 synthesis
Acrolein	Direct oxidation of ethylene
Allyl chloride	High temperature chlorination of propylene
Fatty acids	Oxidation of N-paraffins
Fatty amines	Ammoniation of fatty acid followed by catalytic hydrogenation of aminonitriles
Benzoic acid	Air oxidation of toluene in L.P.
Benzaldehyde	Air oxidation of toluene V.P.
Chloronaphthalenes	Chlorination of naphthalenes
Higher alcohols	High-pressure hydrogenolysis
Methyl and ethyl acrylates	Acetylene, nickel carbonyl and methyl or ethyl alcohol
Trichloroethylene	Catalytic-thermal dehydrochlorination of tetrachloroethane Chlorination of ethylene to 1, 2 dichloroethane and conversion to T.C.E.
Tetrachloroethylene	Chlorination of methane in atmosphere of carbon tetrachloride High temperature chlorination of ethylene dichloride
Chloroform	Methane chlorination
Methyl chloride	Direct methane chlorination Esterification of methanol with hydrochloric acid
P/O-dichlorobenzene	Chlorination of chlorobenzene
Glycerol	Hydrolysis of epichlorohydrin with NaOH Catalytic hydrogenation of nigor From acrolein and isopropanol
Hexamethylene tetramine	NH_3 + formaldehyde
Decahydronaphthalene	Hydrogenation of naphthalene
Carbon tetrachloride	Chlorination of carbon disulfide From chlorinated methanes production
Carbon bisulfide (disulfide)	Sulfur and methane Sulfur and charcoal in electric arc furnace
Benzene hexachloride	Benzene chlorination in presence of actinic light

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (continued)	
Acetophenone	By-product of phenol by cumene peroxidation
Acrolein	Condensation of acetaldehyde with formaldehyde
Ethylacetate	Acetic acid and ethyl alcohol in presence of sulfuric acid
Propyl acetate	Acetic acid and Propyl alcohol in presence of sulfuric acid
Acetin (glyceryl monoacetate)	Glycerol and acetic acid
Propionic acid	Carbonylation of ethyl alcohol with CO at high pressure Oxidation of propionaldehyde
Fatty alcohol	Reduction of fatty acid with sodium metal High pressure catalytic hydrogenation of fatty acids
Butyl acetate	Esterification of acetic acid and butyl alcohol in presence of sulfuric acid
sec-butyl alcohol	Hydrolysis of butylene (in H_2SO_4) with steam
n-butyl alcohol	Condensation of acetaldehyde to crotonaldehyde followed by hydrogenation
n-butyl propionate	Esterification of propionic acid with butyl alcohol (H_2SO_4)
Chloroacetic acid	Chlorination of acetic acid
Sodium Chloroacetate	Esterification of chloroacetic acid
Chloropicrin (nitrotrichloromethane- CCl_3NO_2)	Picric acid and calcium hypochlorite Nitrification of chlorinated hydrocarbons
Thioglycolic acid	Monochloroacetic acid and H_2S followed by neutralization
Adiponitrile	Adipic acid and ammonia
Sodium benzoate	Benzoic acid neutralized with sodium bicarbonate
Sodium sulfoxalate formaldehyde	Zinc hydrosulfite, formaldehyde and caustic soda
Sodium acetate	Neutralization of acetic acid with caustic soda
Tartaric acid	Maleic anhydride and hydrogen peroxide

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (Liquid Phase Reaction Systems)	
Ethanol	Sulfuric acid hydrolysis of ethylene
Isopropanol	Sulfuric acid hydrolysis of propylene
Acetone	Cumene oxidation with cleavage of hydroperoxide in sulfuric acid
Phenol	Raschig process chlorobenzene process Sulfonation process Cumene oxidation with cleavage of hydroperoxide in sulfuric acid
Oxo-chemicals Includes: N-butyl alcohol Isobutyl alcohol 2-ethylhexanol Isooctyl alcohols Decyl alcohols	Oxo-process (carbonylation and condensation)
Acetaldehyde	Ethylene oxidation via Wacker process
Acetic acid	Oxidation of LPG (butane) Oxidation of acetaldehyde Carbonylation of methanol
Methyl ethyl ketone	Sulfuric acid hydrolysis of butene-2, dehydrogenation of sec-butanol Oxidation of LPG (butane)--By-product of acetic acid manufacture
Methyl methacrylate	Acetone cyanohydrin process
Ethylene oxide	Chlorohydrin process
Acrylonitrile	Acetylene-HCN process
Ethylene glycol	Sulfuric acid catalyzed hydration of ethylene oxide
Acrylic acid	CO synthesis with acetylene
Ethyl acrylate	Acetylene and ethanol in presence of nickel carbonyl catalyst Oxidation of propylene to acrylic acid followed by esterification Reaction of ketone with formaldehyde followed by esterification
Styrene monomer	Alkylation of benzene with ethylene, dehydrogenation of ethylbenzene with steam
Adipic acid	Oxidation of cyclohexane/cyclohexanol/cyclohexanone Direct oxidation of cyclohexane with air

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (continued)	
Terephthalic acid	Oxidation of para-xylene with nitric acid Catalytic oxidation of para-xylene
Dimethyl terephthalate	Esterification of TPA with methanol and sulfuric acid Vapor phase methylation of phenol
Para-cresol	Oxidation of para-cymene with cleavage in sulfuric acid
Cresylic acids	Caustic extraction from cracked naphtha
Aniline	Nitration of benzene with nitric acid (L.P.), hydrogenation of nitrobenzene
Chloroprene	Dimerization of acetylene to vinyl acetylene followed by hydrochlorination Vapor phase chlorination of butadiene followed by isomerization and reaction
Bis-phenol-a	Condensation of Phenol and Acetone in presence of HCl
Propylene oxide	Addition of propylene and CO ₂ to aqueous calcium hypochlorite Liquid phase oxidation of isobutane followed by liquid phase epoxidation
Propylene glycol	Hydration of propylene oxide catalyzed by dilute H ₂ SO ₄
Vinyl acetate	Liquid phase ethylene and acetic acid process
Anthraquinone	Catalytic air oxidation of anthracene
Beta naphthol	Naphthalene sulfonation and caustic fusion
Caprolactam	Hydroxyl amine production, cyclohexanone production, cyclohexanone oximation, oxime rearrangement, purification, and ammonium sulfate recovery
Toluene di-isocyanate	Toluene nitrication, toluene diamine production, HCl electrolysis, phosgene production, TDI production, purification
Silicones	Reaction of silicon metal with methyl chloride

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (continued)	
Naphthemic acids	From gas-oil fraction of petroleum by extraction with caustic soda solution and acidification
Ethyl cellulose	From alkali cellulose and ethyl chloride or sulfate
Cellulose acetate	Acetylation of cellulose with acetic acid (followed by saponification with sulfuric acid for diacetate)
Chlorobenzene	Raschig process
Chlorophenol	Direct chlorination of phenol From chloroaniline through diazonium salt
Chlorotoluene	Catalytic chlorination of toluene
Hydroquinone	Oxid. of aniline to quinone followed by hydrogenation
Naphthosulfonic acids	Sulfonation of B-naphthol Caustic fusion of naphthalene sulfonic acid
Nitrobenzene	Benzene and HNO_3 in presence of sulfuric acid
Amyl acetate	Esterification of amyl alcohol with acetic acid
Amyl alcohol	Pentane chlorination and alkaline hydrolysis
Ethyl ether	Dehydration of ethyl alcohol by sulfuric acid
Ethyl butyrate	Esterification of ethyl alcohol with butyric acid
Ethyl formate	Esterification of ethyl alcohol with formic acid
Tetraethyl lead	Reduction of ethyl chloride with amalgam of Na and Pb
Formic acid	Sodium hydroxide and carbon monoxide
Methyl isobutyl ketone	Dehydration of acetone alcohol to mesityl oxide followed by hydrogenation of double bond
Naphthol	High-temperature sulfonation of naphthalene followed by hydrolysis to B-naphthol
Pentachlorophenol	Chlorination by phenol
Sodium pentachlorophenate	Reaction of caustic soda with pentachlorophenol

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (continued)	
Toluidines	Reduction of nitrotoluenes with Fe and H_2SO_4
Hydrazine	Indirect oxidation of ammonia with sodium hypochlorite
Oxalic acid	Sodium formate process
Oxalates	Sodium formate process
Sebacic acid	Caustic hydrolysis of ricinoleic acid (castor oil)
Glycerol	Acrolein epoxidation/reduction followed by hydration Propylene oxide to allyl alcohol followed by chlorination
Diethylene glycol diethyl ether	Ethylene glycol and ethyl alcohol condensation dehydration
Dichloro-diphenyl-trichloroethane (DDT)	Monochlorobenzene and chloral in presence of sulfuric acid
Pentachloroethylene	Chlorination of acetylene
Methylene chloride	Methane chlorination Methanol esterification followed by chlorination
Pentaerythritol	Acetaldehyde and formaldehyde in presence of basic catalyst
Chloral (trichloroacetic aldehyde)	Chlorination of acetaldehyde
Triphenyl phosphate	Phenol and phosphorous oxychloride
Tridecyl alcohol	From propylene tetramer
Tricresyl phosphate	Cresylic acid and phosphorous oxychloride
Amil alcohol	Chlorination of pentanes and hydrolysis of amyl chlorides
Acrylamide	Acrylonitrile hydrolysis with H_2SO_4
Higher alcohols	Sodium reduction process
synthetic amino acids	Acrolein and mercaptan followed by treatment with Na_2CO_3 and NaCN
Organic esters	Alcohol and organic acid, H_2SO_4 catalyst
Trialkylacetic acids	Olefins and CO followed by hydrolysis
Fatty acids	Batch or continuous hydrolysis
Lauric acid esters	Esterification of lauric acid
Oleic acid esters	Esterification of oleic acid

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory C (continued)	
Isocyanates	Phosgene and Amines
Coal tar cyclic intermediates	Coal tar distillation
Subcategory D (Batch Processes)	
Coumarin	Heating salicylic aldehyde, sodium acetate, and acetic anhydride
Resorcinal	Fusing benzene-meta-disulfonic acid with sodium hydroxide
Phosphotungstic acid lakes	Precipitation of basic dyestuffs with solutions of phosphotungstic acid
Methyl violet	Derivatives of paranosaniline
Lake red	Coupling 2-chloro-5-aminotoluene-4 sulfonic acid with 8-naphthol
Lithol rubine	Diazotization of p-toluidine meta sulfonic acid followed by coupling with 3-hydroxy-2-naphthic acid
Eosin toners	Bromination of fluorescein
Amino anthraquinone	Reduction of nitroanthraquinone Substitution of sulfonate with amino group
Amino azobenzene (para)	Catalytic heating of diazoamino-benzene Aniline solution and aniline hydrochloride
Aminoazotoluene (ortho)	From o-toluidine by treatment with nitrite and HCl
Amino phenol (O, M, P)	(meta) Fusion of sulfanilic acid with NaOH and ether extraction (ortho) H ₂ S reduction of O-nitro-phenol and aqueous ammonia (para) Reduction of p-nitrophenol by Fe and HCl Electrolytic reduction of nitro-benzene in sulfuric acid
Anthraquinone (dyes)	Heating phthalic anhydride and benzene in presence of AlCl ₃ catalyst and dehydrating
Azine dyes	From phenazine

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory D (continued)	
Azobenzene	Reduction of nitrobenzene with sodium stannite
Azo dyes (generic)	Diazotation and coupling
Monosodium glutamates	Fermentation of carbon source Acrylonitrile oxoreaction, strecher reaction, hydrolysis
Flavors	Rectification of sulfate turpentine and pyrolysis of terpenes Extraction from natural stuffs
Camphor, synthetic	Pinene to camphene followed by treatment with acetic acid and nitrobenzene
Citral	Separate from lemon grass oil by fractional distillation
Citric acid	Mold fermentation of carbohydrates
Lime citrate (calcium citrate)	By-product production of citric acid
Citronellol	Extraction from oils of citronella, geranium, rose
Peacock blue	Lake of acid glaucine blue dye on alumina hydrate
O/P nitrophenol	Caustic fusion of p-nitrochloro- benzene Dilute nitric acid and phenol at low temperature
Vanillin	Extraction from lignin
Diphenylamine	Reaction of aniline hydrochloride with aniline
Alkylated diphenylamines	Alkylation of diphenylamine obtained by reaction of aniline hydrochloride with aniline
Ethyl nitrite	Ethyl alcohol and alkali nitrites and sulfuric acid
Ferric ammonium oxalate	Ammonium linoxalate and ferric hydroxide
Calcium oxalate	Sodium oxalate and lime
Calcium stearate	Sodium stearate and calcium chloride
Methyl salicylate	Methanol and salicylic acid in presence of sulfuric acid
Calcium tartrate	Reaction of calcium salt and crude cream of tartar

Table 1-3
(continued)

<u>Product</u>	<u>Manufacturing Process</u>
Subcategory D (continued)	
Alkylated phenols	Alkylation with lewis acid catalyst
Acetamide	Distillation of ammonium acetate
Organic esters	Steam distillation of naturally occurring esters
Nitroaniline	p-nitrochlorobenzene and ammonia
Sorbitol	Hydrogenation of fructose-free glucose
Terpineol	Hydration of pinene
Saccharin	From o-toluene sulfonamide From phthalic anhydride via anthranilic acid
Tannic acid	Extraction of powdered nutgalls
Algin (sodium alginate)	Extraction from brown algae
Mustard gas (dichlorodiethyl sulfide)	Ethylene and sulfur chloride Thyoglycol and hydrogen chloride
Ionone	Condensation of citronellal from lemon-grass oil with acetone
Geraniol	From geranium oil, citronellal and palmarosa From myrcene
Sodium citrate	Sodium sulfate and calcium citrate
Calcium citrate	By-product in manufacture of citric acid
Cream of tartar (potassium bitartrate)	From argols by extraction with water
Dimethyl hydrazine	Dimethylamine and chloramine Dimethylamine and sodium nitrite followed by reduction Catalytic oxidation of dimethylamine and ammonia
Nitrophenol	Nitrochlorobenzene and caustic soda

Table 1-4

Products and Processes Covered in Raw Waste Load Sampling

Subcategory A (Continuous Non-Aqueous Processes)

<u>Product</u>	<u>Process</u>	<u>Phase I Survey Visits</u>
Cyclohexane	Hydrogenation of Benzene	1
Ethyl Benzene	Alkylation of Benzene with Ethylene	1
Vinyl Chloride	Acetylene and HCl	1
BTX Aromatics	Co-Product of Ethylene Mfg. Fractional Distillation	1 1
<hr/>		<hr/>
4 Products	5 Manufacturing Processes	6 Visits

Table 1-4

Products and Processes Covered in Raw Waste Load Sampling

**Subcategory B (Continuous Vapor Phase Processes)
WHERE WATER IS USED AS DILUENT OR ABSORBENT)**

<u>Product</u>	<u>Process</u>	<u>Phase I Survey Visits</u>
Ethylene/Propylene	Pyrolysis of Hydrocarbons	7
Butadiene	Co-Product of Ethylene Mfg.	2
	Dehydrogenation of N-Butane	2
Methanol	Steam Reforming of Natural Gas	2
Acetone	Dehydrogenation of Isopropanol	2
Acetaldehyde	Oxidative Dehydration of Ethanol	2
Acetylene	Partial Oxidation of Methane	1
Ethylene Oxide	Catalytic Oxidation of Ethylene	2
Formaldehyde	Oxidation of Methanol	1
Ethylene Dichloride	Direct Chlorination of Ethylene	1
Vinyl Chloride	Cracking of Ethylene Dichloride	1
Styrene	Dehydrogenation of Ethylbenzene	2
<hr/>		<hr/>
12 Products	12 Manufacturing Processes	25 Visits

Table 1-4

Products and Processes Covered in Raw Waste Load Sampling

Subcategory C (Liquid Phase Reaction Systems)

<u>Product</u>	<u>Process</u>	<u>Phase I Survey Visits</u>
Phenol	Chlorobenzene Process	1
Phenol/Acetone	Cumene Oxidation and Cleavage	2
Oxo-Chemicals	Carbonylation and Condensation	1
Acetaldehyde	Oxidation of Ethylene (Wacker Process)	2
Acetic Acid	Oxidation of Acetaldehyde	2
Methyl Methacrylate	Acetone Cyanohydrin Process	1
Ethylene Glycol	Hydration of Ethylene Oxide	1
Acrylic Acid	Carbon Monoxide Synthesis with Acetylene	1
Acrylates	Esterification of Acrylic Acid	1
Terephthalic Acid	Nitric Acid Oxidation of Para-Xylene	1
	Catalytic Oxidation of Para-Xylene	4
Dimethyl Terephthalate	Esterification of TPA	5
Para-Cresol	Sulfonation of Toluene	1
Aniline	Hydrogenation of Nitrobenzene	1
Bisphenol-A	Condensation of Phenol and Acetone	1
Vinyl Acetate	Synthesis with Ethylene and Acetic Acid	1
Caprolactam	Oxidation of Cyclohexane	2
Long-Chain Alcohols	Ethylene Polymerization	1
Tetraethyl Lead	Addition of Ethyl Chloride to Lead Amalgam	1
Coal-Tar Products	Coal Tar Distillation	1
<hr/>		<hr/>
20 Products	20 Manufacturing Processes	31 Visits

CATEGORY D (BATCH PROCESSES)

<u>Product</u>	<u>Process</u>	<u>Phase I Survey Visits</u>
Dyes/Pigments	Batch Mfg.	5

Table 1-5

Major RWL's of Pollutants Based on
Process Wastewater

<u>Category</u>	<u>Flow RWL</u> gals./1,000 lbs	<u>BOD₅ RWL</u> lbs/1,000 lbs	<u>COD RWL</u> lbs/1,000 lbs	<u>TOC RWL</u> lbs/1,000
A Conc. Range (mg/L)	0.25 - 2,000	0.1 - 0.13 (400 - 1,000)	0.3 - 3.7 (200 - 10,000)	0.034 - 0.9 (50 - 2,000)
B Conc. Range (mg/L)	50 - 3,000	0.09 - 7.0 (50 - 500)	0.47 - 21.5 (200 - 5,000)	0.2 - 40 (100 - 2,000)
C Conc. Range (mg/L)	30 - 3,000	1.3 - 125 (3,000 - 10,000)	1.9 - 385 (10,000 - 50,000)	1.5 - 150 (3,000 - 15,000)
D Conc. Range (mg/L)	10,000 - 100,000	52 - 220 (100 - 3,000)	180 - 4,800 (1,000 - 10,000)	60 - 1,600 (200 - 2,000)

SUBCATEGORY A**FIGURE I-1**NON-AQUEOUS PROCESSES

MINIMAL CONTACT BETWEEN WATER AND REACTANTS OR PRODUCTS WITHIN THE PROCESS. WATER IS NOT REQUIRED AS A REACTANT OR DILUENT AND IS NOT FORMED AS A REACTION PRODUCT. THE ONLY WATER USAGE STEMS FROM PERIODIC WASHES OF WORKING FLUIDS OR CATALYST HYDRATION. HEATING AND COOLING ARE DONE INDIRECTLY OR THROUGH NON-AQUEOUS (HYDROCARBON) WORKING FLUIDS. PROCESS RAW WASTE LOADS SHOULD APPROACH ZERO WITH ONLY VARIATIONS CAUSED BY SPILLS OR PROCESS UPSETS.

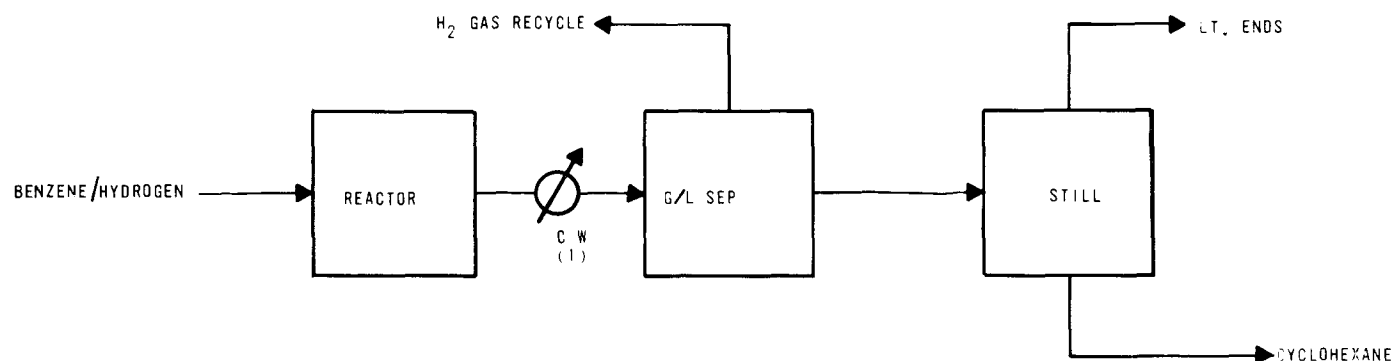
CYCLOHEXANE

FIGURE 1—2

SUBCATEGORY B

PROCESS WATER CONTACT AS STEAM DILUENT AND/OR ABSORBENT

PROCESS WATER USAGE IS IN THE FORM OF DILUTION STEAM, A DIRECT CONTACT QUENCH, OR AS AN ABSORBENT FOR REACTOR EFFLUENT GASES. REACTIONS ARE ALL VAPOR PHASE AND CARRIED OUT OVER SOLID CATALYSTS. MOST PROCESSES HAVE WATER ABSORBER COUPLED WITH STEAM STRIPPING OF CHEMICALS FOR PURIFICATION AND RECYCLE. STEAM IS ALSO USED FOR DE-COKING CATALYST. APPEARS FEASIBLE TO REDUCE PROCESS RAW WASTE LOADS TO NEAR ZERO THROUGH INCREASED RECYCLE AND/OR REUSE OF CONTACT WATER.

24

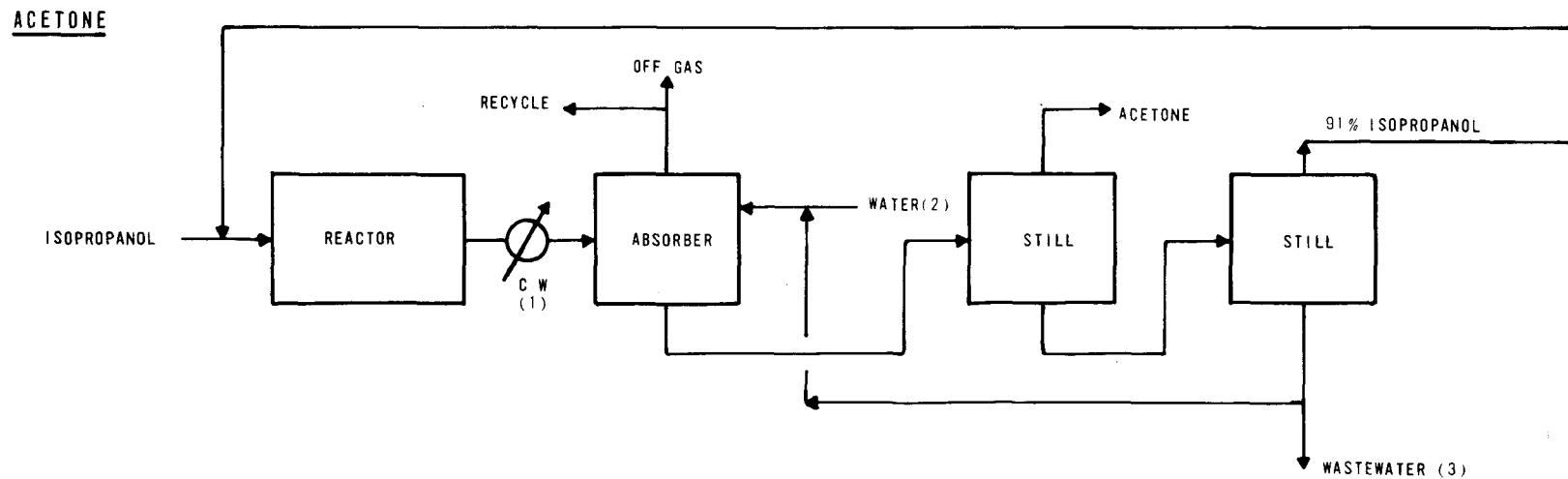


FIGURE 1—3

SUBCATEGORY C

AQUEOUS LIQUID PHASE REACTION SYSTEMS

LIQUID PHASE REACTIONS WHERE CATALYST IS IN AQUEOUS MEDIA SUCH AS DISSOLVED OR EMULSIFIED MINERAL SALT, OR ACID/CAUSTIC SOLUTION. CONTINUOUS REGENERATION OF CATALYST SYSTEM REQUIRES EXTENSIVE WATER USAGE. SUBSTANTIAL REMOVAL OF SPENT INORGANIC SALT BY-PRODUCTS MAY ALSO BE REQUIRED. WORKING AQUEOUS CATALYST SOLUTION IS NORMALLY CORROSIVE. ADDITIONAL WATER REQUIRED IN FINAL PURIFICATION OR NEUTRALIZATION OF PRODUCTS. REQUIREMENTS FOR PURGING LIMITING WASTE MATERIALS FROM SYSTEM MAY PREVENT PROCESS RAW WASTE LOAD FROM APPROACHING ZERO.

25

PHENOL
ACETONE

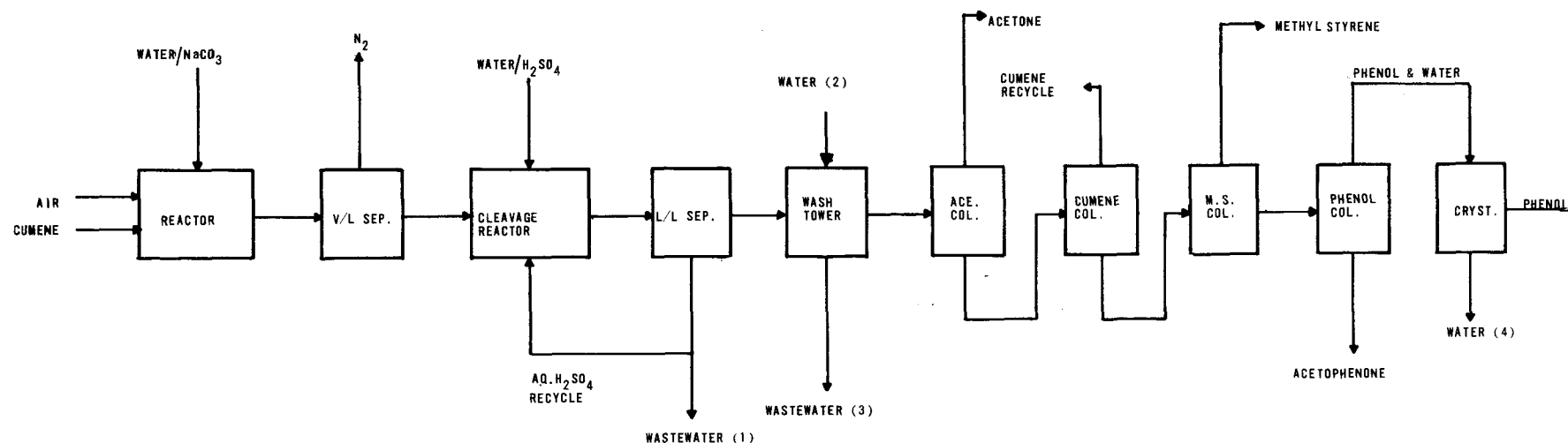
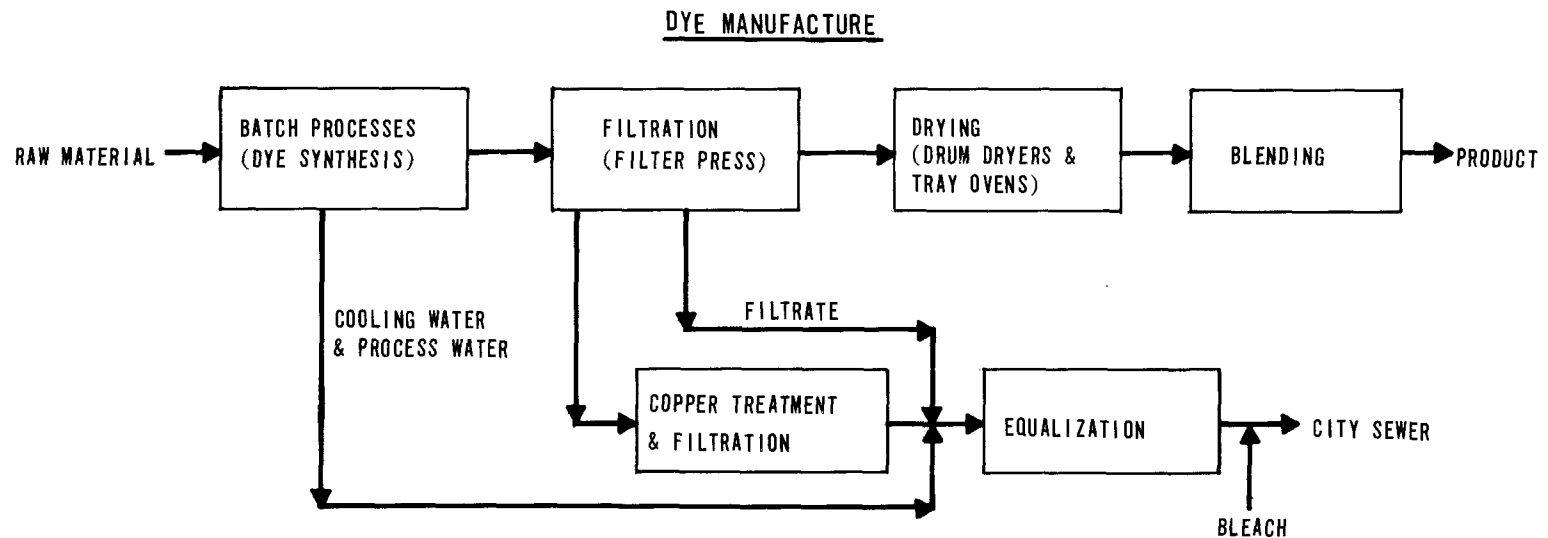


FIGURE 1-4

SUBCATEGORY D

SEMI-CONTINUOUS AND BATCH PROCESSES

PROCESSES ARE CARRIED OUT IN REACTION KETTLES EQUIPPED WITH AGITATORS, SCRAPERS, REFLUX CONDENSERS, ETC. DEPENDING ON THE NATURE OF THE OPERATION. MANY REACTIONS ARE LIQUID PHASE WITH AQUEOUS CATALYST SYSTEMS. REACTANTS AND PRODUCTS ARE TRANSFERRED FROM ONE PIECE OF EQUIPMENT TO ANOTHER BY GRAVITY FLOW, PUMPING, OR PRESSURIZATION WITH AIR OR INERT GAS. MUCH OF THE MATERIAL HANDLING IS MANUAL WITH LIMITED USE OF AUTOMATIC PROCESS CONTROL. FILTER PRESSES USED TO SEPARATE SOLID PRODUCTS FROM LIQUID. WHERE DRYING IS REQUIRED, AIR OR VACUUM OVENS ARE USED. CLEANING OF NON-CONTINUOUS PRODUCTION EQUIPMENT CONSTITUTES MAJOR SOURCE OF WASTEWATER. ANTICIPATED WASTE LOADS FROM PRODUCT SEPARATION AND PURIFICATION WILL BE AT LEAST TEN TIMES THOSE FROM CONTINUOUS PROCESSES.



SECTION II

RECOMMENDATIONS

Effluent limitations commensurate with the best practicable control technology currently available are presented for each industrial subcategory group of the organic chemicals manufacturing industry. Major product-process segments which are applicable to these limitations are listed in Table II-1. Effluent limitations are presented in Table II-2 for the 1977 standard (BPCTCA). It should be noted that process waste waters subject to these limitations include all process water exclusive of auxiliary sources such as boiler and cooling water blowdown, water treatment back wash, laboratories and other similar sources.

End-of-process technology for BPCTCA involves the application of biological treatment systems as typified by activated sludge, trickling filters, aerated lagoons and anaerobic lagoons. Equalization with pH control and oil separation is provided in order to smooth out raw waste variations. Chemical flocculation aids, when necessary, are added to the clarification system in order to control suspended solids.

In-process controls as previously described in Section I are provided to remove those pollutants which interfere with biological waste treatment systems. Biological waste treatment does not preclude the use of equivalent chemical/physical systems. It may be advantageous to provide such systems within the process or at the end of process, especially where land availability is a limiting factor.

Effluent limitations to be attained by the application of the best available technology economically achievable are presented in Table II-3 for the major product-process segments listed in Table II-1 for each subcategory group. End-of-process treatment for BATEA include the addition of activated carbon systems to biological waste treatment processes. Exemplary in-process controls, as discussed in the previous section of this document, are also applicable to this technology. It is emphasized that the model treatment system does not preclude the use of activated carbon within the plant. Such systems are frequently employed for recovery of products, by-products, and catalysts.

The best available demonstrated control technology for new sources includes the most exemplary process controls, as previously enumerated, with biological waste treatment and filtration for removal of suspended solids. Effluent limitations for the major product-process segments are presented in Table II-4.

Table II-1

Subcategories of the Organic Chemicals Manufacturing
Industry (Phase I - Major Product-Processes)

<u>Subcategory A Products</u>	<u>Non Aqueous Processes Process Descriptions</u>
BTX Aromatics	Hydrotreatment of pyrolysis gasoline
BTX Aromatics	Solvent extraction from reformat
Cyclohexane	Hydrogenation of benzene
Vinyl Chloride	Addition of hydrochloric acid to acetylene
<u>Subcategory B</u>	<u>Process with Process Water Contact as Steam Diluent or Absorbent</u>
<u>B1 Products</u>	<u>B1 Process Descriptions</u>
Acetone	Dehydrogenation of isopropanol
Butadiene	Co-product of ethylene
Ethyl benzene	Alkylation of benzene with ethylene
Ethylene and Propylene	Pyrolysis of naphtha or liquid petroleum gas
Ethylene dichloride	Direct chlorination of ethylene
Ethylene oxide	Catalytic oxidation of ethylene
Formaldehyde	Oxidation of methanol
Methanol	Steam reforming of natural gas
Methyl amines	Addition of ammonia to methane
Vinyl acetate	Synthesis of ethylene and acetic acid
Vinyl chloride	Cracking of ethylene dichloride
<u>B2 Products</u>	<u>B2 Process Descriptions</u>
Acetaldehyde	Dehydrogenation of ethanol
Acetylene	Partial oxidation of methane
Butadiene	Dehydrogenation of n-butane
Butadiene	Oxidative - denhydrogenation of n-butane
Styrene	Dehydrogenation of ethylbenzene

Subcategory CAqueous Liquid Phase Reaction
SystemsC1 Products

Acetic acid
Acrylic acid
Coal tar
Ethylene glycol
Terephthalic acid
Terephthalic acid

C1 Process Descriptions

Oxidation of acetaldehyde
Synthesis with carbon monoxide
and acetylene
Distillation of coal tar
Hydrogenation of ethylene oxide
Catalytic oxidation of p-xylene
Purification of crude terephthalic acid

C2 Products

Acetaldehyde
Caprolactam
Coal Tar
Oxo Chemicals
Phenol and Acetone

C2 Process Descriptions

Oxidation of ethylene with oxygen
Oxidation of cyclohexane
Pitch forming
Carbonylation and condensation
Cumene oxidation and cleavage

C3 Products

Acetaldehyde
Aniline
Bisphenol A
Dimethyl terephthalate

C3 Process Descriptions

Oxidation of ethylene with air
Nitration and hydrogenation of benzene
Condensation of phenol and acetone
Esterification of terephthalic acid

C4 Products

Acrylates
p-cresol
Methyl methacrylate
Terephthalic acid
Tetraethyl lead

C4 Process Descriptions

Esterification of acrylic acid
Sulfonation of toluene
Acetone cyanohydrin process
Nitric acid process
Addition of ethyl chloride to
lead amalgam

Table II-2

Effluent Limitations for the Best Practicable Control Technology
Currently Available (BPCTCA) Organic Chemicals Manufacturing
Industry (Phase I- Major Product-Process by Subcategory)

<u>Effluent Characteristics</u>	<u>Effluent Limitations</u> kg/kg production	
	<u>Maximum for any one day</u>	<u>Maximum Average of daily values for any period of thirty consecutive days</u>
<u>Subcategory A</u>		
BOD ₅	0.045	0.02
TSS	0.067	0.03
<u>Subcategory B</u>		
<u>B1 Product-Processes</u>		
BOD ₅	0.13	0.058
TSS	0.20	0.088
<u>B2 Product-Processes</u>		
BOD ₅	0.95	0.42
TSS	1.42	0.64
<u>Subcategory C</u>		
<u>C1 Product-Processes</u>		
BOD ₅	0.28	0.12
TSS	0.42	0.19
<u>C2 Product-Processes</u>		
BOD ₅	0.55	0.25
TSS	0.56	0.25
Phenols (Cumene process only)	0.045	0.02
<u>C3 Product-Processes</u>		
BOD ₅	1.15	0.51
TSS	0.15	0.068
Phenols (Bisphenol A process only)	0.045	0.02
<u>C4 Product-Processes</u>		
BOD ₅	3.08	1.37
TSS	2.80	1.25
Phenols (p-cresol process only)	0.045	0.020
pH for all Subcategories between 6.0 - 9.0		

Table II-3

Effluent Limitations for the Best Available Technology
Economically Achievable (BATEA) - Organic Chemicals Manufacturing
Industry (Phase I- Major Product-Process by Subcategory)

<u>Effluent Characteristics</u>	<u>Effluent Limitations</u> kg/kg production	
	<u>Maximum for</u> <u>any one day</u>	<u>Maximum Average of</u> <u>daily values for any</u> <u>period of thirty</u> <u>consecutive days</u>
<u>Subcategory A</u>		
COD	0.062	0.045
BOD ₅	0.015	0.0085
TSS	0.022	0.013
<u>Subcategory B</u>		
<u>B1 Product-Processes</u>		
COD	0.80	0.58
BOD ₅	0.044	0.025
TSS	0.066	0.04
<u>B2 Product-Processes</u>		
COD	1.32	0.95
BOD ₅	0.32	0.18
TSS	0.48	0.29
<u>Subcategory C</u>		
<u>C1 Product-Processes</u>		
COD	0.52	0.37
BOD ₅	0.093	0.053
TSS	0.14	0.085
<u>C2 Product-Processes</u>		
COD	1.75	0.98
BOD ₅	0.12	0.068
TSS	0.19	0.11
Phenols (Cumene process only)	0.003	0.0017
<u>C3 Product-Processes</u>		
COD	6.07	4.37
BOD ₅	0.067	0.043
TSS	0.05	0.031
Phenols (Bisphenol process only)	0.003	0.0017
<u>C4 Product-Processes</u>		
COD	39.25	28.26
BOD ₅	0.62	0.35
TSS	0.94	0.57
Phenols (p-cresol process only)	0.003	0.0017

pH for all Subcategories between 6.0 - 9.0

Table II-4

Standards of Performance for New Organic Chemicals
Manufacturing Sources
(Phase I - Major Product-Processes by Subcategory)

<u>Effluent Characteristics</u>	<u>Effluent Limitations</u> kg/kg production	
	<u>Maximum for any one day</u>	<u>Maximum Average of daily values for any period of thirty consecutive days</u>
<u>Subcategory A</u>		
BOD ₅	0.037	0.017
TSS	0.034	0.015
<u>Subcategory B</u>		
<u>B1 Product-Processes</u>		
BOD ₅	0.11	0.048
TSS	0.10	0.044
<u>B2 Product-Processes</u>		
BOD ₅	0.76	0.34
TSS	0.72	0.32
<u>Subcategory C</u>		
<u>C1 Product-Processes</u>		
BOD ₅	0.23	0.10
TSS	0.21	0.094
<u>C2 Product-Processes</u>		
BOD ₅	0.45	0.20
TSS	0.28	0.12
Phenols (Cumene process only)	0.045	0.02
<u>C3 Product-Processes</u>		
BOD ₅	0.94	0.42
TSS	0.076	0.034
Phenols (Bisphenol process only)	0.045	0.02
<u>C4 Product-Processes</u>		
BOD ₅	2.56	1.14
TSS	1.40	0.63
Phenols (p-cresol process only)	0.045	0.02

pH for all Subcategories between 6.0 - 9.0

SECTION III
INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement, by not later than July 1, 1977, of effluent limitations for point sources, other than publicly-owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement, by not later than July 1, 1983, of effluent limitations for point sources, other than publicly-owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement, by new sources, of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish, within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable including treatment techniques, process and procedure innovations, operation methods, and other alternatives. The regulations proposed herein set forth effluent limitation guidelines pursuant to Section 304(b) of the Act for the organic chemicals industry.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. Section 307(c) of the Act also requires the Administrator to propose pretreatment standards for new sources discharge to publicly owned waste treatment plants. The Administrator published, in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the organic chemicals industry, which was included in the list published January 16, 1973. This document is published under authority of Section 304(c) of the Act which requires that

information be made available in the form of a technical report on alternate treatment methods to implement effluent limitations and standards of performance for new sources.

Methods Used for Development of the Effluent Limitations and Standards of Performance

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. The point-source category was first subcategorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point-source category. Such subcategorization was based upon raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of: 1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and 2) the constituents (including thermal) of all waste waters (including toxic constituents and other constituents) which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both in plant and end -of-pipe technologies, which are existent or capable of being designed for each subcategory. It also included an identification of the effluent level resulting from the application of each of the treatment and control technologies, in terms of the amount of constituents (including thermal) and of the chemical, physical, and biological characteristics of pollutants. The problems, limitations, and reliability of each treatment and control technology and the required implementation time were also identified. In addition, the nonwater quality environmental impact (such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise, and radiation) was also identified. The energy requirements of each of the control and treatment technologies were identified, as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the "best practicable control technology currently available", "best available technology economically achievable", and the "best available demonstrated control technology, processes, operating methods, or other alternatives". In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques, process changes, nonwater quality

environmental impact (including energy requirements), and other factors.

During the initial phases of the study, an assessment was made of the availability, adequacy, and usefulness of all existing data sources. Data on the identity and performance of waste water treatment systems were known to be included in:

1. Letter surveys conducted by the Manufacturing Chemists Association (MCA).
2. Corps of Engineers Permit Applications.
3. Self-reporting discharge data from various states.

Limited data on process raw waste loads were also known to be included in previous MCA survey returns.

A preliminary analysis of these data indicated an obvious need for additional information.

Refuse Act Permit Applications data are limited to identification of the treatment system used and reporting of final concentrations (which were diluted with cooling waters in many cases); consequently, operating performance could not be determined.

Texas, where there is a high concentration of organic chemical plants, has a self-reporting discharge system. These reports again show only final effluent concentrations and identify the system used; only rarely is there production information available which would permit the essential determination of unit waste loads.

Additional data in the following areas were therefore required: 1) process RWL (Raw Waste Load) related to production; 2) currently practiced or potential in-process waste control techniques; and 3) the identity and effectiveness of end-of-pipe treatment systems. The best source of information was the chemical manufacturers themselves. New information was obtained from direct interviews and sampling visits to organic chemical producing facilities. This additional data was obtained from direct interviews and from inspection and sampling of organic chemical manufacturing and waste water treatment facilities.

Collection of the data necessary for development of RWL and effluent treatment requirements within dependable confidence limits required analysis of both production and treatment operations. In a few cases, the plant visits were planned so that the production operations of a single plant could be studied in association with an end-of-process treatment system which receives only the wastes from that production. The RWL for this plant and associated treatment technology would fall within a single category. However, the unique feedstock and product posi-

tion applicable to individual manufacturers made this idealized situation rare.

In the majority of cases, it was necessary to visit individual facilities where the products manufactured fell into several subcategories. The end-of-process treatment facilities received combined waste waters associated with several subcategories (several products). It was necessary to analyze separately the production (waste generating) facilities and the effluent (waste treatment) facilities. This required establishment of a common basis, the Raw Waste Load (RWL), for common levels of treatment technology for the products within a subcategory and for the translation of treatment technology between categories.

The selection of process plants as candidates to be visited was guided by the trial subcategorization, which was based on anticipated differences in RWL. Process plants which manufacture only products within one subcategory, as well as those which cover several subcategories, were scheduled, to insure the development of a dependable data base.

The selection of treatment plants was developed from identifying information available in the MCA survey returns, Corps of Engineers Permit Applications, state self-reporting discharge data, and contacts within the industry. Every effort was made to choose facilities where meaningful information on both treatment facilities and manufacturing processes could be obtained.

Survey teams composed of project engineers and scientists conducted actual plant visits. Information on the identity and performance of wastewater treatment systems were obtained through:

1. Interviews with plant water pollution control personnel.
2. Examination of treatment plant design and historical operating data (flow rates and analyses of influent and effluent).
3. Treatment plant influent and effluent sampling.

The data base obtained in this manner was then utilized by the methodology previously described to develop recommended effluent limitations and standards of performance for the organic chemical industry. All of the references utilized are included in Section XV of this report. The data obtained during the field data collection program are included in Supplement B.

Description of the Organic Chemicals Industry

General Considerations

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 occurring in nature, and chemical transformation of vegetable fats and oils.

Until the late 1930's, petrochemistry was limited in its scope to the synthesis of oxygenated solvents, most of them previously obtained by fermentation. World War II ushered in the age of synthetic polymeric substitutes for natural and inorganic material: metals, leather, wood, glass, rubber, waxes, gums, fibers, glues, drying oils, etc. The production of these materials on a large scale sufficient to satisfy their enormous potential markets required raw materials far in excess of those available from refinery off-gas. Therefore, additional olefins began to be produced by cracking light saturated hydrocarbons present in the offgas, and later by resorting to similar materials recovered from natural gas.

A parallel phenomenon was the extremely rapid growth in the need for ammonia and nitrogen fertilizers all over the world. Whereas synthesis gas was originally obtained primarily from coal and by upgrading coke oven gases, the surge in ammonia requirements made it necessary to tap other sources of raw materials. In the regions of the world where natural gas was found, this alternate source of synthesis gas became the stream-reforming of methane.

So far, petrochemistry had become exclusively a source of aliphatic chemicals. The next step was the development of processes for extracting aromatic hydrocarbons from catalytic reformat. This was to be followed by methods for correcting the imbalance between toluene and benzene in reformed naphtha by dealkylating the former and producing additional benzene. With these developments, the elimination of coal as a necessary base for the synthetic organic chemical industry was practically completed.

The most economical techniques for producing olefins and synthesis gas are, respectively, cracking in a tubular furnace and steam reforming. For purely technical reasons, these methods were restricted at first to materials no heavier than butane. A natural advantage was conferred on those regions of the world where natural gas was found, or those where liquid fuels had acquired such a large share of the total demand for energy that enough by-products were available for the chemical industry.

In the early 1960's, one of the most important stages in the evolution of petrochemistry was reached. It became possible to apply the techniques of steam reforming and tubular furnace cracking to liquid feedstocks, thereby freeing the industry from the requirement of locating in the vicinity of petroleum refineries or in regions rich in natural gas. This stage was that of "chemical refinery" a chemical complex feeding on liquid feedstocks that are totally converted to petrochemical raw materials.

A further trend within the chemical industry has been the extraordinary simplification of numerous organic syntheses made possible during the last ten years. This is due particularly to developments in catalysis and automatic control. Oxygenated, unsaturated, and nitrogenated compounds, formerly obtained via routes involving several steps, are gradually being produced by direct oxidation, nitration, amination, or dehydrogenation. Petrochemicals generally tend to be made from hydrocarbon raw materials having the same number of carbon atoms as the finished product. This, combined with the construction of ever larger production units, has been the cause of the drop in the price of organic chemicals to an extent that would have seemed unthinkable a few years ago.

However, these trends are counterbalanced by a crisis which is rapidly developing for the organic chemical industry: i.e. concerning the availability of economical new materials. 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 percent 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 percent 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 percent 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 percent of the total 3¢/lb ethylene price prevailing for Gulf Coast markets during the past several years.

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 below illustrates the theoretical effect of an increase of 50¢/bbl in the cost of crude oil:

Cost Increase Associated with 50¢/bbl		
<u>Petrochemical</u>	<u>Current Cost</u>	<u>Increase in Crude Oil</u>
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 basic raw materials which are currently supplied by petroleum refineries or natural gas companies are:

1. LPG (liquid petroleum gases).
2. Gases from cracking processes.
3. Liquid distillates (C₄ - C₉ naphtha).
4. Distillates from special cracking processes.
5. Cyclic aromatic fractions.
6. Natural gas.

These materials are usually obtained by physical separation processes in petroleum refineries. They are then sold or transferred to organic chemicals manufacturers, which in many instances are wholly-owned subsidiaries of the refining company.

The basic raw materials are first chemically converted to a primary group of reactive precursors. These precursors are then utilized in a multitude of specific chemical conversions to produce both intermediate and final products. Table III-1 summarizes several of the basic raw materials, their associated

reactive precursors, and possible intermediates or finished products manufactured by chemical conversion.

The lower members of the paraffin and olefin series of organic raw materials are the basic starting point in the manufacture of a large number of important organic chemicals. Diagrams which depict the many possible derivatives obtained through chemical conversion are presented for:

Methane (Figure III-1)
Ethylene (Figure III-2)
Propylene, n-butylenes, and iso-butylene (Figure III-3)
BTX aromatics (Figure III-4).

These representations are called "end-use diagrams" and serve to illustrate the many complex interactions which are possible between raw materials, precursors, intermediates, and final products.

The precise definition of a specific manufacturer's production activities within this matrix poses a difficult problem.

Traditionally, the industry has been studied according to chemical function. There are cases of firms specializing in the production of compounds having a common chemical function or that are made by a given unit process. For example, some companies produce several nitration derivatives, or fatty amines, or isocyanates. These cases are often the result of a favorable raw material position enjoyed by specific companies.

More important from the standpoint of the actual behavior of chemical companies is horizontal integration. This can be a powerful motivation due either to a desire to provide hedges against changes in market structures (as in the case of firms that produce various types of polymers or synthetic fibers) or to complement a line of products (e.g. when a company making polyols decides also to produce isocyanates).

Despite the significance of these types of motivation in the chemical industry, however, the main influence in recent years has been the need to integrate vertically. Firms that until recently were content to produce intermediates or end-products have been under constant pressure either to integrate backwards by acquiring their own sources of raw materials, or to integrate forward by gaining control of their clients. The percentage of captive utilization of most major chemical intermediates is growing steadily. This is attributable chiefly to the circumstance that unit profits generally are higher at the finished-product end of the chain. Consequently, many large oil and chemical companies have rapidly enlarged the scope of their activities (both by acquisition and by internal expansion), and have gradually increased their position in the market vis-a-vis those companies which have been content to maintain their original structure.

Table III-1

Raw Materials, Precursors, Intermediates, and Finished Products
Frequently Found in The Organic Chemicals Industry

<u>Raw Materials By Distillation</u>	<u>Precursors (Basic Chemicals) By Conversion</u>	<u>Intermediates By Conversion</u>	<u>Finished Products By Conversion</u>
Paraffins and cyclics	Olefins, diolefins, acetylene, aromatics	Various inorganics and organics	Inorganics and organics
Natural gas			Carbon black
Hydrogen		Synthesis gas	NH ₃
Methane			Methanol Formaldehyde
Refinery gases	Acetylene Isobutene	Acetic acid Acetic anhydride	Acetates Fibers
Ethane*	Ethylene	Isoprene	Rubber
Propane*	Propylene	Ethylene oxide, etc.	Rubber and fiber
n-Butane*	n-Butanes	Butadiene	Rubber
Hexane			
Heptanes			
Refinery naphthas			
Naphthenes	Cyclopentadiene	Adipic acid	Fibers
Benzene		Ethylbenzene Styrene Cumene Alkylbenzene Cyclohexane	Styrene Rubber Phenol, acetone
Toluene	Toluene	Phenol Benzoic acid	Plastics
Xylenes	o-m-p-xylene	Phthalic anhydride	Plastics
Methyl naphthanes	Naphthalene	Phthalic anhydride	Plastics

*From LPG and refinery cracked gas.

Note: Aromatics are also obtained by chemical conversions (demethylation, etc.).

FIGURE III-1

PETROCHEMICALS FROM METHANE

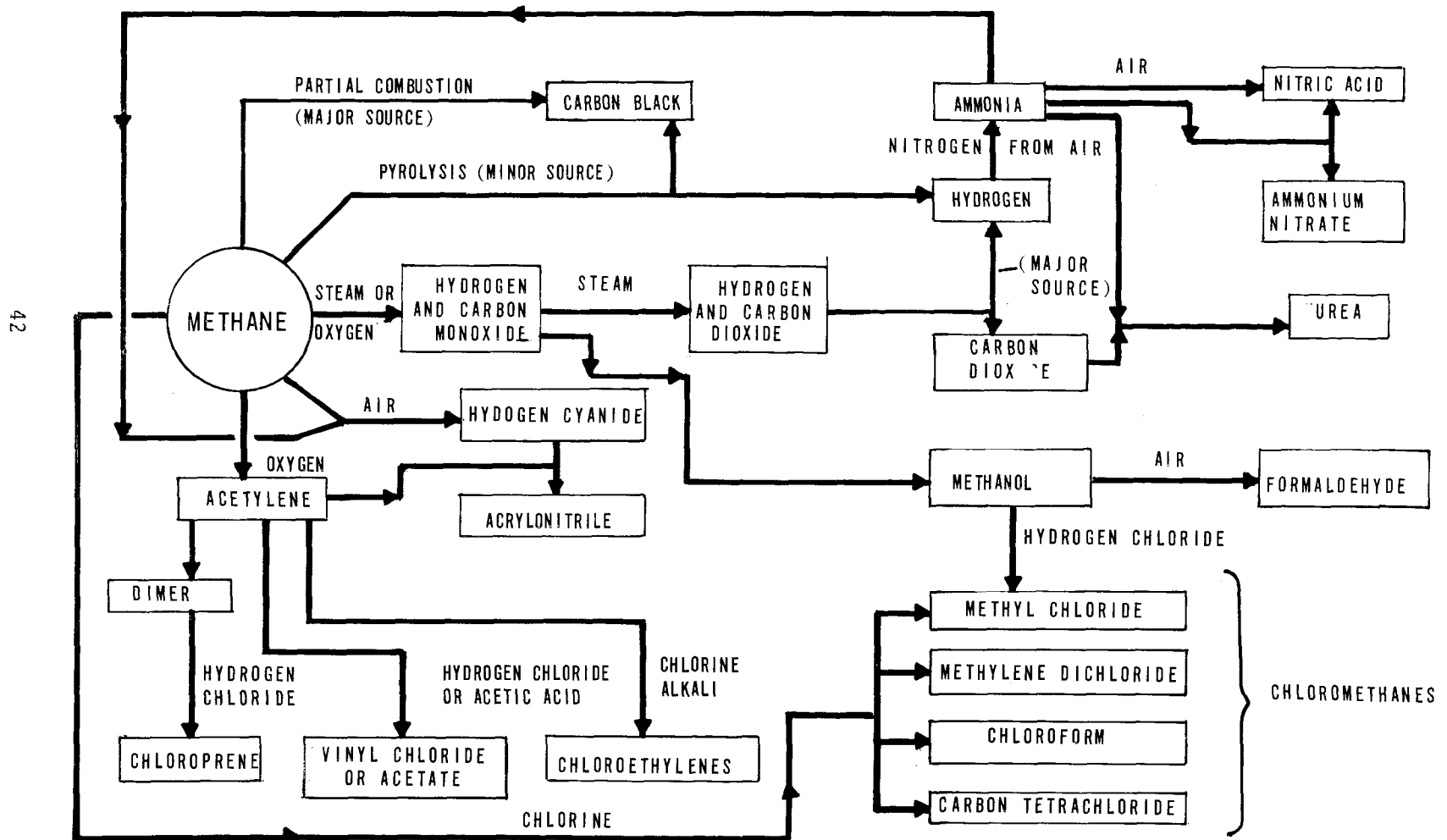


FIGURE III-2
PETROCHEMICALS FROM ETHYLENE

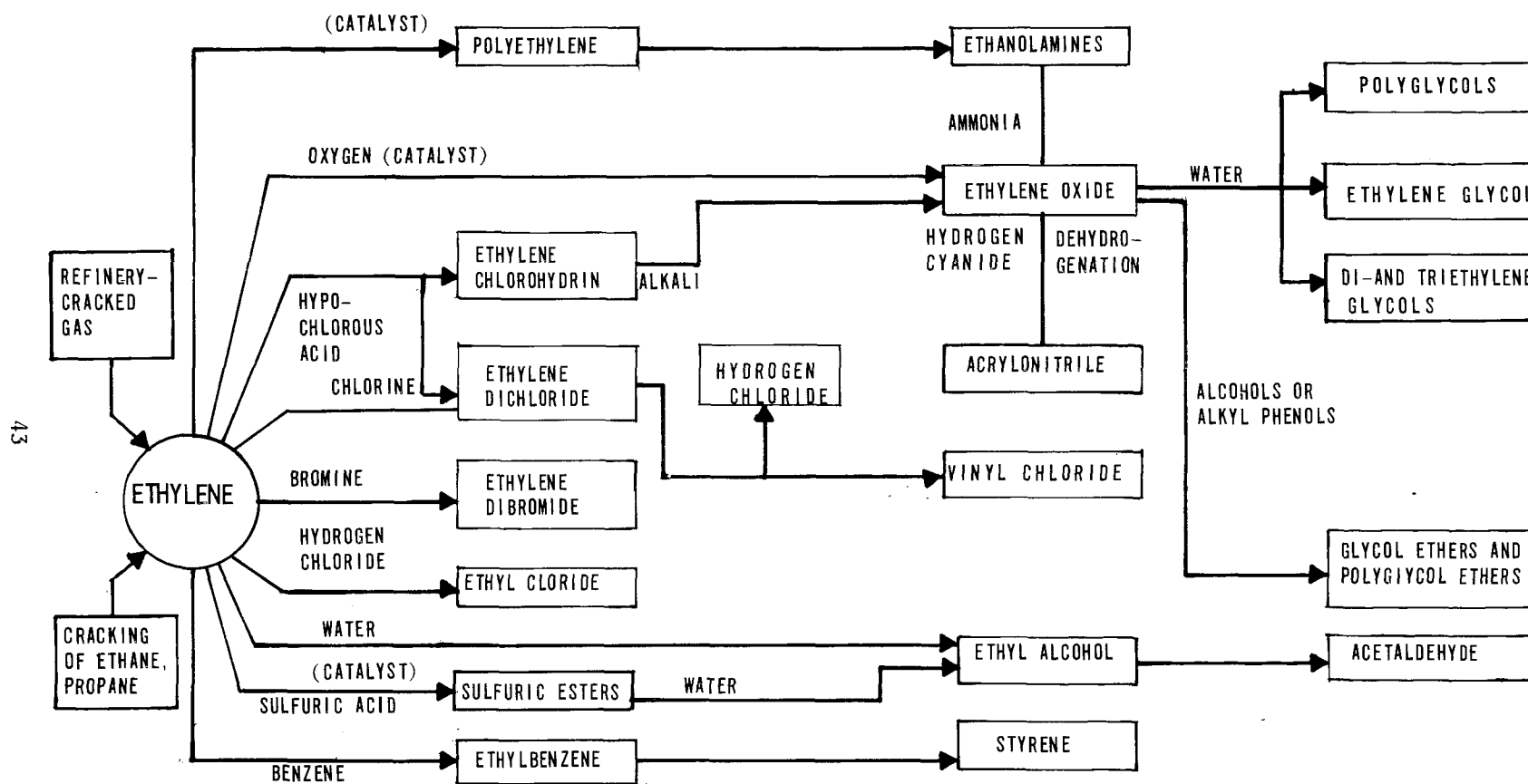


FIGURE III-3
PETROCHEMICALS FROM PROPYLENE AND BUTYLENES

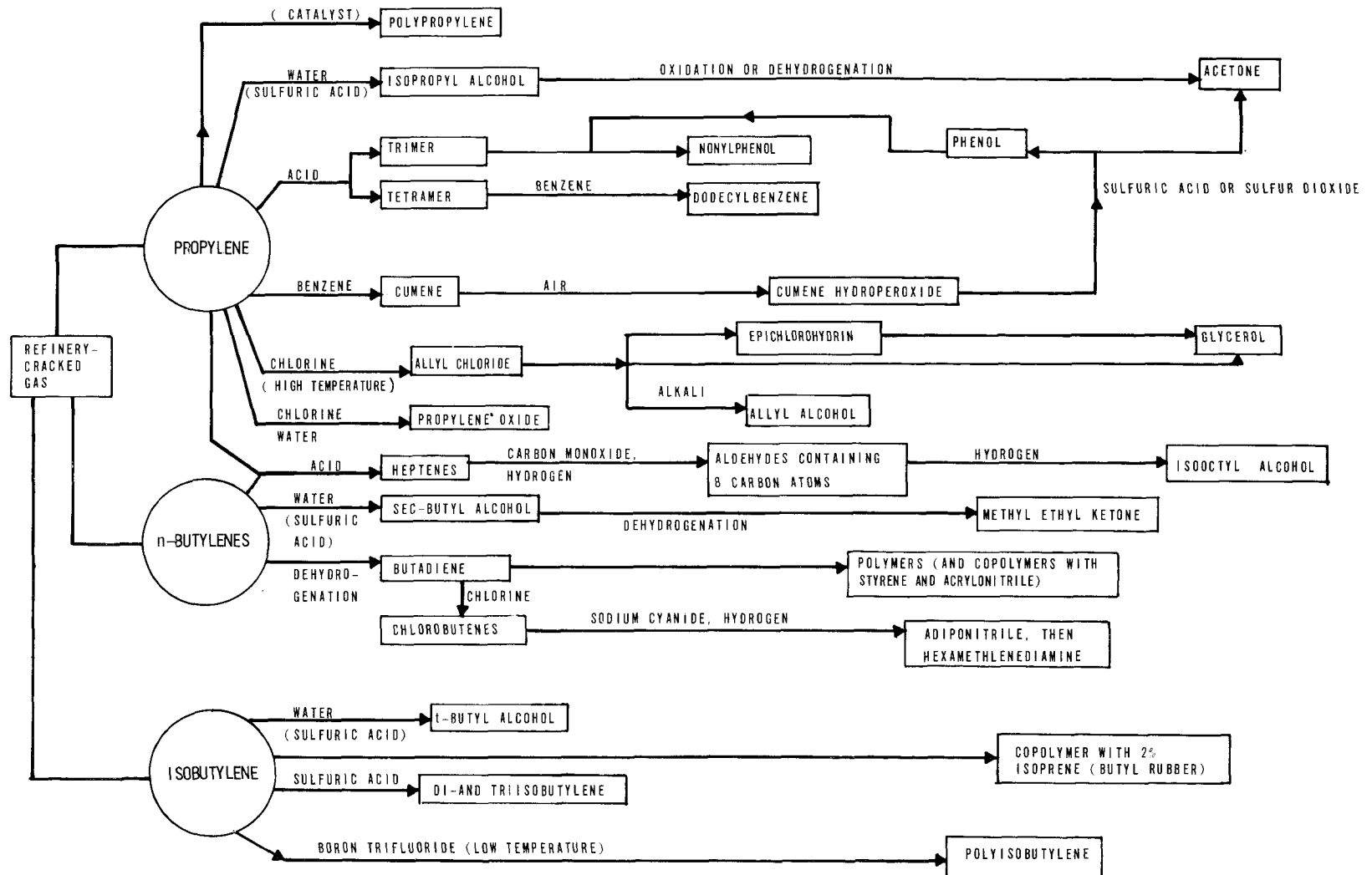
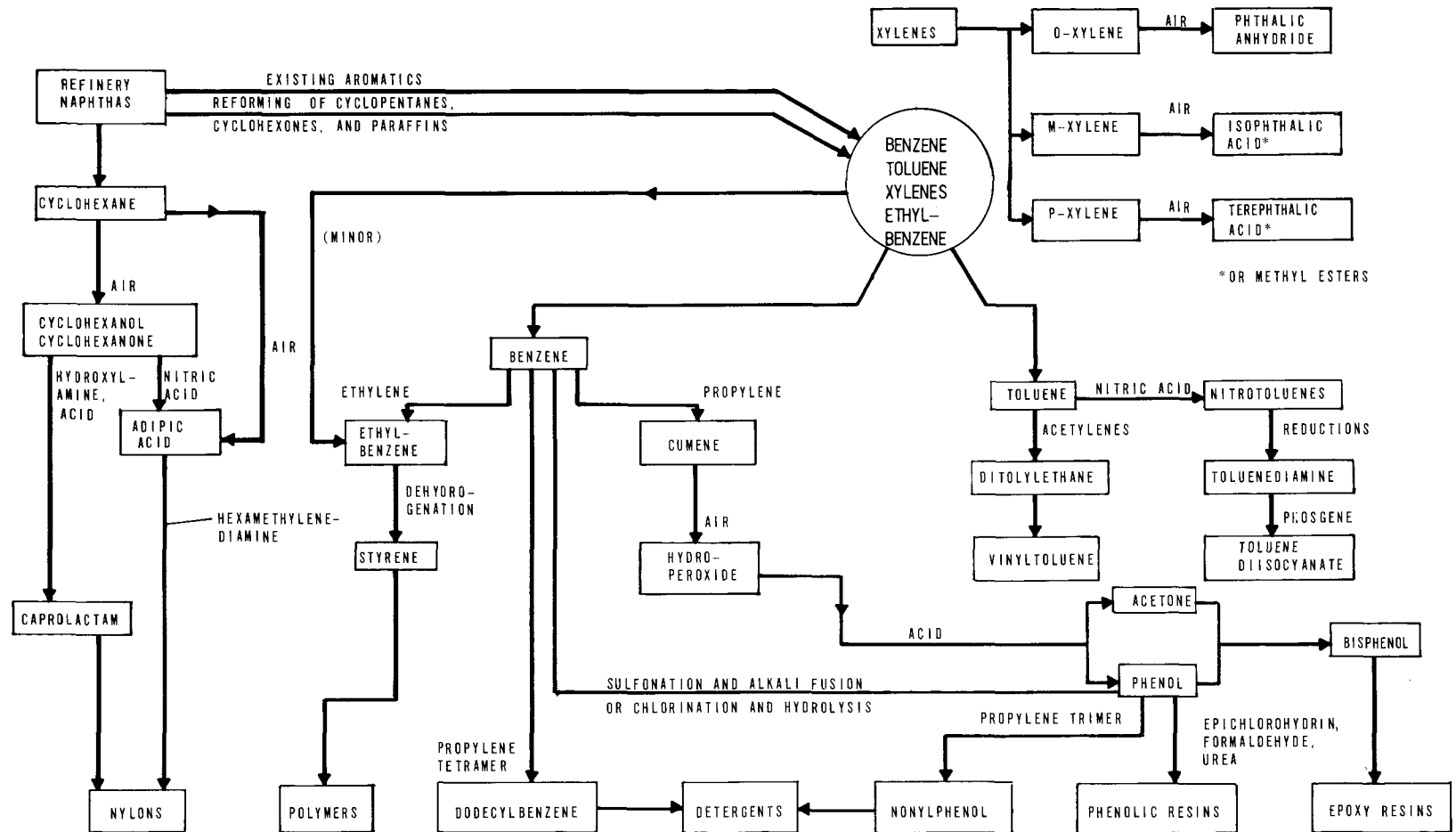


FIGURE III-4
CYCLIC PETROCHEMICALS

45



The specific set of feedstocks, intermediates, and products which are associated with the operation of any facility represents the sum of these considerations as they relate to an individual company. For this reason there is no effective method by which manufacturing operations may be correlated between any two separate plants. Each plant's production and set of process operations constitute a unique contribution toward the profitability of the operation.

The true production associated with a given plant must include the captive utilization of feedstocks and intermediates within the plant's boundaries. Actual production would be the total of all intermediate processing steps between the initial feedstock (e.g. LPG or naphtha) and the final products. A typical sequence of processing operations is illustrated below:

Raw Material: LPG (Ethane and Propane)
Process 1: Steam Cracking

Intermediate: Ethylene
Process 2: Oxidation

Intermediate: Acetaldehyde
Process 3: Oxidation

Final Product: Acetic Acid

In this simplified example, the production at the facility would represent the sum of the ethylene, acetaldehyde, and acetic acid produced by Processes 1, 2, and 3 respectively.

In order to insure the smooth operation of the different segments within a producing facility, manufacturers maintain inventories of feedstocks, intermediate products, and final products available for subsequent processing or for shipment from the plant. Depending on the nature of the operation, these inventories are updated on a monthly, weekly, or even daily basis. The examination of historical production inventories and associated manufacturing processes for a given facility provides the most meaningful picture as to the nature of the activities within its boundaries. This is directly related to the type and quantity of wastes which are generated.

Scope of Work Related to Actual Industry

In order to establish boundaries on the scope of work for this study, the organic chemicals industry was defined to include all commodities listed under SIC 2815 (Cyclic Crudes and Intermediates) and SIC 2818 (Industrial Organic Chemicals Not Elsewhere Classified). A list of the specific products included under these two SIC numbers was presented in Tables I-1 and I-2. The study has been further limited by the exclusion of plastics, fibers, agricultural chemicals, pesticides, fertilizers, detergents, paints, and pharmaceuticals.

The effluent limitations presented in this report for many of these chemicals should be applied only where their production is not associated with refining operations such as crude topping, cracking and reforming.

Because of the diverse nature of the organic chemicals industry, there will always be gray areas where definitive boundaries cannot be established. The Government's Standard Industrial Classification system for classifying industrial enterprises by their major lines of activity puts producers of chemicals, plastics materials, and synthetics in industry group 281. However, Table III-2, a tabulation of the fifty largest producers of chemicals in the U.S. (compiled by the Chemical and Engineering News, April 30, 1973), contains only twenty-one firms from the 281 group. The relative sizes of establishments by numbers of employees are shown in Table III-3. The companies in the list that are not members of the 281 group are classified in industries ranging from meat and dairy products to photographic and optical equipment. Nearly half of them are petroleum refiners. When approaching a specific facility for the purpose of applying effluent limitations, it is necessary to gain some background information on the exact nature of its operations and not to rely entirely on the SIC number under which the company owning the facility is listed.

The data collection effort associated with this study has been divided into two parts, Phase I and Phase II. The information and effluent limitations presented in the report are based on Phase I, where major emphasis was placed upon high production volume commodities. The subsequent effort in Phase II will concentrate on smaller-volume products.

Water Usage Associated with Different Segments of a Chemical Plant

At first glance, an organic chemicals plant often appears to be a chaotic maze of equipment, piping, and buildings that is totally unlike any other facility, even those which manufacture the same product. Nevertheless, there are certain basic components common to almost all chemical plants: a process area; storage and handling facilities for raw materials, intermediates, and finished products; electrical, steam, air, and water systems with associated sewers and effluent treatment facilities; and, in most cases, a laboratory, an office, control rooms, and service roads.

The process area is normally referred to as the "battery limit", while the remainder of the plant is called the "off-sites". The off-sites can be broken down into their components: the storage and handling facilities, the utilities, and the services. This four-area concept in plant layout is illustrated by the plot plan shown in Figure III-5.

The storage facilities associated with any chemical plant obviously depend upon the physical state (i.e. solid, liquid, or gas) of the feedstocks and products. Storage equipment

Table III - 2
Fifty Largest Chemical Producers in the United States

Rank 1972	Rank 1971	Company	Chemical Sales	Net Sales	Chemical Sales as Per Cent of Total Sales	SIC Class
			\$ Millions	\$ Millions		
1	1	DuPont	\$3550	\$ 4,366	81%	281
2	2	Union Carbide	2185	3,261	67	281
3	4	Dow Chemical	2103	2,404	87	281
4	3	Monsanto	1924	2,225	86	281
5	5	Celanese	1279	1,385	92	281
6	6	Exxon	1258	20,310	6	291
7	7	W.R. Grace	1088	2,315	47	281
8	8	Allied Chemical	1001	1,501	67	281
9	9	Occidental Petroleum	831	2,721	31	509
10	10	Hercules	795	932	85	281
11	12	Eastman Kodak	694	3,478	20	383
12	11	FMC	657	1,498	44	281
13	14	Shell Oil	645	4,076	16	291
14	13	American Cyanamid	644	1,359	47	281
15	15	Rohm and Haas	588	619	95	281
16	16	Stauffer Chemical	543	543	100	281
17	19	Phillips Petroleum	490	2,512	19	291
18	20	Borden	475	2,193	22	202
19	17	Mobil Oil	470	9,166	5	291
20	18	Ethyl Corp.	458	632	73	281
21	21	Cities Service	424	1,862	23	291
22	23	Gulf Oil	420	6,243	7	291
23	29	NL Industries	415	1,014	41	285
24	22	Standard Oil (Ind.)	410	4,503	9	291
25	25	PPG Industries	405	1,396	29	321
26	26	Diamond Shamrock	404	617	65	281
27	27	Akzona	391	572	68	281
28	32	B.F. Goodrich	363	1,507	24	301
29	28	Ashland Oil	352	1,780	20	291
30	30	U.S. Steel	350	5,429	6	331
31	31	Air Products	342	351	97	281
32	34	3M Co.	330	2,114	16	383
33	33	Olin	329	1,098	30	281
34	36	Standard Oil of California	304	5,829	5	291
35	41	BASF Wyandotte	301	301	100	
36	44	Airco	283	402	57	281
37	41	Ciba-Geigy	280	625	45	
38	40	Tenneco	277	3,275	8	291
39	35	El Paso Natural Gas	254	1,097	23	492
40	43	Goodyear Tire	250	4,072	6	301
41	47	Merck	235	958	25	283
42	48	Baychem	230	230	100	
43	46	Chemetron	224	314	71	281
44	38	Pfizer	222	1,093	20	283
45		American Hoechst	220	260	85	
46	49	Lubrizol	217	217	100	289
47		Reichhold Chemicals	217	217	100	281
48	50	Atlantic Richfield	216	3,321	7	291
49	37	Swift & Co.	210	3,241	6	201
50	39	Koppers	204	613	33	281

Note: SIC classifications are as follows: 201 Meat; 202 Dairy; 281 Basic chemicals; 283 Drugs; 285 Paints; 289 Other chemicals; 291 Petroleum; 301 Tires; 321 Glass; 331 Iron and steel; 383 Photo equipment; 492 Gas; 509 Miscellaneous wholesalers.

Source: Chemical and Engineering News, April 30, 1973

TABLE III-3
ESTABLISHMENTS BY EMPLOYMENT SIZE
IN THE ORGANIC CHEMICALS
MANUFACTURING INDUSTRY

Establishments By Size (No. of Employees)	<u>SIC 2815</u>	<u>SIC 2818</u>	No.	<u>Total</u> %
< 10	46	174	220	33
< 50	97	289	386	58
< 100	113	339	452	67
< 250	150	409	559	84
< 500	163	447	610	92
< 1,000	170	468	638	96
< 2,500	177	481	658	99
<u>> 2,500</u>	<u>0</u>	<u>7</u>	<u>665</u>	100
Total	177	488	665	
Companies	115	339	454	
Total Employment (1,000)	30	95.1	125.1	
Total Payroll (\$Million)	251.1	844.9	1,096.0	

* 1967 US Census Data

frequently utilized includes: cone-roof tanks, with or without "floating" roofs, for storage of liquid hydrocarbons; cylindrical or spherical gas-holding tanks; and concrete pads or silos for storage of solids.

Waste water emanating from this part of the plant normally results from storm run-off, tank washing, accidental spills, and aqueous bottoms periodically drawn from storage tanks. Although the generation rate is sporadic and the volume small, these waste waters have in most cases contacted the chemicals which are present in this area. For this reason, they are normally sent to a process sewer and given the same effluent treatment as contact-process waste waters.

Utility functions such as the supply of steam and cooling water generally are set up to service several processes. Boiler feed water is prepared and steam is generated in a single boiler house. Noncontact steam used for surface heating is circulated through a closed loop whereby varying quantities are made available for the specific requirements of the different processes. The condensate is nearly always recycled to the boiler house, where a certain portion is discharged as blowdown.

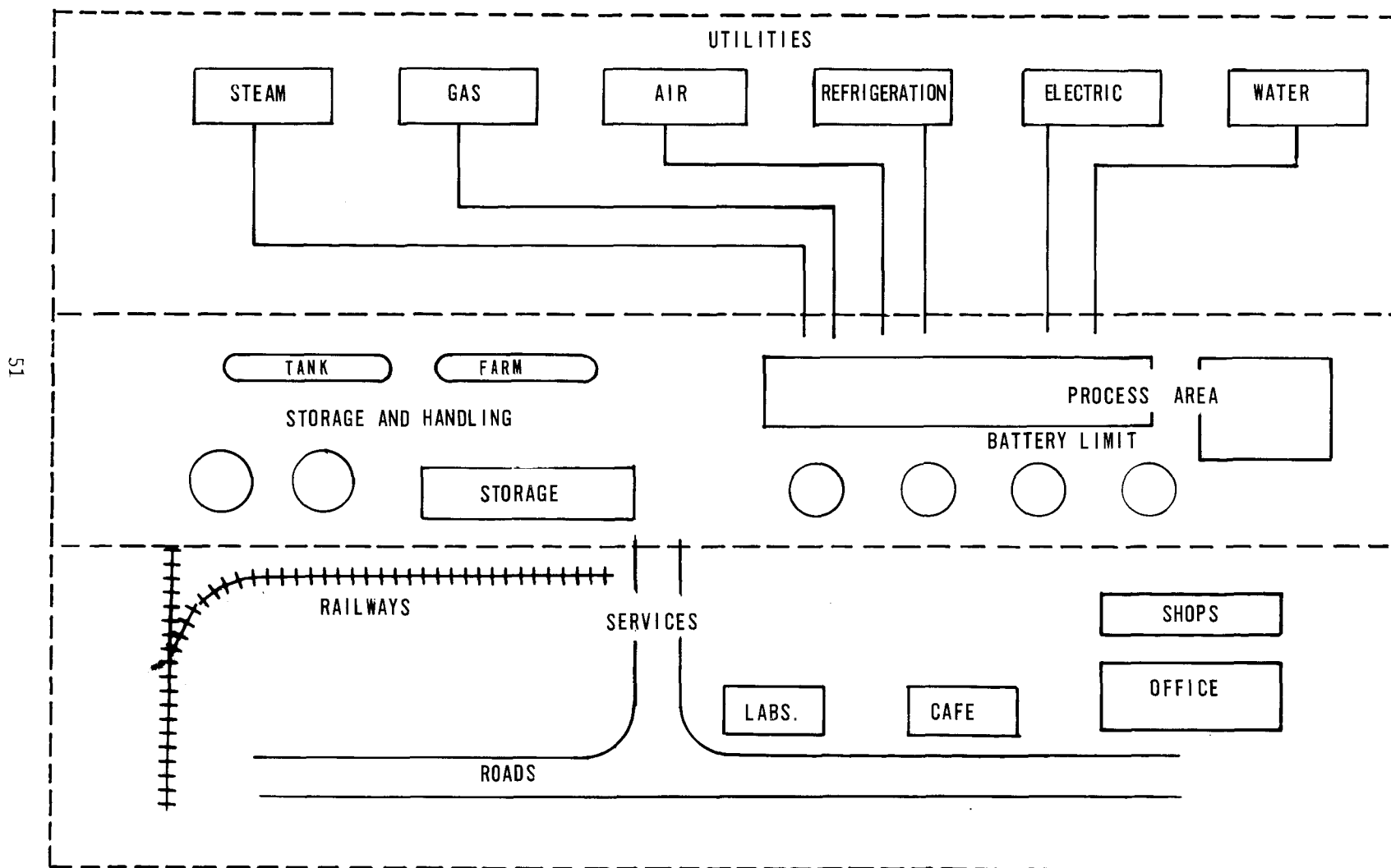
The three major uses of steam generated within a chemical plant are:

1. For noncontact process heating. In this application, the steam is normally generated at pressures of 125 to 650 psig.
2. For power generation such as in steam-driven turbines, compressors, and pumps associated with the process. In this application, the steam is normally generated at pressures of 650 to 1500 psig and requires superheating.
3. For use as a diluent, stripping medium, or source of vacuum through the use of steam jet ejectors. This steam actually contacts the hydrocarbons in the manufacturing processes and is a source of contact process waste water when condensed. It is used at a substantially lower pressure than the foregoing and frequently is exhaust steam from one of the other uses.

Steam is supplied to the different users throughout the plant either by natural-circulation, vapor-phase systems, or by forced-circulation liquid heat-transfer systems. Both types of system discharge some condensate as blowdown and require the addition of boiler makeup water. The main areas of consideration in boiler operation are normally boiler efficiency, internal deposits, corrosion, and the required steam quality.

Boiler efficiency is dependent on many factors. One is the elimination of boiler-tube deposition that impedes heat transfer. The main contributors to boiler deposits are calcium, magnesium, silicon, iron, copper, and aluminum. Any of these can occur in

FIGURE III-5
PLOT PLAN FOR CHEMICAL PLANT
ILLUSTRATING FOUR-AREA LAYOUT



natural waters, and some can result from condensate return-line corrosion or even from makeup water pretreatment. Modern industrial boilers are designed with efficiencies on the order of 80 percent. A deposit 1/8 inch in depth will cause a 2-3 percent drop in this efficiency, depending on the type of deposit.

Internal boiler water treatment methods have advanced to such a stage that corrosion in the steam generation equipment can be virtually eliminated. The control of caustic embrittlement in boiler tubes and drums is accomplished through the addition of sodium nitrate in the correct ratio to boiler water alkalinity. Caustic corrosion in high heat transfer boilers can also be controlled by the addition of chelating agents.

This type of solubilizing internal boiler water treatment has been shown to be more effective than previous precipitation treatment using phosphate.

Other factors influencing boiler efficiency include reduction of the amount of boiler blowdown by increasing cycles of concentration of the boiler feedwater, efficiency of the blowdown heat recovery equipment, and the type of feed used.

Flash tanks are used in many plants to recover, as low-pressure steam, as much as 50 percent of the heat lost from continuous boiler blowdown. The steam is then used for the boiler feed water deaerator or other low pressure applications. Additional heat is recovered in some plants by installing heat exchangers following the blowdown flash tank. The blowdown is used to preheat the makeup boiler feed water in these exchangers.

Steam purity is of prime importance if:

1. The boilers are equipped with superheaters.
2. The boilers supply power generation equipment.
3. The steam is used directly in a process where contamination could affect product quality or destroy some material (such as a catalyst) essential to the manufacture of the product.

The minimum purity required for contact steam (or contact process water) varies from process to process. Limits for suspended solids, total solids, and alkalinity vary inversely with the steam pressure. The following tabulation summarizes boiler water concentration limits for a system providing a steam purity of 0.5-1.0 ppm total solids, which is required for most noncontact steam uses. It should be noted that the boiler operation must incorporate the use of antifoam agents and steam separation equipment for the concentrations shown to be valid.

<u>Parameters</u>	<u>Boiler Pressure, Psig</u>			
	<u>0-300</u>	<u>301-450</u>	<u>451-600</u>	<u>601-750</u>
Total Solids (mg/l)	6,000	5,000	4,000	2,500
Suspended Solids (mg/l)	1,000	200	100	50
Total Alkalinity (mg/l)	1,000	900	800	750

The concentrations of these contaminants found in actual boiler blowdowns were generally within the ranges shown above.

Water conditioning or pretreatment systems are normally part of the Utilities Section of the most plants. From the previous discussions, it is obvious that the required treatment may be quite extensive. Ion-exchange demineralization systems are very widely employed, not only for conditioning water for high pressure boilers, but also for conditioning various process waters. Clarification is also widely practiced and usually precedes the ion exchange operation.

Noncontact cooling water also is normally supplied to several processes from the Utilities area. The system is either a loop which utilizes one or more evaporative cooling towers, or a once through system with direct discharge.

Cooling towers accomplish the cooling of water circulated over the tower by moving a predetermined flow of ambient air through the tower with large fans. The air-water contact causes a small amount of the water to be evaporated by the air. Thus, through latent heat transfer, the remainder of the circulated water is cooled.

Approximately 1,000 BTU are removed from the total water circulation by the evaporation of 1 lb of water. Therefore, if 100 lbs of water are introduced at the tower inlet and 1 lb is evaporated to the moving air, the remaining 99 lbs of water are reduced in total heat content by 1,000 BTU, or about 10 BTU/lb. The 99 lbs of water leaving the tower have been cooled 1°F/lb/BTU removed, and the exit temperature is reduced by about 10°F. This leads to the common rule of thumb: 1 percent evaporation loss for each 10°F.

Since cooling is primarily by transfer of latent heat, cooling tower selection is based on the total heat content or enthalpy of the entering air. At any one enthalpy condition, the wet bulb temperature is constant. Therefore cooling towers are selected and guaranteed to cool a specific volume of water from a hot water temperature to a cold water temperature while operating at a design wet-bulb temperature. Design wet-bulb temperatures vary from 60°F ~ 85°F depending on the geographic area, and are usually equalled or exceeded only 2.5 percent to 5 percent of the total summer operating time.

Hot water temperature minus cold water temperature is termed cooling range, and the difference between cold water and wet-bulb temperature is called approach.

A closed system is normally used when converting from once-through river cooling of plant processes. In the closed system, a cooling tower is used for cooling all of the hot water from the processes. Figure III-6 illustrates this method. With the closed system, makeup water from the river is required to replace evaporation loss at the tower.

Two other water losses also occur. The first is drift, which is droplet carry-over in the air as contrasted to evaporative loss. The cooling tower industry has a standardized guarantee that drift loss will not exceed 0.2 percent of the water circulated. The second loss in the closed system is blowdown to sewer or river. Although blowdown is usually taken off the hot water line, it may be removed from the cold water stream in order to comply with regulations that limit the temperature of water returned to the stream. Blowdown from a tower system will vary depending on the solids concentration in the make-up water, and on the occurrence of solids that may be harmful to equipment. Generally, blowdown will be about 0.3 percent per 10°F of cooling, in order to maintain a solids concentration in the recirculated water of three to four times that of the make-up water.

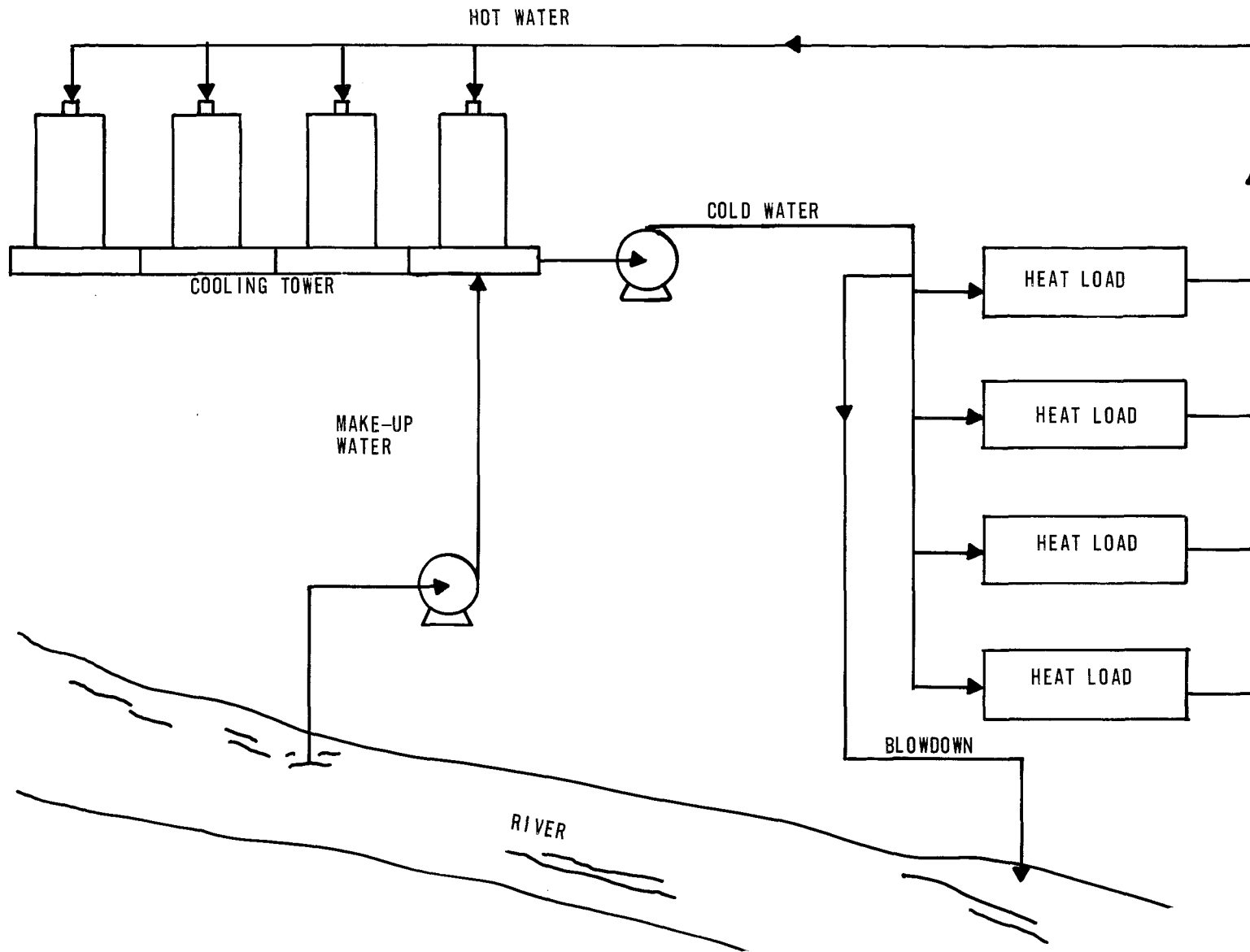
The quantity and quality of the blowdown from boilers and cooling towers depend on the design of the particular plant utility system. The heat content of these streams is purely a function of the heat recovery equipment associated with the utility system. The amounts of waste brine and sludge produced by ion exchange and water treatment systems depend on both the plant water use function and the intake source. Usually none of these utility waste streams can be related directly to specific process units.

Quantitative limitations on parameters such as dissolved solids, hardness, alkalinity, and temperature, therefore, cannot be allocated on a production basis. The limitations on such parameters associated with non-contact utility effluents will be considered under Phase II.

The Service area of the plant contains the buildings, shops, and laboratories in which most of the plant personnel work. The sanitary wastes from this area obviously depend on the number of persons employed. It should be noted that most chemical plants run continuously and have 3 operating shifts per day. There are also wastes associated with the operation of the laboratory, machine shops, laundry, etc. The wastes from the Service area normally are combined with the wastes from the process area prior to treatment.

As was mentioned previously, there are a large number of process combinations possible within the "Battery limits" of the typical multiprocess plant. Choosing one of the many commercially viable processes for the manufacture of a specific chemical at a particular location or time is a decision based on a particular manufacturer's unique situation.

FIGURE III-6
CLOSED SYSTEM



Each process is itself a series of unit operations which causes chemical and physical changes in the feedstock or products. In the commercial synthesis of a single product from a single feedstock, there generally are sections of the process associated with: the preparation of the feedstock; the chemical reaction; the separation of reaction products; and the final purification of the desired product. Each unit operation may have drastically different water usages associated with it. The type and quantity of contact waste water are therefore directly related to the nature of the various processes. This in turn implies that the types and quantities of waste water generated by each plant's total production mix are unique.

The production from a given process module is obviously related to the design capacities of the individual unit operations within it. In many cases the unit operations are arranged as a single train in series. In other cases, some unit operations such as the reaction are carried in several small reactors operating in parallel.

The flow of material between unit operations within a process may be either a continuous stream or through a series of batch transfers. Both types of processes normally have an associated design capacity which is generally expressed as millions of pounds of product per year.

Types of Manufacturing Processes

There are two major types of manufacturing process within the industry:

1. Continuous Processing Operations.
2. Batch Processing Operations.

Facilities utilizing continuous processes manufacture products in much greater volumes than do batch operations. Although the initial manufacture of many chemicals was first done by batch processing, changes to continuous processing were made when markets were enlarged to meet increasing and changing demands. The reduction in plant cost per unit of production was the major driving force behind this change.

Batch processing is still extensively practiced, particularly when the production is small or where safety demands that small quantities be handled at one time. Furthermore, batch operations are more easily controlled when varying reaction rates and rapid temperature changes are key considerations.

Demarcation between batch and continuous operations provides the first working division of the industry into subcategories. Most of the products and processes covered in Phase I are related to continuous operations. This has provided sufficient information to sub divide the continuous processes into three subcategories. These will be fully defined later in this report.

There is frequently a segregation of the equipment associated with large continuous operations to the extent that each process module is located in its own building or plant location. The management of a large continuous process to be competitive, efficacious and profitable, may be the responsibility of an entire division of the company. In such cases, the plant manager may function as a landlord whose responsibility is to provide the required utilities for each process module. In such operations, there is usually complete segregation of contact process waters from noncontact cooling water and steam.

Flow charts are normally used to show the coordinated sequence of chemical conversions and unit operations within a continuous process module. They indicate the points of entrance of raw materials, noncontact media for heating and cooling, and the places where products and wastes are removed. A flow chart can normally be used to divide the process module into four subsections:

- Feed Preparation
- Reaction
- Product Separation
- Product Purification

Each of these subsections can include several unit operations or chemical conversions.

The feed preparation section may contain equipment such as furnaces where the liquid feed is vaporized or heated to reaction temperature, or large steam driven compressors for compressing gaseous feed to the reaction pressure. It may contain distillation columns to separate undesired feed impurities which might damage the catalyst in the reactor or cause subsequent unwanted side reactions. Impurities may also be removed by preliminary chemical conversion (such as the hydrogenation of diolefins) or by physical means such as silica gel driers to remove trace amounts of moisture.

The reaction section of the process module is where the principal chemical conversions are accomplished. The reactor may be as simple as a hollow tube used for noncatalytic vapor-phase reactions. However, most industrial reactions are catalytic and generally require more complex reactor designs. The specific reactor design is usually governed by the required physical state of the reactants and catalyst.

Catalysts are of two types: heterogeneous and homogeneous. Heterogeneous catalysts are usually solids which may be composed of chemically inactive material such as finely ground aluminum or contain metals such as cobalt, platinum, iron, or manganese which are impregnated on a solid support. In heterogeneous reaction systems, the reactants are usually in the vapor phase. The conversion proceeds in three steps: adsorption of the reactants upon the surface of the catalyst; chemical reactions on the sur-

face of the catalyst; and desorption of the products from the catalyst surface.

Homogeneous catalysts exist in the same physical state as the reactants and products. This may require the use of an aqueous or non-aqueous solvent to provide a reaction media. Typical homogeneous catalysts include strong acids, bases, and metallic salts which may be in the form of a solution or a slurry. It should be noted that the recovery, reconcentration, or regeneration of these catalysts may require the use of processing equipment much more elaborate than the reactor itself.

The recovery of reaction products may involve a wide variety of processing operations. If the reactor effluent is a vapor, it may be necessary to condense and quench the products in a direct contact medium such as water. In many instances the desired products are absorbed in water and are subsequently stripped from the water by heating. Liquid reactor effluents are separated from solvents (and catalysts) by distillation. In almost all cases, the conversion of feed is not complete, so that continuous separation and recycle of unconverted feed to the reactor is necessary.

Final purification of the products is normally required both when they are to be sold and when they are used as intermediates. Most specifications restrict contaminant levels to the range of parts per million. Because of this, additional operations such as distillation, extraction, crystallization, etc. are necessary. The product is pumped from the battery limits to tanks in the storage area.

In large-scale continuous processes, all of the subsections of the process module are operated with the use of automated controls; in some cases, complete automation or computer control is utilized. Recording instruments maintain continuous records of process variables such as temperature, pressure, flow of fluids, viscosity, and the composition of various process streams. Instrumentation for the indicating, recording, and control of process variables is an outstanding characteristic of modern chemical manufacture. In many processes, the instrument expense costs up to 5 percent of the total expenditure for the process module. The function of the operators, mechanical technicians, and supervising engineers in this type of operation is to maintain the process module in proper running order.

When chemical manufacturing is on a small scale, or when it is not adaptable to continuous procedures, a batch sequence is frequently used. This requires more supervision on the part of operators and engineers, because the conditions and procedures usually change from the start to the finish. Batch operations with small production and variable products also transfer equipment from the making of one chemical to that of another based on the same type of chemical conversion. Hundreds of specific products may be manufactured within the same building.

This type of processing requires the cleanout of reactors and other equipment after each batch. Purity specifications may also require extensive purging of the associated piping. Rapid changes in temperature during the batch sequence may also require the direct addition of ice or quench water as opposed to slower non-contact cooling through a jacket or coils.

Process waters from batch or continuous processes within the battery limits include not only water produced or required by the chemical reactions but also any water which comes in contact with chemicals within each of the process modules. Although the flows associated with these sources are generally much smaller than those from non-contact sources, the organic pollution load carried by these streams is greater by many orders of magnitude. The process RWL's from the battery limits can be put on a meaningful production basis and form the basis for the effluent limitations developed in this report.

Relationship to Chemical Process Economics

Each process module within the plant functions as a separate economic entity, with a real or artificial price attached to the final product or intermediate which it manufactures. This selling price (or transfer price) is usually expressed as a required realization including the cost of raw materials, manufacturing cost, and return on the capital investment associated with the process module.

The total materials cost is based on the price of the feedstock minus any credits obtained for the concurrent production of co-products or byproducts. Co-products are normally defined to be salable commodities with their own markets. By-products are normally materials such as gases produced by undesired side reactions; these are usually credited only for use as auxiliary fuel.

Manufacturing costs normally include the following items:

1. Labor and supervision.
2. Direct overhead.
3. General overhead.
4. Depreciation.
5. Repairs.
6. Utilities (power, steam, fuel, cooling water, and process water)
7. Miscellaneous chemicals associated with catalyst replacement, etc.

These items are added to give a total manufacturing cost.

The return on the total capital investment for the process module is normally based on some specific pretax return (such as 20 percent) which the manufacturer charges or must pay for the initial use of capital. The total capital investment normally

includes the cost of the process module, initial working capital, and startup costs.

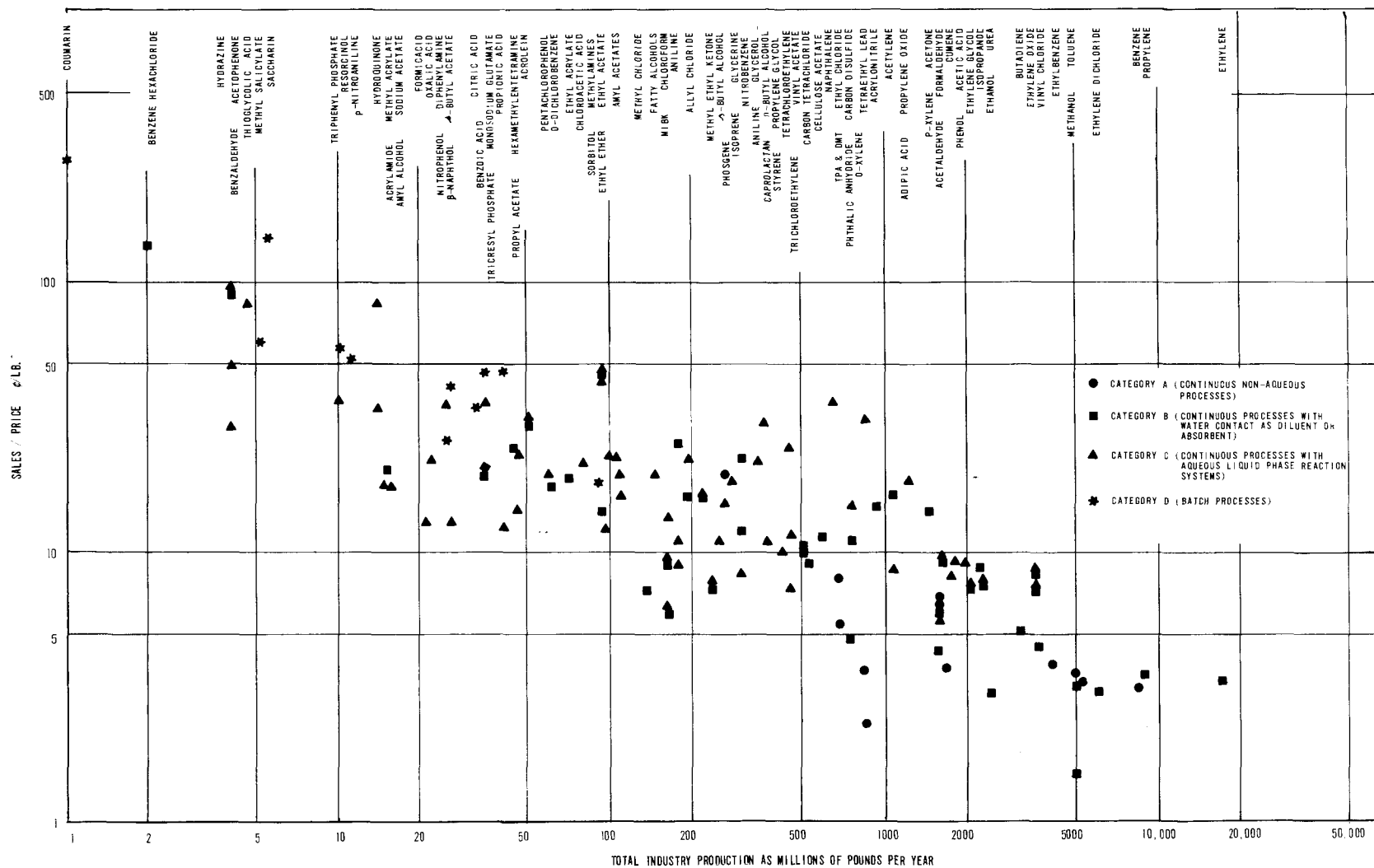
When the three components are added together and divided by the production of the desired product, they provide a required realization or unit price which the manufacturer attaches to that product. Other factors such as market penetration, sales build-up, and overall trends in total industry capacity and industry demand will then drive the actual selling price upward or downward.

When the organic chemicals industry is considered as a whole, there is a definite relationship between the total production and the selling price for a specific chemical. This relationship is illustrated in Figure III-7. As would be anticipated, high-volume chemicals manufactured in large scale continuous processes have a much lower selling price than do small volume batch chemicals. As shown in Figure III-7, this relationship may be correlated with the continuous and batch process categories for the industry.

Required realizations based on typical size process modules (production capacity indicated as millions of pounds per year) are presented for the chemicals studied in this report. These unit costs are expressed as cents per pound. They have been broken down into the three components previously described.

Costs are also presented 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 specific 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.

RELATIONSHIP BETWEEN SELLING PRICE AND TOTAL INDUSTRY PRODUCTION



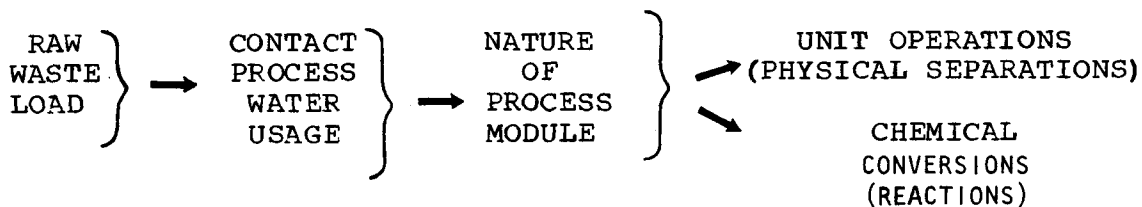
SECTION IV
INDUSTRY SUBCATEGORIZATION

Discussion of the Rationale of Subcategorization

The goal of this study is the development of effluent limitations commensurate with different levels of in-process and end-of-pipe pollution control technology. These effluent limitations will specify the quantity of pollutants which will ultimately be discharged from a specific manufacturing facility, and will be related to the quantity of product produced.

The diverse range of products and manufacturing processes to be covered suggests that separate effluent limitations be designated for different segments within the industry. To this end, a subcategorization of the Organic Chemicals Industry has been developed. The subcategorization is process oriented. Chemical commodities have been grouped according to the RWL associated with their specific manufacturing process.

The relationship between the process raw waste load (RWL), process water usage, and those specific unit operations and chemical conversions which define the nature of the process is shown below:



Manufacturing processes have been examined for type of process water usage associated with each. Process water is defined to be all water which comes in contact with chemicals within the process and includes:

1. Water required or produced (in stoichiometric quantities) in the chemical reaction.
2. Water used as a solvent or as an aqueous medium for the reactions.
3. Water which enters the process with any of the reactants or which is used as a diluent (including steam).
4. Water associated with the catalyst system, either during the reaction or during catalyst regeneration.
5. Water used as an absorbent or as a scrubbing medium for separating certain chemicals from the reaction mixture.

6. Water introduced as steam to strip certain chemicals from the reaction mixture.
7. Water used to wash, remove, or separate chemicals from the reaction mixture.
8. Water associated with mechanical devices such as steam-jet ejectors for drawing a vacuum on the process.
9. Water used as a quench or direct contact coolant such as in a barometric condenser.
10. Water used to clean or purge equipment used in batch type operations.
11. Runoff or wash water associated with battery limits process areas.

The type and quantity of process water usage are related to the specific unit operations and chemical conversions within a process. The term "unit operations" is defined to mean specific physical separations such as distillation, solvent extraction, crystallization, adsorption, etc. The term "chemical conversion" is defined to mean specific reactions such as oxidation, halogenation, neutralization, etc.

Description of Subcategories

Four process subcategories have been established. Subcategories A, B, and C relate to continuous processes, while Subcategory D relates to batch processes. The subcategories are described as follows:

Subcategory A - Nonaqueous Processes

Minimal contact between water and reactants or products within the process. Water is not required as a reactant or diluent and is not formed as a reaction product. The only water usage stems from periodic washes of working fluids or catalyst hydration.

Subcategory B - Processes With Process Water Contact as Steam Diluent or Absorbent

Process water usage is in the form of dilution steam, a direct contact quench, or as an absorbent for reactor effluent gases. Reactions are all vapor-phase and are carried out over solid catalysts. Most processes have an absorber coupled with steam stripping of chemicals for purification and recycle. Steam is also used for de-coking of catalyst.

Subcategory C - Continuous Liquid-Phase Reaction Systems

Liquid-phase reactions where the catalyst is in an aqueous medium such as dissolved or emulsified mineral salt, or acid-caustic solution. Continuous regeneration of catalyst system requires extensive water usage. Substantial removal of spent inorganic salt by-products may also be required. Working aqueous catalyst solution is normally corrosive. Additional water may be required in final purification or neutralization of products.

Subcategory D - Batch and Semicontinuous Processes

Processes are carried out in reaction kettles equipped with agitators, scrapers, reflux condensers, etc. depending on the nature of the operation. Many reactions are liquid-phase with aqueous catalyst systems. Reactants and products are transferred from one piece of equipment to another by gravity flow, pumping, or pressurization with air or inert gas. Much of the material handling is manual with limited use of automatic process control. Filter presses and centrifuges are commonly used to separate solid products from liquid. Where drying is required, air or vacuum ovens are used. Cleaning of noncontinuous production equipment constitutes a major source of waste water. Waste loads from product separation and purification will be at least ten times those from continuous processes.

Sample flow diagrams illustrating typical unit operations and chemical conversions for a process within each category are provided in Figures I-1, 2, 3, and 4. The raw waste loads (RWL) associated with each of the continuous process subcategories (A, B, and C) are based on contact process water only. Most continuous processes are able to achieve segregation and do not include noncontact cooling water or steam. Subcategory D includes all water usage associated with the process in that rapid cooling with direct contact is required in the manufacture of dyes.

Basis for Assignment to Subcategories

The subcategorization assigns specific products to specific subcategories according to the manufacturing process by which they are produced. Where more than one process is commercially used to produce a specific chemical, it is possible that the chemical may be listed in more than one subcategory, because the unit operations and chemical conversions associated with different feedstocks may differ drastically in regard to process water usage and associated RWL.

A comprehensive listing of the chemicals and manufacturing processes which have been assigned to each of the four subcategories is provided in Table I-4. This listing includes both the products and processes for which actual RWL data has been obtained, as well as the remaining chemicals and associated processes included under SIC 2815 and 2818.

It is possible to assign products and processes to subcategories based on a knowledge of the aqueous waste sources within a specific process. This was initially done prior to the collection of any quantitative field data, through a knowledge of the specific unit operations and chemical conversions associated with the process. RWL data obtained by field sampling and manufacturers' historical records were then used to confirm the subcategorization and to provide quantitative boundaries. The products and processes covered in Phase I are listed in Table I-5 by subcategory.

The quantity of process water entering the process is normally set by the requirements of chemical conversion. The most common chemical conversions used within the industry were therefore examined and are themselves subcategorized in the tabulation below:

<u>Subcategory A</u>	<u>Subcategory B</u>	<u>Subcategory C</u>	<u>Subcategory D</u>
Acylation	Amination	Alcoholysis	Alkylation
Alkylation	Hydration	Ammonolysis	Amination
Aromatization	Dehydration	Dehydration	Condensation
Friedel-Crafts	Hydrogenation	Esterification	Nitration
Reactions	Dehydrogenation	Hydroformulation	
Halogenation	Oxidation	Hydration	
	Pyrolysis	Neutralization	
		Nitration	
		Oxidation	

Many of these chemical conversions are quite complex. Consequently, they are defined, along with the rationale for their subcategorization, in the Glossary Section (XVI) of this report. It should be noted that many of the more complex processes and batch sequences incorporate several of these chemical conversions.

Water may also enter the process through unit operations which follow the chemical conversions and are required in the separation or final purification of products. Some of these are:

1. Direct-contact quenching.
2. Absorption of gaseous chemicals in water.
3. Scrubbing of less volatile chemicals from a gaseous product stream.
4. Stripping of more volatile chemicals from a product stream (water enters as steam).
5. Vacuum distillation columns and the associated condensate from steam jet ejectors.
6. Washing of chemicals from solid products.

7. Washing or purging process lines and equipment in batch sequence operations.

Water leaves the process through another group of unit operations associated with the physical separation of water from hydrocarbons. Some of these are:

1. Liquid-liquid separation equipment, such as decant drums.
2. Vapor-liquid separation equipment, such as distillation columns or flash chambers.
3. Solid-liquid separation equipment, such as crystallizers and filters.

To be considered within Subcategory A, the unit operations and chemical conversions within a process module must be essentially anhydrous. Contact water usage shall be only in the form of periodic washes or steaming used to treat non-aqueous catalysts or working solvents. The other sources of waste water are from external washing and maintenance operations within the process battery limits. External water sprays utilized to provide cooling on the outside of process pipes are considered as contact process water. Such waste waters generally are contaminated through contact with chemicals present on the ground within the battery limits; consequently, they should be collected and discharged to a process sewer for subsequent treatment.

Subcategory B processes are characterized by unit operations and chemical conversions where the primary contact between water and chemicals is through vapor-liquid interfaces. Although final separation and discharge of water from the process may be as a liquid from a decant drum, contact within the process is normally: 1) through the mixing of steam with hydrocarbon vapors; 2) gaseous chemicals passing counter-currently through an aqueous absorption or quench medium; or 3) steam used to strip more volatile chemicals from liquid hydrocarbon mixtures. In all of these cases, the ultimate concentration of contaminants in the aqueous stream is governed by the specific vapor-liquid equilibria between the aqueous phases and the chemical phases. Hydrocarbon concentrations as total organic carbon (TOC) are generally less than 1 mg/l or 1,000 mg/l in the aqueous streams associated with this type of processing.

The chemical conversions associated with Subcategory C processes are characterized by intimate contact between water and the reaction mixture or catalyst system. Water is used as a reaction medium in many of these systems because both the chemicals and the catalyst are infinitely soluble. The chemical conversions are generally multi-step reactions and generally more complicated than the vapor-phase reactions in Subcategory B. (The Glossary of Chemical Conversions provides specific examples.) The Subcategory C reactions are also generally less selective in

their yield to desired products and subsequently produce more by-products which must be removed from the system.

Typical unit operations involve liquid-solid interfaces where water is used to wash contaminants from solid chemical products. Because of the much larger quantities of chemicals and catalyst present in aqueous solution, most Subcategory C processes utilize many of the same unit operations as in Subcategory B, for the purpose of recovering these materials prior to discharging the water. There is also much more extensive internal recycling of aqueous process streams.

The hydrocarbon concentrations (as TOC) in the process waste waters which are ultimately discharged are in some cases 10-fold those for Subcategory B or approximately 10 g/l or 10,000 mg/l. The amount of contaminants, when expressed on a production basis, is also higher because of the required removal of by-products which are necessarily present in aqueous solutions.

Subcategory D refers to batch processes. These operations are characterized by small production volumes and highly variable mixtures of products. A typical batch dye plant manufactures a wide variety of products at any specific point in time. This product mix itself may change completely on a schedule basis as short as one week. The segregation and characterization of process waste water associated with the production of any one specific dye is not possible, nor is it practical as a basis for establishing effluent limitations. Instead, the total waste water emanating from the batch plant is considered.

It is an economic necessity that equipment be transferred from the making of one chemical to that of another in multi-product batch plants. Although certain items may be used for only one type of chemical conversion, product purity requires that process lines and vessels be purged and cleaned between batches. Water is the most common cleaning solvent used in such applications, both because of the relatively low cost associated with its use and because other organic solvents cannot provide the required removal of contaminants. Wastewater from cleaning is, therefore, a major contributor to the RWL of subcategory D processes.

Additional considerations include the fact that most of the chemical conversions are carried out in aqueous media and are generally much

more complex than those done continuously. The reactions are generally less selective and produce greater quantities of waste by-products. They also frequently require rapid cooling which can be provided only through the direct addition of ice or refrigerated quench water.

Field sampling within subcategory D in Phase I of this study was limited primarily to dye plants. The sampling results indicate that both contaminant loadings and process waste water flows are higher than for continuous processes. Supplementary information

on other batch operations, to be obtained in Phase II, may show that these processes are not subject to all of the waste-generating operations associated with dyes. If this proves to be the case, additional subcategories will be established.

In subsequent sections, separate effluent limitations are established for each subcategory. The process modules within each subcategory generate a certain range of raw waste load, which is characteristic of the subcategory. The effluent limitations are then based on the characteristics and treatability of each subcategory's RWL.

By its very nature, the subcategorization implicitly considers factors such as raw materials, production processes, and products, as well as the quantity and treatability of the wastes generated. Additional factors, (such as plant size or plant age) were examined, but did not justify further subcategorization based on the Phase I coverage.

It should be noted that the intensely competitive nature of this industry requires continual process modification and improvement of product yields. Process modules may in many instances contain chemical conversion steps or unit operations which were not originally part of the process. Also, no definable trend between waste water flow or RWL (on a production basis) and the production rate from a given process module was detected. The only discernible difference appeared to be between low-volume batch and high-volume continuous processes, which had already been divided into separate subcategories.

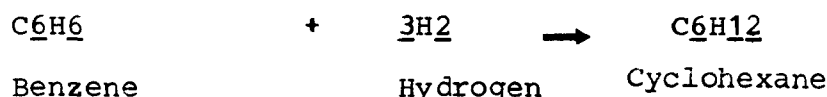
The following pages contain individual profiles of the products and processes studied in Phase I sampling visits. The profiles are grouped according to category. They develop a complete technical and economic picture for each of the processes studied.

SUBCATEGORY A

Product
Cyclohexane

Process
Hydrogenation of Benzene

Cyclohexane can be obtained as a naturally occurring petroleum fraction or through the hydrogenation of benzene. The chemical reaction for the production of cyclohexane from benzene is given below:



The reaction is usually carried out in the liquid phase with a nickelpalladium or platinum catalyst at elevated temperature and pressure. Fresh feed (benzene) is combined with makeup and recycle hydrogen and preheated to reaction temperature by heat exchange first with reactor effluent and then with steam. The reaction effluent is cooled and flashed. Part of the vapor is used as recycle hydrogen, while the forward-flow vent gas is chilled by refrigeration to minimize cyclohexane losses and is available as high-pressure fuel gas. The separated liquid is sent to a column where the light-end impurities are taken overhead.

A flow sheet for this process is shown in Figure IV-1.

The cyclohexane process surveyed utilized a C₆ hydrocarbon feedstock containing a high concentration of benzene. The only contact process waste water associated with the process is a spent caustic wash containing 5-10 wt.% NaOH. The flow raw waste load for this stream is quite low and amounts to only 0.24 gal per 1,000 lb of cyclohexane when expressed on a production basis.

The contact caustic wash was necessary in the operation of this process because of the high sulfur content of the feedstock. This sulfur would reduce the useful life of the precious metal catalyst if it were not removed prior to the hydrogenation reaction. It was not possible, based on this one survey visit, to determine if the sulfur content of the feed was abnormally high and whether or not other cyclohexane units would require this type of caustic treatment of the feed.

The U.S. cyclohexane capacity and estimated economics for cyclohexane are presented in Tables IV-1 and IV-2.

FIGURE IV-1
CYCLOHEXANE

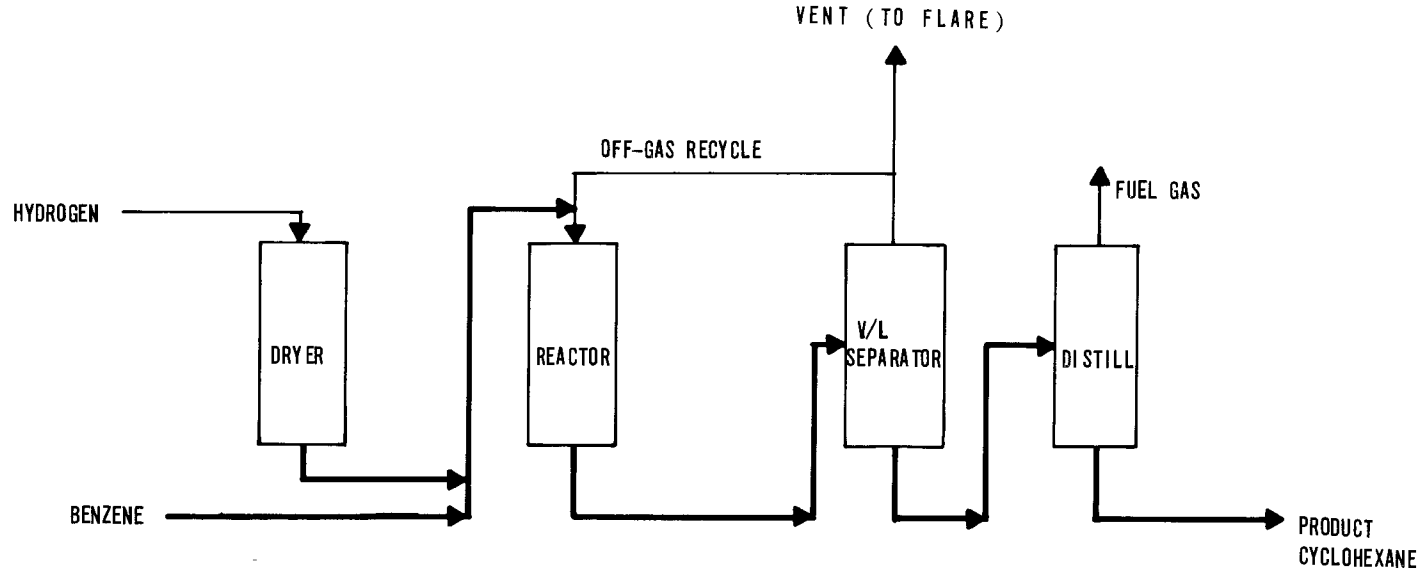


Table IV-1
U.S. Cyclohexane Capacity
(MM gal)

<u>Company</u>	<u>1967¹</u>	<u>1972²</u>	<u>Process</u>
Ashland (Catlettsburg, Ky.)	20	30	Benzene
Arco (Wilmington, Calif.)	15	15	"
Conoco (Lake Charles, La.)	40	shut down	"
(Ponca City, Okla.)	40	shut down	"
Cosden (Big Spring, Texas)	8	8	"
Enjay (Baytown, Texas)	40	40	"
Gulf (Port Arthur, Texas)	33	33	"
Phillips (Borger, Texas)	47	47	Petroleum
(Las Mereas, P.R.)	46	46	Benzene
(Sweeney, Texas)	30	53	Petroleum
Pontiac (Corpus Christi, Texas)	12	12	Benzene
Shell-Corco (Guayanilla Bay, P.R.)	30	30	"
Texaco (Port Arthur, Texas)	40	40	"
Union (Nederland, Texas)	33	33	"
Total ³	434	387	
Total ³ (MM lb)	2,820	2,520	

¹82% based on benzene hydrogenation.

²74% based on benzene hydrogenation.

³6.5 lb/gal.

Source: Oil, Paint & Drug Reporter Profile, Jan, 1, 1969.

Table IV-2
Estimated Economics for Cyclohexane
(100 MM lb. plant)

Total Fixed Capital= \$0.5 MM

Estimated Operation Cost

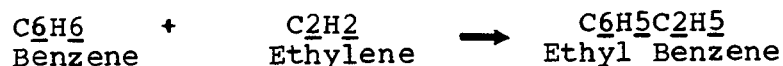
	<u>Cost,</u> <u>¢/lb. cyclohexane</u>
Benzene (at 3.4¢/lb.)	3.15
Hydrogen	0.38
Labor and overhead	0.08
Utilities, catalyst	0.03
Capital charges	<u>0.16</u>
Total	3.80

SUBCATEGORY A

Product
Ethyl benzene

Process
Alkylation of benzene with ethylene

Some ethyl benzene is recovered in refinery fractionation operations, but the majority is manufactured via the alkylation of benzene with ethylene. The alkylation reaction is:



A process flow sheet is shown in Figure IV-2. Ethylene and feed benzene are combined with recycle benzene and polyaromatics, heated to reactor temperature, and introduced to the alkylation reactor. Off-gases from the reactor pass to the scrubbing system. The reactor effluent is passed to the separation section. Unreacted benzene is recycled, ethyl benzene is drawn off as the product, and polyethyl benzenes are recycled or drawn off as waste effluents.

If high purity benzene feedstock is used, the crude product is not required to be washed with caustic solution and water. However, the plant visited during the survey employs a feedstock containing some organic contaminants, and washing is necessary before the crude product is sent to the separation step. The washing step also removes any traces of the BF_3 promoter.

The major waste streams of this process are the spent caustic and washing streams used to wash the crude alkylate. Significant amounts of tars, benzene, ethyl benzene and other polymers will be found in these streams. Heavy aromatics fractions from the separation column are disposed of by incineration.

The data obtained from the plant survey are summarized in the following tabulation:

Flow	37.7 gallons/1,000 lb
COD	5,980 mg/l 1.88 lb/1,000 lb
BOD ₅	433 mg/l 0.136 lb/1,000 lb
TOC	2,091 mg/l 0.66 lb/1,000 lb

Ethyl benzene was recategorized under Subcategory B1 since the washing step is considered a common industry practice.

The alternate route in manufacture of ethyl benzene is a liquid-phase reaction using aluminum chloride catalyst. The process requires much more extensive washing to remove highly acidic aluminum chloride catalyst. It is usually employed in

combination with an ethyl benzene dehydrogenation step to produce styrene. The U.S. ethyl benzene capacity is shown in Table IV-3.

FIGURE IV-2
ETHYLBENZENE

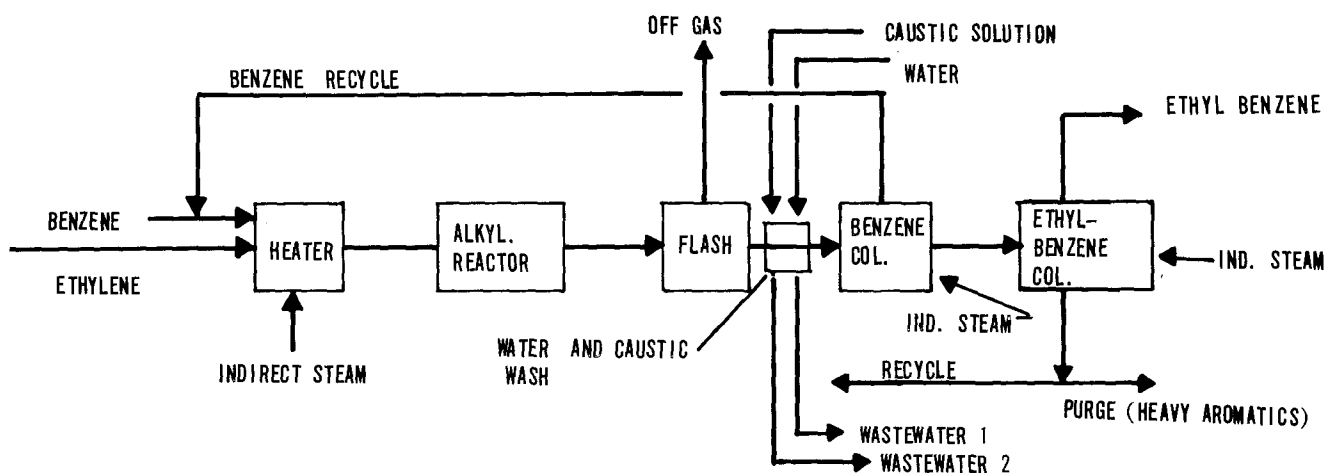


Table IV-3

U.S. Ethyl Benzene Capacity

<u>Producer</u>	<u>Plant Location</u>	<u>Estimated Mid-1970 Capacity**</u>	
		<u>Alkylation</u>	<u>Recovery</u>
Amoco	Texas City, Texas	950	-
Coastal States	Corpus Christi, Texas	-	35
Corco	Penuelas, P.R.	-	100
Cosden	Big Springs, Texas	110	25
Cos-Mar	Carville, La.	650	-
Dow	Freeport, Texas	750	-
	Midland, Michigan	450	-
El Paso	Odessa, Texas	200	-
Enjay	Baytown, Texas	175	70
Foster Grant	Baton Rouge, La.	800	-
Monsanto	Alvin, Texas	-	50
	Texas City, Texas	900	-
Shell	Torrance, California	280	-
Signal	Houston, Texas	-	35
Sinclair-Koppers	Houston, Texas	-	100
	Corpus Christi, Texas	85	30
Sun	Port Arthur, Texas	550	-
Tenneco	Chalmette, La.	-	20
UCC	Institute, W.Va.*	130*	-
	Seadrift, Texas	<u>350</u>	<u>-</u>
TOTAL		6,250	465

* Plant not currently operating but not dismantled.

Not included in total.

** MM lbs/yr.

SUBCATEGORY A

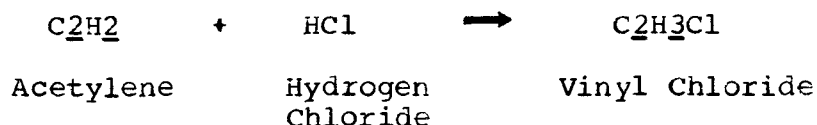
Product

Vinyl Chloride

Process

Acetylene and HCl

The classical acetylene addition reaction proceeds in the vapor phase with high-purity acetylene and anhydrous hydrogen chloride as reactants. The chemical reaction is given below:



A process flow sheet is shown in Figure IV-3. The feed stocks, acetylene and anhydrous hydrogen chloride, are fed into tubular reactors which are packed with mercuric chloride impregnated on granular activated carbon. The reactor effluent is sent to a three column distillation system for purification, and purified vinyl chloride is taken as bottoms of the last column.

Because no water comes into direct contact with the reactants and products and no reaction water is generated, there is no direct-contact process waste water. However, in the plant visited a "Mercury Treatment System" is associated with this process. This system is used for treating rainfall (which picks up traces of mercuric salts on the surface of the concrete pads and equipment) and periodic distillation column and reactor cleanouts. It is also used to treat the water from surface sprays which cool the outsides of process lines within the process battery limits.

Based on flow measurements and sampling of these waste waters, the following RWL was calculated:

Flow RWL (gal/1,000 lb)	240
COD RWL (lb/1,000 lb)	3.7

The waste water is collected by a segregated sewer and is pumped into one of two alternate storage tanks. When the storage tank is full, sodium sulfide is added to precipitate mercuric sulfide. Two activated carbon columns, connected in series, are used to polish the filtrate.

The Mercury Treatment System is a batch operation. The effluent from the activated carbon column is totally recycled to the storage tank until the mercuric concentration has been decreased to approximately 0.5 micrograms/l. The mercury sludge from the filter press as well as saturated activated carbon is placed in drums and buried or removed by a contractor who recovers mercury.

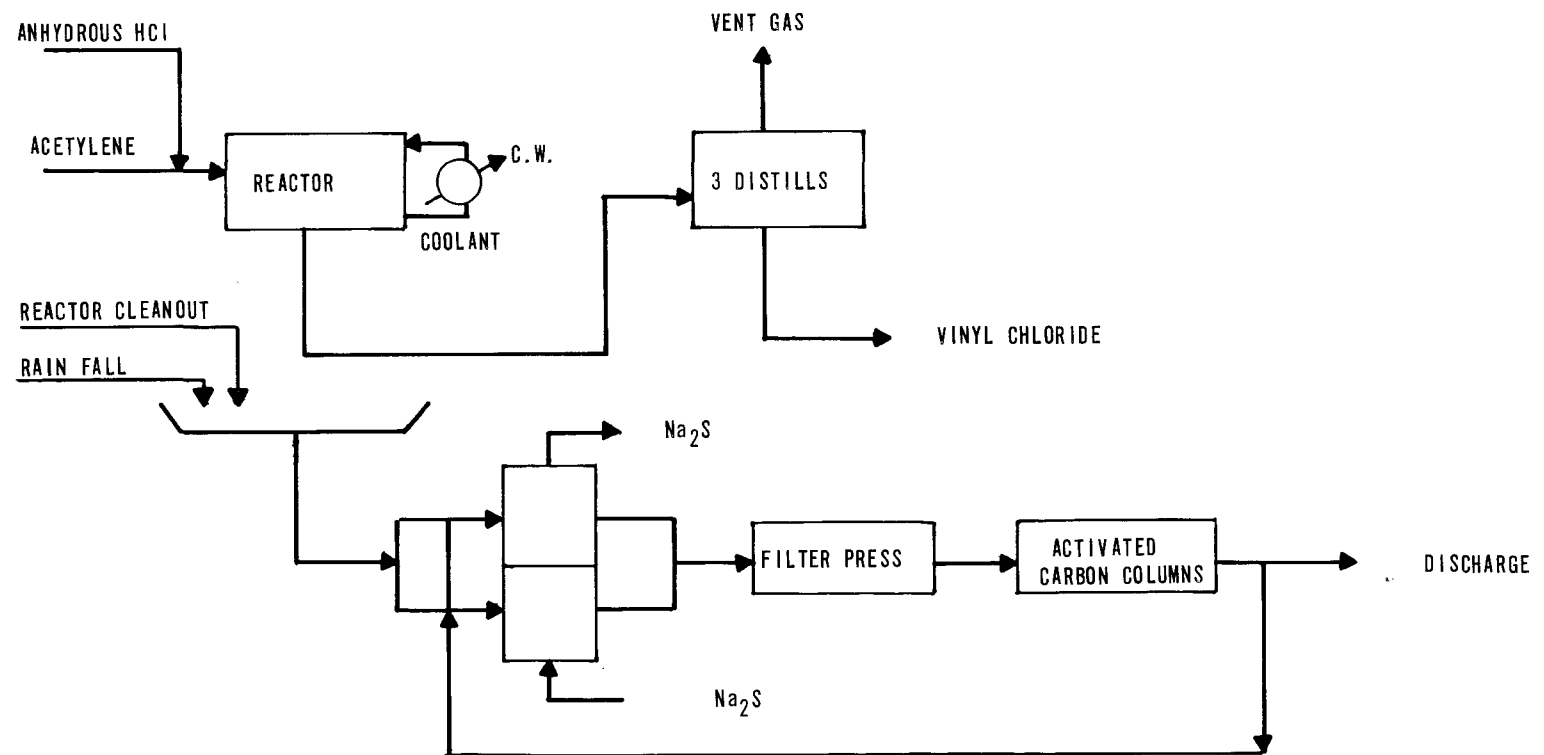
The analytical results for a single batch are presented below:

<u>Before</u> <u>Treatment</u>	<u>After</u> <u>Treatment</u>
-----------------------------------	----------------------------------

COD (mg/l)	1,836	1,306
TOC (mg/l)	448	33
SS (mg/l)	1,124	24
Hg (micro-grams/l)	2,600	4.1

A more recent process for manufacture of vinyl chloride is by the route of thermal cracking of ethylene dichloride. This process will be discussed in Subcategory B.

FIGURE IV - 3
VINYL CHLORIDE, ACETYLENE ADDITION
WITH ANHYDROUS HYDROGEN CHLORIDE



SUBCATEGORY A

<u>Product</u>	<u>Process</u>
Benzene, Toluene and Xylene (BTX) Aromatics	1. Hydrogenation Pyrolysis Gasoline from Ethylene Manufacture 2. Solvent Extraction

A mixture of BTX aromatics and saturates may be obtained as a by-product of ethylene manufacturing (by pyrolysis of naphtha feedstocks). This mixture must first be stabilized by hydrotreating prior to the recovery of BTX aromatics by solvent extraction.

Two-Stage Hydrolysis Gasoline Hydrotreater

The first stage hydrotreating of pyrolysis gasoline differs from convention hydrotreating of virgin stocks in that the feedstock is difficult to handle and cannot be heated to the 500-700°F temperatures needed for conventional hydrotreating. Water injection is not required and the process itself should be non-polluting. In the low temperature processes, diolefins and other reactive compounds are hydrogenated to yield a product which can be stored or handled in conventional refinery and petrochemical processing.

The second stage hydrotreater is similar to the conventional refinery hydroterater with a colbalt/moly catalyst. Under certain conditions it may be necessary to prefractionate the feed to these processes as heavy polymers can rapidly deactivate catalyst. Frequently steam stripping, or steam injection with the fractionator feed is used in these operations. The condensate must then be disposed of.

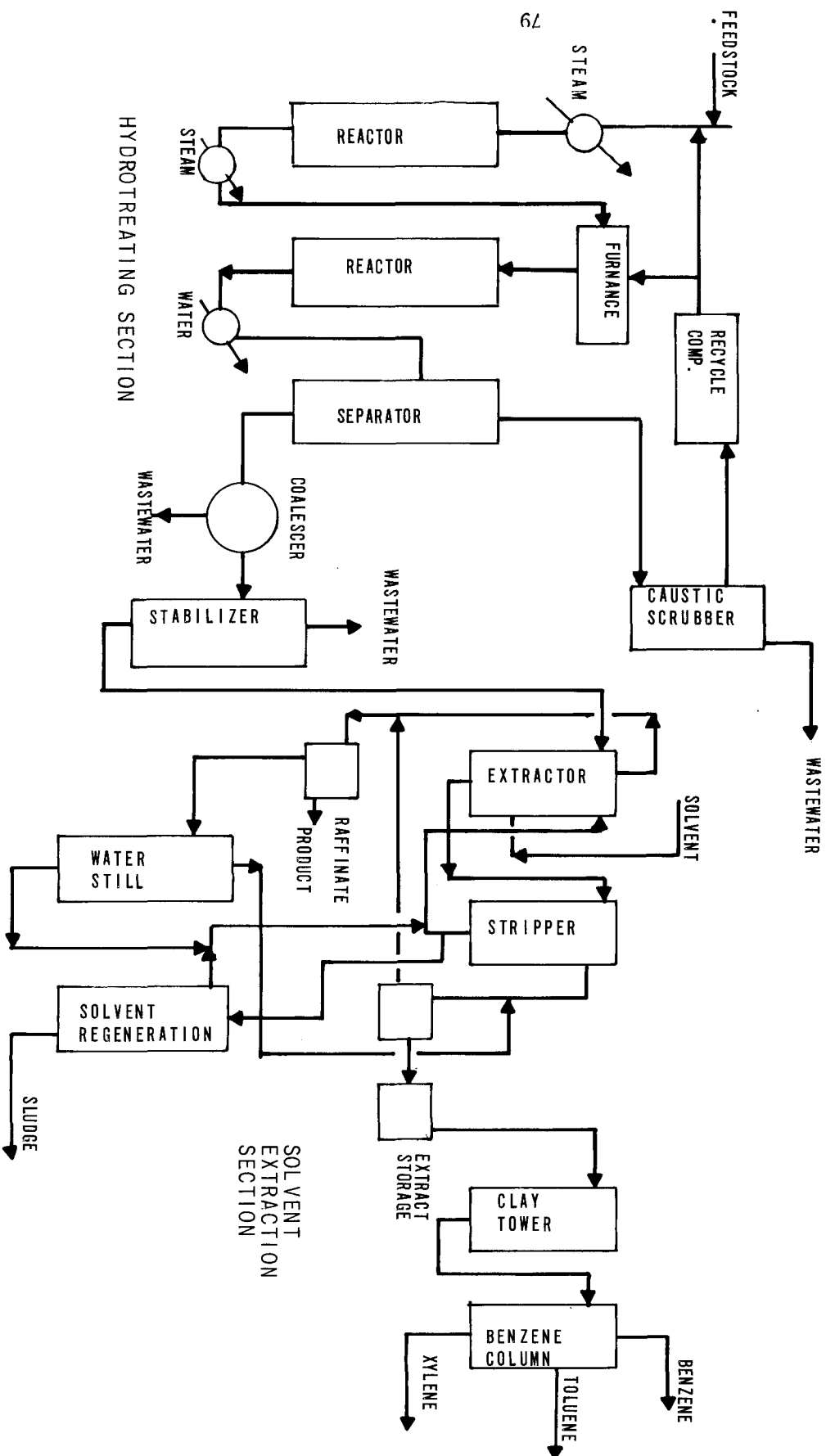
The catalysts used for the first stage hydrotreating operation contain either nickel or a noble metal. They require more frequent regeneration than most refinery catalysts. Once in about four months may be a reasonable number. The steam-air decoking may result in an air pollution problem.

Some plants contain a provision to inject water to wash out ammonium bisulfite salts which might be formed in the reaction. In this case, a coalescer, or water separator, would be used to separate this water. This operation would only be performed intermittently, and would not be a major source of waste water.

A flow diagram for the pyrolysis gasoline hydrotreater is shown in Figure IV-4. The feedstock and recycled hydrogen gas are preheated and passed through a series of hydrotreating reactors containing platinum catalyst. The reactor effluent is cooled and then discharged into a separator, where the gas stream taken overhead is recycled back to the reactor after being scrubbed with caustic solution. The liquid phase from the reactor is passed through a coalescer (where water is used to trap coke

FIGURE IV - 4

BTX PRODUCED BY HYDROTREATING PYROLYSIS GASOLINE WITH SUBSEQUENT SOLVENT EXTRACTION



particles formed in the pyrolysis reactor) and a stabilizer (where light hydrocarbons are removed).

They survey data obtained from a plant with pyrolysis gasoline as feedstock are shown in the following tabulation. The data presented can be considered as the standard for all levels of control technology of this process.

Flow	13.6 gal/1,000 lb
COD	2,755 mg/l 0.31 lb/1,000 lb
BOD ₅	914 mg/l 0.104 lb/1,000 lb
TOC	306 mg/l 0.034 lb/1,000 lb

As shown in Figure IV-3 the only sources of waste water are in the hydrotreating section of the process.

BTX Extraction

The stabilized liquid is then extracted with a solvent (di- and tri-ethylene glycol) to recover the aromatics, and the raffinate (containing paraffins) is sent to a cracking furnace to produce olefins. The dissolved aromatics (BTX) are separated from the solvent by distillation, and the solvent-free aromatics are water washed and then separated into the individual components: benzene, toluene, and xylene. The separated solvent regenerated and recycled to the process, while the sludge produced is disposed by landfill. There are many solvents that will extract aromatics from naphthas at high recoveries and purities, but for many reasons only a few are used commercially. In recent years, several refiners have switched from di- and tri-ethylene glycol to tetra ethylene glycol. A change to tetra ethylene glycol can usually be achieved with minor equipment modifications and no change in royalty status. The most recent development shows that sulfolene has established itself in the U.S. as the preferred solvent for BTX extraction. Although the results and economics of using sulfolene have not been published, it is known that drastic changes in process conditions and a relatively high solvent cost cause a large capital investment for this solvent change. The sulfolene system differs from other solvent systems in that the solvent regeneration is under vacuum. If steam ejectors with barometric condenser are used to produce the vacuum, the resultant oily water will be a significant water pollution source. Therefore, BPCTCA and BATEA levels of control technology for the sulfolene system will require vacuum pumps with surface condensers to produce vacuum for process needs, and the resulting oily stream should be disposed of by incineration.

The U.S. capacity for Benzene and Toluene is presented in Table IV-4.

Table IV-4

U.S. Benzene and Toluene Capacity

<u>Producer</u>	<u>Location</u>	Benzene and toluene capacity, 1965 MM lbs/yr		
		Benzene from petroleum		Toluene
		Extraction	Dealkylation	
Allied	Winnie, Texas	30.0		
Amoco	Texas City, Texas	110.0		145.0
Ashland	Buffalo, N.Y.	75.0		60.0
	Catlettsburg, Ky.	100.0	45.0	80.0
Atlas Processing	Shreveport, La.	75.0		
Conoco	Lake Charles, La.	45.0		
	Ponca City, Okla.	45.0		
Cosden	Big Spring, Texas	65.0	110.0	110.0
Crown Central	Houston, Texas	45.0	95.0	70.0
Dow	Bay City, Mich.		145.0	125.0
	Freeport, Texas		220.0	
Enjay	Baton Rouge, La.	175.0		110.0
	Baytown, Texas	180.0	220.0	360.0
Gulf	Philadelphia, Pa.	110.0	90.0	110.0
	Port Arthur, Texas	230.0		35.0
Hess	Corpus Christi, Texas	220.0		130.0
Leonard	Mount Pleasant, Mich.		20.0	25.0
Marathon	Detroit, Mich.	55.0*		120.0*
	Texas City, Texas	45.0		85.0
Monsanto	Alvin, Texas	250.0	185.0	230.0
Phillips	Sweeney, Texas	160.0		
Pontiac	Corpus Christi, Texas	65.0		95.0
Richfield	Wilmington, Calif.	130.0		175.0
Shell	Houston, Texas	220.0		220.0
	Odessa, Texas	35.0	110.0	70.0
	Wilmington, Calif.	110.0		70.0
	Wood River, Calif.	220.0		110.0
Signal	Houston, Texas	20.0	140.0	110.0
Sinclair	Houston, Texas			145.0
	Marcus Hook, Pa.			45.0
Socony-Mobil	Beaumont, Texas	220.0		180.0
South Hampton	Silsbee, Texas		45.0	45.0
Standard (Calif.)	El Segundo, Calif.	180.0		175.0
	Richmond, Calif.	70.0		60.0
Sun	Marcus Hook, Pa.	110.0		180.0
Sunray-DX	Tulsa, Okla.	80.0	90.0	30.0
Suntide	Corpus Christi, Texas	70.0	110.0	95.0
Tenneco	Chalmette, La.	110.0		60.0
Texaco	Port Arthur, Texas	220.0		145.0
Union-Atlantic	Nederland, Texas	130.0		145.0
Union Carbide	S. Charleston, W. Va.	75.0		70.0
Union Oil	Lemont, Ill.	160.0		70.0
Vickers	Potwin, Kans.	20.0		35.0
Subtotals		4,340.0	1,625.0	4,125.0
Total from petroleum		5,965.0		4,125.0
Total from coal		130.0		50.0
Grand Total		6,095.0		4,175.0

Source: Based on Oil, Paint & Drug Reporter, June 14, 1965; Hydrocarbon Processing, February 1966.

*Toluene and benzene shipped as a blend to Dow at Bay City, Mich., and finally processed there.

SUBCATEGORY A

Product

BTX Aromatics

Process

Solvent Extraction from Reformate

Alternately, solvent extraction may be employed on C₆-C₈ reformate cuts to extract aromatics from low octane paraffins. The raffinate could be fed to synthetic natural gas (SNG) generation or a petrochemical facility or, alternately, recycled to the catalytic reformer. The extraction unit here might be of different design than a unit for chemical production in that high purities and recoveries are not required.

As the refinery picture is complex, similarly it is difficult to predict the growth of extraction processes.

Sulfolene, or other solvent, become a loss in three ways which affect waste disposal:

1. Solvent degradation - Units have provision for solvent regeneration but periodically heavy materials must be purged.
2. Losses to products due to incomplete water wash.
3. Leaks

A recent estimate in a sulfolene unit was that 30 lb of sulfolene make-up were required for 1,000,000 lbs of feed. Published information on Udex operation indicated losses about three times as great. (For Udex, .03lb/barrel of feed, Oil and Grease Journal 5/7/62.) These then represent the material, either as solvent, or degradation products, which can go to waste streams.

It appears that sulfolane has established itself in the U.S. as the preferred solvent for BTX extraction. A recent article (Hydrocarbon Processing, 3/73) advocates diglycloamine as a superior solvent. It would require major design revisions to convert a Udex Unit to sulfolane operation. The article apparently concedes that sulfolane is preferred for completely new installations.

The sulfolane system differs from other solvents in that the solvent regeneration is under vacuum. In a 1000 BPSD feed plant, about 5,000lb/hr of 100lb steam might be required to maintain the necessary vacuum for one design, and this quantity of oily condensate must be disposed of. If surface condensing is not used, but barometric condensers used, the quantity of oily water to be disposed of increases by a factor of 10-50 (water required to condense the steam).

It is difficult to project the future requirements for new solvent extraction units. With high severity reforming required for low-lead or no-lead gasoline, there should be ample benzene in reformate so that there should be no need to extract toluene for conversion to benzene. Furthermore, for other chemical

purposes toluene requirements are small and consequently toluene will be left in the gasoline pool. In high severity reforming the C8 aromatic fraction contains very little paraffins and paraxylene can be produced by crystallization without solvent extraction. With this argument, solvent extraction will only be used on reformat for benzene where the solvent/feed requirements are minimal. Consequently, existing facilities may be adequate and no new units may be required for refineries.

RWL data for the UDEX solvent extraction process are summarized below:

Flow RWL (gal/1,000 lb BTX extract):	60.4
TOC RWL (lbs/1,000 lb BTX extract):	0.144

The U.S. xylenes producers are shown in Table IV-5.

Table IV-5

U.S. Xylene Capacity
(MM gallons/year)

Producer	Plant Location	Source	Estimated Capacity*
Ashland	Catlettsburg, Ky.	a	35
	Buffalo, N.Y.	a	10
Atlantic Richfield	Houston, Texas	a,c	60
British Petroleum	Marcus Hook, Pa.	a	30
Chevron Chemical	El Segundo, Calif.	a	23
	Richmond, Calif.	a	49
Cities Service	Lake Charles, La.	a	72
Coastal States	Corpus Christi, Texas	a	24
Commonwealth	Guayanilla Bay, P.R.	a,b	79
Cosden Oil	Big Spring, Texas	a	18
Crown Central	Houston, Texas	a	10
Enjay Chemical	Baton Rouge, La.	a,b	41
	Baytown, Texas	a	50
Hess Oil	Corpus Christi, Texas	a	30
Leonard Refineries	Mt. Pleasant, Mich.	a	3
Marathon Oil	Detroit, Mich.	a	15
	Texas City, Texas	a	14
Mobil	Beaumont, Texas	a,b	41
Monsanto	Chocolate Bayou, Texas	b	41
Phillips	Guayamas, P.R.	a	55
Pontiac Refining Co.	Corpus Christi, Texas	a	18
Shell Chemical	Houston, Texas	a	70
Signal Oil and Gas	Houston, Texas	a	22
Southwestern Oil	Corpus Christi, Texas	a	18
Standard Oil (Indiana)	Texas City, Texas	a	124
Sun Oil	Marcus Hook, Pa.	a	30
	Corpus Christi, Texas	a	35
Tenneco, Inc.	Chalmette, La.	a	50
Union Oil Co.	Lemont, Ill.	a	39
Union Oil/Arco	Nederland, Texas	a	46
Union Carbide	Ponce, P.R.	b	<u>73</u>
TOTAL			1,225

*From reformat and pyrolysis gasoline.

Does not include coke oven operations.

a = Reformate

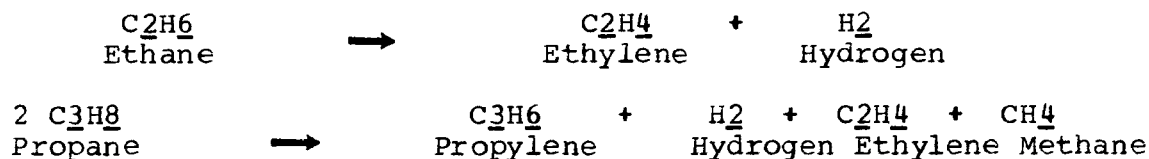
b = Pyrolysis gasoline

c = Toluene Disproportionation

SUBCATEGORY B

<u>Product</u>	<u>Process</u>
Ethylene and Propylene	Pyrolysis of Hydrocarbons

Ethylene and propylene are produced primarily by the pyrolysis of saturated hydrocarbons. In the U.S., ethane and propane currently predominate as feedstock material. The chemical reactions for their pyrolysis are given below:



A process flow sheet is shown in Figure IV-5. The hydrocarbon feedstock is diluted with steam and passed through a pyrolysis furnace, where cracking takes place. Normal temperatures in the cracking section of the furnace are 1,500 to 1,600 F, and residence time is one second or less. The purpose of steam dilution is to depress any coking tendency within the furnace tubes.

In order that only the desired degree of cracking be obtained, the hot reactor effluent gases are cooled rapidly to a temperature which will quench the cracking reaction. Consequently, the cracked gases are cooled in a variety of ways, but usually at some point by direct contact with water in the quench tower.

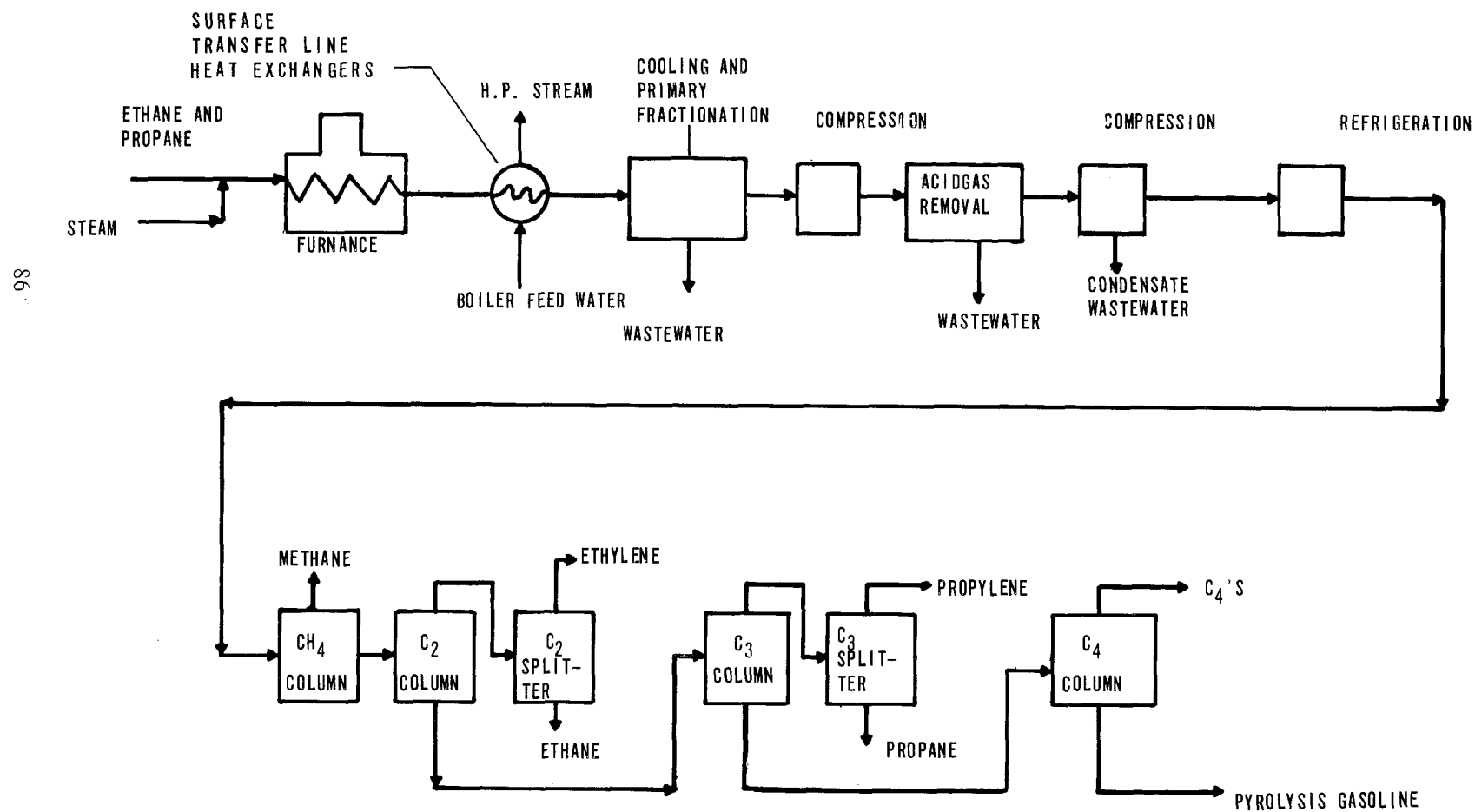
After quenching, the cracked gases are compressed prior to treatment for removal of the contained acidic gases (CO_2 and H_2S). The acid gases are usually absorbed by some combination of systems using monoethanol amine (MEA), caustic, and water. The purified gas stream is then dried and further compressed before fractionation.

After compression, the dried, cracked gas is cooled to cryogenic temperatures, and hydrogen is flashed off and sent either to additional purification facilities or burned as fuel. The dehydrogenated stream flows to the demethanizer, where overhead methane is sent to fuel, and the C_2 +bottoms flow, under pressure, to the de-ethanizer.

At the de-ethanizer the C_3 and heavier materials are taken off as a bottoms stream and are sent to the de-propanizer. The de-ethanizer overhead is selectively hydrogenated in the light acetylene converter, in order to remove trace amounts of acetylene; this stream then goes to the C_2 splitter, where the ethylene and ethane are separated. Ethane is recycled to the cracking furnace, and the overhead from the splitter is the product ethylene and is sent to storage.

FIGURE IV-5

ETHYLENE, PROPYLENE- PYROLYSIS OF HYDROCARBONS



The C₄ + depropanizer bottoms are sent to the debutanizer, and the overhead is selectively hydrogenated in the heavy acetylene splitter in order to remove trace amounts of methyl acetylene and propadiene. The de-propanizer overhead goes to the C₃ splitter where the propane and propylene are separated. The final tower in the fractionation train is the debutanizer, where various C₄ compounds are separated from the dripolene or pyrolysis gasoline fraction. The C₅ and heavier materials may be rejected as waste or may be used as a source of aromatics. U.S. ethylene capacity is shown in Table IV-6.

The major areas of water usage in the cracking process relate to dilution steam requirements and the contact quench waters required in the cooling and primary separation of the cracked gas products.

Pressure and hydrocarbon partial pressure are extremely important variables in the design and operation of ethylene plants. From an ethylene yield viewpoint, it is best to minimize pressure, or more specifically, hydrocarbon partial pressure. Low pressure is an economic problem since it increases the compression requirements following reaction. Instead of running the reaction at low pressure, steam is used as a diluent to reduce the hydrocarbon partial pressure. The steam also serves as a heating the cold feed.

For each feed there is an economic optimum of pressure and steam rate as they affect investments, operating costs and product yields. Typical weight ratios of steam to hydrocarbon feed are as follows: gas feeds - 0.3; naphtha feeds - 0.5; gas oil feeds - 0.7.

After cooling in the surface transfer line heat exchangers, the pyrolysis furnace effluent must be cooled further to a temperature suitable for economic compression. This cooling is generally carried out in a tray tower of more than one section. In addition to cooling the gases, heavy ends present in the furnace effluent must be scrubbed out. Because the quantity of heavy ends is very different when cracking gasoil, naphtha or ethane and propane, the tower design and function is different for each case.

In a plant where ethane or propane is cracked, the pyrolysis effluent contains very little hydrocarbon material that will condense at atmospheric conditions. Thus, when the gas is cooled to compressor suction conditions, only water and trace quantities of hydrocarbons condense. However, it is important that the hydrocarbon be removed from the gas since it is a tarry material that will foul the downstream processing equipment. The plant includes a sketch of a typical quench tower system for an ethane-propane plant. The hot gases enter the tower at the bottom and pass up through a baffled section passing through curtains of downflowing water. The gas is cooled to approximately 200 F (93.5 C) in the baffled section, and then passes to a tray section where cooling to approximately 105°F (40°C) takes place, the

Table IV-6

U.S. Ethylene Capacity (1972)

<u>Company</u>	<u>Feedstock</u>	<u>MM lb</u>
Allied Chemical (Geismar, La.)	ethane-propane	500
Arco (Wilmington, Calif.)	refinery gas	100
Chemplex (Clinton, La.)	ethane-propane	500
Cities Service (Lake Charles, La.)	propane	1,000
Conoco (Lake Charles , La).	ethane-propane	500
Corco (Penueles, P. R.)	naphtha	1,000
Dow (Bay City, Michigan)	naphtha	170
(Freeport, Tx.)	ethane-propane	1,400
(Plaquemine, La.)	ethane-propane	600
DuPont (Orange, Tx.)	ethane-propane	750
Eastman (Longview, Tx.)	ethane-propane	450
El Paso (Odessa, Tx.)	ethane-propane	400
Enjay (Batone Rouge, La.)	ethane, gas oil & naphtha	1,000
(Baytown, Tx.)	refinery gas	85
(Bayway, N. J.)	refinery gas	175
Goodrich (Calvert City, Ky.)	propane	250
Gulf (Cedar Bayou, Tx.)	propane	400
(Port Arthur, Tx.)	refinery gas & propane	1,000
Jefferson Chemical (Port Neches, Tx.)	refinery gas, ethane & propane	500
Mobil (Beaumont, Tx.)	refinery gas & naphtha	500
Monsanto (Alvin, Tx.)	refinery gas	600
(Texas City, Tx.)	refinery gas	100
National Distillers (Tuscola, Ill.)	ethane-propane	350
Northern Petrochemicals (Joliet, Ill.)	ethane-propane	800
Olin (Brandenberg, Ky.)	ethane	90
Phillips (Sweeny, Tx.)	ethane-propane & refinery gas	600
Phillips-Houston (Sweeny, Tx.)	ethane-propane	500
Shell (Deer Park, Tx.)	propane & refinery gas	1,200
(Norco, La.)	ethane-propane & refinery gas	500
(Torrance, Calif.)	propane	70
Sinclair-Koppers (Houston, Tx.)	ethane-propane & refinery gas	500
Sun Olin (Claymont, Delaware)	refinery gas	220
Union Carbide (Institute, W. Va.)	ethane-propane	350
(Ponce, P.R.)	refinery gas & naphtha	1,000
(Seadrift, Tx.)	ethane-propane	900
(S. Charleston, W.Va.)	ethane-propane	400
(Taft, La.)	ethane-propane & naphtha	1,000
(Texas City, Tx.)	ethane-propane	750
(Torrance, Calif.)	refinery gas	150
(Whiting, Ind.)	refinery gas	270
		<u>21,630</u>

Source: Informations Chiemie, May, 1970 p. 157

exact temperature being a function of the available cooling water temperature. Fractionation

between the heavy materials and the gasoline and lighter overhead also takes place in this trayed section. Heat is recovered in two stages so that maximum use is made of the heat in the gas. A larger settling drum is required to provide the separation between water, oil and tar.

In a plant where naphtha is being cracked, significant quantities of fuel oil are produced which can be separated into the quench tower, frequently termed the primary fractionator. There are a number of different designs for this area. One common design is a combination oil and water tower which eliminates overhead condensers and their attendant pressure drop ahead of the compressors. The lower section is a fractionator refluxed with cracked gasoline distillate which knocks down any fuel that might otherwise flow up the tower with the cracked gas. The upper section is a water wash tower or spray condenser, where raw gasoline and dilution steam are condensed. The gasoline and water mixture is withdrawn from the bottom of this section as reflux while the net production goes to a distillate stripper before delivery to battery limits as raw product. The wash water can be used for certain low level heating services such as de-ethanizer and propylene splitter reboiling before returning to the top section of the tower.

Gas oil cracking requires yet another type of design due to the very much larger quantity of gasoline and heavier material. The design of this tower begins to approach the design of crude oil distillation column. There are many possible designs for this, depending upon the products required. The lower sections of the primary fractionator constitute distillation similar to a crude column, while the top sections are water wash sections. The bottoms from the fractionator are shown going to a vacuum flash tower to produce an additional vacuum distillate; this additional product would normally be required only when cracking heavy gasoils and when the fuel oil product is substantial.

The major waste water sources in the cracking process are draw-offs from the water quench tower and the scrubber for removal of acid gases. Other possible sources are the water draw-offs from compressor interstages. The data obtained from the sampling program are summarized in the following tabulation.

<u>Plant No.</u>	<u>Flow</u> gal/1,000 lb	<u>COD</u> lb/1,000 lb (mg/l)	<u>BOD5</u> lb/1,000 lb (mg/l)	<u>TOC</u> lb/1,000 lb (mg/l)
1	364	1.75 (533)	0.39 (130)	0.48 (259)
2	150	2.29 (1,827)	0.35 (279)	2.02 (1,617)

3	554	3.16 (684)	0.88 (189)	1.12 (242)
4	52.5	0.66 (1,502)	0.088 (200)	0.43 (980)
5		N.A.	N.A.	N.A.
6	145	6.16 (5,110)	0.32 (265)	2.14 (1,770)
7	167	0.65 (467)	0.27 (192)	0.75 (538)

Historical RWL data were also collected wherever they were available, and were subjected to analysis for probability of occurrence. The following tabulation presents the results of the analysis.

<u>Plant</u>	<u>Occurrence</u>	<u>Flow</u> gal/1,000 lb	<u>COD</u> lb/1,000 lb	<u>TOC</u> lb/1,000 lb
Plant 3	10%	N.A.	1.6	0.6
	50%	N.A.	4.0	1.05
	90%	N.A.	6.4	1.51
Plant 5	10%	305	0.40	N.A.
	50%	410	1.98	N.A.
	90%	515	3.60	N.A.

The probability analysis for Plant 5 covered monthly average data for a period of 12 months; for Plant 3 it covered seven random daily samples for a period of 3 months. For the other plants there was not sufficient historical data for a full statistical analysis and comparison of the sampling data of all the plants.

Review of the available data reveals significant variations of RWL among the plants. The volume of wastewater per unit of product varies dependent primarily on the extent of scrubber water. At some plants, the use of steam strippers facilitates the reuse of quench water and minimizes the loss of hydrocarbons, thus generating a lower RWL; the organic loading in the wastewater is also affected by the performance of the quench towers and scrubbers. Higher RWL's in some cases are the result of contaminants in the feedstock.

The noncontact steam used in an ethylene plant is generated from extremely pure water because of the high pressure conditions. Most of this steam is recovered as condensate and returned to the boilers. A large quantity of steam, however, is used to contact dilution steam in the cracking reaction. When this steam is condensed from the process gases it is recovered as a fouled condensate and is not suitable for use as boiler feed water or

any other purpose. In some locations, even disposal of this steam is a problem.

Most of the boiler feed water make-up in an ethylene unit is required to replace this condensed material. Since the boiler feed water make-up must be suitable for high pressure steam generation, the net result is the extremely pure water is degraded to fouled condensate. As plants have increased in size and steam pressures have increased, the differential cost in boiler feed water treating has become significant and directed consideration to recovery of this water. The obvious recovery method is to generate steam that is suitable for use as dilution in the cracking furnaces. This steam is required at 100-150 pounds per square inch gauge pressure (psig) and the water quality is not critical as in the case of high pressure steam. By removing the dilution steam requirement from the main steam system, the high pressure steam system becomes a closed loop and the only losses are to leaks and blowdown.

The principles of recovery of the condensed dilution steam for reuse are simple. In order for the condensed material to be used as feed water for a vaporization system, it must be stripped of oils which would rapidly foul an exchanger used to vaporize this water. Then, since the water contains solids that must be purged from the system, heavy blowdown from the vaporizer is required to remove these solids. A well designed water system permits recovery of 90 percent of the steam used in hydrocarbon dilution and reduces the overall boiler feed water make-up requirements to less than 20 percent of the requirements without a clean-up system. Unless boiler feed water make-up is inexpensive because of existing high purity treating facilities, water clean-up is an economic addition to a new plant and is always included.

Since 1967, ethylene plants have incorporated the use of steam condensate strippers in order to reuse waste water effluent and minimize hydrocarbon effluent in waste waters.

These facilities will generally require the use of a steam stripper and steam dilution. In addition, 2 pumps, and a steam reboiler are required. Investments for these facilities for a 5×10^6 lb/yr gas cracker are shown in Table IV-7 as \$240,000. Figures IV-6 and IV-7 are process flowsheets for quench tower loops without and with a condensate stripper.

The increment operating costs are shown in Table IV-8. On ethylene product, it represents an increase of about .01¢ and on the waste water reduction it represents .15¢/U.S. gal of water saved.

The water draw-off from compressor interstages could be combined with the condensate stripping operation since it would only increase the quantity of water handled by about 20-25 percent without incurring any other handling problems. This water would probably be returned to the quench tower for re-processing.

Table IV-7

Investment for Condensate Stripping*

I. Process Water Stripper 4' & 8' I.D. x 39' High Including:	
12 - Trays	
1 - 240 GPM Pump	
1 - 250 GPM Pump	
1 - Filter	
Instruments, Piping, Foundations, etc.	\$160,000
II. Dilution Steam Drum 7' I.D. x 20' High Including:	
2 Heat Exchangers	
Instruments, Piping, Foundations	<u>\$ 80,000</u>
TOTAL	<u><u>\$240,000</u></u>

*For a 500 MM lb/yr ethylene plant using C₂/C₃ feed,
totally installed, U.S. Gulf Coast location,³ 1973.

FIGURE IV-6
WATER QUENCH WITHOUT CONDENSATE STRIPPER
(500MM LB./YR. ETHYLENE PLANT WITH C₂/C FEEDSTOCK)

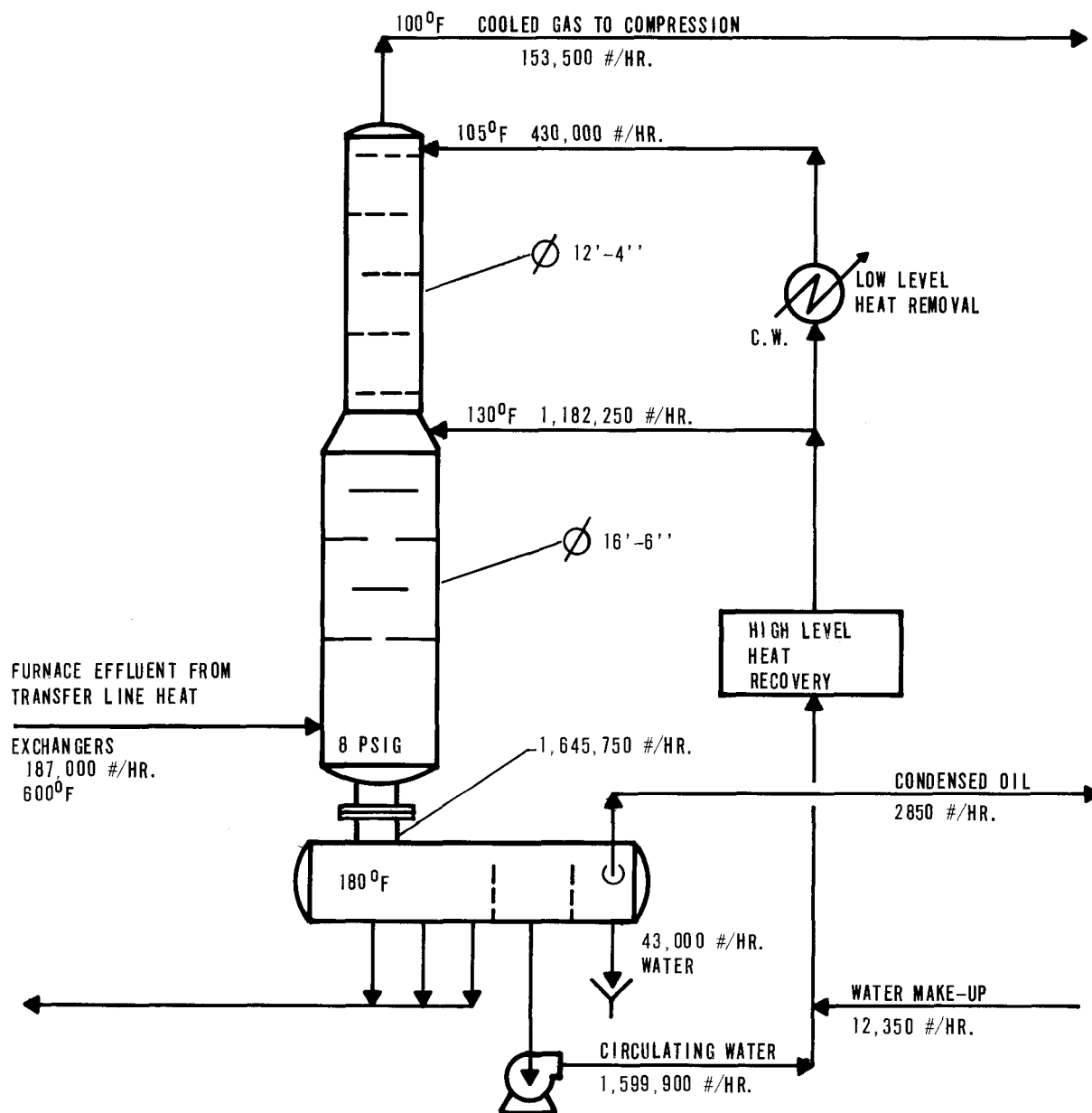


FIGURE IV-7
WATER QUENCH WITH CONDENSATE STRIPPER
(500 MM LB./YR. ETHYLENE PLANT WITH C₂/C₃ FEEDSTOCK)

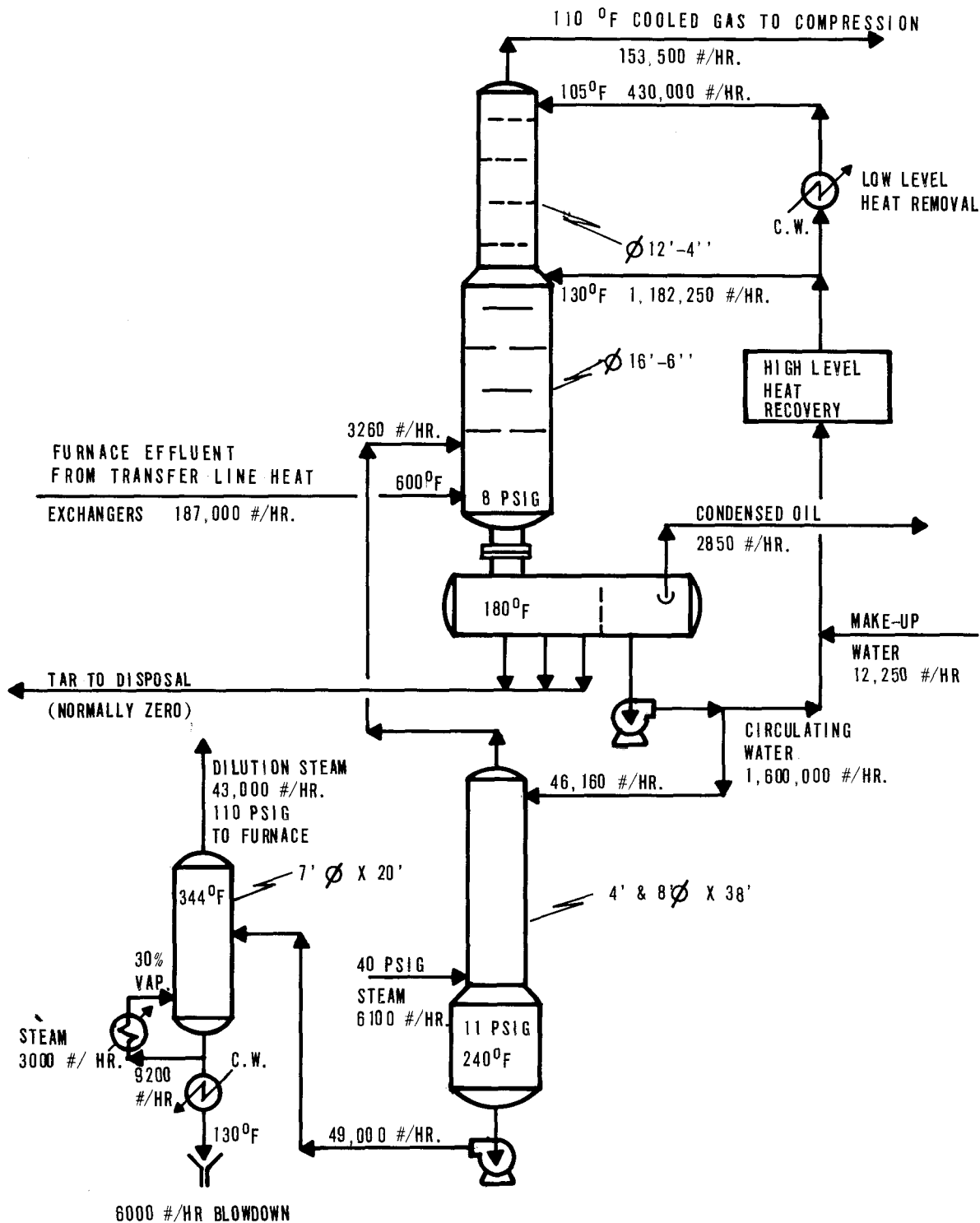


Table IV-8

Incremental Operating Costs
for Condensate Strippers*

Incremental:

Steam - 6500 lb/hr (Stripping + Vaporization)
Electricity-Pumps - 40,000 Kwh
Saving of 74 GPM of wastewater or boiler feedwater

	<u>Operating Cost/Year</u>
Steam	\$32,000
Power	<u>400</u>
	32,400
B.F.W. 74 GPM @ \$.40/MUSG	<u>(14,400)</u> Credit
Net Utility Cost	\$18,000

Investment Items:

Depreciation	24,000
Maintenance, Insurance and Other	<u>11,000</u>
	\$35,000
TOTAL	\$53,000/Year

Cost/lb of C_2 = .011¢

Cost/gallon of water saved = .15¢

*Note: For a 500 MM lb/yr ethylene plant using C_2/C_3 feed.

Table IV-9 presents the U.S. plants which are known to operate with condensate strippers.

To define BADCT and BATEA technology, a steam stripper is required to reuse the waste water from the quench tower. With the installation of steam stripper, contamination attributable to the quench water would be eliminated, and the resulting RWL's would be as follows:

<u>Plant No.</u>	<u>Flow</u> gal/1,000 lb	<u>COD</u> lb/1,000 lb (mg/l)	<u>BOD5</u> lb/1,000 lb (mg/l)	<u>TOC</u> lb/1,000 lb (mg/l)
1	364	1.57 (533)	0.39 (130)	0.48 (159)
2	50	1.83 (4,400)	0.19 (450)	1.77 (4,250)
3	11	0.77 (8,550)	0.43 (4,800)	0.13 (1,450)
4	52.5	0.66 (1,500)	0.09 (200)	0.43 (980)
7	10	0.48 (5,860)	0.12 (1,500)	0.63 (7,700)

The RWL's of plants 1 and 4 are the same as in the previous tabulation because steam stripping has already been implemented at those plants. Plant 6 is missing from this tabulation because sampling at that plant (of the combined streams of quench water and scrubber water) precluded separate calculation of RWL without quench water.

The high waste water flow of Plant 1 is attributed to high water usage in the scrubber; recycle of scrubber water could reduce the waste water flow but not the organic loading. The calculated data for Plants 3, 4, and 7 can be considered as representative of the RWL for the process and can be used as criteria for BATEA and BADCT control technology.

Table IV-9

U.S. Ethylene Plants Using Condensate Strippers

1.	Allied, Geismar	600 MM lb/yr Ethylene
2.	DuPont, Orange	750 MM lb/yr Ethylene
3.	Northern Petrochemical	800 MM lb/yr Ethylene
4.	Monsanto, Alvin	650 MM lb/yr Ethylene
5.	Union Carbide, Seadrift	1,400 MM lb/yr Ethylene
6.	Union Carbide, Texas City	1,250 MM lb/yr Ethylene
7.	Shell, Deer Park	1,000 MM lb/yr Ethylene
8.	Continental, West Lake	550 MM lb/yr Ethylene
9.	Cities Service, Lake Charles	440 MM lb/yr Ethylene
10.	Dow, Freeport	1,000 MM lb/yr Ethylene
11.	Union Carbide, Taft	500 MM lb/yr Ethylene
12.	Enjay, B.R.	1,200 MM lb/yr Ethylene
13.	Dow, Freeport	500 MM lb/yr Ethylene
14.	Amoco, Texas City	750 In construction
15.	Shell, Norco	1,000 Announced

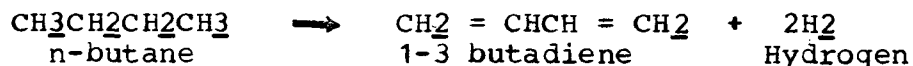
SUBCATEGORY B

<u>Product</u>	<u>Process</u>
Butadiene	1. Co-Product of Ethylene Manufacture
	2. Dehydrogenation of n-Butane

Butadiene is produced as the by-product of the cracking of hydrocarbons or by dehydrogenation of C₄ hydrocarbons, such as n-butane or butylenes, or as a co-product of ethylene manufacture.

1. Dehydrogenation of n-butane

The one-step catalytic dehydrogenation of n-butane is carried out in the vapor phase with solid chromium-on-alumina catalyst. The reactors operate under vacuum at approximately 3 pounds per square inch absolute (psia) to obtain low hydrocarbon partial pressures. This prevents excessive coking on the catalyst. The chemical reaction is given below:



A process flowsheet is shown in Figure IV-8. The feedstock (n-butane) and recycled butane and butenes are fed into a battery of fixed-bed reactors. The reactor effluent is oil-quenched, compressed, and sent to an absorption column, where hydrocarbon vapor is absorbed with light oil. The effluent from the absorber is then passed through a series of distillations where unreacted butane and butene are separated for recycle to the dehydrogenation reactors. Butadiene is separated from the butene splitter overhead by extractive distillation with furfural or cuprous ammonium acetate (CAA) extraction.

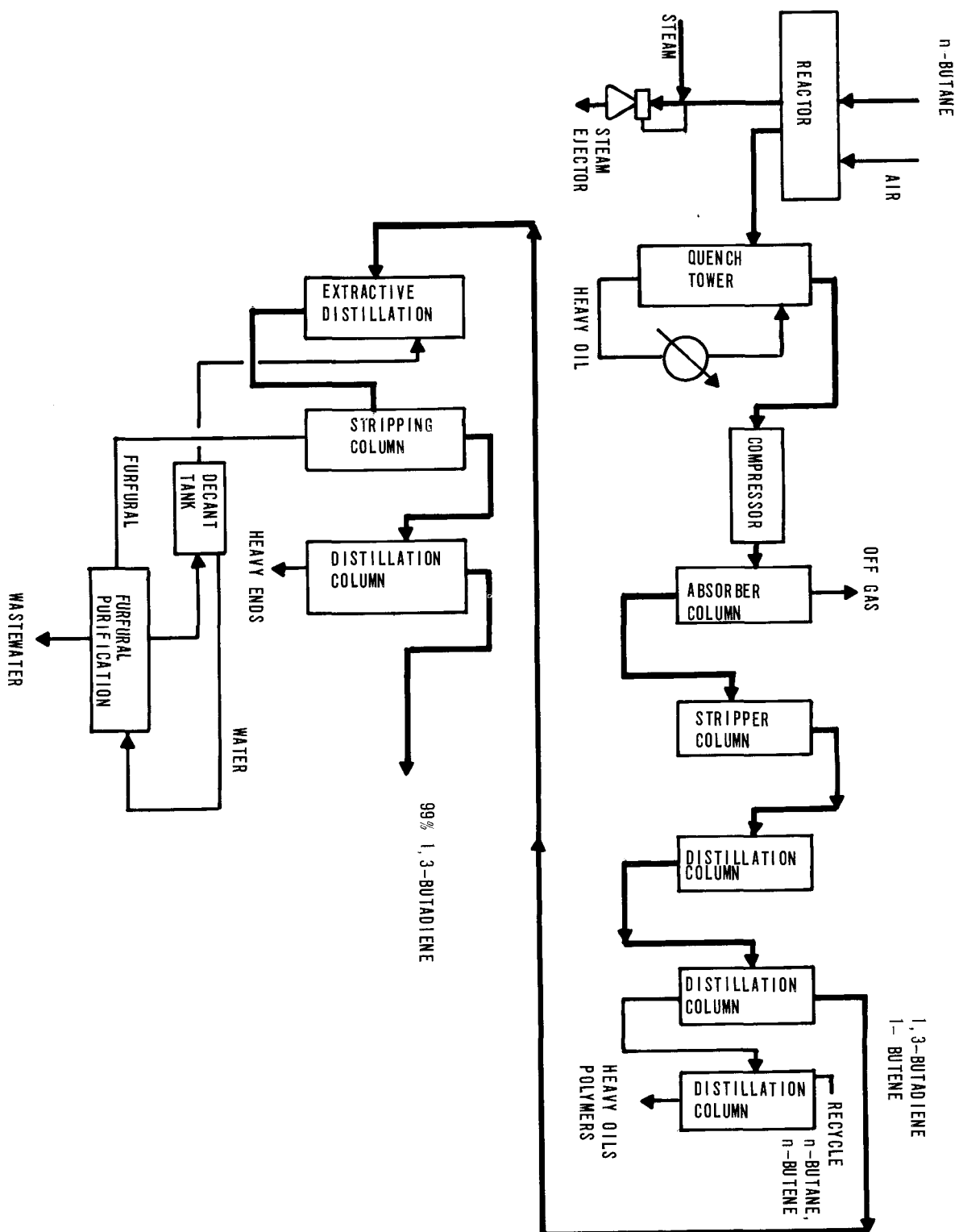
A different process for producing butadiene from C₄ hydrocarbons was employed by one plant visited. The process dehydrogenates butane to butylenes using superheated steam as a diluent. After separation from light and heavy by-products, the butylenes are converted to butadiene by oxidative dehydrogenation. This reaction is illustrated below:



2. Co-product of ethylene manufacture

Butadiene is also produced by extraction from the C₄ and heavier residue produced in ethylene manufacture. As shown in Figure , the C₄ residue goes to an extractive distillation with furfural or cuprous ammonium acetate (CAA) extraction. The effluent is then sent to a steam stripper

FIGURE IV-8
BUTADIENE, DEHYDROGENATION OF n-BUTANES



and fractionator, where heavy ends are removed. The stream taken overhead from the fractionator is further washed with water to remove solvents.

The dehydrogenation of n-butane produces waste waters from scrubbing the gases used to periodically burn coke from the catalyst surface, and from the steam ejector-barometric condenser systems used to obtain vacuum in the reactors. The process also produces wastewaters from the final recovery of butadiene product. Waste waters generated by the process wherein butadiene is formed as a co-product of ethylene manufacture are essentially the same as those from the final recovery unit in the dehydrogenation process. Survey data obtained from plant visits are summarized in the following tabulation:

Plant No.---	Process	Flow	COD	BOD ₅	TOC
		gal/1,000lb (mg/l)	lb/1,000lb (mg/l)	lb/1,000 lb (mg/l)	lb/1,000 lb (mg/l)
1.	Dehydrogenation, Extractive Distillation	1,160	3.23 (334)	2.96 (306)	
2	Dehydrogenation, Extractive Distillation	1,451	245 (20,200)	72 (5,960)	
3	Co-product of ethylene Extractive Distillation	88	1.120 (1,525)	0.547 (745)	0.554 (755)
4	Co-product Ethylene Extractive Distillation	339	3.899 (1,378)	1.183 (418)	1.545 (546)
5	Co-product of Ethylene Extractive Distillation	183	1.042 (683)	0.165 (102)	0.313 (205)

Since furfural has a relatively high boiling point, it can be easily separated from product butadiene by distillation. Furfural loss in the waterwashing step is minimal. The process (Plant 4) utilizing extraction with cuprous ammonium acetate must be equipped with a water scrubber to remove CAA from the final product and therefore produces considerable more waste water as well as a higher RWL. The data presented by Plants 3, 4, and 5 confirm the above argument and can be considered, respectively, as representatives of BPCTCA for the ethylene co-product process with extractive distillation and extraction. However, to define BPCTCA and BATEA control technology, a steam stripper should be used to recover solvents, furfural, or CAA from the scrubber water, which would then be recycled. With this in-process can be reduced to the following levels:

Flow	65 gallons/1,000 lb
COD	0.43 lb/1,000 lb
BOD ₅	0.18 lb/1,000 lb

As indicated in the data tabulation, RWL's presented by the two dehydrogenation plants show a significant variation. Although these two plants represent two different dehydrogenation routes, as described in the preceding paragraph the variation is due mainly to less effective operation of wash columns and strippers rather than to differences in the processes. Consequently, the data presented by Plant 1 should be considered as representative of BPCTCA.

Since the dehydrogenation reactor is operated at approximately 3 psia, steam ejectors with barometric condensers are used to produce the vacuum, and these generate an excessive amount of waste water. A vacuum pump system, such as that described in the Styrene section can substantially reduce the amount of waste water and also eliminate organic losses in the exhaust stream.

To define BADCT and BATEA control technology for the dehydrogenation process, steam ejectors should be replaced with vacuum pumps and a steam stripper should be installed to recover organic solvent, as described in the ethylene co-product processes.

An alternate route for butadiene manufacturing is the dehydrogenation of n-butene. It is a vapor phase reaction with a catalyst of iron oxide promoted by chromium oxide, magnesium-iron oxide, or calcium nickel phosphate. Butadiene is produced through several dehydrogenation reactors (in parallel) containing fixed bed catalysts. The reaction gases are quenched and cooled in a series of quench towers. The condensate containing C4-hydrocarbons is charged to a fractionating column where it is stabilized. The stabilized condensate is then treated for the removal of polymerized materials. Finally, the crude butadiene is purified by absorption or extractive distillation.

The U.S. butadiene capacity and the estimated economics for a one-step dehydrogenation plant are presented in Tables IV-10 and IV-11.

Table IV-10

U. S. Butadiene Capacity (1965)

<u>Company</u>	<u>Location</u>	<u>MM lbs/yr.</u>
From butane		
El Paso	Odessa, Texas	130.0
Firestone	Orange, Texas	220.0
Phillips	Borger, Texas	224.0
Petro-Tex	Houston, Texas	220.0
Shell	Torrance, Calif.	140.0
ARCO	Channelview, Texas	242.0
Sub Total		1,176.0
From butylenes		
Copolymer	Baton Rouge, La.	120.0
Goodrich-Gulf	Port Neches, Texas	320.0
Enjay	Baytown, Texas	66.0
PCI (Cities Service)	Lake Charles, La.	160.0
Texas-U. S.	Port Neches, Texas	320.0
Petro-Tex	Houston, Texas	280.0
Sub Total		1,266.0
Olefin plant C ₄		
Chevron Chem.	El Segundo, Calif.	32.0
Dow	Freeport, Texas	64.0
Enjay	Baton Rouge, La.	110.0
Mobil	Beaumont, Texas	50.0
Monsanto	Alvin, Texas	100.0
Union Carbide	Seadrift, Texas, etc.	140.0
Tidewater	Delaware City, Del.	14.0
Sub Total		510.0
Grand Total		2,952.0

Source: Oil, Paint and Drug Reporter, October 24, 1966.

Table IV-11

Estimated Economics for Butadiene
(100. MM lb. plant, One-Step Dehydrogenation)

Total Fixed Capital=\$17. MM

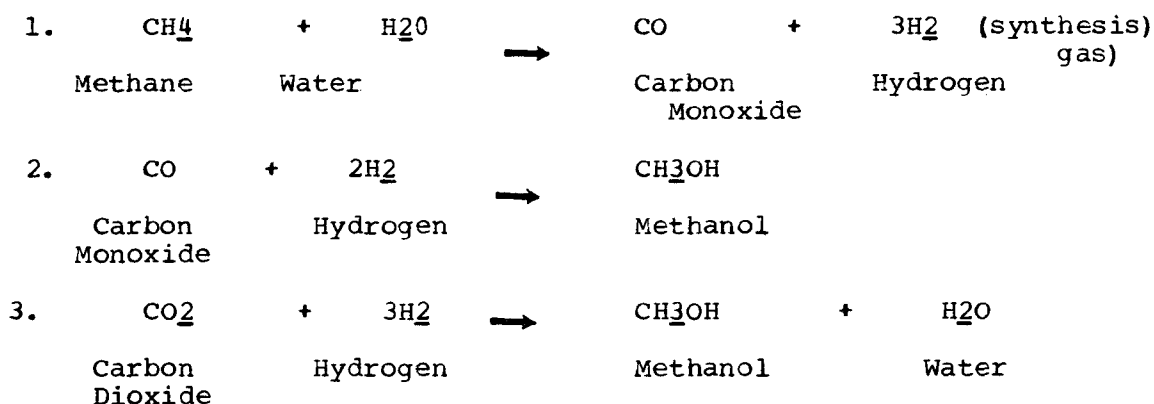
Estimated Operation Cost

	<u>Cost</u> <u>¢/lb. butadiene</u>
Butane (at 1.4¢/lb.)	2.6
Utilities	0.7
Catalyst, chemicals and royalties	1.2
Labor and overhead	0.8
Capital charges	5.8
Hydrogen Credit	-0.4
TOTAL	10.7

SUBCATEGORY B

<u>Product</u>	<u>Process</u>
Methanol	Steam Reforming of Natural Gas

All of the processes for synthetic methanol involve the basic steps of steam reforming of natural gas plus addition of carbon dioxide to adjust the C/H ratio, compression, synthesis in a catalytic converter, and distillation for purification. The following reactions summarize the basic chemistry:



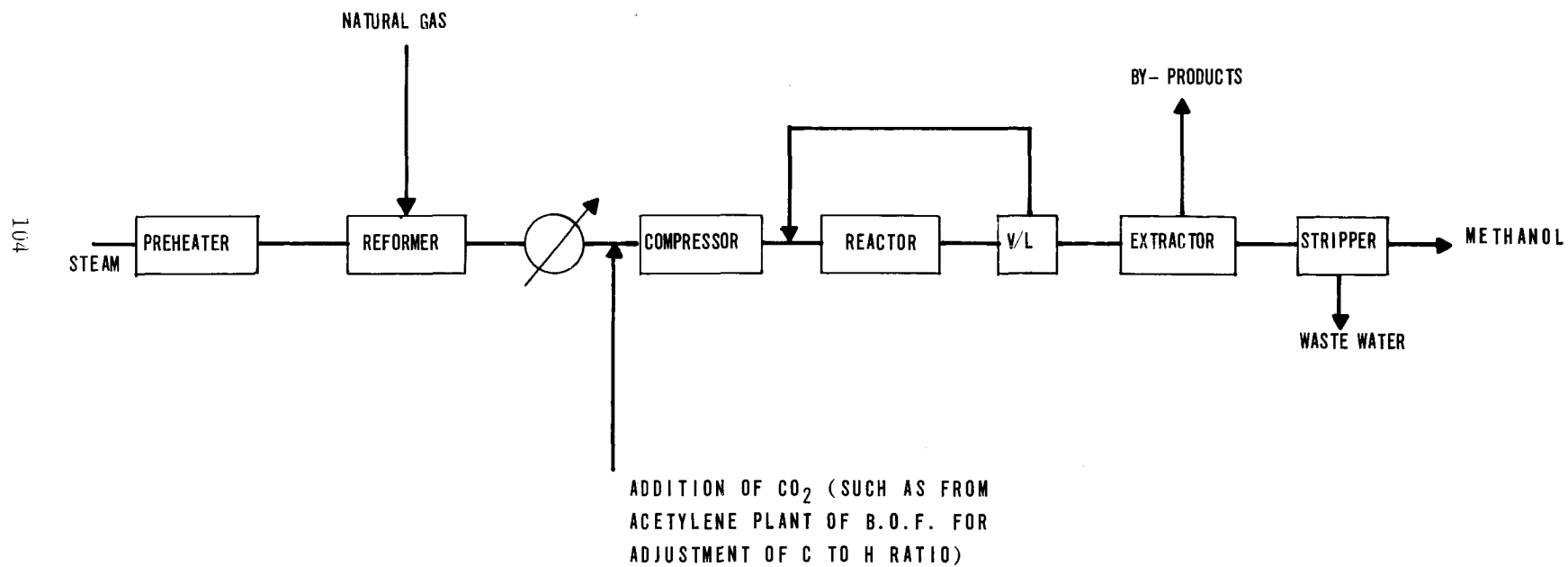
The optimum atomic ratio for C/H in methanol synthesis is 1/4 as indicated above. However, carbon dioxide is added to take care of extra hydrogen resulting from steam reforming of natural gas.

The traditional conversion to methanol is carried out at high pressure (4,500 psig) in the presence of a chromium oxide-zinc oxide catalyst at about 650°F. However, a new process operates at only 750 psig and 500°F. by using a new active copper catalyst. The much lower pressures allow the use of centrifugal compressors rather than reciprocating compressors, and also allow use of hydrogen-rich synthesis gas without having to add carbon dioxide. Also, the conversion of natural gas to methanol is much higher in the low-pressure process than that in the high-pressure process.

A flow sheet for methanol synthesis is shown in Figure IV-9. The synthesis gas, after compression, is charged together with recycle gas to the reactor. The methanol-bearing gas leaving the reactor is cooled by heat exchange with air or water. The condensed crude methanol is separated from unreacted gas, which is recycled to the reactor. The flashed, gas-free crude methanol from the separator is purified by distillation.

The only waste water stream from methanol plants using 100% natural gas feedstock is the aqueous stream from the final methanol distillation column. Processes which utilize off-gases from acetylene manufacture as feedstock introduce impurities into

FIGURE IV-9
METHANOL



the system. These impurities must be removed before crude methanol can be purified. Usually, the impurities are first oxidized by a strong oxidizing agent; this is followed by sedimentation, filtration, and cation exchange. The results of survey data are shown in the following tabulation:

	Plant I	Plant 2
FLOW	59 gallons/1,000 lb	42.2 gallons/1,000 lb
COD	320 mg/l 0.16 lb/1,000 lb	4,930 mg/l 1.74 lb/1,000 lb
BOD ₅	119 mg/l 0.059 lb/1,000 lb	2,620 mg/l 0.92 lb/1,000 lb
TOC	107 mg/l 0.053 lb/1,000 lb	583 mg/l 0.21 lb/1,000 lb

Plant I utilizes the low-pressure system with natural gas as feedstock; Plant 2 uses off-gases from acetylene manufacturing as part of its feedstock. The RWL of Plant I is representative of the low-pressure process, and can be considered as standard for BADCT and BATEA. The higher RWL of Plant 2 is due to impurities introduced with the off-gases. A preliminary fractionator can take the place of a series of treatments of crude methanol, and the impurities can be removed from the fractionator and disposed of by incineration. The RWL could then be expected to approach that of the low-pressure process. There is no significant difference in waste water characteristics between the high- and low- pressure processes. Only minimal carryover of metal catalyst is expected.

The U.S. production of methanol and the estimated economics are shown in Tables IV-12 and IV-13, respectively.

Table IV-12
U.S. Methanol Capacity (1972)

<u>Company</u>	<u>Location</u>	<u>MM gallons</u>
Allied	South Point, Ohio	25
Borden	Geismar, La.	160
Celanese	Bishop, Texas	100
	Clear Lake, Texas	200
Commercial Solvents	Sterlington, La.	50
DuPont	Orange, Texas	130
	Beaumont, Texas	200
	Huron, Ohio	30
Escambia	Pensacola, Fla.	50
Georgia-Pacific	Plaquemine, La.	100
Hercules	Plaquemine, La.	80
Monsanto	Texas City, Texas	100
Rohm and Haas	Deer Park, Texas	22
Tenneco	Pasadena, Texas	60
Union Carbide	Texas City, Texas	<u>42</u>
TOTAL		1,349*

*8.9 billion lb/yr

Source: Oil, Paint and Drug Reporter, Chemical Profile,
September 27, 1971.

Table IV-13
Estimated Economics for Methanol
(costs in ¢/gal)

	Capacity in tons/day			
	150	300	800	800
Output, MM gal/yr	15	30	80	80
Process	lp	hp	lp	hp
Compressor	c	r	c	r
Capital cost, \$ million	\$ 5.40	\$ 8.80	\$14.50	\$15.20
Variable costs, ¢/gal*	2.65	4.18	2.65	2.87
Labor, maintenance, supervision	2.50	1.73	0.89	0.93
Fixed costs (plant, depreciation)	4.31	3.32	1.94	2.05
Cost to manufacture	9.46	9.23	5.48	5.85
S, G & A	0.50	0.50	0.50	0.50
20% return, BFIT	7.20	5.87	3.62	3.80
Sales value (FOB)	17.20	15.60	9.60	10.20
Sales value (FOB) (same basis, naphtha @ 6.5¢/gal)	21.00	19.90	13.40	14.70

Symbols: lp = low-pressure
hp = high-pressure
c = centrifugal
r = reciprocal

*Natural gas at 20¢/1,000 cu.ft.

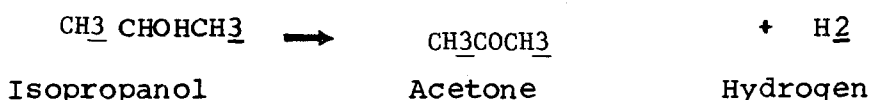
Source: B. Hedley, W. Povers and R.B. Stobaugh; Hydrocarbon Processing,
Sept. 1970, p. 277.

SUBCATEGORY B

Product
Acetone

Process
Dehydrogenation of Isopropanol

Acetone is produced by dehydrogenation of isopropanol. Fresh and recycle isopropanol are vaporized and fed to a tubular reactor at typical operating conditions of 5 psig and 450-550°C. A brass catalyst is commonly used. Conversion of isopropanol is about 90 percent per pass, and selectivities to acetone are above 95 percent. The reactor effluent is passed into an absorption tower to clean up the hydrogen formed in the reaction. The water solution from the absorption tower is then purified by conventional fractionation techniques, and unconverted isopropanol is recycled back to the reactor. Figure IV-10 summarizes the important process units in the dehydrogenation process, and the chemical reaction is given below:



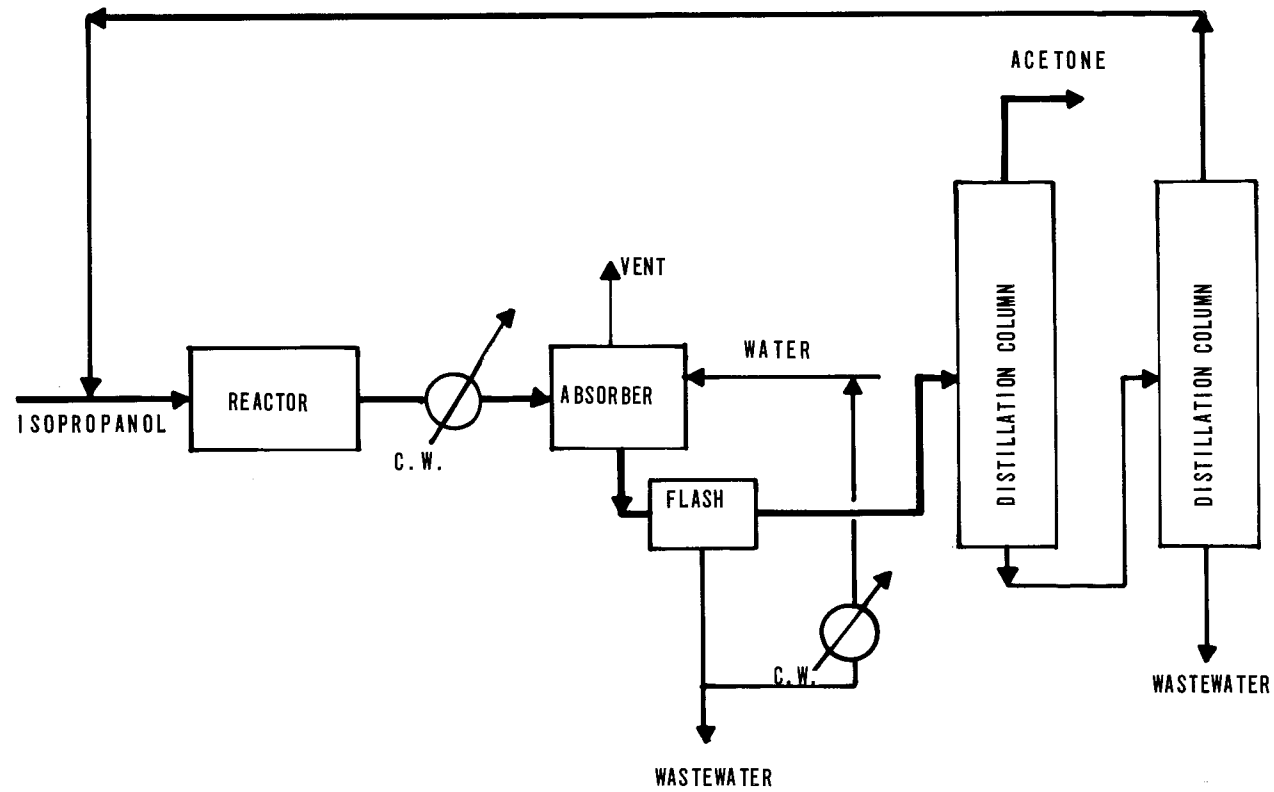
In this process, water is used to absorb product acetone and unreacted isopropanol from the hydrogen produced. After fractionation, one or two waste water streams are produced as bottoms from the isopropanol stripping still or as bottoms from the intermediate flash column. The waste water contains acetone, isopropanol, and small quantities of heavier organic substances. RWL of this process from survey data in plant visits is summarized as follows:

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	230 gallons/1000 lb	120 gallons/1000 lb
COD	246 mg/l 0.47 lb./1000 lb	1,720 mg/l 1.72 lb./1000 lb
BOD ₅	91 mg/l 0.18 lb./1000 lb	338 mg/l 6.34 lb/1000 lb
TOC	132 mg/l 0.25 lb./1000 lb	473 mg/l 0.47 lb./1000 lb

Based on process information, it is concluded that the RWL of Plant 1 is representative of BPCTCA. Since the contaminants in the bottoms of the isopropanol stripping still have low concentrations of volatile organic compounds, this stream can be totally recycled to the absorber as absorbing water. The waste water stream from the intermediate flash column can also be recycled to reduce fresh water usage. Contaminant concentration in the intermediate flash column waste water is a function of the column design; recycle of the above mentioned streams will not

FIGURE IV-10
ACETONE, DEHYDROGENATION OF ISOPROPANOL

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change the characteristics of the existing waste stream. With this process modification, RWL of BADCT and BATEA can be expected to achieve the following values:

Flow	100 gallons/1000 lb
COD	103 mg/l 0.086 lb./1000 lb
BOD ₅	53 mg/l 0.044 lb./1000 lb
TOC	52 mg/l 0.043 lb./1000 lb

The difference in RWL between the two plants is attributed to poor performance of the isopropanol stripping still of Plant 2.

Average process water usage of this process is about 1.18 pounds water per pound of acetone, while cooling water usage amounts to 119 pounds water per pound of product.

Acetone can also be produced by several alternate routes. The most important recent development has been production of acetone as a co-product in the cumene-to-phenol process. Another alternate process is the oxidation of isopropanol. The oxidation process is also vapor-phase and is carried out with brass or copper catalysts.

The economics of the acetone market are conditioned by the fact that the acetone produced as a co-product in the cumene-to-phenol process can be credited at a low price. The U.S. acetone capacity by various processes is shown in Table IV-13. Estimated economics for acetone via vapor-phase dehydrogenation appear in Table IV-14. The estimated economics for acetone via vapor-phase dehydrogenation and the U.S. acetone capacity by various processes are shown in Tables IV-14 and IV-15.

Table IV-14

U.S. Acetone Capacity
(MM lb)

<u>Company</u>	<u>Location</u>	<u>1967</u>	<u>1968</u>	<u>1970</u>	<u>1972</u>	<u>Process</u>
Amoco	Texas City, Texas	-	-	-	240	Isopropanol
Allied Chemical	Philadelphia, Pa.	150	190	190	300	Cumene
Celanese	Bishop, Texas	35	35	35	35	Propane
Chevron	Richmond, Calif.	35	35	35	35	Cumene
Clark Oil	Chicago, Ill.	35	35	35	35	Cumene
Dow	Freeport, Texas	-	-	-	240	Cumene
Eastman	Kingsport, Tenn.	90	90	90	90	Isopropanol
Enjay	Bayway, N.J.	110	110	110	110	Isopropanol
Georgia Pacific	Plaquemine, La.	-	-	120	120	Cumene
Hercules	Gibbstown, N.J.	30	30	30	-	Cumene
Monsanto	Alvin, Texas	35	80	80	225	Cumene
Shell Chemical	Houston, Texas	30	30	30	30	Cumene
	Dominquez, Calif.	150	150	150	150	Isopropanol
	Norco, La.	100	100	100	100	Isopropanol
	Houston, Texas	180	180	245	400	Isopropanol
Skelly Oil	El Dorado, Kansas	30	30	30	30	Cumene
Union Carbide	Marietta, Ohio	-	-	-	175	Cumene
	Bound Brook, N.J.	87	87	87	87	Cumene
	Institute, W. Va.	120	120	120	120	Isopropanol
	Texas City, Texas	130	130	130	130	Isopropanol
	Whiting, Ind.	120	120	120	120	Isopropanol
	Ponce, P.R.	-	-	-	120	Cumene
USS Chemicals	Haverhill, Ohio	-	-	120	120	Isopropanol
Total		1,467	1,552	1,857	3,012	

	<u>1967</u>	<u>1968</u>	<u>1970</u>	<u>1972</u>
% cumene based	29.4	33.4	34.3	46.4
% isopropanol based	68.3	64.3	63.8	52.5
% propane based	2.3	2.3	1.9	1.1

Source: Oil, Paint & Drug Reporter, Oct. 4, 1970.

Table IV-15

Estimated Economics for Acetone
(50. MM lb. plant)

Total Fixed Capital=\$0.6 MM

Estimated Operation Cost

	<u>Cost,</u> <u>c/lb. acetone</u>
Isopropanol	4.7
Utilities	0.9
Labor and overhead	0.3
Capital charges	0.4
Hydrogen	-0.2
Total	6.1

SUBCATEGORY B

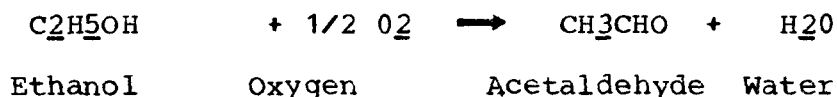
<u>Product</u>	<u>Process</u>
Acetaldehyde	1. Oxidative-Dehydrogenation of Ethyl Alcohol
	2. Dehydrogenation of Ethyl Alcohol

Acetaldehyde is produced in the United States by processes using ethylene, ethyl alcohol, or liquified petroleum gas as feedstock. The breakdown of 1970 U.S. capacity for each route is shown below:

<u>Feedstock</u>	<u>Process</u>	<u>Percent of 1970 U.S. Capacity</u>
Ethylene	Oxidation	56
Ethyl Alcohol	Oxidative- Dehydrogenation	36
LPG	Oxidation	8

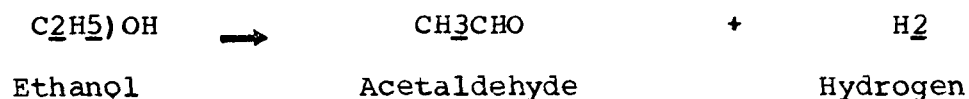
The following discussion is of the ethyl alcohol route; the remaining routes will be discussed under Subcategory C.

In the oxidative-dehydrogenation process, ethanol and air enter an oxidation furnace. The primary reaction is given below:



The reaction is vapor-phase and is carried out over a solid silver gauze catalyst at about 1,000°F. The reactor effluent is condensed and is passed to a phase separator. The gaseous phase is absorbed in refrigerated water. Off-gases pass from the system, and the wash is combined with the liquid stream. The combined liquid stream is fractionated into product acetaldehyde, alcohol for recycle, and waste water.

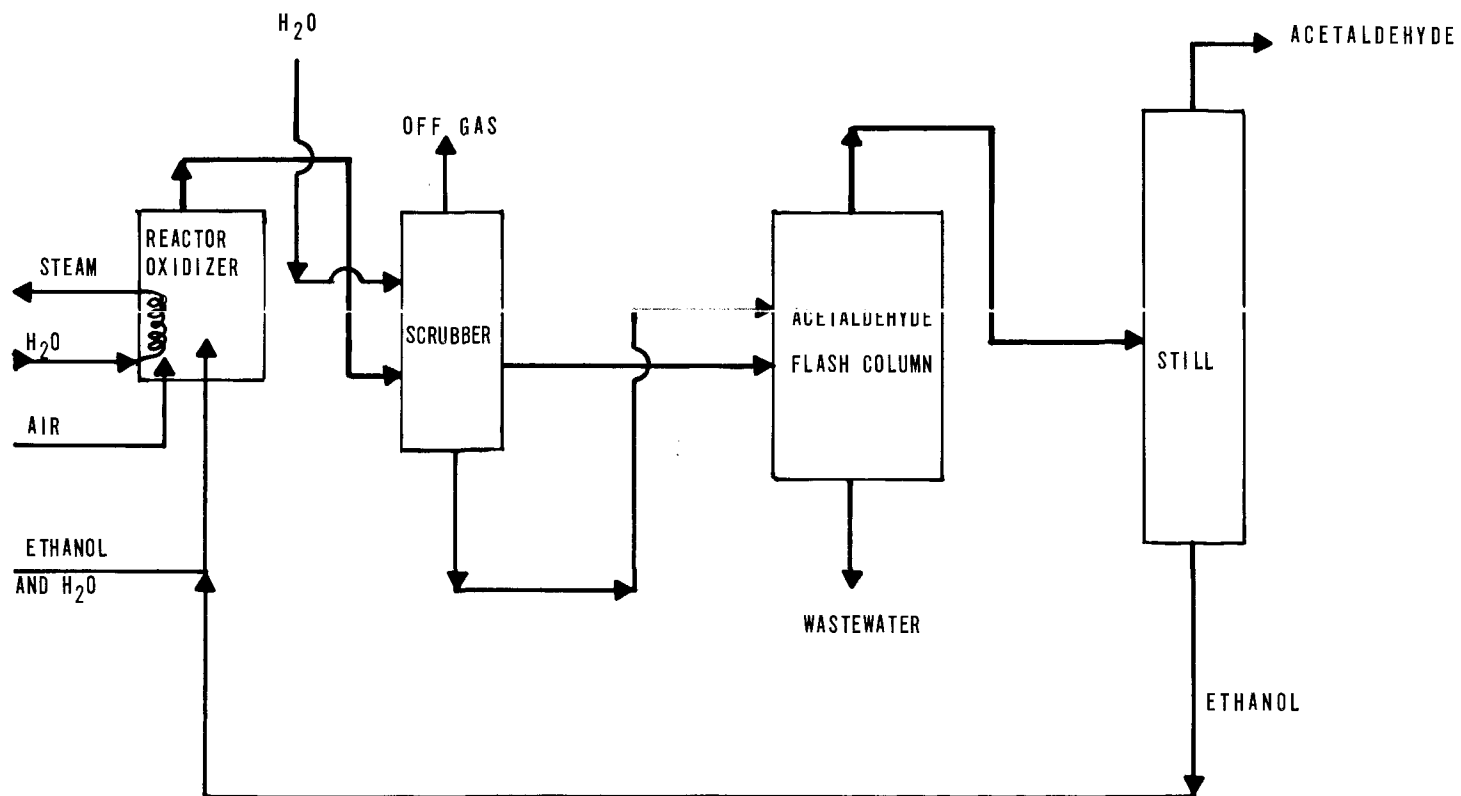
Dehydrogenation of ethanol is based on the chemical reaction:



This reaction is also vapor phase and is carried out over a solid copper catalyst promoted by cobalt or chromium on an asbestos support at 500°F.

A flow sheet for the oxidative dehydrogenation process is shown in Figure IV-11.

FIGURE IV-11
ACETALDEHYDE, OXIDATIVE DEHYDROGENATION



These processes yield from 85 to 95 percent of the stoichiometric amount of acetaldehyde. The only waste water stream generated in these processes is either from the acetaldehyde flash column or the ethanol recovery still, and contains liquid by-products such as acetic acid. The survey data are shown in the following tabulation:

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	1,600 gallons/1,000 lb	140 gallons/1,000 lb
COD	186 mg/l 2.48 lb/1,000 lb	N.A. N.A.
BOD ₅	84 mg/l 1.12 lb/1,000 lb	N.A.
TOC	N.A.	14,400 mg/l 16.7 lb/1,000 lb

Although direct comparison of COD, BOD₅, or TOC values between two plants was not possible, the magnitude of the above parameters and the general relations between COD and TOC, and between BOD₅ and TOC, show a significant difference in RWL for the two plants. The difference is attributed mainly to differing efficiencies of acetaldehyde flash columns and ethanol recovery stills. By improving operating conditions of those stills, Plant 2 should be able to reduce its RWL to the representative RWL of Plant 1.

BADCT and BATEA control technology are defined by an in-process modification of the water scrubbing system, entailing division of the scrubber into a fresh-water scrubbing portion and a bulk recycle water portion. Such a division can significantly reduce fresh-water usage by permitting recycle of four-fifths of the existing waste stream. The amount of waste water flow from the scrubber is thus one-fifth of the original flow. However, because the concentrations of contaminants in this waste stream will increase proportionally, no reduction in RWL will occur.

Total process water and cooling water usages of the two plants are summarized as follows:

<u>Plant</u>	<u>Process Water</u> <u>lb/lb product</u>	<u>Cooling Water</u> <u>lb/lb product</u>
Plant 1	13	104
Plant 2	1	100

Process water is applied mainly to the scrubber. The more water used, the larger the amount of waste flow.

Acetaldehyde capacity in the U.S. is presented in Table IV-16.

Acetaldehyde capacity in the U.S. is presented in Table IV-16.

Table IV-16
Acetaldehyde Capacity
(MM lb)

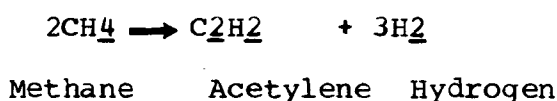
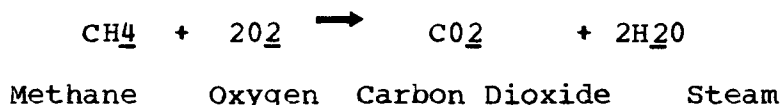
<u>Company</u>		<u>1967</u>	<u>1972</u>	<u>Process</u>
Celanese	Bay City, Texas	210	210	Ethylene
	Bishop, Texas	200	200	LP-gas
	Clear Lake, Texas	175	375	Ethylene
	Pampa, Texas	10	10	Byproduct petroleum gas
Commercial Solvents	Agnew, Calif.	1	1	Ethanol
Dupont Company	Louisville, Ky.	10	10	Byproduct petroleum gas
Eastman	Kingsport, Tenn.	200	-	Ethanol
	Longview, Texas	250	500	Ethylene
Goodrich	Calvert City, Ky.	1	1	Byproduct petroleum gas
Hercules	Parlin, N. J.	35	-	Ethanol
Monsanto	Texas City, Texas	5	5	Byproduct petroleum gas
Publicker	Philadelphia, Penn.	80	80	Ethanol
Shell	Norco, La.	5	5	Byproduct petroleum gas
Union Carbide	Institute, W. Va.			
	S. Charleston, W. Va.	650	650	Ethanol
	Texas City, Texas			
Totals		1,832	2,047	

SUBCATEGORY B

Product
Acetylene

Process
Partial Oxidation of Methane

Acetylene is manufactured by burning preheated natural gas and pure oxygen in specially designed burners. The natural gas is partially oxidized with oxygen, and the evolved heat cracks the hydrocarbon to acetylene.



Cracking occurs at 1,500°C with a residence time of 0.01 to 0.1 seconds. The resulting gases are rapidly quenched with water to prevent acetylene decomposition. A gas cooler and a series of distillation columns are then used to separate acetylene from by-products.

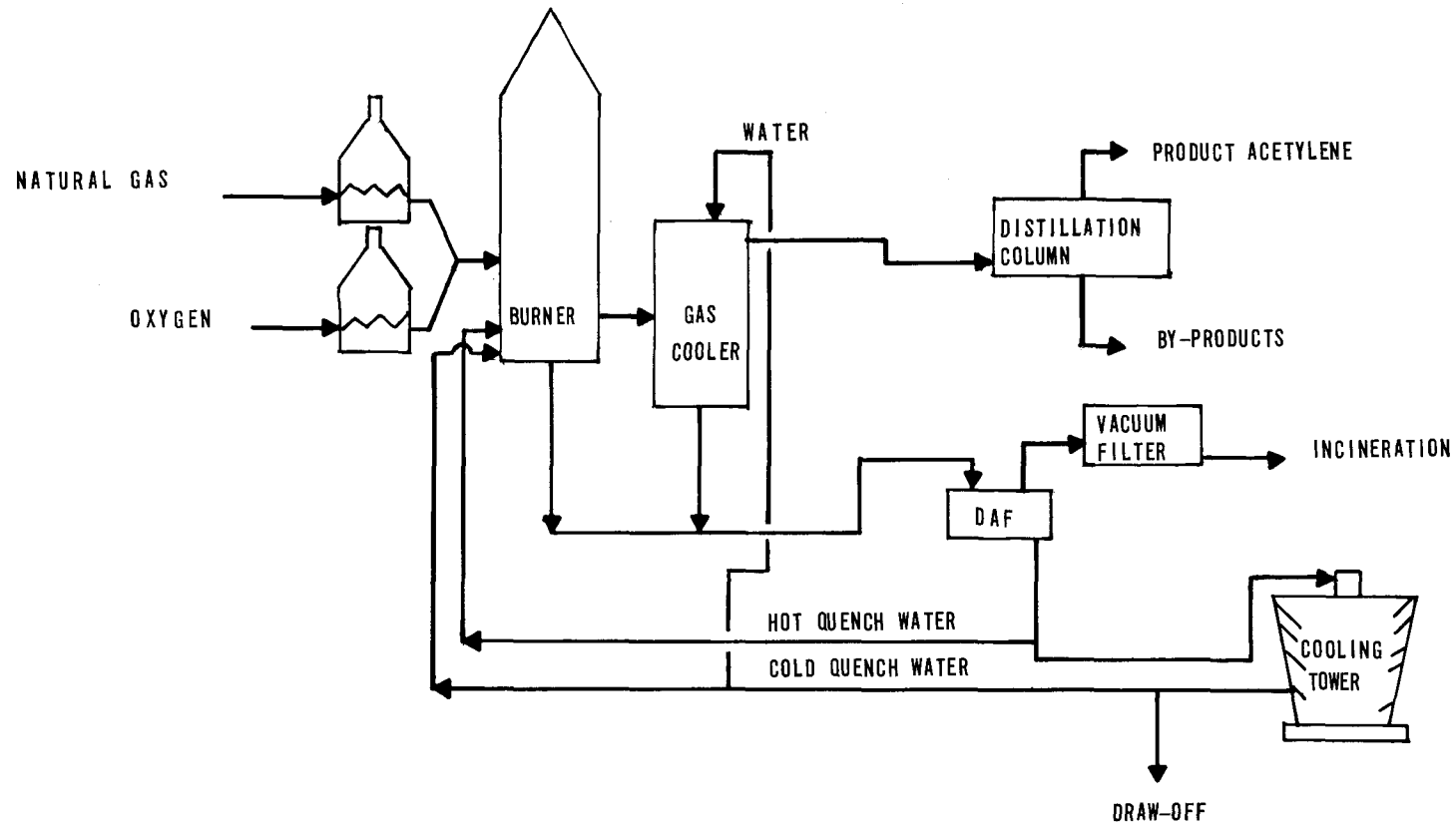
Large quantities of carbon (coke) are produced by burning of the natural gas, and these fine particles are trapped in the quench stream. An air flotation unit or similar device must be provided to remove coke from the quench water before the water can be sent to a cooling tower and recycled. The solids removed can be dewatered and disposed of by incineration. The only waste water stream from the process results from the cooling water system, which must be continually bled and replenished with fresh water to avoid build-up of dissolved substances.

A flow sheet of this process is shown in Figure IV-12.

The results of survey data on cooling tower draw-off stream are shown in the following tabulation:

Flow	561 gallons/1,000 lb
COD	1,274 mg/l 5.95 lb/1,000 lb
BOD ₅	410 mg/l 1.92 lb/1,000 lb
TOC	393 mg/l 1.80 lb/1,000 lb

FIGURE IV-12
ACETYLENE



Comparing these data with those for the cooling water just prior to being discharged to the cooling tower inlet indicates that a significant amount of hydrocarbons are evaporated into atmosphere. In order to further reduce the RWL and not sacrifice ambient air quality, a steam stripper can be installed to remove hydrocarbons from the waste stream before the waste water is sent to the cooling tower. The collected hydrocarbons can then be disposed of by incineration. RWL of BADCT and BATEA will require this in-process modification to achieve lower waste loads.

Acetylene can also be produced by two other routes. The first is pyrolysis of a mixture of lime and coke at 2,000°C in an electric furnace to form calcium carbide. The calcium carbide is ground under anhydrous conditions and then treated with a limited quantity of water to produce acetylene. Calcium hydroxide is a by-product. The second, called the Wulff Process, produces acetylene by pyrolysis of ethane, propane, naphtha, or similar material. An alternating cycle is used wherein hydrocarbons are heated by a hot tile checker work (1,100°C) to produce acetylene. Following this, there is a combustion step during which the bricks are heated in air to burn off tar deposits. The pyrolysis gases are contacted initially with dimethyl formamide (DMF) to remove water, diacetylene, and other products. This is followed by absorption of the acetylene in DMF and final recovery of the acetylene by stripping.

Acetylene production had grown 10% annually from 1960 to 1965. This growth has been stimulated primarily by demand for vinyl chloride, vinyl acetate, and chloroprene. However, acetylene demand has exhibited a marked decline since then. 1972 acetylene capacity in U.S. is presented in Table IV-17.

Table IV-17

U.S. Acetylene Capacity (1972)

<u>Company</u>	<u>MM lb</u>	<u>Process</u>
Diamond Shamrock (Houston, Texas)	40	Partial oxidation
Dow (Freeport, Texas)	15	" "
Monochem (Geismar, La.)	165	" "
Rohm and Haas (Houston, Texas)	35	" "
Tenneco (Houston, Texas)	100	" "
Union Carbide (Seadrift, Texas)	15	Ethylene byproduct
(Taft, La.)	18	Wulff
(Texas City, Texas)	80	Partial oxidation
Other	<u>735</u>	Calcium carbide
Total	1,203	

Source: Oil, Paint & Drug Reporter, April 5, 1971, p. 9.

SUBCATEGORY B

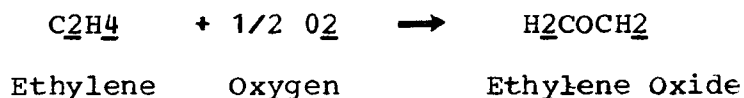
Product

Ethylene Oxide

Process

Catalytic Oxidation of Ethylene

Most ethylene oxide manufacture is based on the direct vapor-phase oxidation of ethylene over a silver oxide catalyst:



Oxidation takes place in the main reactor. Partial oxidation of ethylene to ethylene oxide and total oxidation to carbon dioxide and water are the two primary reactions. Ethylene oxide is recovered from the reactor effluent by absorption in a dilute aqueous solution.

A flow sheet for the oxidation process is shown in Figure IV-13.

In the process using high purity oxygen, the main absorber off-gas passes through a carbon dioxide removal system and is recycled to the reactor to reduce the ethylene partial pressure. When air is used as the oxidant, a secondary reactor system is employed to scavenge the remaining ethylene in the main absorber off-gas. Ethylene oxide is separated from water in the desorber, and the residual gases are discharged from the system. The combined liquid stream is fed to the ethylene oxide still, where the oxide product and residual water are separated.

The only waste stream generated in the direct oxidation process is the draw-off from the ethylene oxide separator bottoms. Process raw waste loads of this process obtained from plant visits are shown in the following tabulation:

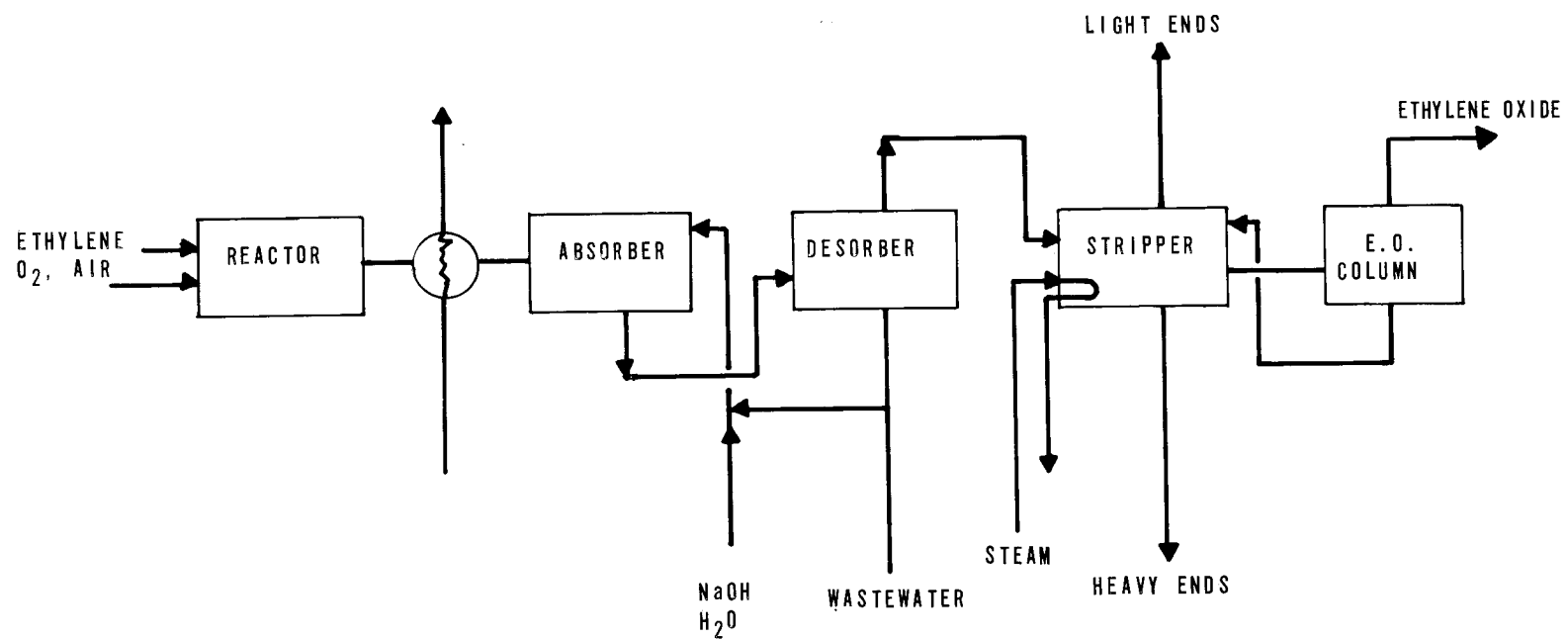
Plant 1

Plant 2

Flow	17.8 gallons/1,000 lb	131.0 gallons/1,000 lb
COD	52,000 mg/l 7.7 lb/1,000 lb	4,800 mg/l 5.26 lb/1,000 lb
BOD ₅	4,800 mg/l 0.71 lb/1,000 lb	650 mg/l 0.71 lb/1,000 lb
TOC	19,650 mg/l 2.91 lb/1,000 lb	2,699 mg/l 2.95 lb/1,000 lb

The survey data show the same order of magnitude of raw waste loads in these two plants. However, the Plant 1 ethylene oxide separator operates more effectively and, consequently, generates a lesser volume of wastewater. Further reduction of RWL of Plant 1 is deemed unfeasible, and it should be considered as a representative RWL of this process in BPCTCA standards.

FIGURE IV-13
ETHYLENE OXIDE



Ethylene oxide manufacture is usually accompanied by ethylene glycol manufacture. Since the waste water from ethylene oxide contains 2% or more of ethylene glycol, this waste stream is usually sent to an ethylene glycol plant for further processing instead of being discharged into sewer lines. BADCT and BATEA standards, therefore, should require zero discharge from the direct oxidation process.

The high sulfate concentration in waste streams would disrupt the normal operation of biological treatment systems. Therefore, pretreatment or proper dilution with other waste streams is required.

Total process water usage (including steam directly supplied to the process) of this manufacturing process is approximately 0.25 lb water per lb of ethylene oxide, while cooling water usage is 0.096 lb water per lb of ethylene oxide.

An alternate route in the manufacture of ethylene oxide (used only by one chemical plant) is the chlorohydrin process. Ethylene, chlorine, and water are passed into a packed reactor, where they form ethylene chlorohydrin. The ethylene chlorohydrin is then reacted with hydrated lime to produce ethylene oxide. This process produces an aqueous lime slurry. The generation of this minimum-value by-product has led some producers to phase this process out.

Ethylene oxide production has grown nearly threefold in the last decade. Accompanying this growth has been a continuous increase in plant size, which has led to a corresponding decline in sales price. The U.S. ethylene oxide capacity and estimated economics for ethylene oxide are shown in Tables IV-18 and IV-19.

Table IV-18
Ethylene Oxide Capacity
(MM lb)

<u>Company</u>	<u>Location</u>	<u>1970</u>	<u>1972</u>
Calcasieu Chemical	Lake Charles, La.	150	150
Celanese	Clear Lake, Texas	300	300
Dow	Freeport, Texas	425	425
	Placequimine, La.	150	150
Eastman	Longview, Texas	60	60
GAF	Linden, N.J.	65	-
Houston Chemical	Beaumont, Texas	80	80
Jefferson Chemical	Port Neches, Texas	500	500
Matador Chemical	Orange, Texas	45	45
Northern Natural Gas	Joliet, Illinois	240	240
Olin Mathieson	Brandenberg, Ky.	100	100
Shell	Geismar, La.	125	125
Sun Olin	Claymont, Del.	80	80
Union Carbide	Institute, W.Va.	220	220
	Seadrift, Texas	330	430
	S. Charleston, W.Va.	60	60 ¹
	Texas City, Texas	700	500 ¹
	Torrance, Calif.	50	50
	Whiting, Ind.	150	150
	Ponce, P.R.	100	100
	Taft, La.	<u>350</u>	<u>450</u>
TOTAL		4,280	4,215

¹One unit shut down at this site.

Source: Oil, Paint & Drug Reporter, Oct. 1, 1969.

Table IV-19

Estimated Ethylene Oxide Economics
(300-MM-lb plant; 1972 construction)

Total Fixed Investment Cost

<u>Process</u>	<u>\$ MM</u>
Chlorohydrin	15.20
Catalytic air oxidation	38.60

Estimated Operation Cost

	<u>Cost</u>	
	<u>¢/lb ethylene oxide</u>	
	<u>Chlorohydrin</u>	<u>Air Oxidation</u>
Raw materials	9.61 ¹	3.30 ²
Utilities	0.78	0.28
Labor	0.20	0.14
Maintenance (6% ISBL + 3% OSBL)	0.24	0.64
Overhead (45% maint. + labor)	0.20	0.35
Taxes & insurance (1.5% of invest.)	0.08	0.20
Depreciation (10 years)	<u>0.50</u>	<u>1.32</u>
TOTAL	11.61	6.23

¹ Ethylene at 0.75 lb/lb and 3.3¢/lb; and chlorine at 1.8 lb/lb and 3.25¢/lb.

² Ethylene at 1.0 lb/lb and 3.3¢/lb.

SUBCATEGORY B

<u>Product</u>	<u>Process</u>
Formaldehyde	Oxidation of Methanol
In the plant visited, formaldehyde is manufactured by oxidation of methanol. The process is a gas-phase reaction, operated with an iron-molybdenum oxide catalyst and a lean methanol-air mixture. The chemical reaction is given below:	
$\text{CH}_3\text{OH} + 1/2 \text{O}_2 \longrightarrow \text{HCHO} + \text{H}_2\text{O}$	
Methanol Oxygen	Formaldehyde Water

A flow sheet for the methanol oxidation process is shown in Figure IV-14. A mixture of methanol and water is vaporized by a closed steam loop, which circulates between the reactor and feed vaporizer. The reactants, mixed with air, flow through a thin layer of catalyst crystals in the reactor. The product gases are cooled by water, and product formaldehyde is recovered as a 50-52 percent aqueous solution by two-stage absorption. Product concentration is adjusted by controlling the amount of water supplied to the second stage absorber. The remaining unabsorbed gases from the absorber are disposed of by incineration.

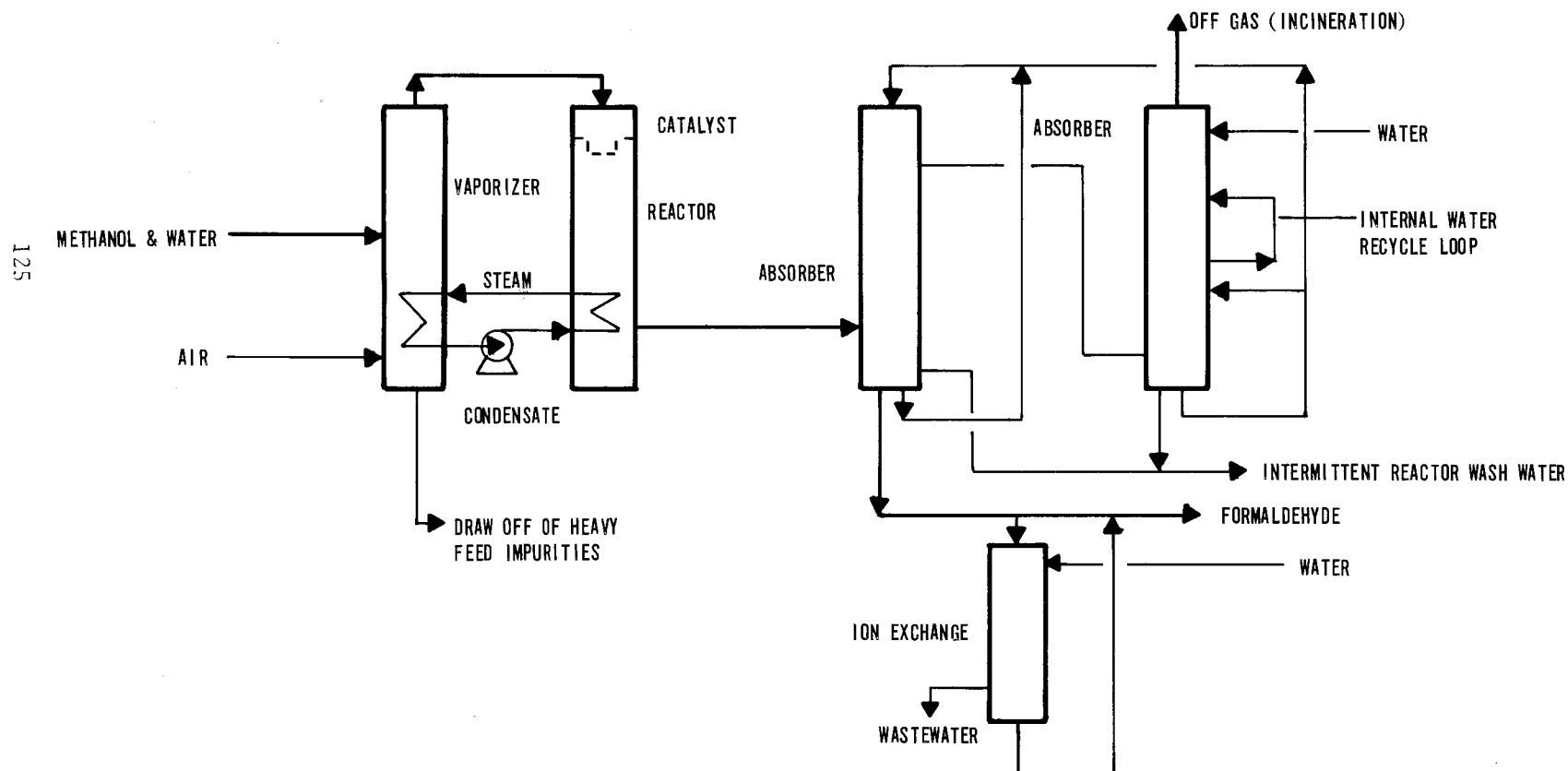
A portion of the formaldehyde product may be passed through an anion exchanger to produce high purity formaldehyde by removing formic acid and sodium formate.

Waste water streams generated in this process are intermittent. For example, waste water from the washing of the absorber occurs at most twice per year. The contaminants in this stream are formic acid, methanol, formaldehyde, and ammonia. Wastewater created by regenerating the ion exchange units occurs three times per month at the plant visited. Another possible waste stream is withdrawn as an aqueous slip stream from the bottom of the feed vaporizer whenever heavy impurities (such as acetone and oxygenated organics) occur in the methanol feed; the total flow of this waste stream, estimated by plant personnel, is about 131 gallons per 1,000 pounds of formaldehyde. A sample was not taken for analysis, since a continuous and representative sample is not available.

The alternate approach for formaldehyde manufacture from methanol involves a combined dehydrogenation and oxidation reaction over a silver or copper catalyst. This process operates with a rich methanol-air mixture.

About 90 percent of the formaldehyde produced in the U.S. is based on methanol as a raw material. The balance of the formaldehyde production is as a co-product of butane oxidation. The basic chemical reaction is summarized as follows:

FIGURE IV-14
FORMALDEHYDE, METHANOL OXIDATION





The U.S. formaldehyde capacity and the estimated economics for formaldehyde production of a 100 million pounds per year (100 percent) unit based on iron-molybdenum catalyst process are shown in Tables IV-20 and IV-21.

Table IV-20

U. S. Formaldehyde Capacity

<u>Producer</u>	<u>Plant Location</u>	<u>Estimated Capacity*</u> <u>(MM lbs. 37% Soln./Yr.)</u>
Allied	Ironton, Ohio	310
American Petrofina	Calumet City, Ill.	75
Borden	Bainbridge, N. Y.	40
	Demopolis, Ala.	80
	Diboll, Texas	70
	Fayetteville, N. C.	200
	Fremont, Calif.	80
	Kent, Washington	70
	La Grande, Oregon	40
	Louisville, Ky.	70
	Missoula, Mont.	80
	Sheboygan, Wisc.	120
	Springfield, Oregon	250
Celanese	Bishop, Texas	1,170
	Newark, N. J.	115
	Rock Hill, S. C.	115
Commercial Solvents	Agnew, Calif.	30
	Seiple, Pa.	65
	Sterling, La.	30
DuPont	Belle, W. Va.	490
	LaPorte, Texas	200
	Perth Amboy, N. J.	150
	Toledo, Ohio	150
GAF	Calvert City, Ky.	100
Georgia Pacific	Coos Bay, Ore.	80
	Columbus, Ohio	100
	Crosett, Ark.	160
Gulf	Vicksburg, Miss.	45
Hercules	Hercules, Calif.	95
	Louisiana, Mo.	170
Monsanto	Addyston, Ohio	100
	Eugene, Ore.	100
	Springfield, Mass.	280

Table IV-20
(con't)

<u>Producer</u>	<u>Plant Location</u>	<u>Estimated Capacity* (MM lbs. 37% Soln. /Yr.)</u>
Occidental	N. Tonawanda, N. Y.	135
Reichhold	Charlotte, N. C.	10
	Hampton, S. C.	40
	Kansas City, Kan.	40
	Moncure, N. C.	100
	Racoma, Wash.	40
	Tuscaloosa, Ala.	70
	White City, Ore.	50
Rohm and Haas	Bristol, Pa.	25
	Philadelphia, Pa.	25
Skelly	Springfield, Ore.	70
Tenneco	Fords, N. J.	160
	Garfield, N. J.	175
U.C.C.	Boundbrook, N. J.	150
Wright	Acme, N. C.	150
	Malvern, Ark.	<u>100</u>
TOTAL		<u><u>6,570</u></u>

*Capacity data are as reported by Stanford Research Institute,
C.E.H. for late 1970

Table IV-21

Estimated Economics for Formaldehyde Production
(100 MM lb. 100% Formaldehyde Plant)

Total Fixed Capital=\$0.45 MM

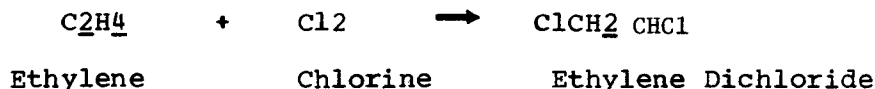
	Estimated Operation Cost	
	Captive methanol (3.0¢/lb.)	Merchant methanol (4.5¢/lb.)
Methanol	3.5	5.2
Catalyst and Chemicals	0.3	0.3
Utilities (including demineralized process water)	0.4	0.4
Labor and overhead	0.8	0.8
Capital charges	<u>1.5</u>	<u>1.5</u>
TOTAL	6.5	8.2

SUBCATEGORY B

Product
Ethylene Dichloride

Process
Direct Chlorination of Ethylene

The direct chlorination of ethylene is carried out in the presence of a ferric chloride catalyst suspended in liquid ethylene dichloride.



The gas stream from the reactor is passed through a caustic scrubber, where the unreacted gases and a trace amount of hydrogen chloride are removed by a caustic solution. The liquid stream from the reactor is first sent to a distillation column to remove heavy ends and then to a wash tower, where a caustic solution is used to remove some impurities. The crude product is finally discharged to a distillation column for purification. A process flow sheet is shown in Figure IV-15.

There are two waste streams in this process. One is liquid effluent from the scrubber and the other is the waste water from the wash tower. The results of a survey at one plant are shown in the following tabulation:

Flow	96 gallons/1,000 lb
COD	6,050 mg/l 4.84 lb/1,000 lb
BOD ₅	Inhibitory
TOC	1,106 mg/l 0.89 lb/1,000 lb

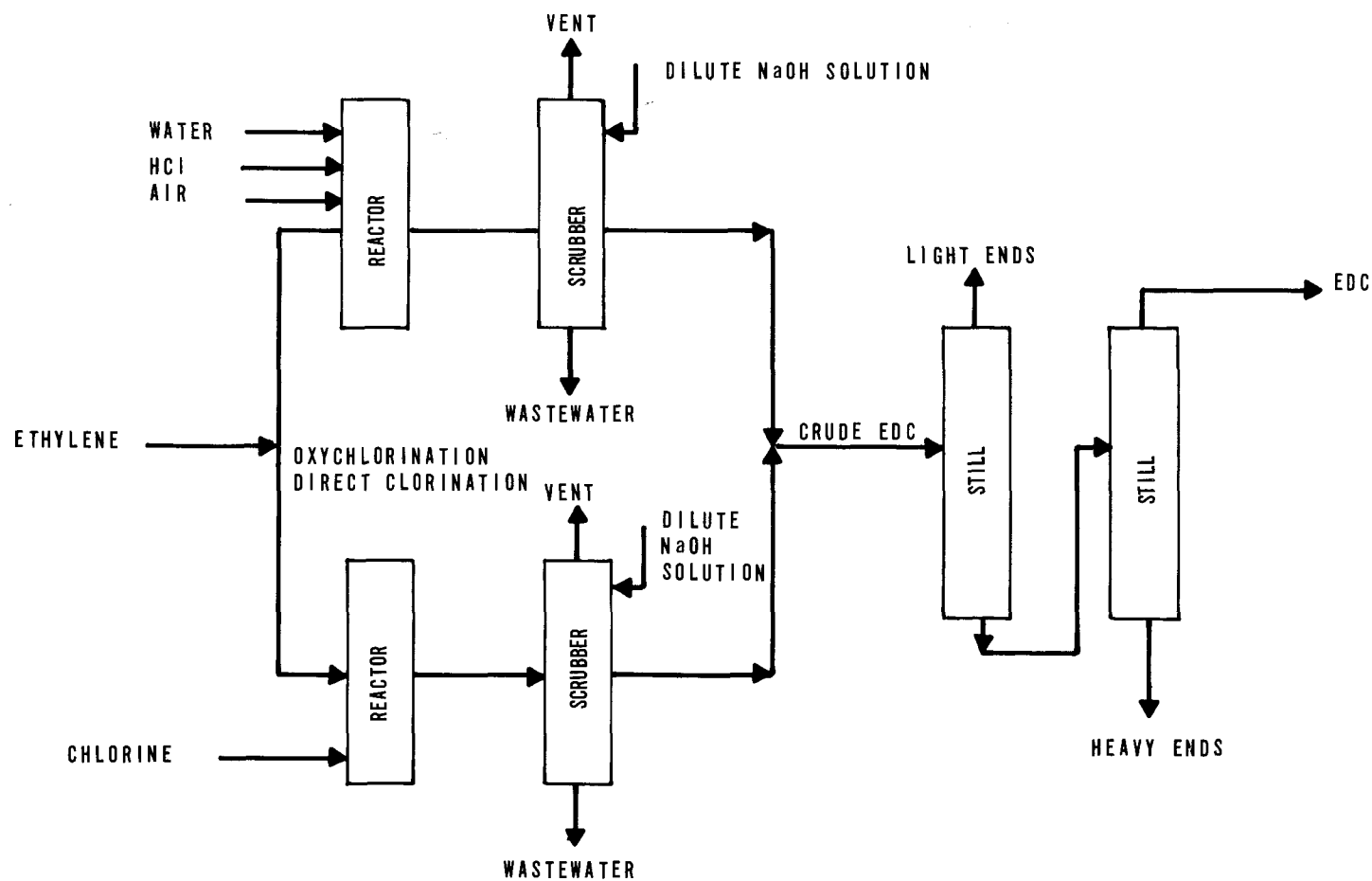
A surface heat exchanger can be used to condense water vapor in the offgas to the scrubber, while the remaining uncondensed gas from the reactor (which contains primarily unreacted ethylene and chlorine) can be totally recycled to the reactor. The scrubber and its waste water can then be eliminated. With this modification, RWL of BADCT and BATEA for this process can be expected to have low values of 0.072 pounds of COD and 0.106 pounds of TOC per 1,000 pounds of ethylene dichloride.

Total process water usage of this process is 0.82 pound of water per pound of ethylene dichloride, and cooling water usage is 93 pounds of water per pound of product.

An alternate route in manufacturing EDC is oxychlorination of ethylene with hydrochloric acid and air over a supported copper chloride catalyst. The characteristic waste water stream from

FIGURE IV-15
ETHYLENE DICHLORIDE (EDC) BY OXYCHLORINATION AND DIRECT CHLORINATION

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this process will contain most of the same impurities found in the direct chlorination process.

Ethylene dichloride has moved from fifth to third place in consumption of ethylene in the last decade. This growth has been at the expense of acetylene. The common point of intersection is vinyl chloride, which accounts for 75% of ethylene dichloride usage. Ethylene dichloride production has grown more than four-fold since 1961 with a concomitant decline in price to about 3¢ per pound. The U.S. ethylene dichloride capacity and estimated economics of EDC are presented in Tables IV-22 and IV-23, respectively.

Table IV-22

U.S. Ethylene Dichloride Capacity (1972)

<u>Company</u>		<u>MM lb.</u>
Allied	(Baton Rouge, La.)	500
American Chemical	(Long Beach, Calif.)	325
Continental Oil	(Lake Charles, La.)	1,000
Diamond Shamrock	(Deer Park, Texas)	110
Dow	(Freeport, Texas)	2,100
	(Plaquemine, La.)	1,100
Ethyl Corp.	(Baton Rouge, La.)	500
	(Houston, Texas)	250
B.F. Goodrich	(Calvert City, Ky.)	800
PPG	(Lake Charles, La.)	500
	(Guayanilla, P.R.)	835
Shell	(Deer Park, Texas)	1,700
Union Carbide	(S. Charleston, W. Va.)	150
	(Texas City, Texas)	150
Vulcan	(Geismar, La.)	240
	Total	10,260

Source: Oil, Paint, and Drug Reporter, Sept. 20, 1971.

Table IV-23

Estimated Economics for Ethylene Dichloride
(100. MM lb. plant)

Total Fixed Capital=\$1.0 MM

Estimated Operation Cost

	<u>Cost,</u> <u>¢/lb. EDC</u>
Ethylene	1.2
Chlorine	1.8
Utilities	0.1
Labor and overhead	0.1
Capital charges	<u>0.2</u>
Total	3.4

CATEGORY B

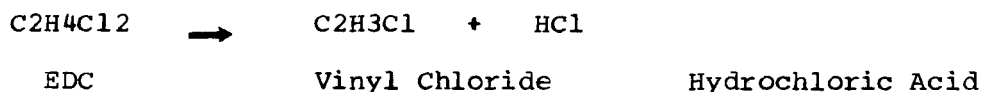
Product

Vinyl Chloride

Process

Cracking of Ethylene Dichloride

Recent developments in ethylene technology, coupled with the low cost and ready availability of ethylene, dictate ethylene as feedstock in all new vinyl chloride plants. Vinyl chloride monomer is produced by cracking purified Ethylene Dichloride (EDC) in a pyrolysis furnace as follows:



After quenching by direct contact cooling, the furnace products are separated into HCl and high-purity vinyl chloride monomer. The liquid streams from the quencher are fractionated to separate the vinyl chloride product from unreacted EDC, which is then recycled. A flow sheet for this process is shown in Figure IV-16.

The major waste water sources are the effluents from scrubbing systems required for hydrogen chloride removal, recycle purification of EDC, and the effluent from associated aqueous acid by-product production units. The survey data for one plant are presented in the following tabulation.

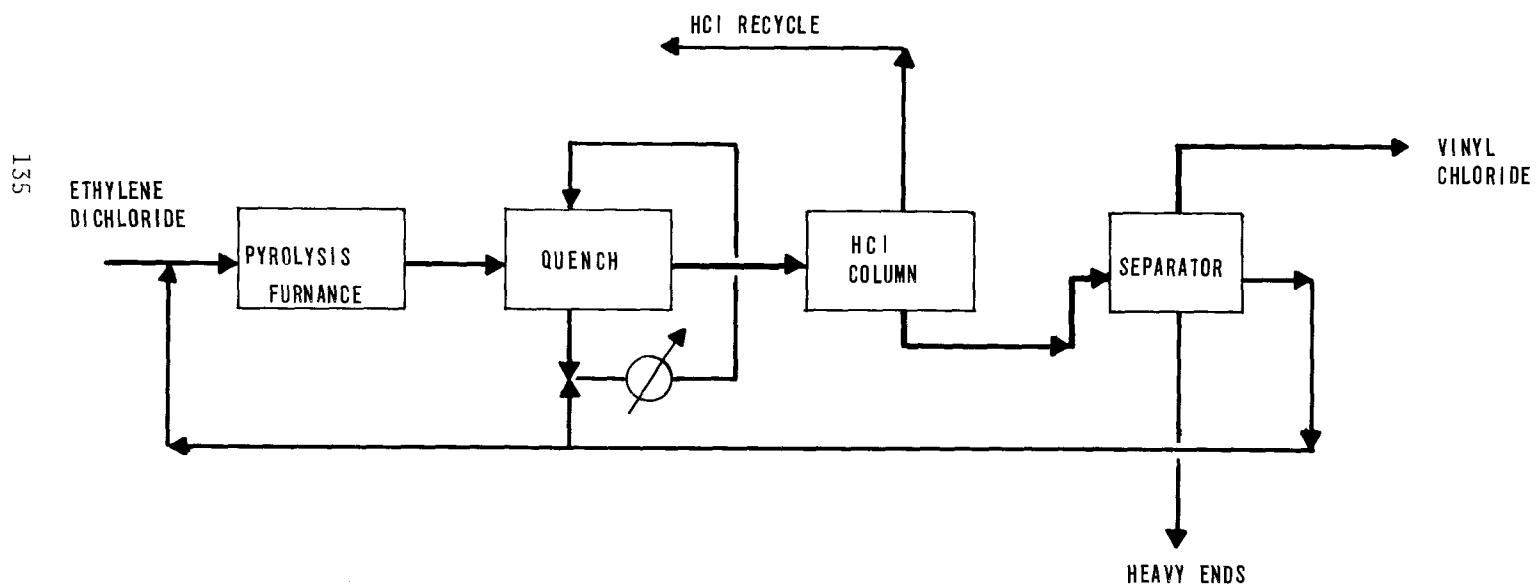
FLOW	336 gallons/1,000 lb
COD	2,733 mg/l 7.661 lb/1,000 lb
BOD ₅	Not available
TOC	120 mg/l 0.33 lb/1,000 lb

A large fraction of the RWL shown above is contributed by the aqueous acid production unit. If the by-product were left in an anhydrous form, the anhydrous acid by-product could actually replace the aqueous acid by-product. The RWL of this process will be reduced to 85 gallons of flow per 1,000 lb of product, 0.203 lb COD/1,000 lb, and 0.054 lb TOC/1,000 lb; this level of RWL will be considered as the standard of BADCT and BATEA control technology for vinyl chloride manufactured by EDC cracking.

Total process water usage in existing processes is 2.80 pounds per pound of vinyl chloride, and cooling water usage amounts to 3,464 pounds per pound of product.

FIGURE IV-16

VINYL CHLORIDE BY THERMAL CRACKING OF ETHYLENE DICHLORIDE



An alternate route in manufacturing of vinyl chloride is the classical acetylene addition reaction. This has been covered under the discussion in Category A.

Table IV-24 presents the U.S. vinyl chloride capacity, and Table IV-25 estimated economics for various processes.

Table IV-24

U.S. Vinyl chloride capacity¹
(MM lb)

<u>Company</u>	<u>1967</u>	<u>1969</u>	<u>1972</u>	<u>Process</u>
Allied Chemical (Moundsville, W. Va.)	100	-	-	Acetylene
(Geismar, La.)	-	300	550	Ethylene
American Chemical (Long Beach, Calif.)	170	170	170	Ethylene
Continental Oil (Lake Charles, La.)	-	600	600	Ethylene
Cumberland Chemical (Calvert City, Ky.)	60	-	-	Acetylene
Diamond Shamrock (Deer Park, Tx.)	100	100	-	Acetylene
Dow Chemical (Freeport, Tx.)	200	200	525	Ethylene
(Plaquemine, La.)	250	300	575	Ethylene
Ethyl Corp. (Baton Rouge, La.)	270	270	270	Ethylene
(Houston, Tx.)	150	150	150	Ethylene
General Tire (Ashtabula, Ohio)	75	-	-	Acetylene
B. F. Goodrich (Calvert City, Ky.)	400	400	400	Ethylene
(Niagara Falls, N.Y.)	40	-	-	Acetylene
Goodyear (Niagara Falls, N.Y.)	70	-	-	Acetylene
Monochem (Geismar, La.)	250	250	250	Acetylene
PPG (Lake Charles, La.)	-	300	300	Ethylene
PPG-Corco (Puerto Rico)	-	-	500	Ethylene
Shell (Deer Park, Tx.)	-	-	700	Ethylene
Tenneco (Houston, Tx.)	200	200	200	Acetylene
Union Carbide (S. Charleston, W. Va.)	120	120	120	Ethylene &
(Texas City, Tx.)	230	230	-	Acetylene
Totals	2,685	3,590	5,310	

¹ Based on Oil, Paint & Drug Reporter, March 17, 1969.

Table IV-25

Estimated vinyl chloride economics
(500-MM-lb plant; 1972 construction)

Total fixed capital

Process	\$ MM
Ethylene oxychlorination	17.9
Acetylene	18.9
Ethane (transcat)	18.0

Production cost

Process:	¢/lb		
	<u>Ethylene</u>	<u>Acetylene</u>	<u>Ethane</u>
Raw materials			
Ethane (0.59 lb/lb at 0.9¢/lb)	-	-	0.53
Ethylene (0.49 lb/lb at 3.0¢/lb)	1.46	-	-
Chlorine (0.67 lb/lb at 2.5¢/lb)	1.68	-	1.45 ¹
Acetylene (0.44 lb/lb at 8.0¢/lb)	-	3.52	-
HCl (0.60 lb/lb at 2.5¢/lb)	-	1.49	-
Subtotal	3.14	5.01	1.98
Labor	0.09	0.06	0.09
Utilities	0.22	0.08	0.22
Maintenance (6% ISBL + 3% OSBL)	0.17	0.18	0.17
Overhead (45% maint. + labor)	0.12	0.11	0.12
Taxes & ins. (1.5% of investment)	0.05	0.06	0.05
Depreciation (10 years)	0.36	0.38	0.36
Total	4.15	5.88	2.99

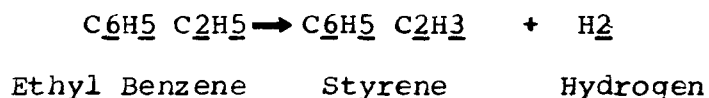
¹0.58 lb/lb at 2.5¢/lb.

SUBCATEGORY B

Product
Styrene

Process
Dehydrogenation of Ethyl Benzene

Styrene is produced by vapor-phase dehydrogenation of ethyl benzene over supported zinc oxide, magnesium oxide, and iron oxide catalysts. Steam is used as the diluent.



A flow sheet for styrene via the dehydrogenation of ethyl benzene is shown in Figure IV-17. Feedstock ethyl benzene and superheated steam are mixed in a dehydrogenation reactor. After being condensed, the reactor effluent goes to a separator, where three phases are formed. The uncondensed gases are passed through a scrubber where organic vapors are removed by the scrubbing water. The water phase is removed from the separator and discharged from the system, and the organic dehydrogenated mixture passes to the distillation section.

Since the dehydrogenation reaction operates at about 60% ethyl benzene conversion, it is necessary to fractionate the process unreacted ethyl benzene for recycle. Styrene will polymerize at temperatures approaching its normal boiling point; therefore, it is necessary to operate the styrene ethyl benzene distillation under vacuum to prevent styrene loss due to polymerization.

The draw-offs from separator and scrubber are two of the three major waste water pollution sources in the process. The other source is a steam-ejector system used to produce vacuums for distillation columns. The survey data derived from plant visits are summarized as follows:

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	2,810 gallons/1,000 lb	657 gallons/1,000 lb
COD	219 mg/l 5.13 lb/1,000 lb	426 mg/l 2.34 lb/1,000 lb
BOD ₅	69 mg/l 1.62 lb/1,000 lb	70 mg/l 0.381 lb/1,000 lb
TOC	22 mg/l 0.53 lb/1,000 lb	22 mg/l 0.12 lb/1,000 lb

The smaller amount of waste water in Plant 2 is attributed to its use of steam jets with surface heat exchangers in contrast to the steam jets with barometric condensers used in Plant 1, and also to effective operation of the scrubber system. Use of untreated river water as quenching water for the barometric condensers at Plant 1 introduces some contaminants into the waste water stream. Plant 2 discharges uncondensable vapors (consisting of some organic contaminants) from surface heat exchangers into the atmosphere.

To achieve BADCT and BATEA control technology, the steam jets (with either surface or barometric condensers) should be replaced by vacuum pumps. RWL for BADCT and BATEA can then be expected to be lower than that represented by Plant 2.

An example based on a 5×10^6 lb per year styrene plant has been devised for illustrating the advantages of vacuum pumps over steam jets. A description is given in the following paragraphs.

A two-stage steam ejector system is currently used to obtain the vacuum in the distillation section. The ejector system illustrated uses surface exchangers for both inter and after condensers. A schematic flow sheet, depicting steam and effluent flow rates and effluent composition, is presented in Figure IV-18. The effluent steam from the ejectors contains a fair amount of organics and represents a source of pollution. The cost of operating the two-stage ejector system is presented in Table IV-26. Some producers reportedly fractionate the ejector effluent stream and recycle the organics back to the process. However, it is not known if this technique is widespread or successful. Note that the use of barometric condensers will result in an excessively large effluent stream.

The vacuum pump most suitable for this application is a two-stage unit which uses a rotating mass of liquid to draw the vacuum. In this case, the compressant liquid would be essentially ethyl benzene. Most of the organics in the inlet vapor stream from the tower condense in the compressant fluid and can be recycled back to the process. Process flow sheets showing the use of vacuum pumps are presented in Figure IV-19. The amount of organic substances actually leaving the vacuum system in the exhaust air is extremely small and is itemized in Table IV-27. The amount shown in this table as recycled is actually discharged from the system via the steam ejector system. The operating costs of using vacuum pumps are summarized in Table IV-28.

It is evident that a two-stage, liquid-sealed vacuum pump is more economical than a two-stage steam ejector using surface condensers. The economic advantage is due to the extremely low loss of ethyl benzene and styrene in the exhaust stream from the vacuum pumps. In other words, this modification not only has an economic advantage, but also reduces the RWL of the process. Styrene is used exclusively for homo-, co-, and terpolymers and is produced on the Gulf Coast. Production capacity has grown rapidly to accommodate demand. Installed styrene capacity is

FIGURE IV- 18
STYRENE- ETHYLBENZENE DISTILLATION, VACUUM VIA TWO-STAGE STEAM EJECTORS

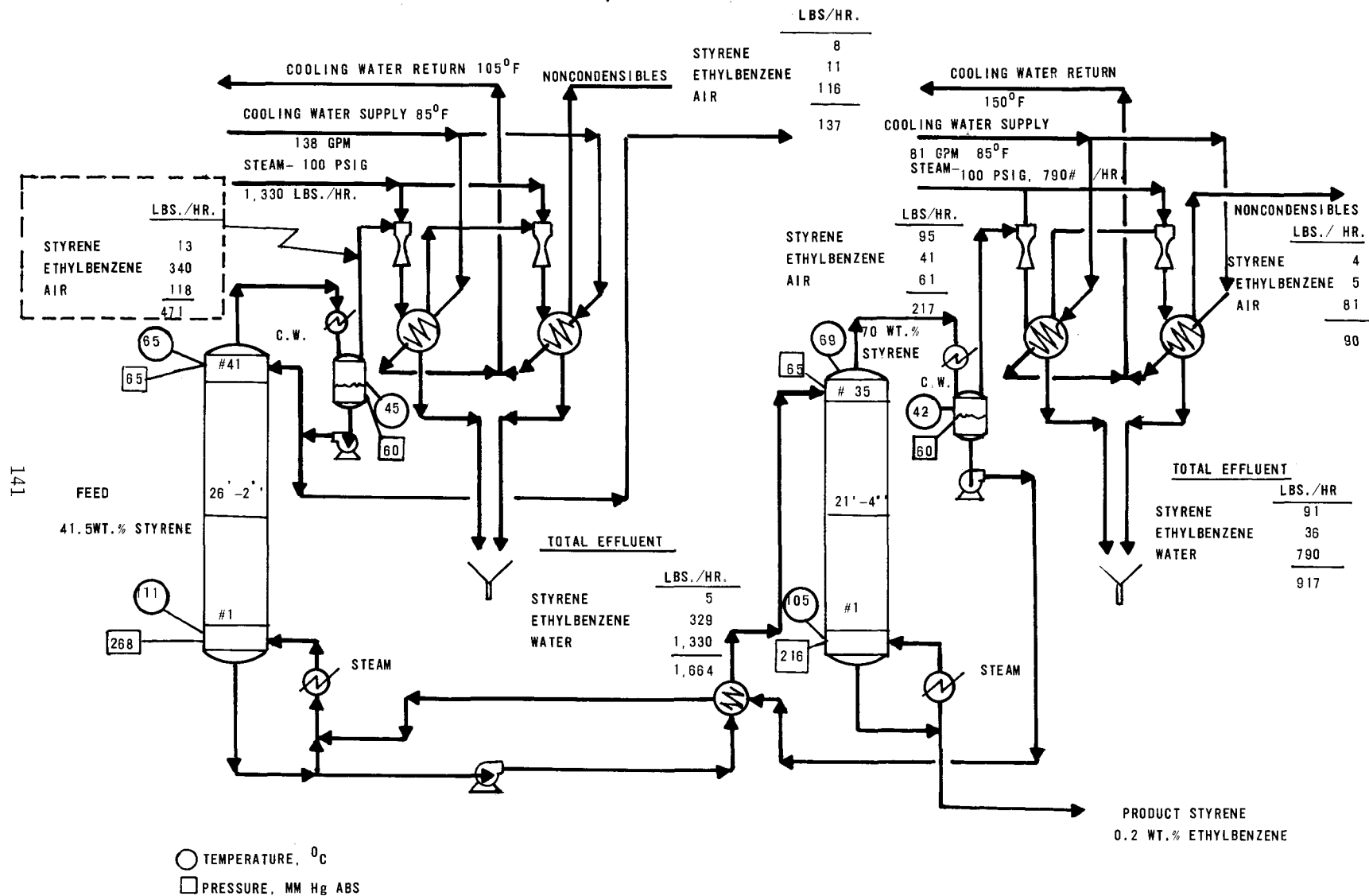


FIGURE IV-19
 STYRENE - ETHYLBENZENE DISTILLATION, VACUUM VIA VACUUM PUMPS

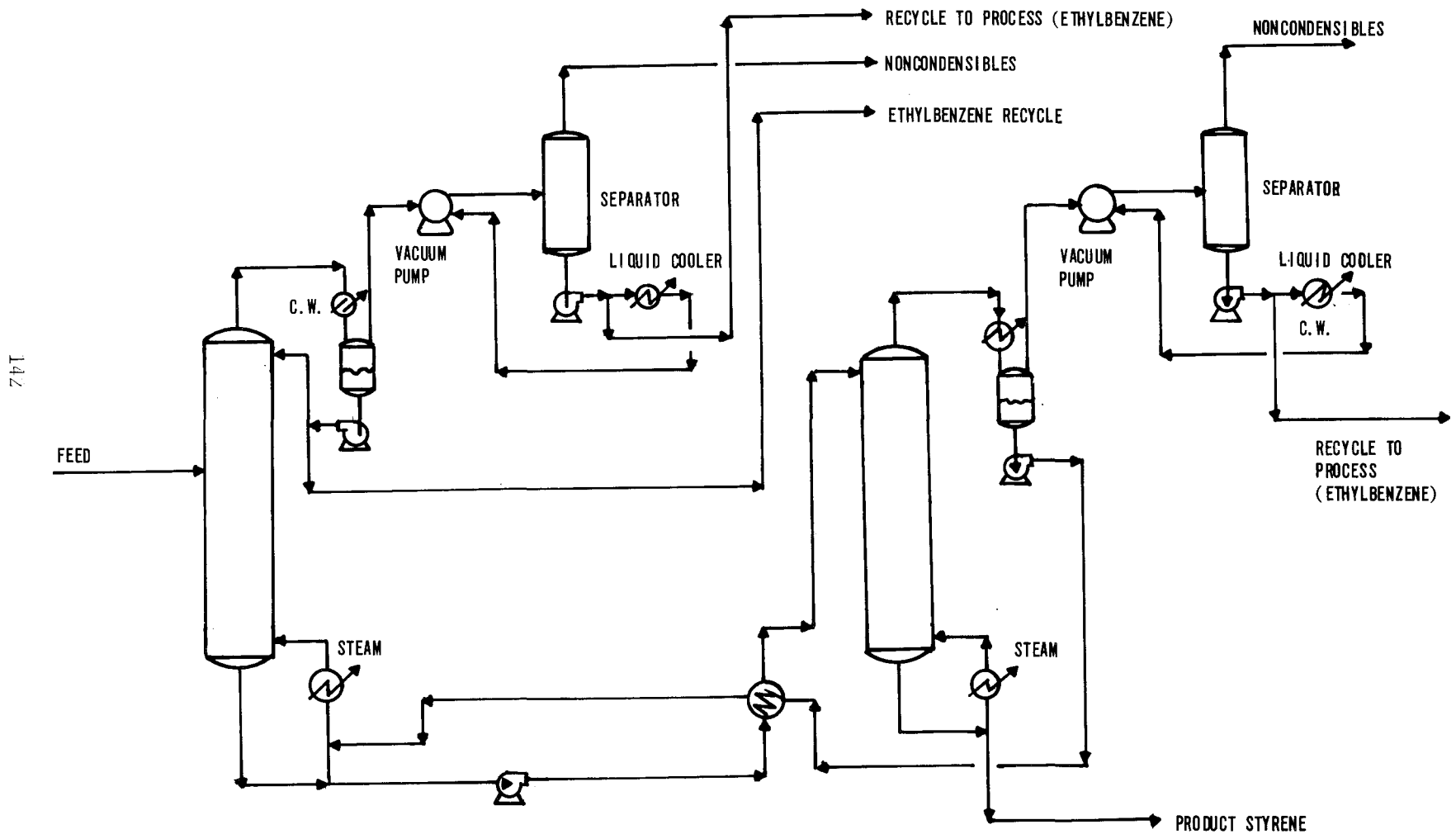


Table IV-26

Operating Cost of Two-Stage Steam Ejectors
Styrene-Ethyl Benzene Distillation
500 MM lbs/yr Styrene, 8,200 hrs/yr

	Two-Tower System			
	Tower No. 1		Tower No. 2	
Investment, \$ (for ejectors etc.)	10,000		7,400	
<u>Utilities</u>	<u>Lb/Hr</u>	<u>\$/Yr</u>	<u>Lb/Hr</u>	<u>\$/Yr</u>
Steam, x 55¢/M lb	1,330	6,000	790	3,600
Cooling Water, 2.5¢/M gal	<u>GPM</u>	<u>\$/Yr</u>	<u>GPM</u>	<u>\$/Yr</u>
$\Delta T=20^{\circ}\text{F}$	150	1,800	89	1,100
Total Utilities, \$/Yr	7,800		4,700	
<u>Investment Related</u>	<u>\$/Yr</u>		<u>\$/Yr</u>	
Maintenance Material and Labor, 2% of Investment	200		150	
Plant Overhead, 65% of Maintenance	130		100	
Insurance and Taxes, 1.5% of Investment	150		110	
Depreciation, 10% of Investment	<u>1,000</u>		<u>740</u>	
Total Investment Related Expenses, \$/Yr.	1,480		1,100	
<u>Product Losses</u>	<u>Lb/Hr</u>	<u>\$/Yr</u>	<u>Lb/Hr</u>	<u>\$/Yr</u>
Styrene, 7.0 ¢/lb	13	7,500	95	54,500
Ethylbenzene, 3.5 ¢/lb	340	<u>97,600</u>	41	<u>11,800</u>
Total Product Losses, \$/Yr	105,100		66,300	
Total Operating Costs, \$/Yr	<u>114,380</u>		<u>72,100</u>	
	186,480			
Total Operating Costs, ¢/lb styrene produced			0.037	

Table IV-27

Organics in Exhaust Air From Vacuum Pumps
 500 MM Lbs/yr Styrene-8,200 hrs/yr
 (1bs/hr)

Two-Tower System

	<u>Tower No. 1</u>	<u>Tower No. 2</u>
<u>Styrene</u>		
In	13	95
Out In Exhaust	<u>8</u>	<u>4</u>
Amount Recycled	5	91
<u>Ethylbenzene</u>		
In	340	41
Out In Exhaust	<u>11</u>	<u>5</u>
Amount Recycled	329	36

Table IV-28

Operating Costs For Vacuum Pumps*
 Styrene-Ethyl Benzene Fractionation
 500 MM Lbs/yr Styrene, 8,200 hrs/yr.

	Two Tower System			
	Tower No. 1		Tower No. 2	
Investment, \$ (vacuum pumps etc.)	30,000		23,000	
<u>Utilities</u>				
Power, 0.800 ¢/kwh	<u>kwh</u> 51	<u>\$/yr</u> 3,350	<u>kwh</u> 29	<u>\$/yr</u> 1,900
Cooling Water, 2.5 ¢/Mgal ΔT=20°F.	<u>GPM</u> 13	<u>\$/yr</u> 160	<u>GPM</u> 7	<u>\$/yr</u> 90
Total Utilities, \$/yr	3,510		1,990	
<u>Investment Related Expenses</u>	<u>\$/yr</u>		<u>\$/yr</u>	
Maintenance Materials and Labor, 4% of Investment	1,200		920	
Plant Overhead, 65% of Maintenance	780		690	
Insurance, Taxes, 1.5% of Investment	450		920	
Depreciation, 10% of Investment	<u>3,000</u>		<u>2,300</u>	
Total Investment Related Expenses, \$/yr	5,430		4,830	
<u>Product Losses</u>				
	<u>Lbs/yr</u>	<u>\$/yr</u>	<u>Lbs/yr</u>	<u>\$/yr</u>
Styrene, 7¢/lb.	8	4,600	4	2,300
Ethylbenzene, 3.5¢/lb.	11	<u>3,160</u>	5	<u>1,440</u>
Total Product Losses, \$/yr	7,760		3,740	
Total Operating Costs, \$/yr	<u>16,700</u>		<u>10,560</u>	
	27,260			
Total Operating Cost, ¢/lb styrene product	0.005			

*Per letter from Nash Engineering Co. of 5-29-73 to Chem Systems

presented in Table IV-29, and estimated economics for a competitive 5 x 10⁸ lb plant are shown in Table IV-30.

Table IV-29

U.S. Styrene Capacity¹
(MM lb)

<u>Company</u>		<u>1967¹</u>	<u>1970¹</u>	<u>1972</u>
Amoco	(Texas City, Texas)	300	800	800
Cosden	(Big Spring, Texas)	100	100	100
Cos-Mar	(Carville, La.)	-	500	500
Dow	(Freeport, Texas)	500	650	650
	(Midland, Mich.)	300	350	350
El Paso	(Odessa, Texas)	85	120	120
Foster-Grant	(Baton Rouge, La.)	200	250	250
Gulf Oil	(Donaldsville, La.)	-	-	500
Marbon	(Baytown, Texas)	125	135	shut down
Monsanto	(Texas City, Texas)	650	800	1,300 ²
Shell	(Torrance, Calif.)	210	240	240
Sinclair-Koppers	(Houston, Texas)	70	110	110
	(Kobuta, Pa.)	200	430	430
Sun Oil	(Corpus Christi, Texas)	60	80	80
Union Carbide	(Sea Drift, Texas)	300	300	300
	(Institute, W. Va.)	110	shut down	shut down
Total		3,210	4,865	5,730

¹Oil, Paint & Drug Reporter, July 7, 1969 and earlier profiles.
²New plant that replaced 800 MM-lb unit.

Table IV-30

Estimated Economics For Styrene¹
(500 MM-lb plant; 1972 construction period)

- A. Total fixed capital=\$35.0 MM
B. Production costs

	<u>¢/lb styrene</u>
Raw materials ²	3.95
Labor	0.13
Utilities	0.91
Maintenance (6% ISBL + 3% OSBL)	0.34
Overhead (45% maint + labor)	0.56
Taxes (1.5% of invest)	0.10
Depreciation (10 yr)	<u>0.70</u>
Total	6.69

¹Dehydrogenation process.

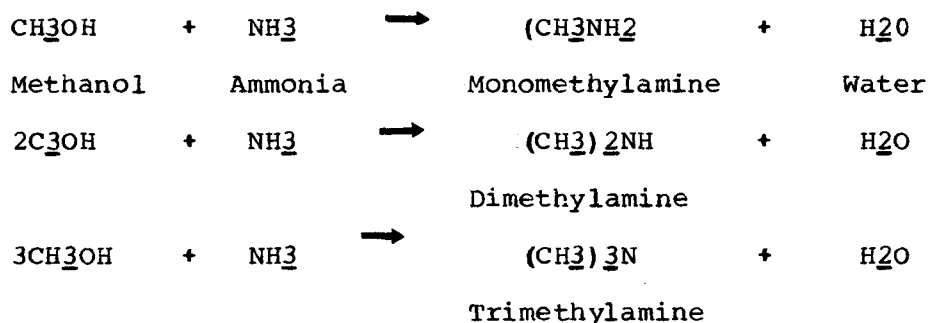
²1.10 lb ethylbenzene at 3.50¢/lb + catalyst and chemicals.

SUBCATEGORY B

Product
Methyl Amines

Process
Synthesis of Methanol and Ammonia

Methyl amines are synthesized by methanol and ammonia in the presence of catalyst to form a mixture of mono-, di-, and trimethylamine.

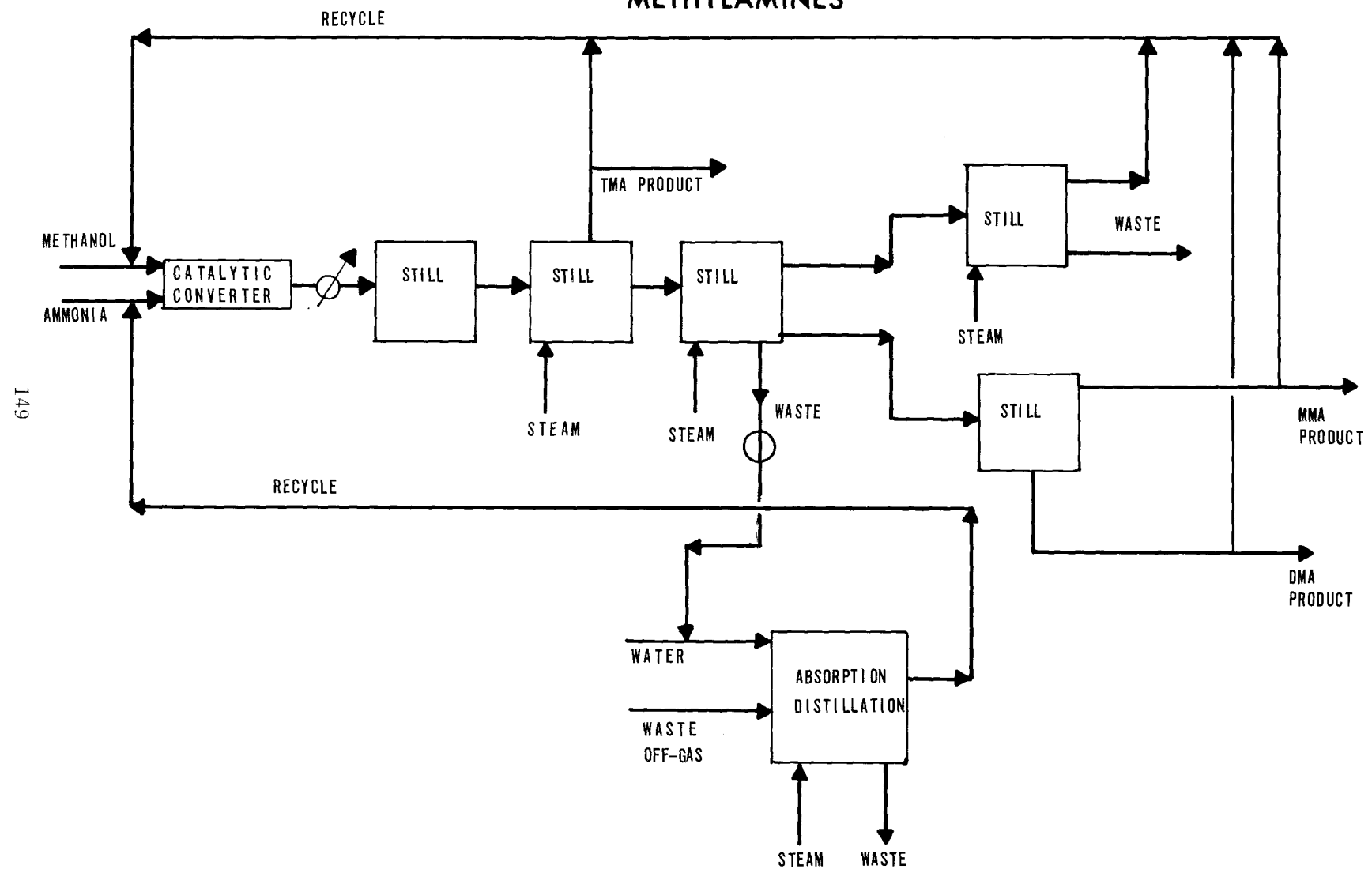


Reactants are first preheated by the converter effluent, thereby recovering some of the exothermic reaction heat. The product stream is then flashed to remove the noncondensibles and is sent to the recovery system. First, ammonia is taken overhead and recycled, together with some trimethylamine. Next, water is added to break the TMA-Ammonia azeotrope, and pure TMA is taken overhead from a distillation column. The mixture of mono- and dimethylamine is first dehydrated and then fractionated to separate DMA and MMA. The ratios of three amines can be varied by changing reaction conditions. The process flow diagram is shown in Figure IV-20.

This process uses water to scrub ammonia from all off-gases. The liquid effluent from the absorber is then flashed to recover ammonia. The major waste water source, containing a significant amount of unrecoverable ammonia, is the bottoms from the flash column. The other two waste water streams are the bottoms from the separation fractionators. The characteristics of the waste water are summarized in the following tabulation.

	<u>Sample No. 1</u>	<u>Sample No. 2</u>
Flow	429 gallons/1,000 lb	429 gallons/1,000 lb
COD	6,303 mg/l 22.56 lb/1,000 lb	1,178 mg/l 4.21 lb/1,000 lb
BOD ₅	99 mg/l 0.351 lb/1,000 lb	174 mg/l 0.62 lb/1,000 lb
TOC	11,634 mg/l	3,808 mg/l

FIGURE IV-20
METHYLAMINES



41.65 lb/1,000 lb

13.63 lb/1,000 lb

The above data show significant variation. The extraordinarily high ratio of COD/BOD₅ is due to the ammonia contaminant which contributes to the measurement of COD but not to that of BOD₅. It is believed that Sample I was taken under the upset operating condition of the ammonia flash column.

Total process water usage, including steam directly supplied to the process, is 3.1 pounds water per pound of methylamines, while cooling water usage amounts to 16,700 pounds water per pound of product.

Minor process modifications such as reusing waste waters from fractionators as ammonia absorption water can reduce the amount of waste water. The ammonia content in the waste water can be treated only by end-of-pipe treatment.

Investment for a methylamines plant depends somewhat on the intended product mixture; a unit to produce 10 million pounds per year costs around \$1.5 million. A summary of U.S. production capacity and estimated production costs for dimethylamine are presented in Tables IV-31 and IV-32.

Table IV-31
U.S. Methyl Amines Capacity (1970)

<u>Company</u>	<u>Location</u>	<u>Capacity</u> MM lbs.
Commercial Solvents	Terre Haute, Ind.	18
DuPont	Belle, W. Va.	75
	Strang, Texas	26
Escambia	Pace, Fla.	50
GAF	Calvert City, Ky.	10
Pennwalt	Wyandotte, Mich.	<u>10</u>
TOTAL		189

Table IV-32
Estimated Economics for Methylamines
(10 MM lb. Plant)

Total Fixed Capital = \$1.5 MM

Estimated Production Cost

	<u>Cost</u> ¢/lb. DMA
Methanol (captive, 3.04/lb.)	4.6
Ammonia (merchant, 4.0¢/lb.)	1.6
Utilities	1.5
Labor and Overhead	1.2
Capital charges	<u>5.0</u>
Total	13.9

SUBCATEGORY B

Product
Vinyl Acetate

Process
Synthesis with Ethylene and Acetic Acid

Fresh ethylene, oxygen, and acetic acid are combined with their respective recycle streams, and then are vaporized and fed to a fixed-bed reactor. Typical operating conditions are 5 psig and 250°C. Conversion per pass is about 5 percent, with very high (99 percent) selectivity. The catalyst is usually a mixture of palladium, copper, and iron chloride on alumina. The acetic acid-to-water mole ratio in the reactor is kept at about 40:1 to suppress acetaldehyde formation. Reactor effluent vapor is partially condensed to recover some of the acetic acid for recycle. Further cooling and fractionation separate a crude product stream from ethylene, which is recycled to the reactor. The crude product stream is then fed to a series of fractionators for further removal of acetic acid and light ends. Hydroquinone is usually added as a polymerization inhibitor before vinyl acetate is sent to storage. The process flow diagram is shown in Figure IV-21.

Since the process is a vapor-phase reaction, waste water is minimal. The major waste water stream is generated as bottoms from one of the fractionators. The light ends and heavy ends separated out are either recycled, sold, or disposed of by incineration.

Results of survey data are summarized in the following tabulation:

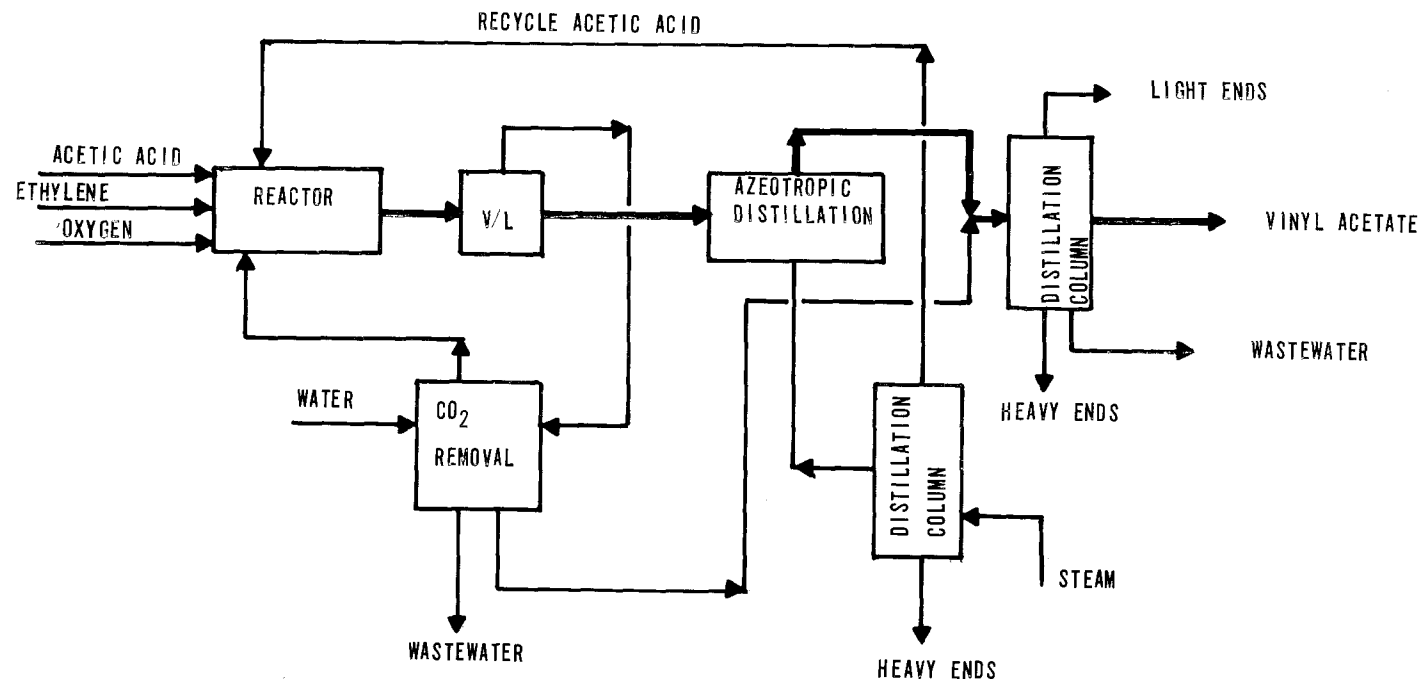
Flow	28 gallons/1,000 lb
COD	516 mg/l 0.13 lb/1,000 lb
BOD ₅	150 mg/l 0.04 lb/1,000 lb
TOC	220 mg/l 0.25 lb/1,000 lb

This level of RWL can be considered as standards for BADCT and BATEA control technology for this process.

The classical alternate route in manufacturing of vinyl acetate is the simple vapor-phase reaction of acetylene and acetic acid in the presence of a zinc acetate catalyst on a carbon support. Acetylene conversion is about 60 percent per pass at high (96 percent) selectivity.

A third route is by liquid-phase synthesis of ethylene and acetic acid. The reaction is carried out in a palladium chloride solution at 450 psig and 250°C. Conversion per pass is about 5 percent with 97-98 percent selectivity. Acetaldehyde co-product

FIGURE IV -21
VINYL ACETATE, FROM ETHYLENE AND ACETIC ACID



yield is controlled by suitable adjustment of the water content, and this co-product is oxidized in-situ to form acetic acid, which is used for the main reaction. The literature indicates that this route produces the best economics.

The U.S. vinyl acetate capacity and comparative economics of the acetylene and ethylene processes are presented in Tables IV-33 and IV-34.

Table IV-33
U.S. Vinyl Acetate Capacity

Producer	Location	1967 MM lb	1969 MM lb	1970 MM lb	1972 MM lb	Process
Air Products	Calvert City, Texas	95	95	95	-	Acetylene
Borden Chemical	Geismar, La.	90	115	115	115	Acetylene
	Geismar, La.	-	-	75	75	Acetylene
Celanese Chemical	Bay City, Texas	100	100	100	-	Ethylene
	Pampa, Texas	65	65	-	-	Acetaldehyde- acetic anhydride
	Clear Lake, Texas	-	-	200	200	Ethylene
DuPont Company	Niagara Falls, N.Y.	75	75	75	-	Acetylene
	La Porte, Texas	-	-	-	400	Ethylene
Monsanto Company	Texas City, Texas	65	65	80	-	Acetylene
National Starch	Long Mott, Texas	50	50	60	60	Acetylene
Union Carbide	S. Charleston, W.Va.	55	55	55	-	Acetylene
	Texas City, Texas	145	195	300	300	Acetylene
U.S. Industrial Chemical	La Porte, Texas	-	-	300	300	Ethylene
Total		740	815	1,455	1,450	
% acetylene		78	80	59	38	

Source: Oil, Paint & Drug Reporter Profile, Jan. 1, 1970 and other trade publications

Table IV-34

Comparative Vinyl Acetate Economics
(300-MM-lb plants; 1972 construction period)

Estimated Total Investment Cost

Acetylene process = \$12.6 MM

Ethylene process (gas phase) = \$17.3 MM

Estimated Production Costs
¢/lb vinyl acetate

Acetylene Route Ethylene Route

Raw materials

Acetic acid (6.0¢/lb)	4.31	4.23
Ethylene (3.0¢/lb)	-	1.02
Acetylene (8.0¢/lb)	2.56	-
Catalyst and chemicals	<u>0.32</u>	<u>0.29</u>
Total materials	7.19	5.54
Labor	0.17	0.19
Utilities	0.29	0.70
Maint. (6% ISBL + 3% OSBL)	0.20	0.27
Overhead (45% of maint. + labor)	0.17	0.21
Taxes and ins. (1.5% of investment)	0.07	0.09
Depreciation (10 years)	<u>0.42</u>	<u>0.57</u>
Total	8.51	7.57

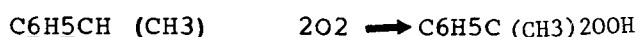
SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Phenol	1. Cumene Oxidation and Cleavage 2. Chlorobenzene Process

1. Cumene Oxidation and Cleavage

The cumene process is currently the most popular route and the one upon which most expansions will be based. The manufacture of phenol from cumene is carried out by a process involving the following basic steps:

- a. Oxidation of cumene with air to form cumene hydroperoxide.



Cumene Oxygen Cumene Hydroperoxide

- b. Cleavage of cumene hydroperoxide to form phenol and acetone.



Cumene Hydroperoxide Phenol Acetone

A process flow sheet is shown in Figure IV-22. Cumene and air are fed to a liquid-phase reactor, operating at 25-50 psig and 130-140°C, in the presence of a small amount of alkali, to produce the hydroperoxide intermediate. Reactor liquid effluent is fed to a fractionating tower, where unreacted cumene is recovered and recycled to the reactor.

Cumene hydroperoxide from the fractionator is fed to a hydrolysis reactor where the cumene hydroperoxide is cleaved to phenol and acetone with the aid of a sulfuric acid catalyst. Typical operating conditions are 5 psig and 150-200°F, and conversion is essentially complete, with minimal formation of undesired by-products. The crude phenol-acetone mixture is passed through an ion exchange system and then fed to a series of tower fractionation trains, where pure phenol and co-produced acetone are separated from light and heavy ends and other by-products.

2. Chlorobenzene Process

The process flow diagram of chlorobenzene process is shown in Figure IV-23, and the basic reactions are summarized below:

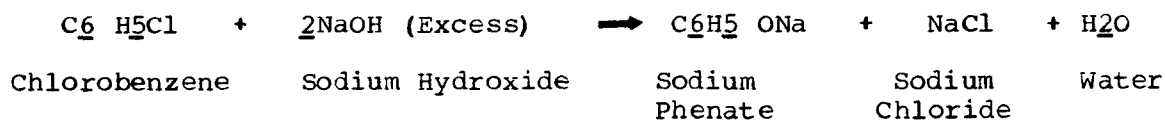
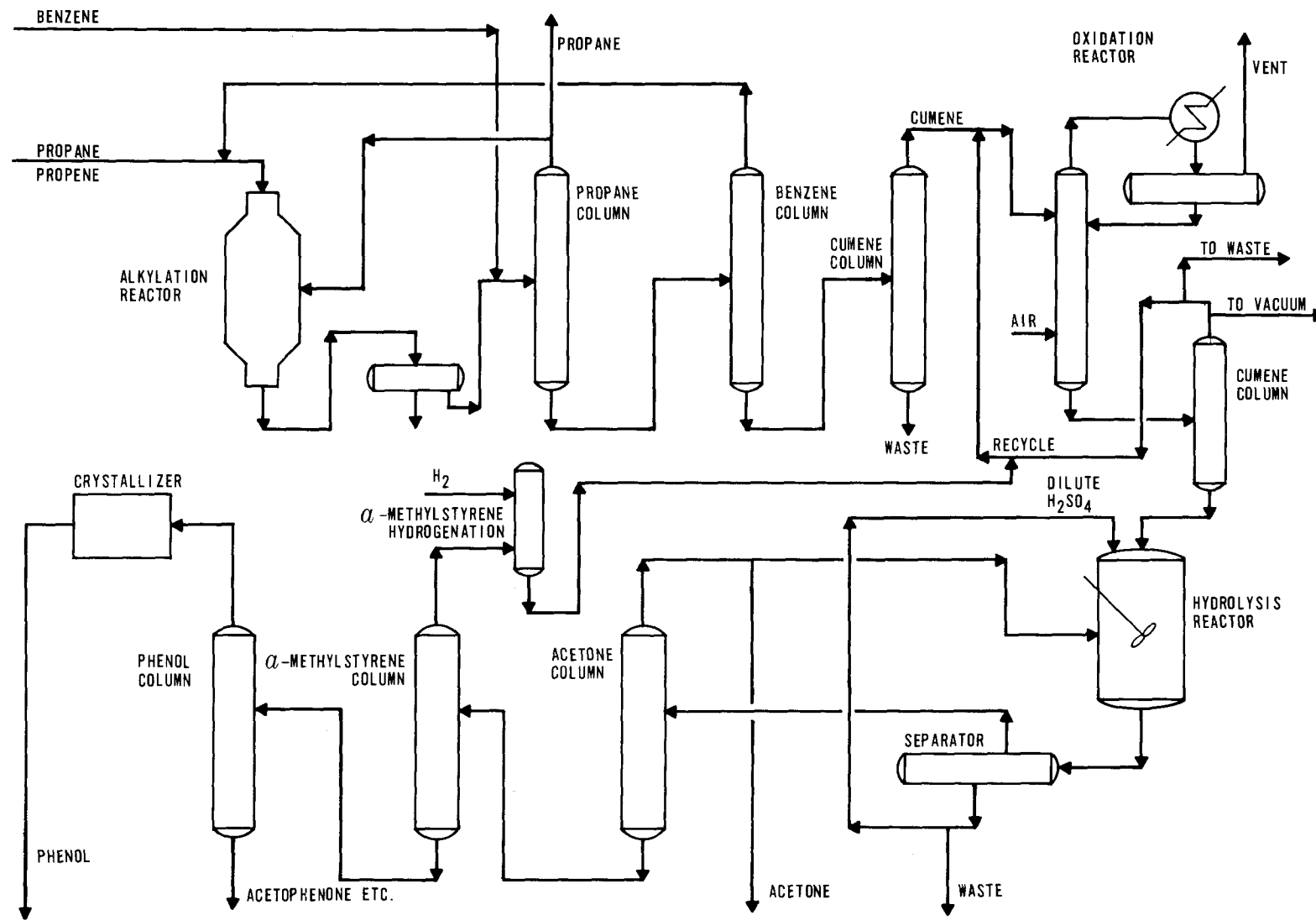
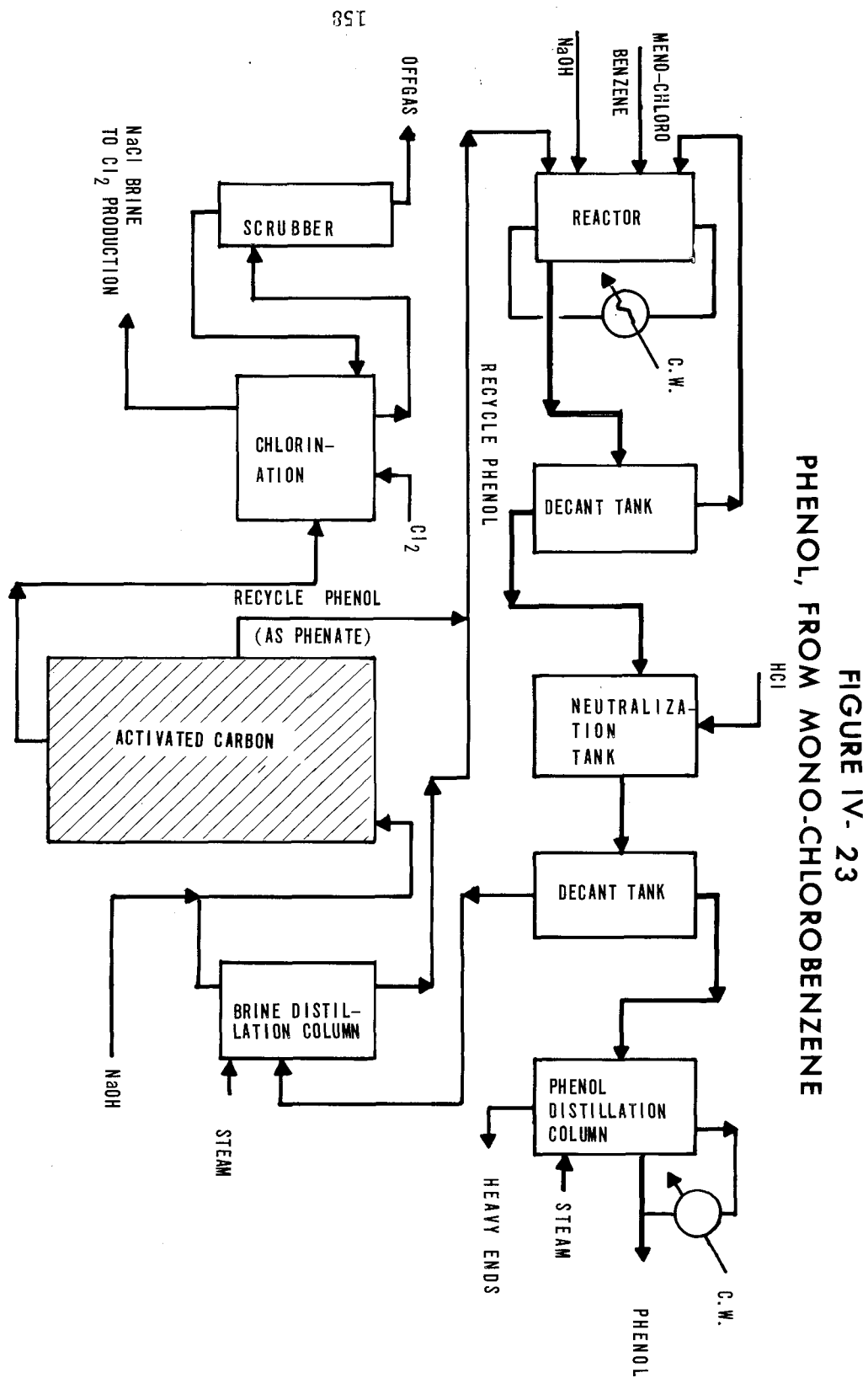
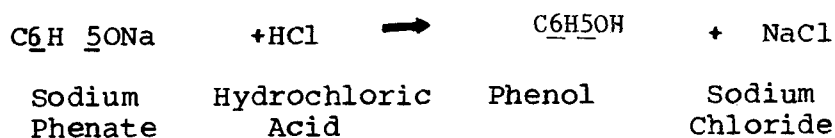


FIGURE IV-22

PHENOL, VIA CUMENE







The feed materials (chlorobenzene and excess caustic solution) are fed into a liquid-phase reactor, and the effluent is discharged into a decanter. The upper layer of unreacted chlorobenzene is recycled back to the reactor. The bottom layer of sodium phenate is neutralized to produce a mixture of phenol and brine; this mixture is then decanted. The upper layer is sent to a fractionator, where pure phenol is obtained, and the bottom brine stream is passed through an activated carbon bed to remove the remaining phenol, which is eventually recycled back to the reactor.

The chlorobenzene process is used by only one company in the U.S. The major waste water source in this process is the brine solution from the second decanter, which is contaminated with phenol and acetic acid. However, an activated carbon system and chlorination reactor, both being considered as parts of an integral system of the process, are used to remove phenol by adsorption and to destroy the acetic acid component. The effluent from the system is totally recycled for chlorine production. The adsorbed phenol is desorbed with caustic solution to form sodium phenate, which is recycled back to the reactor. Therefore, the process is free of discharge and can be considered as a standard for BADCT and BATEA.

The cumene oxidation process recycles the water present in the hydroperoxide reactor. Water from the dilute sulfuric acid in the cleavage reactor is also recycled. The only significant waste water stream is generated by water scrubbing the vapor effluent from the cleavage reactor; this stream contains dissolved sulfuric acid, sulfates, and oxygenated organic compounds.

The major parameters of surveyed RWL data from two cumene oxidation plants are summarized in the following tabulation. The results of the analyses also show that phenol and oil contaminants in waste waters from both plants are in excess of general discharge criteria for biological treatment processes and would interfere with the normal functioning of such processes.

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	279.6 gallons/1,000 lb	164 gallons/1,000 lb
COD	4,770 mg/l 11.1 lb/1,000 lb	84,304 mg/l 11.5 lb/1,000 lb
BOD ₅	2,410 mg/l 5.6 lb/1,000 lb	17,575 mg/l 24 lb/1,000 lb

TOC	194 mg/l	77,406 mg/l
	0.45 lb/1,000 lb	105.6 lb/1,000 lb

The survey data show a significant difference in RWL between two plants. The lower RWL of Plant 1 is attributed to the installation of dephenolizer facilities (steam stripper). These facilities are considered as part of the process rather than end-of-pipe treatment, since phenol is recovered at this unit and recycled back to the oxidation reactor. The higher RWL of Plant 2 is attributed mainly to the disposal of concentrated light ends and heavy ends from acetone and phenol fractionators into the sewers, instead of by incineration as commonly practiced. RWL represented by Plant 1 can be logically considered as standard for BPCTCA control technology.

The activated carbon system mentioned in the chlorobenzene process has been claimed to be effective in reducing phenol concentration from about 100 mg/l down to 1 mg/l. The saturated activated carbon beds can be regenerated with caustic solution by desorbing phenol into phenate salt. The salt is then recycled to the oxidation reactor. With this system, phenol is recovered for reuse, and the RWL of the process is reduced as well. Consequently, BADCT and BATEA should require a steam stripper/dephenolizer with an activated carbon system to achieve a low RWL standard.

Gross cooling water usages for the two processes discussed above differ greatly: 3.85 and 463 pounds of water per pound of phenol, respectively, for the chlorobenzene and cumene processes.

Several other process routes in manufacturing of phenol are currently practiced. These include the Hooker-Raschig process, toluene oxidation, and sulfonation. Again, the cumene route is by far the most important, and it is predicted that all phenol capacity installed over the next ten years will be based on this process. The current U.S. phenol production capacity and its estimated economics are presented in Tables IV-35 and IV-36.

The Hooker-Raschig and sulfonation processes are briefly described in the following paragraphs.

The Hooker-Raschig process is a two-step, vapor-phase reaction. A benzene chlorination reaction is carried out at 400°F with air, over a copper and iron chloride catalyst. The copper-iron catalyst oxidizes the hydrogen chloride to chlorine and water. The chlorine attacks the benzene ring to yield chlorobenzene and additional hydrogen chloride. The chlorobenzene is then hydrolyzed over silica at 900°F to yield phenol and hydrogen chloride. There is no net production of hydrogen chloride since it is continually converted to usable chlorine. The net products are, therefore, phenol and water.

The sulfonation process is a liquid-phase reaction. Benzene is first reacted with sulfuric acid to produce benzenesulfonic acid,

which is then converted to phenol by caustic fusion. The sulfuric acid employed in this process is totally lost.

Table IV-35
U.S. Phenol Capacity*

<u>Producer</u>	<u>Plant Location</u>	<u>Estimated Capacity</u> MM lbs/yr	<u>Process Route</u>
Allied	Frankford, Pa.	420	Cumene
Chevron	Richmond, Cal.	50	Cumene
Clark Oil	Blue Island, Ill.	70	Cumene
Dow	Kalama, Wash.	40	Toluene oxidation
	Midland, Mich.	230	Chlorobenzene
Hercules	Gibbstown, N.J.	100	Cumene
Hooker	N. Tonawanda, N.Y.	65	Raschig
Monsanto	S. Shore, Ky.	65	Raschig
	Alvin, Texas	375	Cumene
	Monsanto, Ill.**	115	Sulfonation
Reichold	Tuscaloosa, Ala.	90	Sulfonation
Shell	Houston, Texas	50	Cumene
Skelly	El Dorado, Kansas	50	Cumene
Union Carbide	Bound Brook, N.J.	150	Cumene
	Marietta, Ohio	125	Raschig
Natural phenol produced		<u>90</u>	
TOTAL		<u><u>2,085</u></u>	

*As of mid-1970. Estimated based on trade literature.

**Reported shut down.

Table IV-36

Estimated Economics for Phenol Production
(400-MM-lb plant; 1972 construction)

FIXED INVESTMENT COSTS

<u>Process</u>	<u>\$MM</u>
Cumene	26.6
Toluene	30.0
Raschig	36.1

PRODUCTION COSTS

	<u>Cumene</u> <u>¢/lb</u>	<u>Toluene</u> <u>¢/lb</u>	<u>Raschig</u> <u>¢/lb</u>
Raw materials	5.81 ¹	3.45 ²	3.67 ³
Labor	0.29	0.29	0.29
Utilities	0.92	0.71	0.78
Maintenance (6% ISBL + 3% OSBL)	0.32	0.36	0.43
Overhead (45% maint. and labor)	0.27	0.30	0.32
Taxes and insurance (1.5% of investment)	0.10	0.11	0.13
Depreciation (10%)	<u>0.67</u>	<u>0.76</u>	<u>0.91</u>
TOTAL	8.38	5.98	6.53
By-product credit ⁴	<u>2.74</u>	<u>-</u>	<u>-</u>
NET	5.64	5.98	6.53

¹1.45 lb cumene/lb at 3.7¢/lb + catalyst and chemicals.

²Includes 1.3 lb toluene at 2.5¢/lb.

³0.94 lb benzene/lb at 3.4¢/lb + catalyst and chemicals.

⁴0.60 lb acetone/lb phenol at 4.6¢/lb.

SUBCATEGORY C

Product

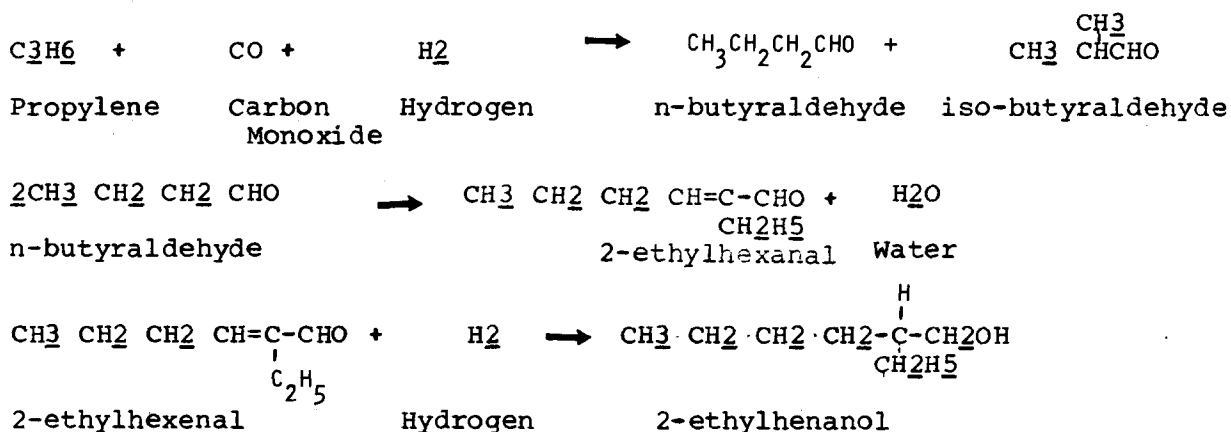
Oxo Chemicals

Process

Carbonylation and Condensation

The oxo process is a broadly applicable technology which is used to produce aldehydes which are usually converted to the corresponding alcohols. The process is used on a number of feedstocks, the two most important being propylene and alpha olefins, to produce linear alcohols for plasticizers and surfactant usage.

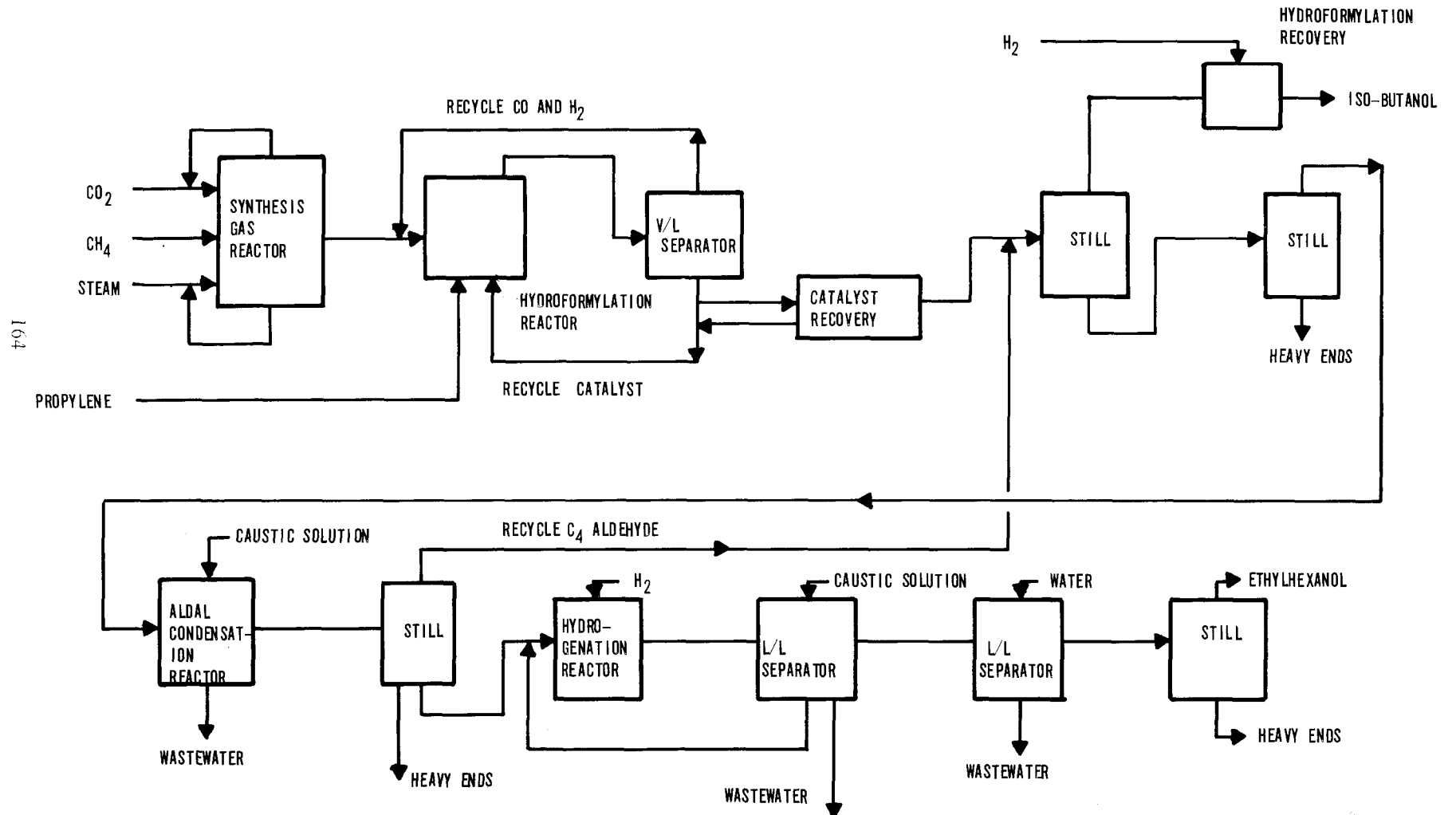
2-ethylhexanol, produced primarily from propylene via n-butyraldehyde, is the most important oxo chemical in terms of volume. A process flowsheet describing the manufacture of 2-ethylhexanol is shown in Figure IV-24 and the basic chemical reactions are given below:



Carbon dioxide, natural gas, and steam are passed into a synthesis gas reactor to produce water gas (1:1 ratio of H₂O and CO) which is then mixed with propylene in a liquid-phase reactor in the presence of a cobalt solution. The reaction is carried out under pressure and the reactor is maintained approximately isothermal. A liquid-gas mixture of aldehydes and unreacted materials is taken overhead from the reactor, cooled, and then separated in successive high- and low-pressure flashing stages, whence unreacted synthesis gas is recycled to the oxo reactor. The catalyst cobalt is then removed continuously from the liquid phase. The liquid product, containing n-butyraldehyde, iso-butyraldehyde, and solvent, is separated in two distillation columns.

N-butyraldehyde is then sent to a condensation reactor, where the subsequent reaction is carried out at moderate temperature and atmospheric pressure in the presence of strong base such as sodium or potassium hydroxide. Continuous removal of the water

FIGURE IV-24
OXO - CHEMICALS



produced during reaction drives the aldol condensation to completion. The unreacted C^o4^o aldehyde is separated from the product 2-ethylhexenal by distillation and is recycled to the condensation reactor.

The 2-ethylhexenal produced is then hydrogenated to 2-ethylhexanol in the presence of a solid nickel catalyst in a pressurized reactor at 50 to 100 atmospheres. After being washed with caustic solution and water, the reactor effluent is sent to a fractionator to recover the product 2-ethylhexanol.

The major waste water streams in oxo-chemical manufacturing are the water removed from the aldol condensation and the water used in washing the crude product before fractionation into final product. The waste water may contain some intermediates, product, and by-product losses. No significant catalyst loss from the reactor is expected. Heavy ends from various stills are disposed of by incineration.

The characteristics of the waste water obtained from the plant survey are summarized in the following tabulation. It should also be noted from the results of analyses that the oil concentration in the waste stream is beyond the limits of the general discharge criterion for biological treatment processes.

Flow	420 gallons/1,000 lb
COD	1,212 mg/l 4.25 lb/1,000 lb
BOD ₅	900 mg/l 3.15 lb/1,000 lb
TOC	549 mg/l 1.92 lb/1,000 lb

Other than reusing the aldol condensation water as wash water, it is deemed unfeasible to further reduce RWL of the process by any in-process modification. Consequently, RWL presented can be considered as standards for BADCT and BATEA control technology for this manufacturing process.

An alternate route in oxo chemical manufacturing is based on a new catalyst system. By carrying out the hydroformation reaction in an alkaline medium using phosphine-promoted cobalt carbonyl processes, 2-ethylhexanol and butanol can be produced directly in one step. Olefin feed and the recycled catalyst stream are charged to the first of a series of packed reactors at control rates. Synthesis gas (H₂/CO molar ratio = 2/1) is fed separately to each reactor. The stream taken overhead from the final reactor is directly sent to the product recovery column. The bottoms from the product recovery column will contain the catalyst complex dissolved in a mixture of alcohols and heavy ends. This stream is recycled to the first reactor with periodical purging to remove the built-up heavy ends.

The U.S. capacity for production of oxo chemicals is presented in Table IV-37 and the estimated economics for a 40 million pounds-per-year plant to produce 2-ethylhexanol from propylene is shown in Table IV-38.

Table IV-37

The U.S. Oxo-Chemicals Capacity
(Millions of pounds)

<u>Company</u>	<u>Location</u>	<u>Capacity</u>
Dow Badische	Freeport, Texas	200
Eastman	Longview, Texas	275
Enjay	Baton Rouge, La.	200
Getty-Air Products	Delaware City, Del.	40
Oxochem	Penuelas, P.R.	250
Shell	Geismar, La.	150
	Houston, Texas	200
Union Carbide	Ponce, P.R.	140
	Seadrift, Texas	120
	Texas City, Texas	200
USS Chemicals	Haverhill, Ohio	<u>70</u>
TOTAL		1,845

Source: Oil, Paint and Drug Reporter, Chemical Profile,
April 1, 1971

Table IV-38

The Estimated Economics for Oxo-Chemicals
(40. MM lb. 2-ethylhexanol-from-propylene plant)

Total Fixed Capital=\$5.7 MM

	<u>Estimated Operation Cost</u> <u>Cost</u> <u>c/lb. 2-ethylhexanol</u>
Propylene	2.1
Synthesis gas	1.5
Catalyst and chemicals	2.4
Utilities	1.6
Labor and overhead	1.2
Capital charges	<u>4.7</u>
Total	13.5

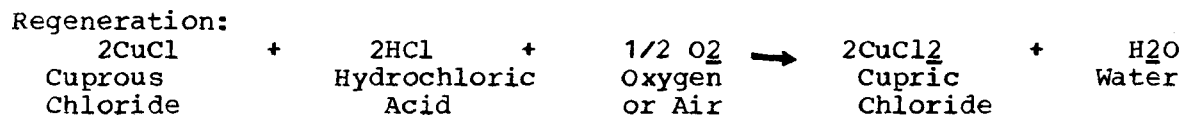
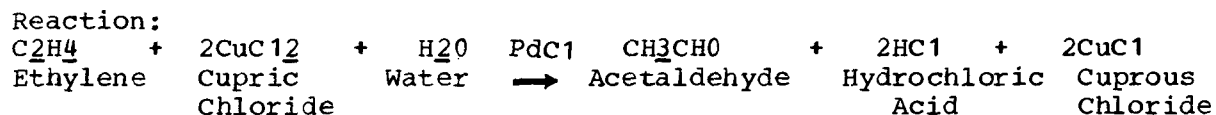
SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Acetaldehyde	Oxidation of Ethylene (Wacker Process)

The Wacker process employs an aqueous catalyst solution of palladium chloride, promoted (for metal oxidation) by copper chloride. The chemistry involved in the process can be summarized as follows:



Ethylene Oxygen or Air Acetaldehyde
The catalyst acts as the oxygen carrier and causes selective conversion of ethylene to acetaldehyde. The reaction steps essentially are:

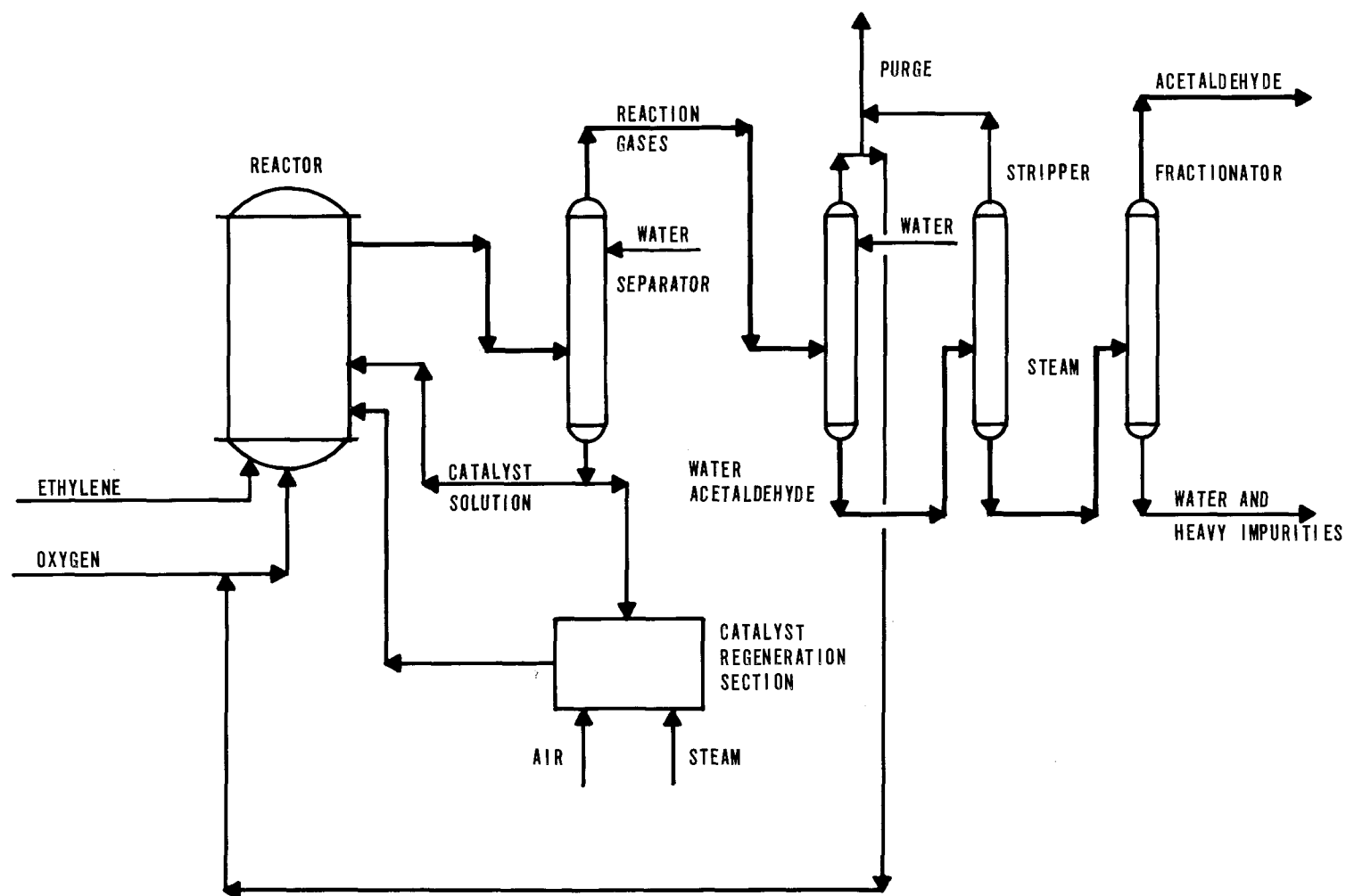


There are two basic process variations, and choice depends upon such factors as oxygen cost, utilities prices, and available ethylene purity. In the single-stage process, pure oxygen is employed as the oxidant. The reactor effluent is condensed and water-scrubbed. Unreacted gas is recycled into the reactor. By-products and water are separated from the acetaldehyde product by distillation. Both the reaction and regeneration are effected at the same time.

In the two-stage process, the oxidant is air. The reaction is carried out with catalyst solution and ethylene in one reactor, and the regeneration is carried out with air in a separate reactor. Lowerpurity ethylene can be used with this version of the process. However, this process forms more by-products and requires high operating pressures.

The process flow sheet for two-stage Wacker process is shown in Figure IV-25. The major waste water sources in this process are the effluents from the scrubber that is required for removal of unreacted ethylene and uncondensed acetaldehyde vapor, and from the aqueous bottoms of the acetaldehyde still. The

FIGURE IV - 25
ACETALDEHYDE (SINGLE-STAGE WACKER PROCESS)



characteristics of the wastewater are shown in the following tabulation.

	<u>Plant I</u>	<u>Plant 2</u>	<u>Plant 3</u>
Flow	90 gallons/1,000 lb	61 gallons/1,000 lb	35 gallons/1,000 lb
COD	58,718 mg/l	11,400 mg/l	20,240 mg/l
BOD ₅		3,700 mg/l	11,500 mg/l
TOC		7,000 mg/l	12,500 mg/l

The foregoing data show the same order of magnitude of raw waste loads in Plants 2 and 3, and this level of RWL can be considered as standard for BPCTCA. The high RWL of Plant I is mainly due to sloppy operation of the acetaldehyde still. To define BADCT and BATEA control technology, it is required that a steam stripper be installed to recover and reuse the organic contaminants in the waste water. A description of the steam stripper, as well as its estimated economics has been given in the section on aniline.

Because of the aqueous-phase reaction, catalyst metals are present in the waste water from the acetaldehyde still bottoms as a result of carry-over from the reactor. The aqueous catalyst solution is also quite acidic and corrosive. Survey data also shows that, in addition to metallic contaminants in waste water stream, sulfate and oil contaminants are found at concentrations in excess of general criteria for biological treatment processes. Pretreatment or dilution to reduce their concentrations is required.

Average process water usage for this process, including steam directly supplied to the process, is 0.92 pounds per pounds of acetaldehyde, while cooling water usage amounts to 330 pounds per pound of product.

Alternate routes for manufacturing of acetaldehyde as well as U.S. production capacity have been discussed under Acetaldehyde in Subcategory B. Estimated economics for production of acetaldehyde by the ethylene route are shown in Table IV-39.

Table IV-39

Estimated Economics for Acetaldehyde
(200 MM-lb plant; 1972 construction)

Fixed Capital Investment

<u>Process</u>	<u>\$ MM</u>
Ethylene	14.80

Estimated Operation Cost

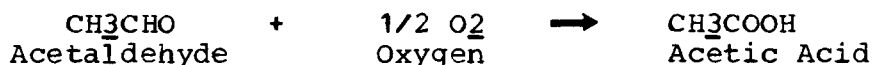
	<u>Cost</u> <u>¢/lb ethylene</u>
Raw materials ¹	2.45
Utilities	0.82
Labor	0.24
Maintenance (6% ISBL + 3% OSBL)	0.35
Overhead (45% labor and maintenance)	0.27
Taxes and insurance (1.5% of investment)	0.11
Depreciation (10 years)	<u>0.75</u>
TOTAL	4.99

¹Includes 0.68 lb ethylene/lb at 3.3¢/lb.

SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Acetic Acid	Oxidation of Acetaldehyde

Acetic acid is produced by the liquid-phase oxidation of acetaldehyde, using either air or oxygen according to the reaction given below:



The reaction is carried out in the liquid phase at 150°F and 60 psig, with manganese acetate dissolved in aqueous solvent as catalyst.

The process flow sheet is shown in Figure IV-26. Acetaldehyde and solvent are fed to the oxidation reactors with a manganese acetate catalyst solution. The reactor effluent (containing unreacted oxygen, nitrogen, acetaldehyde, and solvent) is cooled, and the acetaldehyde and solvent are condensed and recycled back to the reactor. The non-condensibles are water-washed before being discharged into the atmosphere. The degassed liquid stream as well as water from the scrubber are sent to a light-ends column, where the light ends are distilled overhead. The bottoms from these distillation columns are sent to a dehydration column in which water is removed overhead using benzene as the azeotropic agent. The aqueous phase in the distillate stream is sent to a solvent stripping column, where acetic acid is removed as distillate while the bottoms are sent to a waste disposal unit.

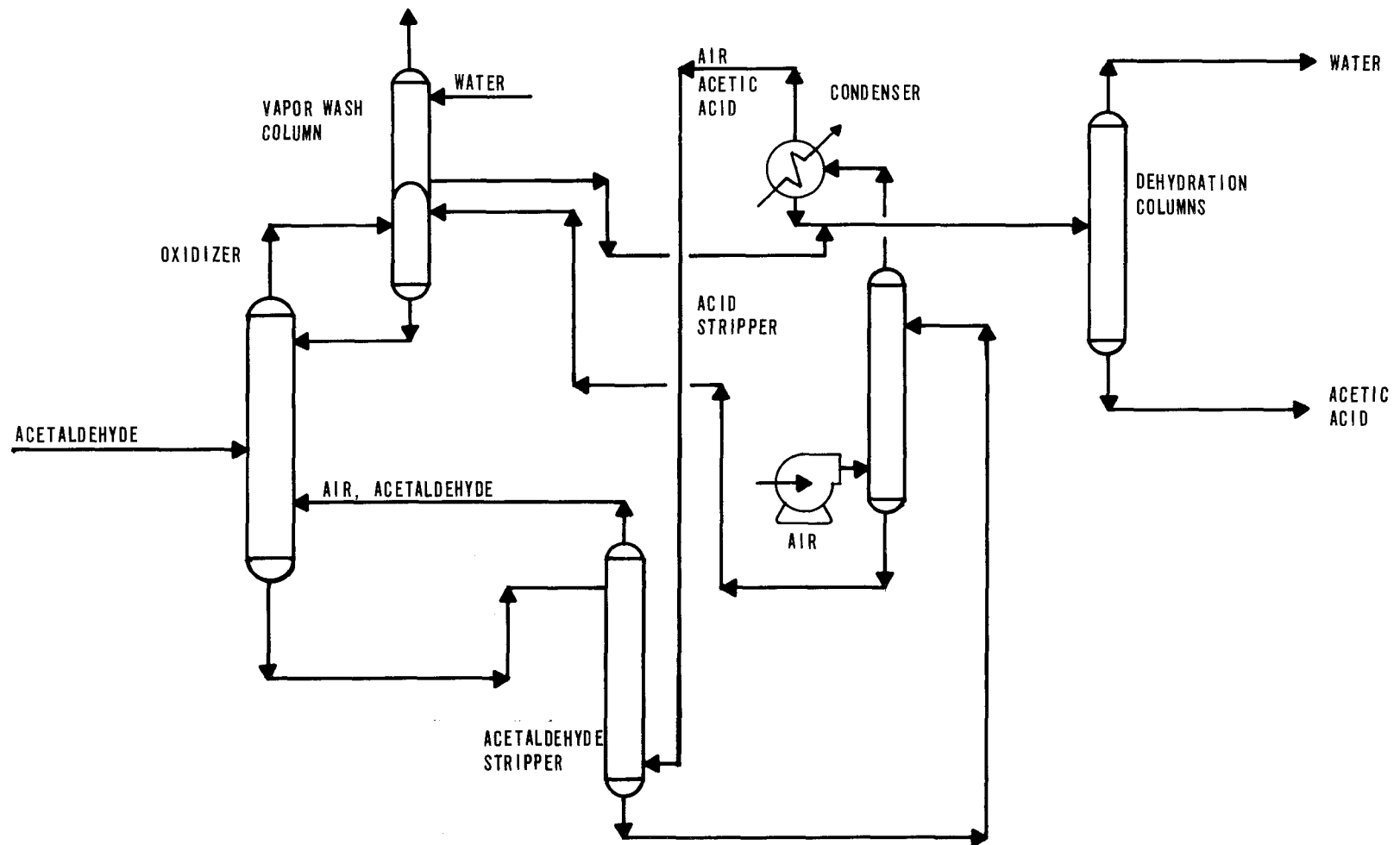
The major waste water source in this process is the water taken overhead from the dehydration column. The possible contaminants are unrecovered formic acid and acetic acid. The characteristics of the waste water obtained from plant surveys is presented in the following tabulation:

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	500 gallons/1,000 lb	10.2 gallons/1,000 lb
COD	186 mg/l 0.78 lb/1,000 lb	306,100 mg/l 26.18 lb/1,000 lb
BOD ₅	84 mg/l 0.35 lb/1,000 lb	64,000 mg/l 5.44 lb/1,000 lb

The foregoing data show a significant variation in RWL between two plants. Examination of each process shows that the concentrated light ends and heavy ends from distillation columns

FIGURE IV .26

ACETIC ACID, ACETALDEHYDE OXIDATION



are discharged into sewer lines by Plant 2 instead of being disposed of by incineration as commonly practiced. If these concentrated streams are excluded, the RWL of Plant 2 as shown below is comparable to RWL of Plant 1.

Flow	1.48 gallons/1,000 lb
COD	7,500 mg/l 0.925 lb/1,000 lb
BOD ₅	26,700 mg/l 0.33 lb/1,000 lb

There is a slight difference in manufacturing process between Plants 1 and 2. Plant 1 utilizes ethanol as part of its feedstock and generates at most 35 gallons of reaction water per 1,000 pounds of product, based on 100% ethanol feedstock. Also, instead of combining scrubber water with aqueous reactor effluent, Plant 1 sends scrubber water directly to an acetaldehyde recovery still and disposes of the bottom stream of the distillation column. This modification allows Plant 1 to use more scrubbing water in the scrubber and results in a high amount of wasteflow.

Based on the foregoing analysis, the RWL of Plant 1 can be considered the standard of BADCT and BATEA of this process. The standards of BADCT and BATEA should require recycling of scrubber water in Plant 1. This modification when implemented will reduce the flow of BPCTCA to one-tenth its current level, and the RWL by one half.

Total process water usage of this process is directly proportional to the amounts of waste water generated. The survey data show a variation from 4.2 pounds of process water per pound of acetic acid at Plant 1 to 0.024 at Plant 2. The gross cooling water usages are 54 and 185 pounds per pound of product for Plants 1 and 2, respectively.

Several other process routes to acetic acid are also practiced commercially. The specific processes utilized by each firm with their respective capacities are presented in Table IV-40. The CO-Methanol and Petroleum Gases (n-butane) processes are discussed briefly in the following paragraphs.

Direct liquid-phase oxidation of n-butane in petroleum gases is normally carried out at 300-350°F under a pressure of 700-800 psig, and the chemical reactions taking place are extremely involved. The reactor effluent is sent to a vapor-liquid separator, the gaseous products from this separator are scrubbed with a heavy hydrocarbon to recover unreacted n-butane, and the liquid product from the separator is split into an organic and aqueous phase. The organic phase is recycled, while the aqueous phase is fractionated to remove intermediate by-products.

The CO-Methanol process is the most recent commercial route. Carbon monoxide and a liquid stream containing the catalyst system of cobalt iodide and cobalt carbonyl hydride are fed to a sparged reactor operating at 500°F and 10,000 psig. Product acetic acid is recovered by fractionation. The methanol feedstock is normally not introduced directly to the oxidizer, but rather is used to scrub the reactor offgases, which contain catalyst in the form of methyl iodide vapor.

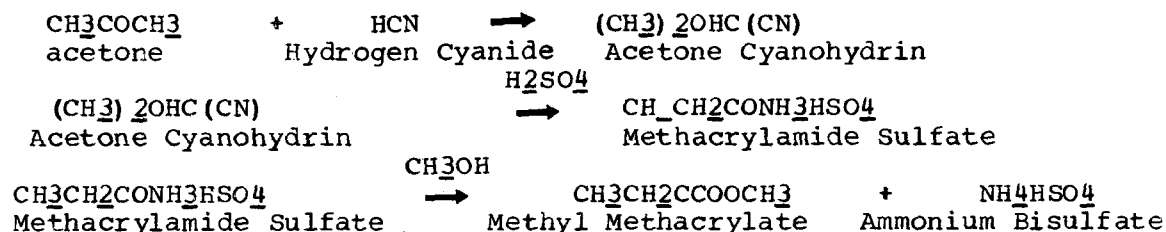
Table IV-40
Acetic Acid Capacity (1972)

<u>Producer</u>	<u>Location</u>	<u>MM lb</u>	<u>Process</u>
Borden	Geismar, La.	100	CO-methanol
Celanese	Bishop, Texas	200	Petroleum gases
	Pampa, Texas	600	Petroleum gases
	Clear Lake, Texas	300	Acetaldehyde
Eastman	Kingsport, Tenn.	325	Acetaldehyde-ethanol
FMC	Bayport, Texas	45	Acetaldehyde
Hercules	Parlin, N.J.	20	Acetaldehyde
Monsanto	Texas City, Texas	300	CO-methanol
Publicker	Philadelphia, Pa.	80	Acetaldehyde-ethanol
Union Carbide	Brownsville, Texas	400	Petroleum gases
	Texas City, Texas	100	Petroleum gases
	S. Charleston, W.Va.	140	Petroleum gases
	Taft, La.	90	Acetaldehyde
Others		<u>100</u>	
TOTAL		2,800	

SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Methyl Methacrylate	Acetone Cyanohydrin Process

Methyl Methacrylate is produced by the acetone cyanohydrin process. The overall chemical reactions are given below:



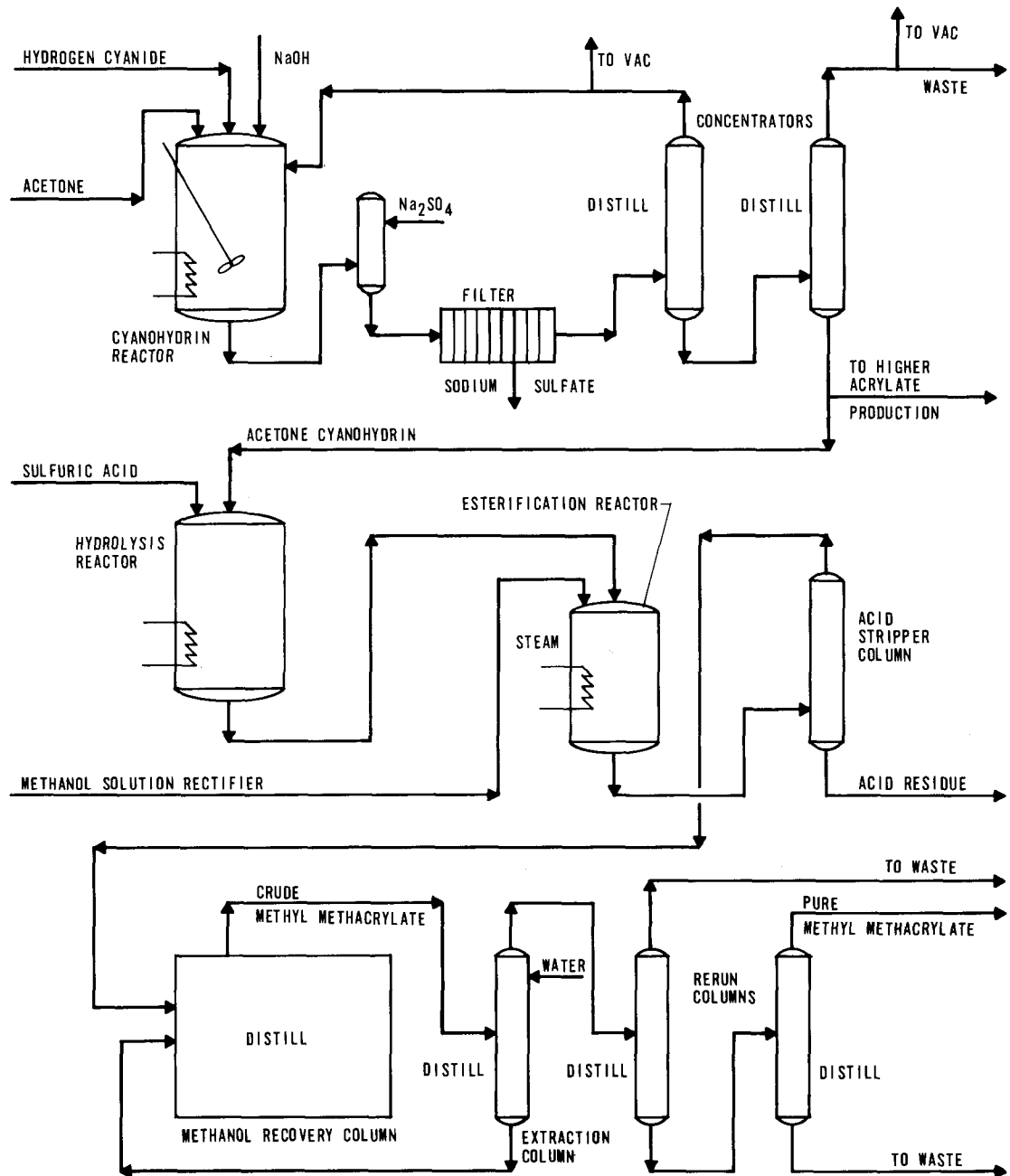
A process flow diagram is shown in Figure IV-27. Acetone cyanohydrin is produced by the reaction of hydrogen cyanide and acetone with an alkaline catalyst in a cooled reaction kettle. The excess catalyst is neutralized, and crude acetone cyanohydrin passes to holding tanks. The salt formed by neutralization of the catalyst is removed in a filter press before the crude acetone cyanohydrin is fed to a two-stage distillation unit. Most of the water and acetone are removed and recycled overhead from the first column, and the remainder of the water is removed at high vacuum from the second column.

Acetone cyanohydrin and concentrated sulfuric acid are pumped into a cooled hydrolysis kettle to make the intermediate, methacrylamide sulfate, which is then sent to an esterification kettle to react with methanol continuously. To prevent polymerization, inhibitors are added at various points in the process. The esterified stream is pumped to the acid stripping column, from which the acid residue, made up of sulfuric acid (40% by weight), ammonium sulfate (28%), water (20%) and organic substances (10%) is sent to a Spent Acid Recovery unit (SAR). The recovered sulfuric acid is recycled back to the hydrolysis reactor.

The overhead stream from the acid-stripping column is then distilled to remove methyl metacrylate and unreacted methanol, which is recycled. The last traces of methanol in the methyl metacrylate are removed by water extraction, after which the monomer is finally purified in a rerun tower.

The acid residue from the acid-stripping column is the major waste stream generated in the process, and this waste stream is either sent to the SAR unit previously mentioned or is discharged into sewers. The waste streams generated as bottoms from various stills are combined with the acid residue for spent acid recovery. Water samples from streams leading to and leaving the SAR unit were taken for analysis, and the results are shown in the following tabulation:

FIGURE IV-27
METHYL METHACRYLATE - ACETONE CYANOHYDRIN PROCESS



	<u>Into SAR</u>	<u>From SAR</u>
Flow	260 gallons/1,000 lb	213 gallons/1,000 lb
COD	178,000 mg/l	110 mg/l
BOD ₅	20,700 mg/l	15 mg/l
TOC	69,998 mg/l	18 mg/l

A high concentration of floating solids was observed in the stream leading to the SAR, and it was impossible to obtain a well-mixed sample. Therefore, samples from the stream were actually taken from the aqueous phase beneath the floating solids. The floating solids removed in the SAR were disposed of by incineration. High concentrations of metal contaminants such as copper and iron are indicated by the results of the analysis. Although a large portion of these metals are removed along with floating solids in the SAR unit, the metal concentrations in the streams discharged to sewers are still beyond the general discharge criteria for biological processes. Although sulfuric acid concentration had been reduced from 40% by weight in the influent to the SAR to 1% by weight in the effluent, the sulfate concentration in the discharge stream was still high enough to inhibit the normal functioning of the biological treatment process.

Because of the highly exothermic reactions involved, the process requires a large amount of cooling water. The survey data show that gross cooling water usage amounts to 366 pounds per pound of methyl metacrylate. Process water is introduced into the system in the form of direct steam stripping in the amount of 0.56 pounds per pound of product.

To define BADCT and BATEA, this process should have a Spent Acid Recovery unit. Two types of SAR units have been devised, and descriptions of the equipment processing required, and estimated economics are presented in the following paragraphs.

1. Spent Acid Recovery by Neutralization

As shown in Figure IV-28, spent acid is neutralized with ammonia gas to form ammonium sulfate. The effluent from the neutralization tank is sent to crystallization and filtration units to separate ammonium sulfate from the aqueous solution. The economics of this unit are shown in Table IV-41.

2. Spent Acid Recovery by Complete Combustion The spent acid solution (see Fig. IV-28) is heated to such a high temperature (about 1,000°C) that sulfuric acid decomposes into SO₂, O₂, and water vapor. Simultaneously, the organic substances are oxidized, and the contained ammonia converted to N₂ and water. The SO₂ gas stream is passed over a catalytic converter to oxidize the SO₂ to SO₃, which is then absorbed to form

FIGURE IV-28
SPENT ACID RECOVERY UNITS

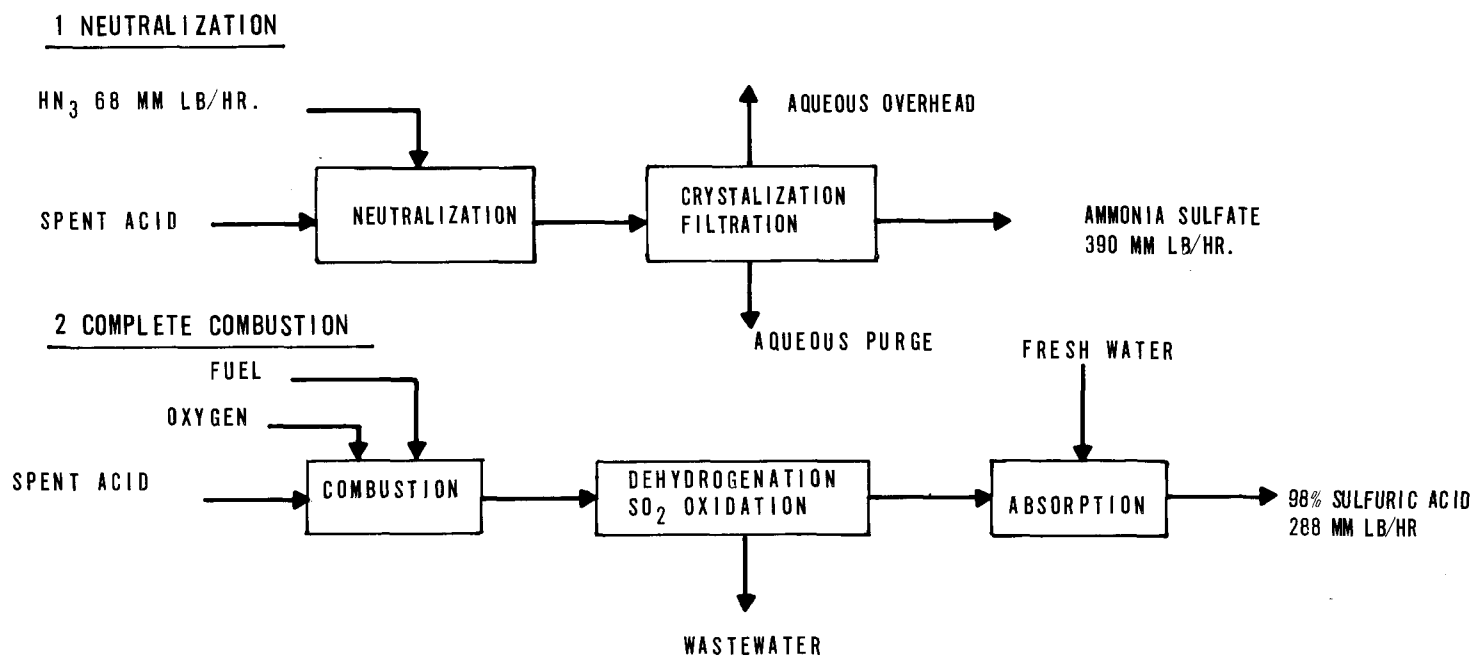


Table IV-41

Economics of Spent Acid Recovery by Neutralization*

Investment

Battery Limits	= \$2,200,000
Off-site	= <u>800,000</u>
Total Investment	\$3,000,000

Operating Costs

Utilities	<u>\$/yr</u>
Steam: 720,000 M lb @ 60¢/M lb	= \$ 430,000
Power: 10,000,000 Kwh @ 0.8¢/Kwh	= 80,000
Cooling Water: 2,000,000 M gal @ 3¢/M gal	= <u>60,000</u>
	\$ 570,000

Chemicals

NH ₃ : 68,000,000 lb @ 2¢/lb	= \$1,360,000
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Amortization	= 440,000
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Labor	= <u>200,000</u>
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Sub-total	\$2,000,000
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Return on Total Investment @ 20%	= \$ 600,000
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Total Annual Cost	= <u>\$3,170,000</u>
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Net Revenue from Recovered Ammonium Sulfate 390 MM lbs/yr @ 0.70¢/lb	= \$2,730,000
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*Based on 485,000,000-lbs/yr Spent Acid Recovery plant.

concentrated acid for recycle. The economics of this unit are shown in Table IV-42.

The economic analyses are based on the following flow rate and composition of spent acid.

H ₂ SO ₄	=	245,000 lb/hr
(NH ₄) ₂ SO ₄	=	16,500 lb/hr
H ₂ O	=	13,500 lb/hr
Organic substances	=	6,150 lb/hr
		<hr/>
		60,650 lb/hr

The acetone cyanohydrin process is the only methacrylate process used commercially in the U.S. An alternate route used in Japan is nitric acid oxidation of isobutylene to metacrylic acid, followed by esterification with methanol.

Producers of methyl methacrylate in the U.S. are shown in Table IV-43. The estimated economics of production, based on a unit that produces 40 million pounds per year, are presented in Table IV-44

Table IV-42

Economics of Spent Acid Recovery by Complete Combustion*

Investment

Battery Limits	= \$3,000,000
Off-site	= <u>1,000,000</u>
Total Investment	\$4,000,000

Operating Costs

Utilities	<u>\$/yr</u>
Fuel: 800,000 MM BTU/yr @ 50¢/MM BTU	= \$ 400,000
Power: 3,000,000 Kwh @ 0.8¢/Kwh	= 24,000
Cooling Water: 750,000 M gal @ 3¢/M gal	= <u>22,500</u>
	\$ 446,500
Amortization	= \$ 600,000
Labor	= <u>100,000</u>
	\$ 700,000
Return on Total Investment @ 20%	= \$ 800,000
Total Annual Cost	= <u>\$1,946,500</u>
Net Revenue on Recovered H ₂ SO ₄	
144,000 tons/yr @ \$20/ton	= \$2,880,000

*Based on 485,000,000-lbs/yr Spent Acid Recovery plant.

Table IV-43
U.S. Methyl Methacrylate Capacity

<u>Producer</u>	<u>Location</u>	<u>Capacity</u> MM lbs/yr.	<u>Route</u>
Rohm and Haas	Houston, Texas Louisville, Ky. Bristol, Pa.	240.0	Acetone-HCN
DuPont	Belle, W. Va.	80.0	Acetone-HCN
American Cyanamid	Fortier, La.	40.0	Acetone-HCN
Escambria *	Pensacola, Fla.	<u>20.0</u>	Isobutylene oxidation
TOTAL		380.0	

* Shut Down

Source: Oil, Paint and Drug Reporter, March 6, 1967

Table IV-44
Estimated Economics for Methyl Methacrylate Production
40. MM lb. plant
Total fixed capital=\$3.2 MM

I. Acetone Cyanohydrin Process

Estimated Operation Cost
Cost
¢/lb. methyl methacrylate

Acetone	5.7
HCN	2.9
Methanol	2.6
Catalyst and chemicals (net)	1.2
Utilities	0.6
Labor and overhead	1.0
Capital charges	<u>2.6</u>
TOTAL	16.6

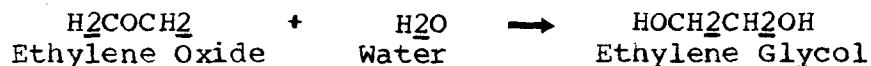
II. Isobutylene Process

	<u>Cost</u>
	¢/lb. methyl methacrylate
Raw materials	9.3
Utilities	1.8
Labor and overhead	<u>1.0</u>
Total	12.1

SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Ethylene Glycol	Hydration of Ethylene Oxide

Ethylene glycol is produced from ethylene oxide by liquid-phase, acidcatalyzed hydration.



Ethylene oxide and water are reacted at about 300 psig and 180°C in the presence of sulfuric acid solution. By selection of the oxide-to-water ratio, it is possible to control the production of the mono-, di-, and higher glycols produced. Excess water is required for temperature control and to prevent the formation of undesirable by-products. Reactor effluent is dehydrated in a multiple-effect evaporator system. The effluent from the dehydration section is fed to a series of fractionators. The first tower removes water and traces of the light-ends, the second produces fiber-grade mono-ethylene glycol, and the subsequent towers produce diethylene and higher glycols.

A flow sheet for this process is shown in Figure IV-29.

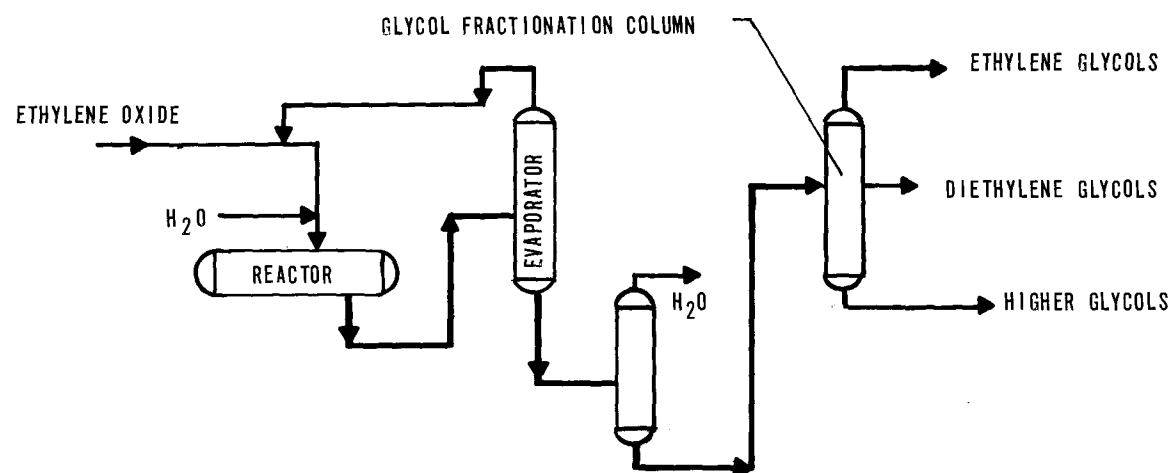
The condensate from the dehydrator is partially recycled, and the remainder of this stream is the only source of water pollution in the process. The characteristics of this waste stream obtained from survey data is shown in the following tabulation:

Flow	584 gallons/1,000 lb
COD	1,800 mg/l 8.77 lb/1,000 lb
BOD ₅	69 mg/l 0.34 lb/1,000 lb
TOC	929 mg/l 4.53 lb/1,000 lb

The high flow of the waste stream is caused by steam jets with barometric condensers which are utilized to produce vacuum for the multipleeffect evaporator system. If vacuum pumps with surface heat exchangers were to replace steam jets and barometric condensers, the flow of this waste stream could be significantly reduced. The condensate from the dehydrator could then be totally recycled back to the reactor. Consequently, BADCT and BATEA standards should require zero discharge from this process.

The manufacture of ethylene glycol is invariably associated with ethylene oxide production, and glycol growth rates are moderate. The U.S. ethylene glycol capacity is presented in Table IV-45.

FIGURE IV-29
ETHYLENE GLYCOLS, FROM ETHYLENE OXIDE



Estimated economics for ethylene glycol, based on ethylene oxide availability at 8.5¢ per pound, are presented in Table IV-46.

Table IV-45
U.S. Ethylene Glycol Capacity

<u>Producer</u>	<u>Location</u>	<u>Mid-1970 Estimated Capacity MM lb/yr</u>
Allied	Orange, Texas	60
Calcasieu	Lake Charles, La.	180
Celanese	Clear Lake, Texas	300
Dow	Freeport, Texas Plaquemine, La.	500 175
Eastman	Longview, Texas	75
GAF	Linden, N.J.	35
Houston-PPG	Beaumont, Texas	85
Jefferson	Port Neches, Texas	360
Matador	Orange, Texas	35
Olin	Brandenburg, Ky.	110
Shell	Giesmar, La.	100
Union Carbide	Institute, W.Va.	230
	Ponce, P.R.	130
	S. Charleston, W.Va.	120
	Texas City, Texas	220
	Torrance, Calif.	50
	Seadrift and Taft, Texas	130
Wyandotte	Giesmar, La.	<u>150</u>
TOTAL		<u><u>3,045</u></u>

Table IV-46

Estimated Economics for Ethylene Glycol
(80 MM lb plant)

Total Fixed Capital = \$0.8 MM

	<u>Estimated Production Cost</u> ¢/lb ethylene glycol
Ethylene oxide	6.3
Utilities	0.2
Labor and overhead	0.2
Capital charges	<u>0.3</u>
TOTAL	7.0

SUBCATEGORY C

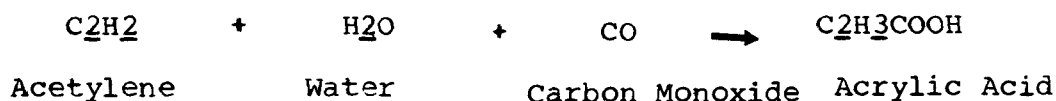
Product

Acrylic Acid

Process

Carbon Monoxide Synthesis with Acetylene

Acrylic acid is synthesized from acetylene and carbon monoxide in a catalytic solution. The chemistry can be represented by the following reaction:



The acetylene feedstock is first dissolved in THF (tetrahydrofuran) in an absorption tower. This solution and carbon monoxide are then mixed in a reactor, and the reaction is carried out at approximately 450°F and 1,500 psig in the presence of a nickel bromide and cupric bromide solution. The off-gas from the reactor is passed through a THF absorber to remove acrylic acid vapor and unreacted acetylene, and is then scrubbed by caustic water for further removal of THF and carbon monoxide from the gas stream. The liquid reactor effluent, a mixture of acrylic acid, byproduct acetaldehyde, and catalyst solution, is fed to a separation column. The overhead is extracted with water to recover THF and is distilled to yield purified acetaldehyde. The raffinate from the separation column is sent to a series of vacuum distillation and extraction columns. The THF and catalyst solution are recovered and recycled to the acid reactor. Technical grade glacial acrylic acid is produced in final distillation columns.

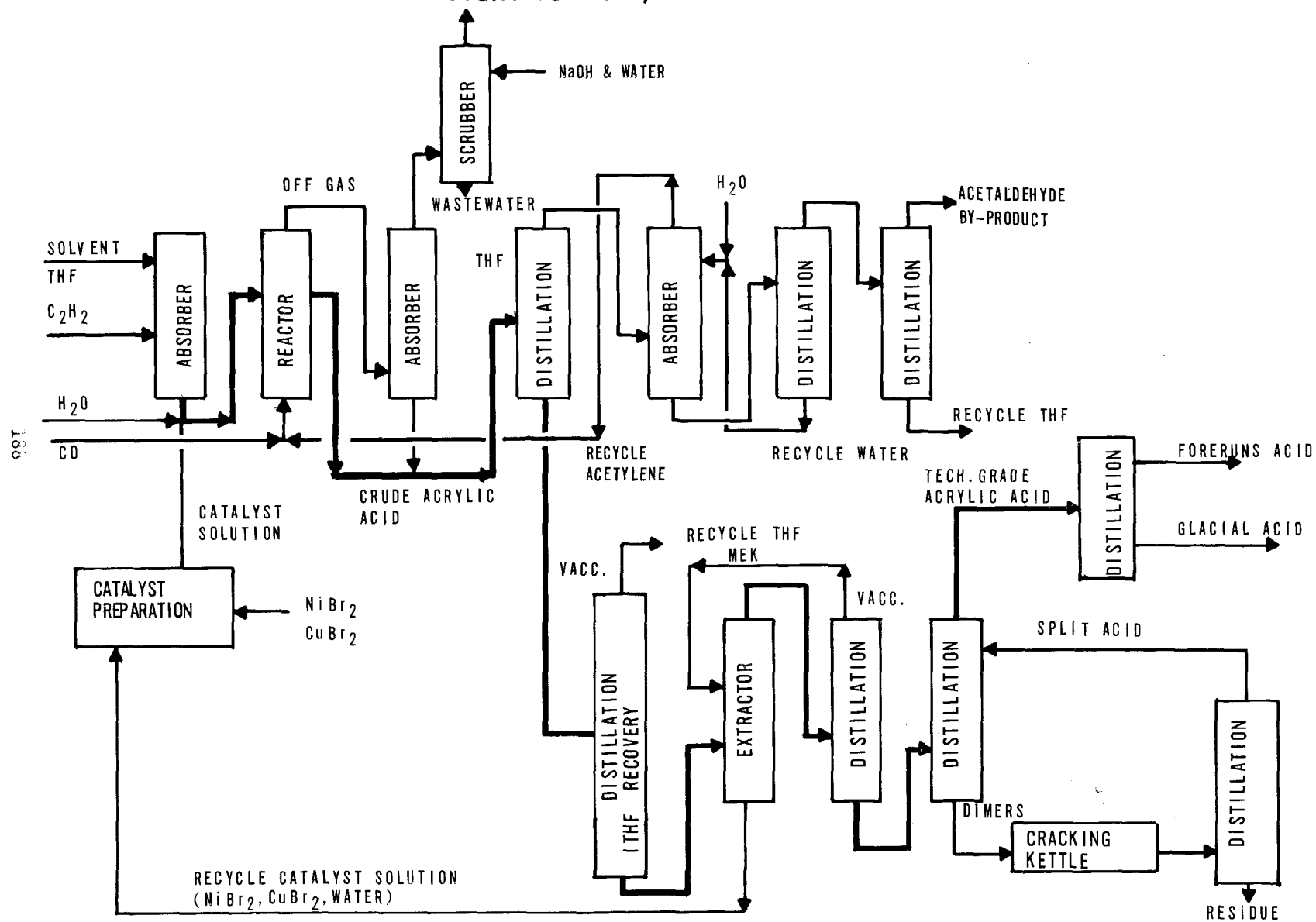
The process flow diagram is shown in Figure IV-30.

The major waste water source is the caustic scrubber water. The contaminants are THF and Na_2CO_3 . The characteristics of waste water samples obtained during recent plant surveys are summarized in the following tabulation:

Flow	475 gallons/1,000 lb
COD	414 mg/l 1.64 lb/1,000 lb
BOD ₅	186 mg/l 0.737 lb/1,000 lb
TOC	387 mg/l 1.53 lb/1,000 lb

Historical data over a period of two months show that TOC ranges from 1.73 to 6.92 pounds per 1,000 pounds of acrylic acid and probability analysis indicates that 50 percent occurrence is equivalent to 3.08.

FIGURE IV-30
ACRYLIC ACID, FROM ACETYLENE



The high waste water flow rate is attributed to the utilization of steam jets used to produce a vacuum in the distillation columns. Converting steam jets to vacuum pumps can certainly reduce the amount of waste water generated, although the RWL in terms of COD, BOD₅, etc. will remain the same. Other than reducing waste water flow rate, in-process modification is deemed unfeasible to further reduce RWL, and consequently, the data presented can be considered as standards for BADCT and BATEA.

A wide range of technology is used to produce acrylic acid. The other important route is based on propylene technology. A mixture of propylene, air, and steam is fed to two tubular catalytic reactors in series and cooled by circulation of molten salt. Most of the acrylic acid is condensed and separated from the gaseous stream by quenching. The resulting aqueous solution is then subjected to an extraction with solvent, followed by distillation for purifying the product and recovering the solvent.

U.S. manufacturing capacity of acrylic acid and the individual specific processes used are presented in Table IV-47, and an estimated economic comparison of the acetylene- and propylene-based technologies is shown in Table IV-48.

Table IV-47

U.S. Acrylic Acid and Acrylates Capacity

<u>Producer</u>	<u>Plant Location</u>	<u>Est. Capacity *</u> <u>(MM lbs./yr.)</u>	<u>Process</u> <u>Used</u>
Celanese	Pampa, Texas	80	b-propiolactone
Dow Badische	Freeport, Texas	40	Acetylene-CO
Dow Chemical	Freeport, Texas	10	Propylene
Goodrich	Calvert City, Ky.	10	b-Propiolactone
Rohm and Haas	Bristol, Pa.	250	Acetylene-CO
	Houston, Texas		
Union Carbide	Institute, W. Va.	70	Ethylene oxide-HCN
	Taft, La.	<u>200</u>	Propylene
TOTAL		<u>660</u>	

*Capacities as of mid-1970 estimated by Stanford Research Institute, CEH. CEH comments that the Dow facility is not due for start-up until late 1970 and the Carbide cyanohydrin plant will be shut down when the propylene plant is up to full capacity by early 1971.

Table IV-48

Estimated Acrylic Acid Economics
(150-MM lb. plant; 1972 Construction)

<u>Total Investment Cost</u>		
<u>Process</u>	<u>\$MM</u>	
Acetylene	10.0	
Propylene	16.9	

<u>Production Cost</u>		
	<u>¢/lb.</u>	
<u>Route:</u>	<u>Acetylene</u>	<u>Propylene</u>
Raw materials	6.85 ¹	3.24 ²
Utilities	0.80	1.12
Labor	0.27	0.33
Maintenance (6% ISBL + 3% OSBL)	0.32	0.54
Overhead (45% maint. + labor)	0.27	0.39
Taxes and insurance (1.5% of invest.)	0.10	0.17
Depreciation	<u>0.67</u>	<u>1.14</u>
¹ TOTAL	9.28	6.93
0.42 lb./lb. at 8.0¢/lb.		
² 0.88 lb./lb. at 3.0¢/lb.		

SUBCATEGORY C

Product
Acrylates

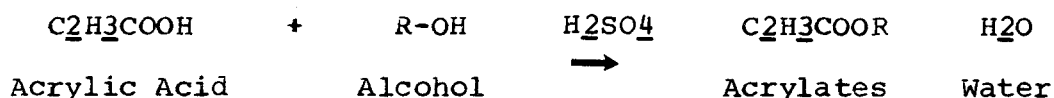
Process
Esterification of Acrylic Acid

Acrylates are manufactured by esterification of acrylic acid. There are four main acrylates plus a large number of specialty, smaller-volume derivatives. The main four are ethyl, 2-ethylhexyl, methyl, and n-butyl in decreasing order of market share. The 2-ethylhexyl and butyl acrylates are produced in a separate facility from the methyl and ethyl esters due to their differences in volatility and solubility.

In the manufacture of methyl or ethyl acrylates, acrylic acid is reacted with an excess amount of methanol or ethanol in a concentrated sulfuric acid solution. The effluent from the reactor goes to an extraction column, where caustic removes the excess alcohol. The effluent water stream is sent to a distillation column; alcohol is recovered overhead and recycles, while the acrylate stream is purified in two distillation columns by removal of light and heavy ends.

In the manufacture of butyl, 2-ethylhexyl, and higher acrylates, the esterification is conducted in the presence of cyclohexane, which is used to remove the water of reaction. The reactor effluent is first neutralized with caustic and then sent to a series of distillation columns. Acrylate is purified, while the excess alcohol is recovered and recycled.

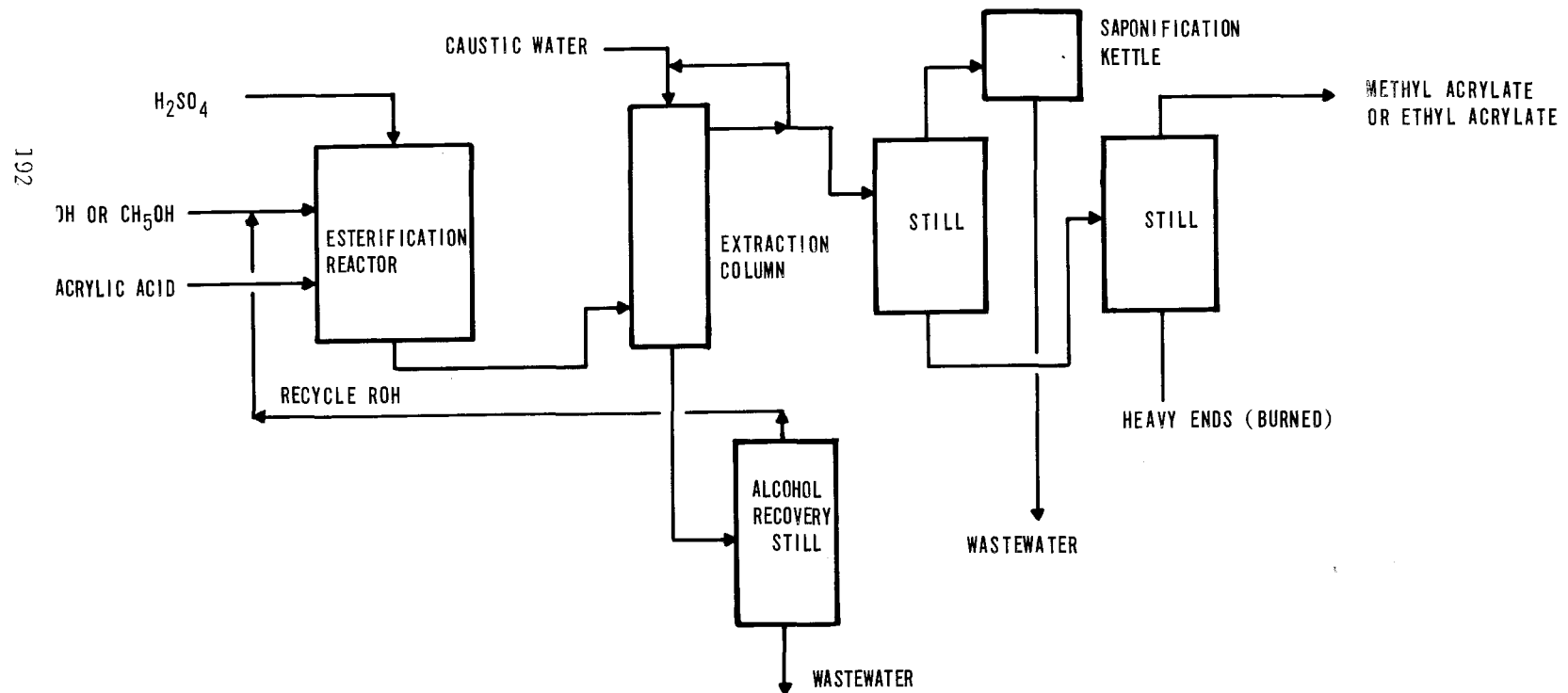
The major process units of the first process are shown in Figure IV-31, and the chemical reaction can be expressed by the following formula:



The two main sources of water pollution in acrylate manufacture are the bottoms of the alcohol recovery still and the effluent of the saponification kettle. The possible contaminants in the waste stream are acrylic acids, alcohols, and sodium salts of various acids. The results of the plant survey are presented in the following tabulation:

Flow	2,856 gallons/1,000 lb
COD	4,870 mg/l 117.5 lb/1,000 lb
BOD ₅	1,942 mg/l 47.1 lb/1,000 lb

FIGURE IV-31
ACRYLATES



TOC

3,290 mg/l
79.5 lb/1,000 lb

Historical data over a period of two months show that total carbon in the waste stream ranges from 15.50 to 46.36 pounds per 1,000 pounds of acrylate produced. Probability analysis of the data indicates that 50 percent occurrence is equivalent to 30.8 pounds per 100 pounds of product.

From the data presented in the preceding paragraphs, it is known that inefficient operation of distillation columns causes significant losses of organics such as alcohol, acrylic acid, and acrylates into the waste stream. Recovery of these organics can be achieved by modification of the distillation columns or by installation of a steam stripper. The amount of waste flow can also be reduced by recycling the waste water to an extraction column.

BADCT and BATEA in-process controls should require a steam stripper to recover organic contaminants in the waste stream and thus achieve a low RWL.

The U.S. acrylate capacity is presented in the same table used for acrylic acid (Table IV-47).

SUBCATEGORY C

<u>Product</u>	<u>Processes</u>
Terephthalic Acid	1. Nitric Acid Oxidation of Para-Xylene 2. Catalytic Oxidation of Para-Xylene

Terephthalic acid (TPA) constitutes virtually the sole use for p-Xylene. Based on the mode of oxidation, manufacturing processes can be divided into the following two classifications:

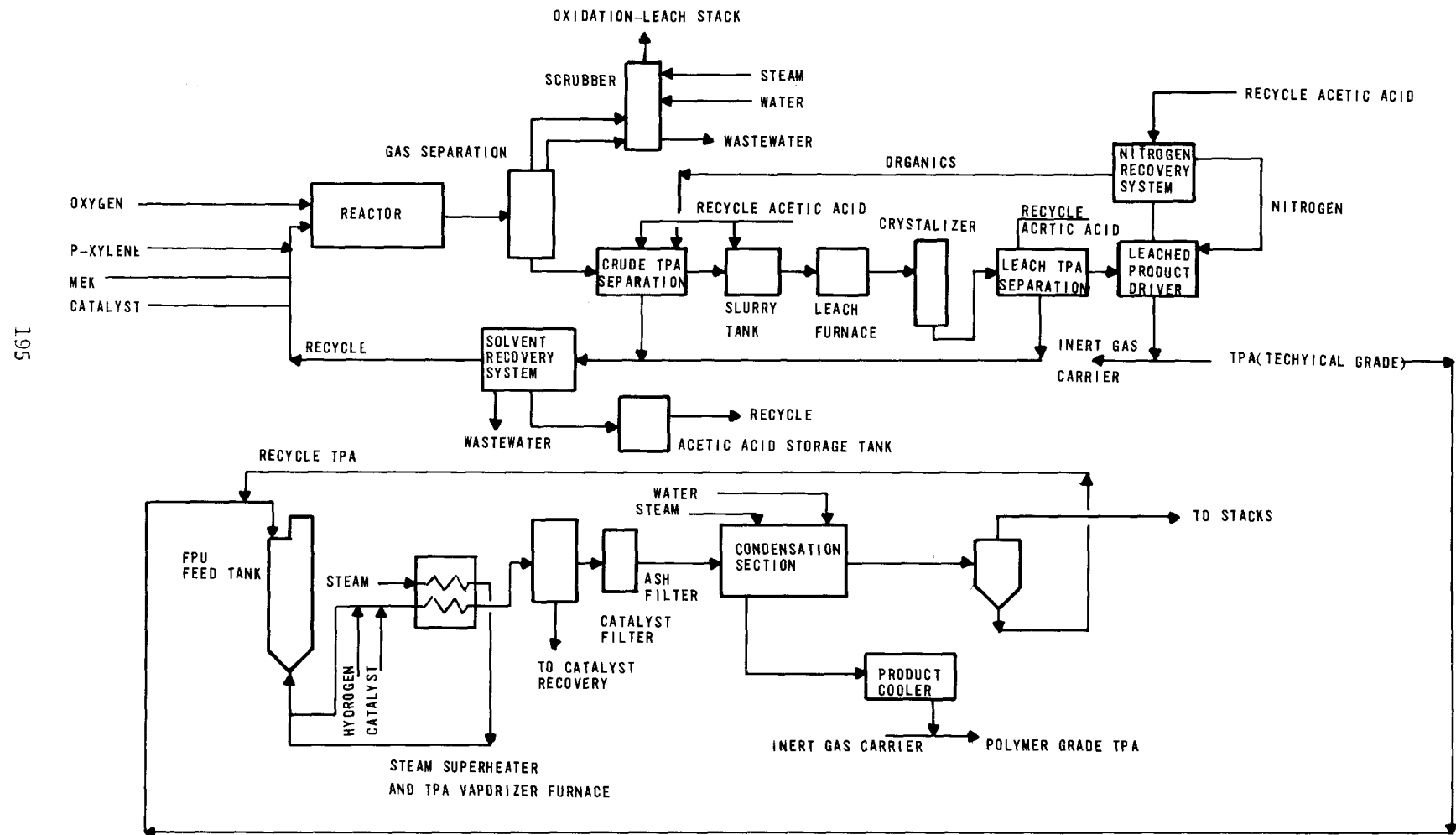
1. Oxidation of p-Xylene with nitric acid,
2. Catalytic oxidation of p-Xylene.

Only one company is using the nitric acid oxidation of p-xylene in the United States. This process is a liquid-phase reaction at approximately 300°F and 125-200 psig in dilute HNO₃ (about 30-40 weight percent). Oxygen or air is passed into the reactor, where oxidation of p-xylene and lower oxides of nitrogen takes place simultaneously. The nitric oxides can be used for nitric acid regeneration.

The second reaction, represented by at least three commercial processes, utilizes acetic acid as a reaction medium and also involves a heavy metal oxidation catalyst. The most widely used commercial process is the Mid-Century process, in which the oxidation is reported to be based upon a bromine-promoted heavy metal catalyst, such as cobalt-manganese. Reaction conditions are 350-450°F and 200-400 psig. The second process utilizes acetaldehyde as a promoter in place of bromine compounds, and the reaction is carried out at 250-350°F and 100-200 psig. The third process uses methyl ethyl ketone as the catalyst activator and operates at 200-300°F and 50-150 psig.

A typical flow sheet for the catalytic oxidation process is shown in Figure IV-32. Preheated acetic acid, p-xylene and bromine catalyst, together with high-pressure air are charged to a well-agitated reactor operating at moderate temperature and pressure. The reactor contents are continuously discharged from the bottom of the reactor as a hot slurry into a crystallizer vessel, where cooling takes place by flashing off part of the acetic acid, unreacted xylene, and some water of reaction. The terephthalic acid slurry is passed to a centrifuge for removal of acetic acid and xylene. The filter cake is washed to remove the remaining reactants and then is dried to give the terephthalic acid product. The spent reaction liquor and condensate from the crystallizer vessel are distilled to remove water, recover unreacted Xylene and acetic acid, and remove any other by-products. The acetic acid is recycled. The off-gas from the reactor is scrubbed with water before being discharged into the atmosphere. TPA obtained from this process is considerably purer than that produced by nitric acid oxidation, usually more than 99 weight percent TPA in contrast to 93 weight percent TPA of the other process.

FIGURE IV-32
TEREPHTHALIC ACID, P-XYLENE TO POLYMER GRADE TPA



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At some plants, the TPA product is further purified to produce fibergrade material. The TPA is washed with hot water to remove traces of catalyst and acetic acid. The hot water slurry is then heated and pumped into fixed-bed reactors and hydrogenated. This is followed by crystallization and drying to recover the fibergrade TPA.

The major waste water streams in the oxidation process are the bottoms from the solvent recovery unit and the effluent of the off-gas scrubber, and the major waste source in the purification process is the discharged mother liquid from the centrifuge. The characteristics of the wastewater obtained from plant visits are summarized in the following tabulation.

<u>Plant</u>	<u>Process</u>	<u>Flow</u>	<u>COD</u>	<u>BOD5</u>	<u>TOC</u>
		gal/1,000 lb		lb/1,000 lb (mg/l)	
1	Catalytic	43.4	1.95 (5,400)	1.30 (3,600)	1.52 (4,200)
1	Purification	715	8.22 (1,380)	5.15 (865)	3.53 (510)
2	Catalytic				
	10% Occurrence	186	0.915	0.51	0.55
	50% Occurrence	186	1.72	0.82	0.86
	90% Occurrence	186	2.52	1.18	1.16
3	Catalytic	1,090	227 (24,950)	68.3 (7,500)	34 (3,730)
4	Nitric Acid	659	104 (18,900)	58.7 (10,700)	44.9 (8,180)

Plant 2 has five indential modules operating in parallel. Data obtained at this plant over a two day period were analyzed for probability of occurrence.

Historical RWL data on process waste water flow and COD were obtained for the catalytic oxidation process at Plant 1. At this plant, there are actually two oxidation process modules, which operate in parallel. The data from these two units were subjected to analysis for probability of occurrence. The following tabulation summarizes the results of this analysis:

	<u>Probability of Occurrence</u>			<u>Ratio</u>
	10%	50%	90%	90/50
Flow RWL, gallons/1,000 lb				

Oxidation Unit A	132	174	217	1.25
Oxidation Unit B	95	137	181	1.32
Purification Unit	754	969	1,185	1.22

COD RWL,
lb/1,000 lb

Oxidation Unit A	8.5	12.5	16.5	1.33
Oxidation Unit B	4.9	11.2	25.5	2.28
Purification Unit	12.8	27.4	58.5	2.14

The probability analysis was conducted on monthly average data taken by the manufacturer over a period of twenty-four months. Comparison of the sampling results and historical results for Plant 1 shows that both the measured process waste water flow and the COD RWL were significantly lower at the time of sampling. This is attributed to the fact that the historical data include surface runoff from the battery limits area. This amounts to approximately 85 gallons/1,000 lb of product, with an associated COD loading of 3.5 lb per 1,000 lb of product.

The differences in RWL among the plants can be explained. The nitric acid oxidation process produces nitric oxides which are supposed to be used in producing nitric acid. However, it is likely that these nitric oxides are discharged into sewer at the plant which was visited during the survey. This results in a high organic loading in the waste water. The high RWL of Plant 3 is due to poor process performance. Since both Plant 3 and Plant 4 are scheduled to be phased out in the very near future, further investigation of possible in-process modifications to reduce RWL is not warranted.

Both Plant 1 and Plant 2 utilize steam ejector systems to obtain vacuum for process needs. In contrast to discharging the exhaust stream into the atmosphere, as at Plant 1, Plant 2 employs barometric condensers to condense the exhaust stream. This causes a significant difference in the amounts of waste water generated.

To define BADCT and BATEA of the oxidation process, vacuum pumps with surface condensers should take the place of steam ejectors and barometric condensers, to reduce the amount of waste flow as well as to preserve the ambient air quality. If a steam stripper like that described in the discussion of aniline should be installed to recover organic contaminants in the waste water of the purification process, RWL can be reduced approximately by about three-fourths.

Process water usages as well as gross cooling water usages are varied among plants and processes. Information obtained from the plant survey is shown in the following tabulation. Plants are identified with the same identification as that used for RWL.

<u>Plant</u>	<u>Process Water Usage</u>	<u>Cooling Water Usage</u>
--------------	----------------------------	----------------------------

	lb/lb product	lb/lb product
1 (Oxidation)	N.A.	N.A.
1 (Purification)	N.A.	N.A.
2	N.A.	188
3	N.A.	N.A.
4	4	20,000

Several approaches to manufacture of TPA are under investigation, but none of them has been commercialized in the United States. The current U.S. capacity for TPA is presented in Table IV-49. The estimated economics for TPA manufacture by the oxidation process are shown in Table IV-50.

Table IV-49
U.S. Terephthalic Acid Capacity

<u>Producer</u>	<u>Plant Location</u>	<u>Est. Crude TPA Capacity (MM Lbs./Yr.)</u>
Amoco	Decatur, Ala.	735
	Joliet, Ill.*	135
DuPont	Gibbstown, N. J.	110
	Old Hickory, Tenn.	210
Eastman	Kingsport, Tenn.	155
Mobil	Beaumont, Texas	130
Total		<u>1475</u>

*May be shut down or switched to isophthalic acid production.

Source: Chem Systems' estimates as of mid-1970.

Table IV-50

Estimated Economics for Terephthalic Acid
(400-MM lb plant--1972 construction)

<u>Investment cost</u>	
<u>Process</u>	<u>\$ MM</u>
Oxidation (Bromine compound)	52.9
Oxidation (Methylethyl Ketone)	58.6

<u>Production costs</u>		
	<u>¢/lb</u>	
	<u>Amoco¹</u>	
	<u>Mobil²</u>	
Raw materials	6.62	7.57
Utilities	0.65	0.88
Labor	0.09	0.09
Maint. (6% ISBL + 3% OSBL)	0.64	0.71
Overhead (45% maint. + labor)	0.33	0.36
Taxes & insurance (1.5% of invest.)	0.20	0.22
Depreciation (10 yr)	1.32	1.47
Total	9.85	11.30
By-product credit	-	1.20
Net	9.85	10.10

¹Includes 0.67 lb p-xylene at 6.5¢/lb.

²P-xylene at 6.5¢/lb and methylethyl ketone at 10¢/lb;
0.67 lb p-xylene/lb and 0.25 lb MEK/lb; .20 lb acetic
acid at 6.0¢/lb as by-product credit.

SUBCATEGORY C

Product
Dimethyl Terephthalate

Process
Esterification of TPA

The high-purity monomer required for the development of polyester fibers and films is produced by converting terephthalic acid (TPA) to dimethyl terephthalate (DMT). However, with improved technology for the manufacture of fiber-grade TPA, it is expected that most of the new fiber and film capacity installed will be based on purified TPA.

In the process for the esterification of TPA to DMT, preheated TPA and methanol are fed to a reactor in the presence of sulfuric acid as a catalyst. DMT in the reactor effluent is recovered and purified by conventional methods such as crystallization and distillation.

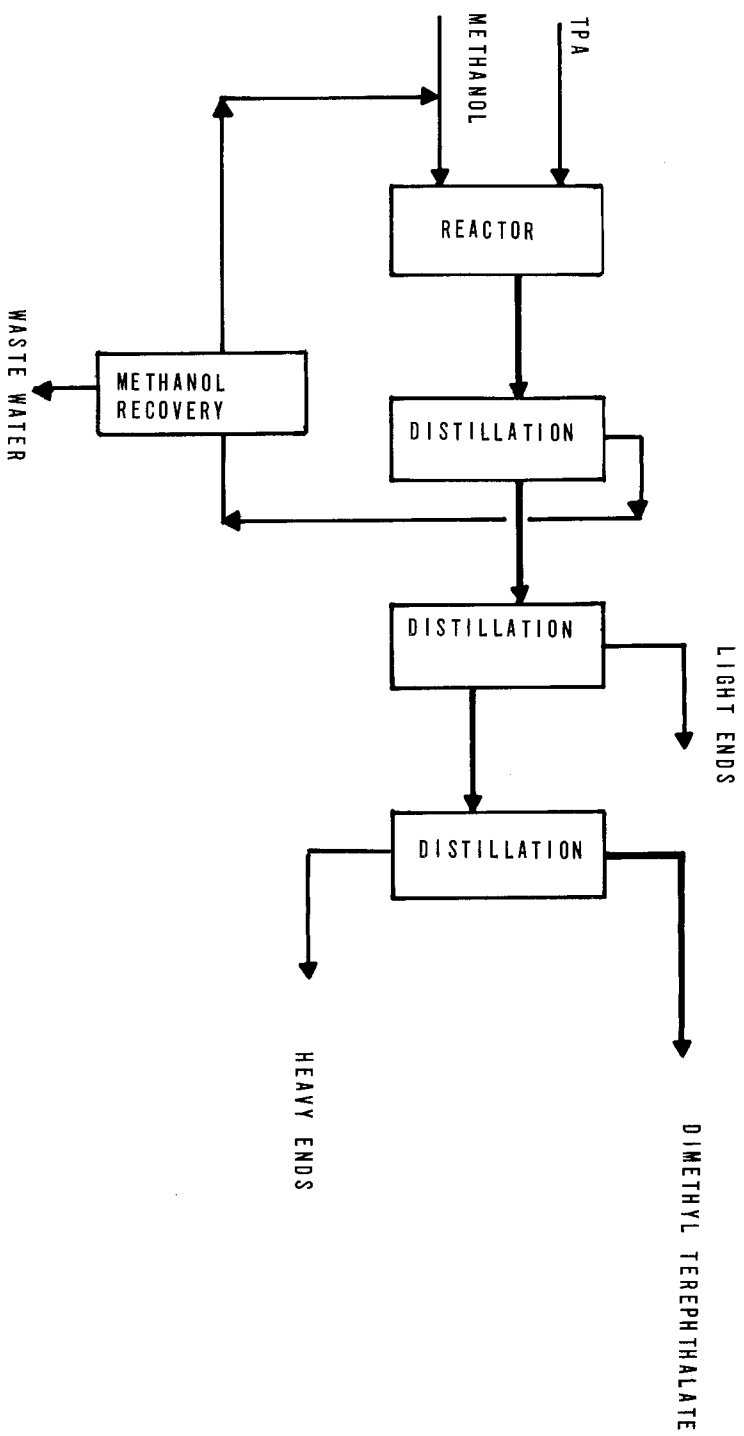
A flow sheet for this process is shown in Figure IV-33.

The water separated after condensation and the benzene used in the reactor to prevent the methanol from vaporizing too rapidly are the major water pollution sources. The waste water may contain some alcohol, benzene, and proproduct or by-product losses. Another water pollution source is the waste stream resulted from cleaning up scattered product resulting from leaks in various portions of the equipment. The characteristics of the waste water obtained from plant surveys are shown in the following tabulation:

	<u>Plant 1</u>	<u>Plant 2</u>	<u>Plant 3</u>
Flow, gal/1,000 lb	68.8	388	1,070
COD,			
lb/1,000 lb	8.93	55.2	0.91
mg/l	15,000	17,000	102
BOD ₅ ,			
lb/1,000 lb	4.81	31.0	0.19
mg/l	8,400	9,580	21
TOC,			
lb/1,000 lb	3.88	22.5	0.62
mg/l	6,800	6,950	69

Historical RWL data on process waste water flow and COD were obtained at Plant 1. At this plant, there are actually two modules, with different production capacities, operating in parallel. The results of the analysis for probability of occurrence are summarized in the following tabulation:

FIGURE IV.33
DIMETHYL TEREPHTHALATE, ESTERIFICATION OF TEREPHTHALIC ACID



	<u>Flow RWL</u>		<u>COD RWL</u>	
	<u>(gal/1,000 lb)</u>		<u>(lb/1,000 lb)</u>	
	<u>Unit A</u>	<u>Unit B</u>	<u>Unit A</u>	<u>Unit B</u>
10% Occurrence	167	150	13.5	16.1
50% Occurrence	313	248	34.	33.7
90% Occurrence	461	344	86.5	70.5
Ratio 90%/50%	1.47	1.39	2.54	2.06

The analysis was based on consecutive 30-day average data collected by the manufacturer over a period of 24 months. The data show that there is only a slight variation between two units of different sizes at the same plant. However, the measured RWL is significantly lower than that from historical data. Again, the difference is due to the fact that historical data includes surface runoff caused by rainfall and housekeeping.

The survey data also reveal significant variations among plants. The high waste water flow of Plant 3 is caused by steam jets with barometric condensers, while the low flow of Plant 1 is due to discharging steam jets directly into the atmosphere. The variation in organic loadings between Plant 1 and Plant 3 is due mainly to different performance efficiencies of the solvent recovery units and to varying effectiveness of preventive measures for process leakages. The high RWL presented by Plant 2 is attributed to the low-purity TPA manufactured by nitric acid oxidation. Plant 2 is scheduled to be phased out in the very near future.

To define BADCT and BATEA, it is certain that vacuum pumps with surface heat exchangers should be utilized in producing vacuum for process needs and that good performance of solvent recovery units should be required. Also, excellent preventive maintenance should be emphasized to reduce RWL.

Process water usage and gross cooling usage are presented in the following tabulation:

<u>Plant</u>	<u>Process Water Usage</u> lb/lb product	<u>Cooling Water Usage</u> lb/lb product
Plant 1	N.A.	N.A.
Plant 2	2	23,000
Plant 3	N.A.	150

An alternate route in the manufacture of DMT is the Hercules process. This synthesis involves liquid-phase oxidation of p-Xylene in acetic acid with a cobalt acetate or naphthenate as a catalyst to produce ptoluic acid. This is subsequently esterified with methanol to produce diethyl hydrogen terephthalate, which is finally esterified to form DMT.

The U.S. capacity for DMT is shown in Table IV-51.

Table IV-51

U.S. Dimethyl Terephthalate Capacity
(Million lbs./yr.)

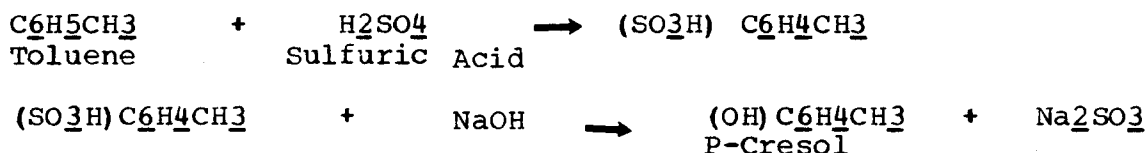
<u>Producer</u>	<u>Plant Location</u>	<u>Estimated Capacity</u>		
		<u>p-Xylene</u>	<u>Crude TPA</u>	<u>Total</u>
Amoco	Joliet, Ill.	--	150	150
	Decatur, Ala.	--	150	150
DuPont	Gibbstown, N.J.	--	250	250
	Old Hickory, Tenn.	--	250	250
Eastman	Kingsport, Tenn.	--	300	300
Hercules	Burlington, N.J.	100	--	100
	Spartenburg, S.C.	100	--	100
	Wilmington, N.C.	<u>400</u>	<u>--</u>	<u>400</u>
Total		<u><u>600</u></u>	<u><u>1100</u></u>	<u><u>1700</u></u>

SUBCATEGORY C

Product
Para-Cresol

Process
Sulfonation of Toluene

As in the case with other coal-tar derivatives, the supply of coke-oven by-product cresylics has failed to keep up with demand. P-cresol was the first isomer to be synthesized commercially and is produced by sulfonation of toluene. The basic chemical equations are given below:



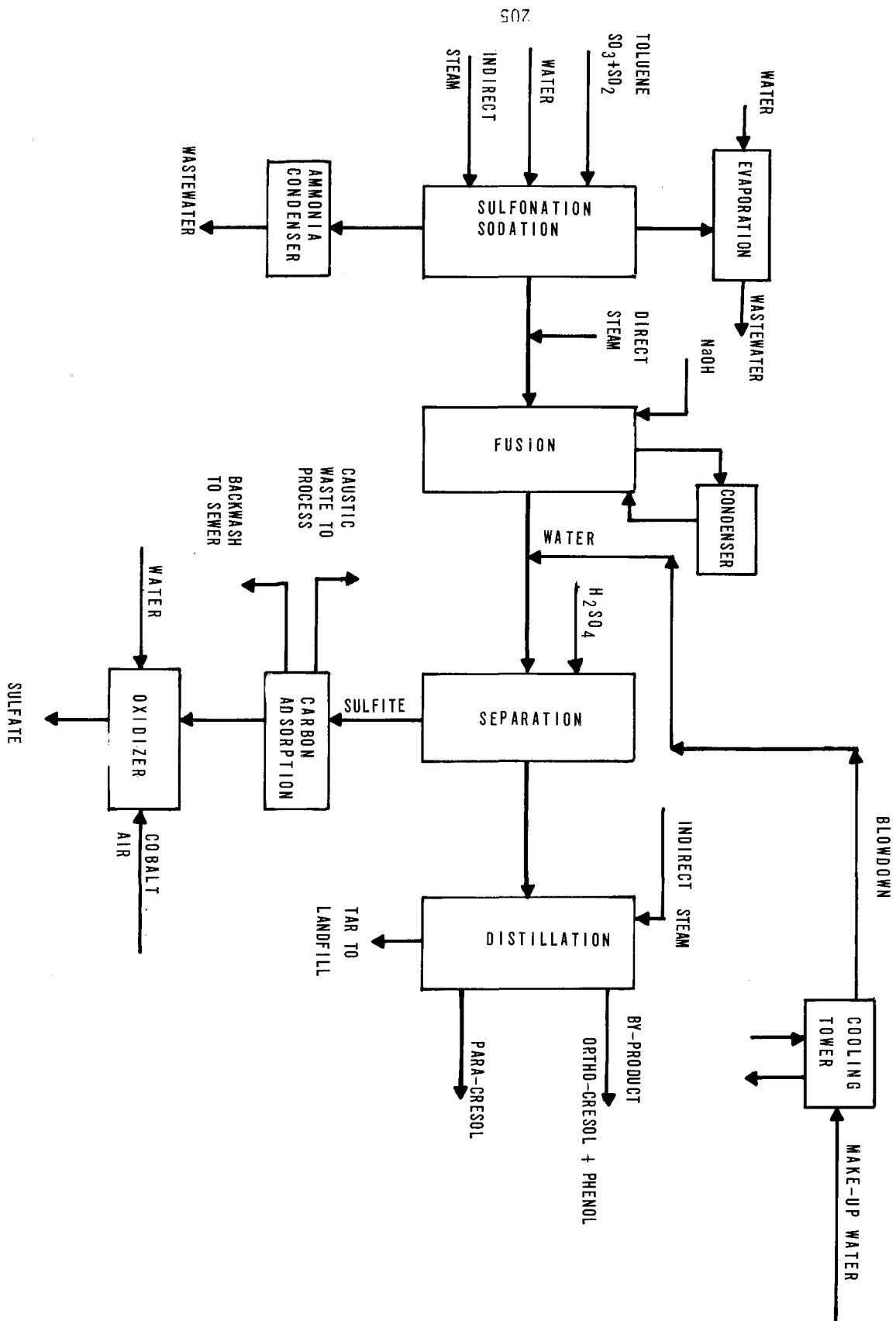
A process flow sheet is shown in Figure IV-34. Toluene and a gas mixture of sulfur dioxide and sulfur trioxide are fed into a sulfonation reactor. The reactor effluent gas is passed through a caustic scrubber to remove unreacted sulfur dioxide. The liquid effluent from the reactor is first diluted with steam and then sent to a caustic fusion column, where crude p-cresol is produced. The crude product is then sent to a washing-separation column, where excess caustic solution is neutralized and two phases are formed. The aqueous phase is discharged from the system, and the organic phase is fractionated to obtain pure p-cresol.

Since the sulfonation reaction approaches 100 percent conversion of sulfur dioxide and trioxide, the vent gas scrubber water does not present a significant water pollution source. The major waste water stream is the aqueous phase discharged from the sulfuric washing/separation column. The average composition of this stream is 77 percent water, 15.2 percent sodium sulfite, 5.1 percent sodium sulfate, 0.4 percent cresylic compounds, and 1.7 percent other organic substances such as cresols, phenols, etc. The data obtained from Plant 1 are shown in the following tabulation:

Flow	1,291 gallons/1,000 lb
COD	23,800 mg/l 256 lb/1,000 lb
BOD ₅	11,400 mg/l 123 lb/1,000 lb
TOC	5,020 mg/l 54 lb/1,000 lb

The sulfite and organic contaminants cause the high oxygen demand in the waste water, while the cresol contaminant (10 mg/l) constitutes an odorous nuisance in the atmosphere.

FIGURE IV.34
 PARA-CRESOL



According to the literature, the organic contaminants in the waste water exhibit very strong anti-oxidant properties and present a difficulty to ordinary biological treatment processes. Several possible methods of controlling this waste water discharge have been investigated. The most promising scheme appears to be activated carbon adsorption of organic contaminants prior to oxidation, followed by chemical regeneration of cresylic compounds adsorbed on the carbon, to return a valuable product to the process, eliminate the odor problem, and reduce the discharge of pollutants.

A demonstration plant and its economics are briefly described in the following paragraphs. The system consists of two 4ft-diameter by 30ft high columns of 304 L stainless steel. Each column is loaded to a height of 18.5 ft. with approximately 6,000 pounds of activated carbon. The system was designed to have sufficient capacity for a one-day operational cycle, requiring one column to be regenerated each 24 hours. Ten percent sodium hydroxide solution is used to regenerate spent activated carbon, and the desorbed cresylic compounds are recycled back to the process. During a seven-month period, the columns were operated at an average superficial velocity of 3.2 gpm/ft. Influent concentrations during the period were 3,500 to 6,500 mg/l cresylic compounds, and effluent concentrations were between 0 and 700 mg/l cresylic compounds. During this time, 271,600 pounds of p-cresol were returned to the process. This amount of p-cresol represents a value of \$114,000.

As demonstrated, the activated carbon system not only can recover p-cresol from the waste water and turn it into profit, but also can decrease the RWL of the system. Furthermore, it improves the treatability of the waste water. Consequently, to define BATEA and BADCT control technologies, an activated carbon system should be incorporated into the process.

Two other process routes for the manufacture of p-cresol are currently practiced: vapor-phase methylation of phenol over alumina catalysts, and liquid-phase oxidation of meta- and para-cumene.

Producers of p-cresol in the U.S. and the economic of production are presented in Tables IV-52 and IV-53

Table IV-52

U.S. Cresol Capacity (1972)

<u>Company</u>	<u>MM lb</u>	<u>Process</u>
Hercules, Inc. (Gibbstown, N.J.)	6	p-cymene oxidation
Koppers (Follansbee, W. Va.)	10	phenol and methanol
Pitt-Consol (Newark, N.J.)	80	phenol and methanol
Sherwin Williams (Chicago, Ill.)	<u>10</u>	toluene sulfonation
Total	106	

Table IV-53

Economic Evaluation of Activated Carbon System
for Wastewater from p-Cresol*

I. Annual Operational Cost	
Depreciation (10 year straight line)	\$ 14,400
Maintenance (5% of installed cost)	7,000
Utilities	1,050
Raw Materials (NaOH and Filter Aid)	17,250
Labor (using existing manpower)	0
Carbon Make-Up	<u>4,000</u>
	\$ 43,700
II. Annual Net Revenue	\$210,320
(500,770 pounds p-cresol recovered/year, sale price= \$0.42/pound)	
III. Analysis	
Gross Profit= \$210,320 -- \$43,700=	\$166,620
Tax (50%)	= <u>83,310</u>
After Tax Profit	= \$ 83,310
After Tax Cash Flow= \$83,310 + \$14,400=	\$97,710
After Tax RDI=	$\frac{\$97,710}{\$144,000} \times 100\% = 67.9\%$
Payout Time	= $\frac{\$144,000}{\$97,710} = 1.47 \text{ yrs.}$

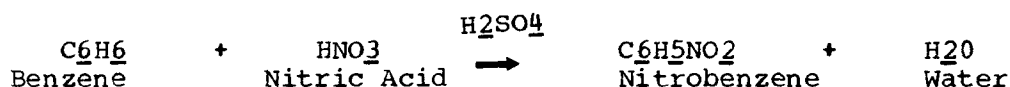
*"Recovery of P-Cresol from Process Effluent," Baber, C.D., Clark, E.W., Jesernig, W.V., and Huether, C.H., Presented at the 74th AIChE, New Orleans, La., March 1973.

SUBCATEGORY C

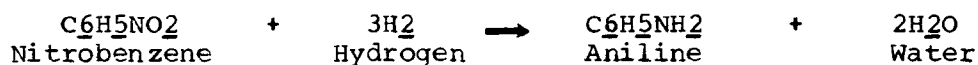
Product
Aniline

Process
Nitration and Hydrogenation of Benzene

Benzene is first converted to nitrobenzene in a mixture of nitric and sulfuric acids:



The reactor effluent is decanted into a liquid/liquid separator, where crude nitrobenzene is separated from the acid solution. The acid solution is concentrated by steam stripping and recycled back to the reactor. Crude nitrobenzene is washed, vaporized, and fed to a fluidized-bed reactor containing a copper-silica hydrogenation catalyst, where the following hydrogenation reaction occurs:



The unreacted hydrogen is recycled to the reactor. Reactor effluent goes to a separator, where two phases are formed. The organic phase contains water, and is fractionated in a two-tower system to remove heavy residue and water from the aniline product. The aqueous layer, formed by the water of reaction, contains some aniline and is discharged into sewers.

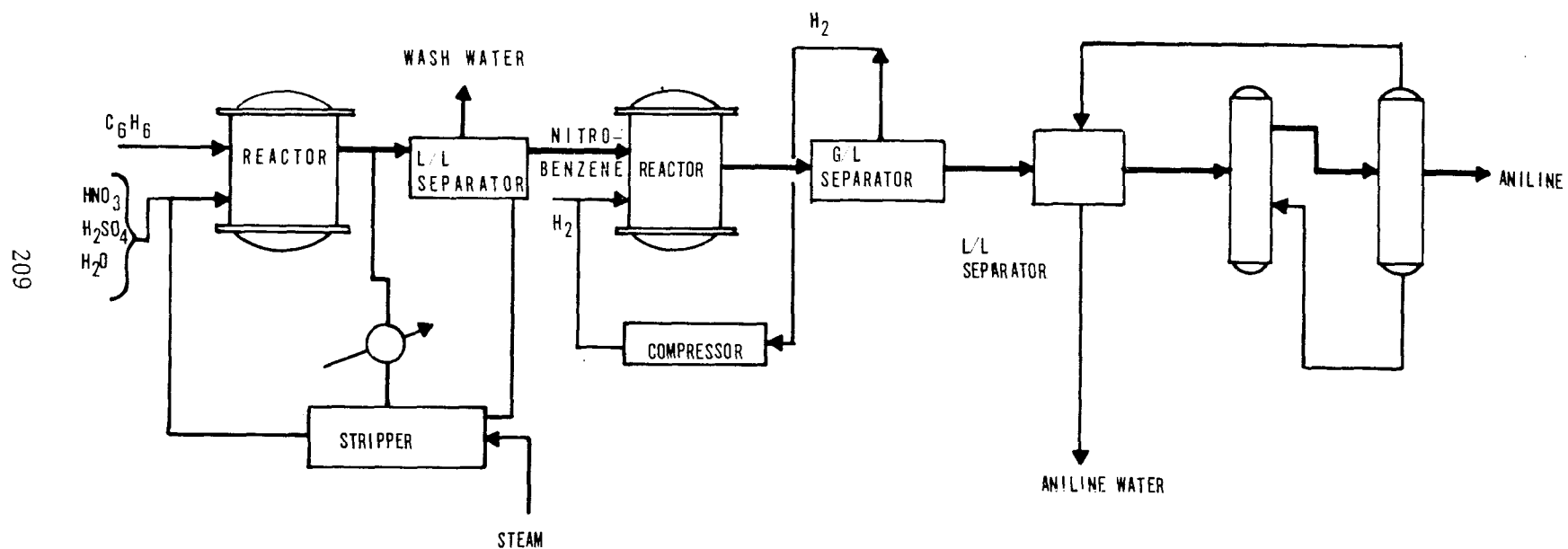
The process flow diagram is shown in Figure IV-35.

The major waste water sources in this process are the crude nitrobenzene wash water and aniline water formed in the final separator. RWL survey data of this process are shown in the following tabulation:

Flow	190 gallons/1,000 lb
COD	13,400 mg/l 21.2 lb/1,000 lb
BOD ₅	15 mg/l 0.02 lb/1,000 lb
TOC	12,150 mg/l 19.2 lb/1,000 lb

Results of analyses indicate that, in addition to the parameters shown above, sulfate concentrations in waste water streams are at levels inhibitory to biological treatment processes. The high RWL of this process is attributed to the high aniline

FIGURE IV - 35
ANILINE



concentration (3 percent) in aniline water from the final separator. It is a common practice to recover aniline by extraction either with incoming nitrobenzene or with benzene. However, such recovery was not practiced at the plant visited during the survey.

BADCT and BATEA in-process controls are defined by implementing an aniline recovery system to reduce process RWL. Instead of using a nitrobenzene extraction scheme, an effective steam-stripping system has been devised, and the following is a description of the equipment and processing required.

Water from a 10⁸ lb/yr aniline plant is steam stripped in a 2.5' x 40' tower. The feed to the stripper is 17 gpm containing 3.1 percent aniline by weight. The bottoms from the stripper will contain about 0.2 percent aniline. The overhead, essentially a 50/50 mixture of aniline and water is sent to incineration. Figure IV-36 is a process flowsheet of the proposed aniline stripper system.

With this modification, RWL can be expected to achieve the following values:

Flow	184 gallons/1,000 lb
COD	1,390 mg/l 2.13 lb/1,000 lb
TOC	1,490 mg/l 2.29 lb/1,000 lb

The totally installed cost for the stripper, including heat exchange, pumps, instrumentation, piping, foundations, electrical wiring, structures, etc. is \$115,000. The total annual operating cost, including depreciation, is about \$45,000. For the 10⁸ lb/yr aniline plant, this adds about .05¢/lb to the cost of the aniline. Table IV-54 presents the economics of the proposed aniline stripper.

The alternate routes in manufacturing aniline are the traditional technique of nitrobenzene liquid-phase reduction with iron filings and the liquid-phase nitrobenzene hydrogenation technique. U.S. aniline capacity from these processes is presented in Table IV-55. Assuming that nitric acid and sulfuric acids are available at \$30 per ton, estimated production costs for a 40.0 million pounds per year aniline plant, including benzene nitration facilities, are shown in Table IV-56.

FIGURE IV-36
ANILINE STRIPPER

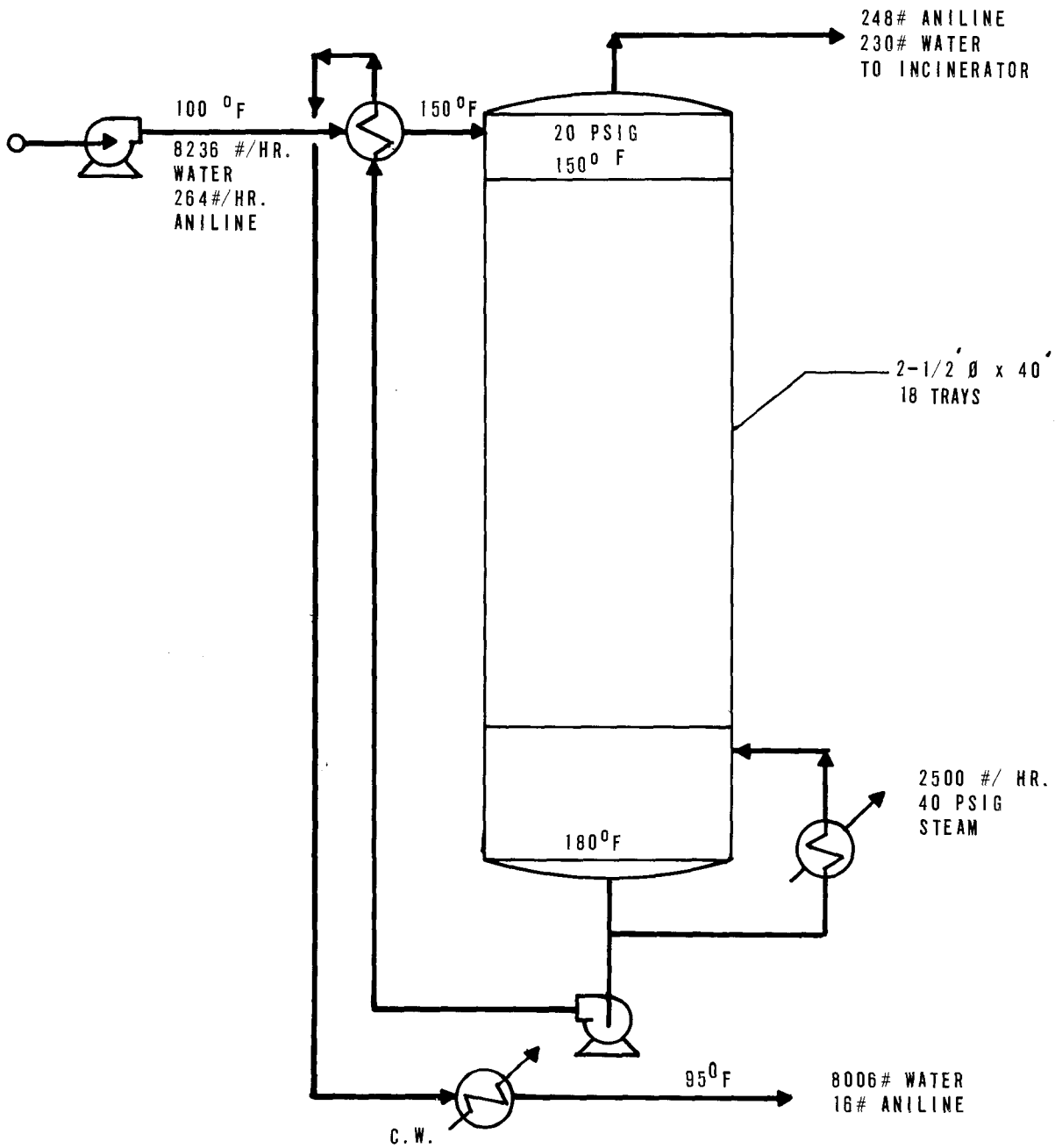


Table IV-54
Aniline Stripper Economics

Investment

Tower Cost, including trays, pumps, exchanges, instruments, piping, foundations, etc.	=	\$115,000 Totally Inst.
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Operating Costs

Utilities

		\$/Yr
Steam: 2500 #/hr. x \$.55/M# x 8000	=	\$11,000
Power: 800,000 kwh x \$.01/kwh	=	8,000
Cooling Water: 20 X 10 ⁶ Gals. x \$.25/M Gals	=	5,000
		\$24,000

Investment Related

Maintenance Material & Labor 4%	=	\$ 4,600
Plant Overhead 65% of Maintenance	=	3,000
Insurance, Taxes 1.5%	=	1,700
Depreciation 10% on BLCC	=	11,500
Total Expenses		\$44,800

¢/Gal Handled 0.55 ¢/Gal.

¢/lb Aniline removed 2.36¢/lb

In 100 MM #/yr Facility 0.045¢/lb Product Aniline

Table IV-55
U.S. Aniline Capacity (1972)

<u>Company</u>	<u>Location</u>	<u>MM lb</u>
Allied	Moundsville, W. Va	60
American Cyanamid	Bound Brook, N.J. Willow Island, W.Va.	60 40
DuPont	Gibbstown, N.J. Beaumont, Texas	130 200
First Chemical	Pascagoula, Miss	35
Mobay	New Martinsville, W. Va.	70
Rubicon	Geismar, La.	40
Total		<u>585</u>

Table IV-56
Estimated Economics for Aniline
(40. MM lb. plant)

Total Fixed Capital=\$3.2 MM

Estimated Operation Cost

	<u>Cost</u> <u>¢/lb. aniline</u>
Benzene	3.1
Nitric Acid	2.4
Hydrogen	0.8
Catalyst and chemicals	0.3
Utilities	0.4
Labor and overhead	0.6
Capital charges	2.6
	<u>10.2</u>

SUBCATEGORY C

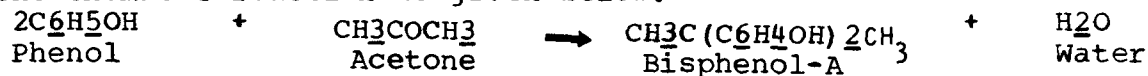
Product

Bisphenol-A

Process

Condensation of Phenol and Acetone

Diphenyl propane, also known as bisphenol-A, is produced by reacting phenol with acetone in the presence of acid catalyst, and the chemical reaction is given below:



A number of by-products are formed in conjunction with the main reaction. The earlier processes eliminated these impurities by batchwise crystallization, while the new process, the Hooker process, employs a continuous distillation and extractive crystallization under pressure to purify the product.

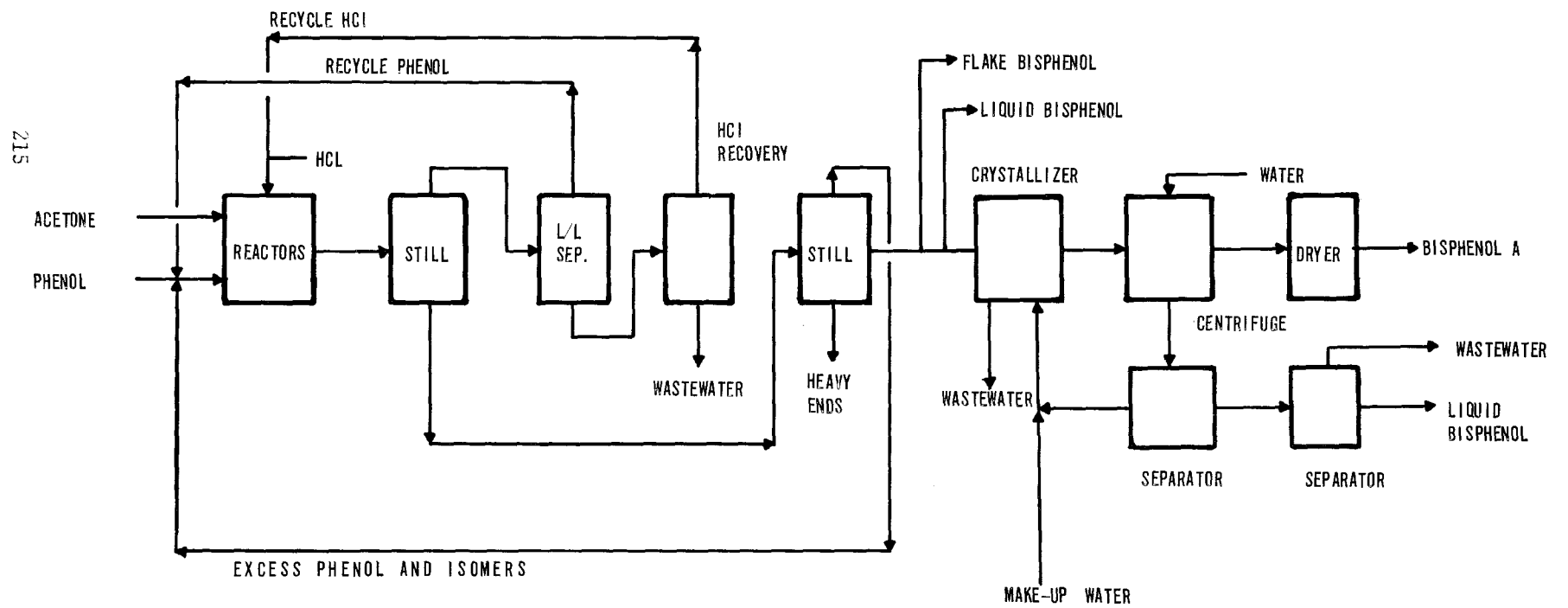
A process flow diagram of the Hooker process is shown in Figure IV-37. Phenol and acetone at a molar ratio of approximately three to one are mixed, saturated with hydrogen chloride gas, and sent to the reaction vessel. Reaction conditions are about 40°C, close to atmospheric pressure, with a mercaptan used as a catalyst. The crude product is stripped of HCl and water of reaction. The overhead is decanted into an organic phase (consisting mainly of phenol which is recycled) and an aqueous phase. The latter goes on to an HCl-recovery unit, and water is sent to disposal.

Bottoms from the stripper are sent to a series of purification distillation chambers, where excess phenol, isomers, and heavy ends are removed from the system for either recycle or disposal. Distillate from the last chamber is sent to the extraction operation, which produces a slurry of pure crystals. The filtrate from the centrifuge is partially recycled to the crystallizer, and the remainder is concentrated in an evaporator to produce liquid bisphenol-A.

The water separated from the HCl recovery unit, the extracted aqueous phase from the crystallizer, and the condensate from the final evaporator are the major waste water sources. The characteristics of the waste water obtained from survey data are presented in the following tabulation:

Flow	66.8 gallons/1,000 lb
COD	30,699 mg/l 17.11 lb/1,000 lb
TOC	9,216 mg/l 5.13 lb/1,000 lb
Phenol	12,713 mg/l 7.1 lb/1,000 lb

FIGURE IV-37
BISPHENOL A



The high concentration of phenol produces an inhibitory effect and interferes with the BOD₅ measurement. The organic contaminants in the waste water are mainly phenol, bisphenol, and organic solvent. Incomplete separation of the aqueous and organic phases in the decanter causes the high loss of organics into the waste water. Organic vapor escaping from the final evaporator also contributes a significant amount of contaminants.

To define BADCT and BATEA, a steam stripper should be required to recover and recycle these organic contaminants in the two major waste streams. The specification and the estimated economics of a steam stripper have been presented in the discussion of Aniline.

The total process water usage of this process is approximately 0.25 pounds per pound of bisphenol-A, while the gross cooling water usage is about 197 pounds per pound of product.

The U.S. Bisphenol-A capacity and estimated economics are presented in Tables IV-57 and IV-58.

Table IV-57
U.S. Bisphenol-A Capacity

<u>Producer</u>	<u>Location</u>	<u>Estimated Capacity*</u> MM lb/yr
Dow	Midland, Mich.	58
General Electric	Mt. Vernon, Ind.	25
Monsanto	St. Louis, Mo.	30
Shell	Houston, Texas	100
Union Carbide	Marietta, Ohio	<u>25</u>
	TOTAL	<u>238</u>

*As of mid-1969. Reported by Chemical Profiles 7/1/69.
Shell is reportedly expanding to 100 MM lb/yr by 1/1/71,
and Dow is reportedly planning a new 100 MM lb/yr plant
for Freeport, Texas due in 1972.

Table IV-58

Estimated Economics for Bisphenol-A
(20 MM lb plant)

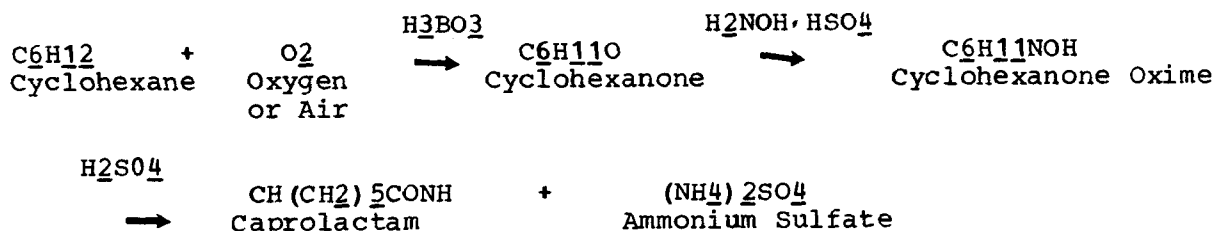
Total Fixed Capital = \$1.9 MM

	<u>Estimated Operation Cost</u> ¢/lb bisphenol-A
Phenol	7.2
Acetone	1.4
Catalyst and chemicals	0.1
Utilities	1.0
Labor and overhead	0.9
Capital charges	<u>3.1</u>
TOTAL	13.7

SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Caprolactam	Oxidation of Cyclohexane

Caprolactam is produced in the Beckman process by the addition of hydroxylamine sulfate to cyclohexanone, which is derived from cyclohexane. The basic chemical equations are given below:



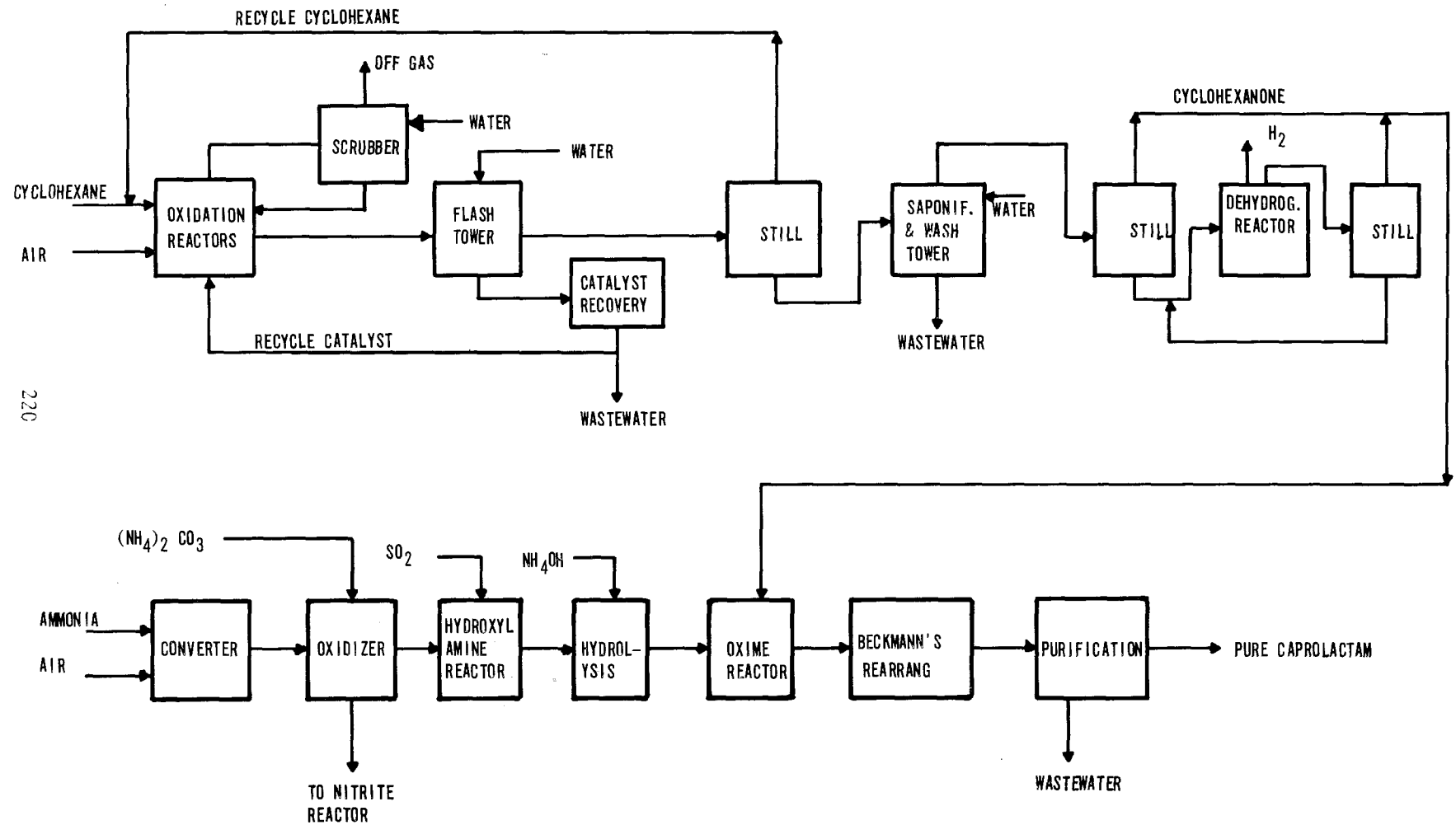
A process flowsheet is shown in Figure IV-38. Feed and recycled cyclohexane are mixed with air in an oxidation reactor in the presence of boric acid, which minimizes adipic acid production. The oxidation is carried out at approximately 150 psig and 160°C. The gaseous effluent is scrubbed to separate unreacted cyclohexane from what is essentially nitrogen. The liquid effluent is flashed with water and separated into an organic phase and an aqueous catalyst phase, which is then sent to a catalyst recovery unit. The organic phase is essentially a mixture of unreacted cyclohexane, cyclohexanone, and cyclohexanol. This mixture is first distilled to recover unreacted cyclohexane and followed by saponification and fractionation to separate cyclohexanone from cyclohexanol, which is then converted to cyclohexanone by dehydrogenation.

The hydroxylamine sulfate is obtained from ammonium nitrates and sulfur dioxide. Ammonia gas and air are fed to a converter where ammonia is burned at about 700°C in the presence of a catalyst and converted to disulphonate by contacting with ammonium carbonate and sulfur dioxide in series. The disulphonate is then hydrolyzed to hydroxylamine.

By addition of cyclohexanone to hydroxylamine sulfate, cyclohexanone oxime is first produced and rearranged in nearly quantitative yield to caprolactam in the presence of concentrated sulfuric acid. The product is neutralized, and the ammonium sulfate solution is extracted with benzene to recover the lactam product and discharged to a concentration and recovery step.

The major water pollution sources in this process are the draw-offs from catalyst recovery unit, saponification and wash tower, and the final product purification step. The contaminants in the waste stream are small amounts of diacids formed during the oxidation step, sodium salts, and unrecovered intermediate products. The characteristics of the waste water obtained from the plant survey are summarized in the following tabulation:

FIGURE IV-38
CAPROLACTAM



	Plant 1	Plant 2
Flow	1,334 gallons/1,000 lb	2,500 gallons/1,000 lb
COD	358 mg/l 4.0 lb/1,000 lb	N.A.
BOD ₅	147 mg/l 1.64 lb/1,000 lb	11.2 lb/1,000 lb
TOC	109 mg/l 1.22 lb/1,000 lb	N.A.

Since it is deemed unfeasible to reduce RWL of this process by any in-process modification, the RWL presented in the preceding tabulation can be considered as standard for BADCT and BATEA.

Several other commercial routes to caprolactam are available, and process highlights of each route are summarized in the following paragraphs.

In the Toyo Rayon process, nitrosylchloride is first manufactured by reacting ammonia gas with air at 700°C and atmospheric pressure using platinum-rhodium gauze as a catalyst, then with concentrated sulfuric acid, and finally with hydrogen chloride. The nitrosylchloride gas mixture is then reacted with cyclohexane to give the cyclohexane oxime hydrochloride. The reaction is carried out in the liquid phase, using the visible light emitted by mercury lamps to induce the photonitrosation. Subsequently, cyclohexanone oxime hydrochloride is treated with oleum to produce a sulfuric acid solution of caprolactam, which is then purified by a series of purification steps.

The Snia Viscosa process is based on the nitrosation of hexahydrobenzoic acid with sulfuric acid in oleum. The feed toluene is oxidized with air and then hydrogenated over a palladium catalyst to form hexahydrobenzoic acid. Caprolactam is then formed by reacting hexahydrobenzoic acid with nitrosylsulfuric acid, which is prepared by bubbling N₂O₃ into the cyclohexane carboxylic acid dissolved in oleum.

The other route (referred to as the Caprolactone Process) produces caprolactam without any ammonium sulfate by-product. Caprolactone is first produced by oxidation of cyclohexanone with peracetic acid, which is produced by acetaldehyde oxidation. The resulting caprolactone is distilled under vacuum and reacted with ammonia at high pressure to form caprolactam, which is purified using conventional distillation techniques.

Although many processes exist for caprolactam production, the only process used commercially in the U.S. as shown in Table IV-59 is the Beckmann process. The relative economics for the Beckmann, Caprolactone and Toyo Rayon processes are summarized in

Table IV-60 which shows that the Beckmann has the lowest investment cost.

Table IV-59
Caprolactam Capacity
(MM lb.)

<u>Company</u>	<u>Location</u>	<u>1967</u>	<u>1972</u>	<u>Process</u>
Allied Chemical	Hopewell, Va.	300	300	Beckmann
Columbia NIPRO	Augusta, Ga.	44	150	Beckmann
Dow Badische	Freeport, Texas	90	176	Beckmann
DuPont	Beaumont, Texas	50	shut down	Nitrocyclohexane
Union Carbide	Taft, La.	<u>50</u>	<u>shut down</u>	Caprolactone
TOTAL		534	626	

Table IV-60

Estimated Economics for Caprolactam
(150-MM-lb. plant; 1972 construction)

TOTAL FIXED CAPITAL

<u>Process</u>	<u>\$ MM</u>
Beckmann	37.4 ¹
Caprolactone	39.8 ²
Toyo Rayon	40.0

¹ Investment includes cyclohexanone and oximation.

² Investment includes peracetic acid and caprolactone units.

PRODUCTION COST
¢/lb. caprolactam

	<u>Beckmann</u>	<u>Caprolactone</u>	<u>Toyo Rayon</u>
Raw materials	11.43 ¹	10.71 ²	9.14
Utilities	1.60	1.91	2.25
Labor	0.58	0.40	0.36
Maintenance (6% ISBL + 3% OSBL)	1.20	1.28	1.28
Overhead (45% of maint. & labor)	0.80	0.76	0.74
Taxes and insurance (1.5% of inv.)	0.38	0.41	0.41
Depreciation (10 yr.)	<u>2.50</u>	<u>2.66</u>	<u>2.66</u>
TOTAL	18.49	18.13	16.84
By-product credit	<u>4.44</u>	<u>6.22</u>	<u>1.58</u>
NET	14.05	11.91	15.26

¹ Includes cyclohexane (0.88 lb. at 3.3¢/lb.), NH₃ (1 lb. at 2 ¢/lb.) and oleum (1.7 lb. at \$36/ton). Ammonium sulfate credit at \$23/ton.

² Includes cyclohexane (1.0 lb. at 3.3¢/lb.) and acetaldehyde (0.62 lb. at 8.0¢/lb.). Acetic acid credit at 6¢/lb.

³ Includes cyclohexane (0.95 lb. at 3.3¢/lb.) ammonia (1 lb. at \$40/ton and oleum (1.7 lb. at \$36/ton). Ammonia sulfate credit at \$23/ton.

SUBCATEGORY C

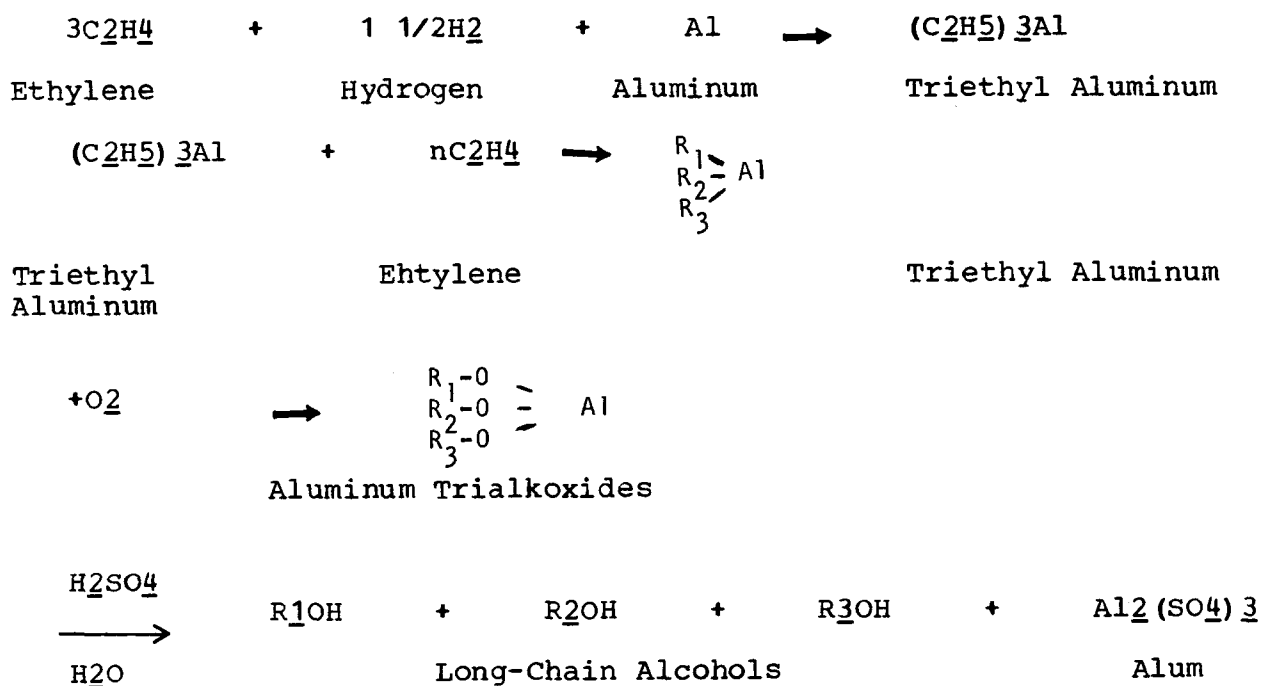
Product

Long Chain Alcohols

Process

Ethylene Polymerization

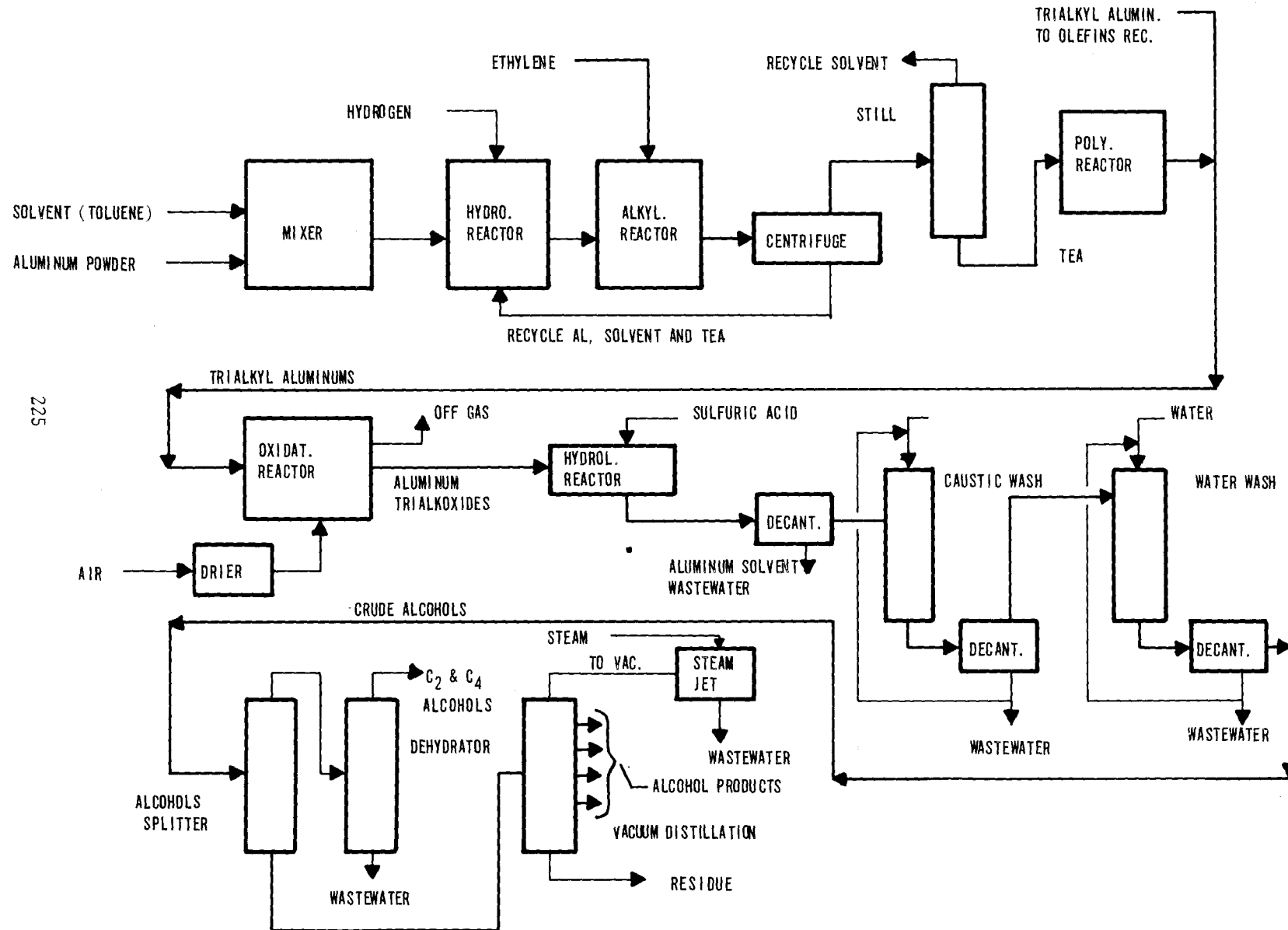
Long-chain alcohols are manufactured from ethylene in the presence of Ziegler catalysts. The process begins by reacting aluminum metal with ethylene and hydrogen to form triethyl aluminum (TEA). Ethylene is added to this compound at high pressures to give trialkyl aluminum compounds, which are then oxidized with dry air to aluminum trialkoxides. These are hydrolyzed by sulfuric acid to primary alcohols having an even number of carbon atoms. The basic chemical equations are summarized as follows:



•A simplified flow diagram is shown in Figure IV-39. An atomized aluminum powder is first activated in a non-aqueous slurry media and next hydrogenated with dry hydrogen gas under pressure to give diethyl aluminum hydride. The hydride is then contacted with ethylene to produce TEA. Approximately two moles of TEA are recycled to the hydrogenator and one mole goes to the polymerization step. Recycle TEA solvent and aluminum are separated by means of a centrifuge.

In the polymerization section, TEA is reacted with ethylene under pressure to make trialkyl aluminum, which is then oxidized to produce alkoxides. A non-aqueous solvent such as toluene is circulated and recycled in this section. In the hydrolysis section, the alkoxides are hydrolyzed with sulfuric acid and water to yield alcohols and a solution of alum and water. The

FIGURE IV-39
LONG CHAIN ALCOHOL



alum solution is separated from the alcohols in a decanter. The sulfuric acid residue is first neutralized with dilute caustic solution and next washed with hot water to remove sodium sulfate. In both the neutralization and wash steps, the alcohols are separated from the aqueous phase in decanters.

The crude alcohols are then dehydrated and fractionated in a series of distillation columns to obtain pure alcohol products. Steam jets are used to produce vacuum in the stills.

The major water pollution sources in this process are the draw-offs from decanters and the condensate of the steam jets. Depending upon the desired concentration of the alum solution recovered, the cycle of decanter draw-off waters, and the modes of condensing ejected steam, the volume of waste water per unit production will vary.

Straight-chain alcohols are also obtained by the oxo reaction starting from straight-chain - olefins and by direct oxidation of normal paraffins. Producers of long-chain synthetic alcohols in the U.S. are presented in Table IV-61.

Table IV-61
U.S. Long-Chain Alcohol Capacity

<u>Producer</u>	<u>Location</u>	<u>1965 Capacity MM lbs/yr.</u>	<u>Type of Alcohol</u>	<u>Process</u>	<u>Raw Material</u>
Continental	Lake Charles, La.	100.00	Primary	Ziegler	Ethylene
Ethyl	Houston, Tex.	50.00	Primary	Ziegler	Ethylene
Shell	Houston, Tex.	50.00	80% Primary 20% Secondary	Oxo	Cracked wax
Shell*	Geismar, La.	100.00	80% Primary 20% Secondary	Oxo	Cracked wax
Union Carbide	Texas City, Tex.	40.00	Secondary	Oxidation	n-paraffins

*Due on stream in 1966.

Source: Oil, Paint, and Drug Reporter, August 26, 1965.

SUBCATEGORY C

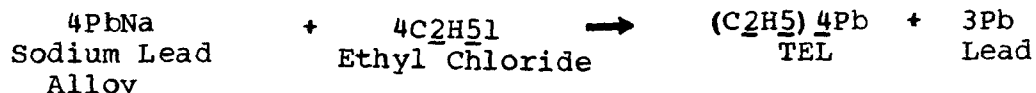
Product

Tetraethyl Lead

Process

Addition of Ethyl Chloride to
Lead in Sodium - Lead Alloy

Over 90 percent of all tetraethyl lead is produced by some version of a conventional forty-year-old batch process in which an alkyl halide reacts with sodium-lead alloy. The reaction, occurring in a horizontal autoclave provided with a reflux condenser to recover any vaporized alkyl halide, yields a mixture of TEL, salt, and lead. The reaction, carried out at 60 psig and 70°C, is given below:



The product mixture is fed batchwise to a still, where the tetraethyl lead is separated from the by-product lead and sodium chloride by direct steam stripping. The tetraethyl lead and stripping steam are condensed and sent to a decanter, where tetraethyl lead is drawn off as a bottoms stream. The upper aqueous layer in the decanter, containing unreacted ethyl chloride and dissolved organic by-products, is discharged into a process ditch.

The salty sludge bottoms from the still are sent to a lead recovery unit, and the centrate is combined with the supernatant from the TEL decanter before being discharged into a settling basin for final recovery of solid lead.

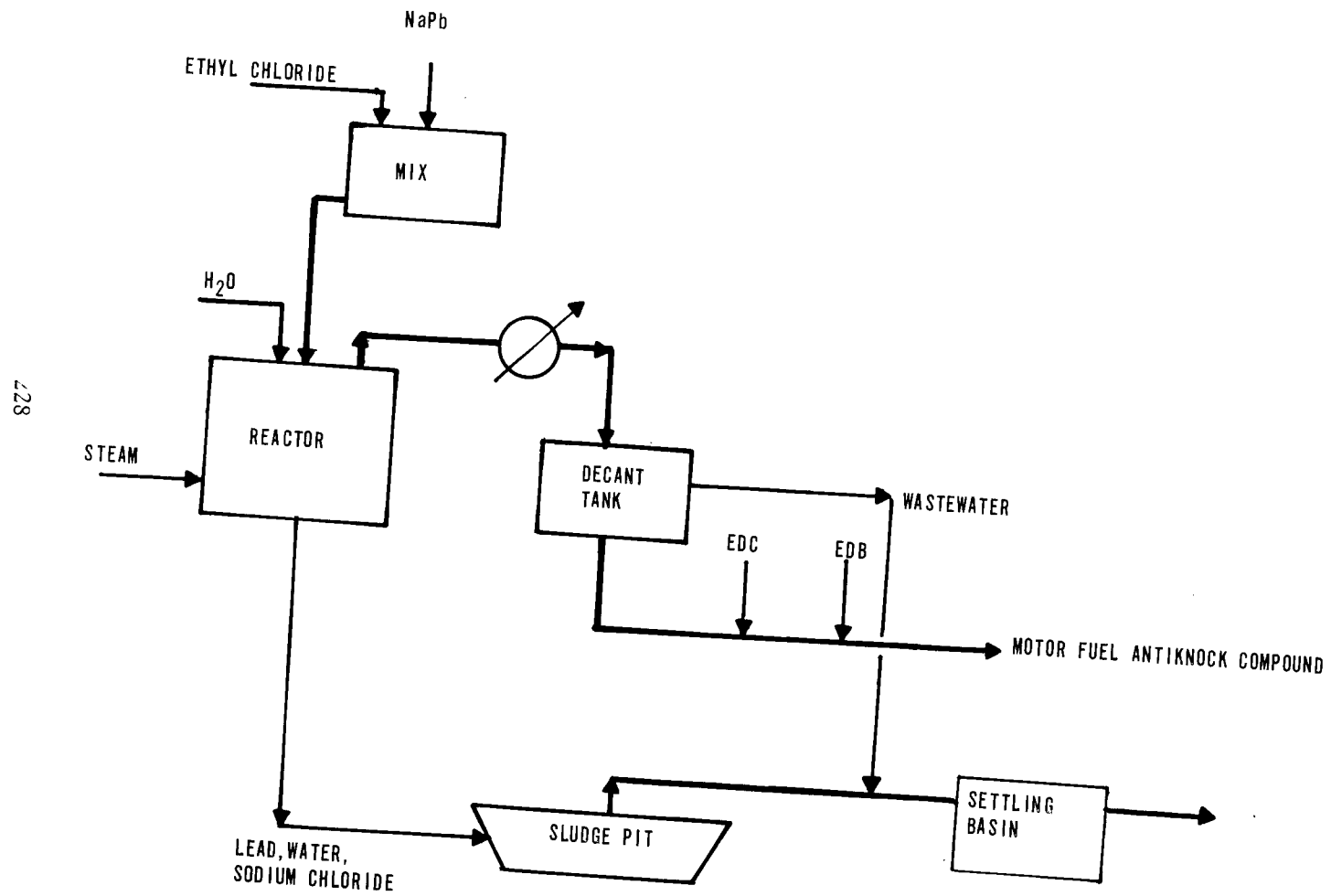
The process flow sheet is shown in Figure IV-40.

Since recovery of by-product lead is considered an integral part of the TEL manufacturing process, the effluent from the settling basin is considered as the waste water source of the process. The waste water characteristics obtained from the plant visit are shown in the following tabulation:

Flow	12,000 gallons/1,000 lb
COD	1,100 mg/l 110 lb/1,000 lb
BOD ₅	40 mg/l 4 lb/1,000 lb
TOC	56 mg/l 5.6 lb/1,000 lb

The high amount of waste water is due mainly to the nature of batch processes, which require a large quantity of water in cleaning up the reactor between reaction batches. Another cause of high water use is the vent-gas scrubber at the "lead" recovery

FIGURE IV- 40
TETRAETHYL LEAD



unit. The intermittent dosage of "still-aids" such as soap or iron to control the plating out of lead on the still walls, as well as unrecovered ethyl chloride, TEL, and metallic lead, all contribute to the high chemical oxygen demand.

In defining levels of control technology, it is suggested that recycling of the aqueous layer in the decanter to reduce fresh water usage, and consequently the amount of waste water discharged, can be considered for BPCTCA. BADCT and BATEA should have a steam stripper for effective recovery of unreacted ethyl chloride and product TEL from the stream prior to their discharge into the settling basin.

An alternate process, which is based on the electrolysis of an alkyl Grignard reagent, is used by only one company in the world. This involves a totally different approach and offers at least three advantages: 1) it gives higher product yields; 2) it does not make by-product lead, hence eliminating the inefficient recovery and recycle of metallic lead; and 3) it can produce TEL as well as alkyl lead compounds. The first processing step is the preparation of the Grignard reagent. Agitated propane-cooled reactors receive metallic magnesium that reacts exothermically with fresh and recycled alkyl halide in the presence of an electrolytic solvent consisting of a mixture of ethers such as tetrahydrofuran and diethyleneglycol dibutyl ether. The yield of alkylmagnesium halide is over 98%. The effluent of the electrolysis cell is sent to a stripper, where a separation of alkyl halide and alkyl lead is performed.

The U.S. tetraethyl lead capacity and the estimated economics for tetraethyl lead production are presented in Tables IV-62 and IV-63.

Table IV-62

U.S. Tetraethyl Lead Capacity

	<u>Plant Location</u>	<u>Est. 1970 Capacity (Million Pounds/Year)</u>
DuPont	Antioch, Calif.	340
	Deepwater, N.J.	
Ethyl	Baton Rouge, La.	390
	Houston, Texas	
Houston Chem.	Beaumont, Texas	100
Nalco Chem.	Houston, Texas	<u>65</u>
Total		895

Table IV-63

Estimated Economics for Tetraethyl Lead
(40. MM lb. plant)

Total Fixed Capital=\$10.0 MM

Estimated Operation Cost

	<u>Cost, ¢/lb. TEL</u>
Ethyl chloride	4.9
Sodium	3.8
Lead (17¢/lb.)	11.4
Utilities	1.5
Labor and overhead	1.6
Capital charges	<u>8.3</u>
Total	31.5

SUBCATEGORY C

<u>Product</u>	<u>Process</u>
Coal Tar Products	Coal Tar Distillation

Coal tar is a mixture of many chemical compounds (mostly aromatic) which vary widely in composition. The process of coal tar distillation separates these fractions into commercially valuable products.

In the plant visited, crude coke-oven tar is fractionally distilled into solvent, carbolic oil, road tar, creosote, and pitch fractions. These products are then purified or further fractionated into fine products. The processes of coal tar distillation, anthracene refining, pitch forming, and naphthalene refining, together with their associated waste water sources, are briefly described in the following paragraphs; simplified process diagrams are presented in Figures IV-41 through IV-44.

Crude coke-oven tar and dilute caustic solution are fed into a dehydration column. The vapor stream taken overhead from the column is condensed, and water is removed from the solvent and discharged to a sewer line. The liquid stream is sent then to a vacuum still and to a series of fractionators where crude carbolic oil, road tar, creosote, and pitch fraction are generated. There are two steam jets associated with the distillation columns; the condensates of these jets contain organic contaminants and are the major water pollution sources.

In the anthracene refining process, creosote is first washed with water in a crystallizer, and the creosote anthracene slurry is passed through filters and centrifuges to produce crude anthracene. The crude product is then sent to a crystallizer, where furfural is used to purify the product. Refined solid anthracene is obtained after solid separation and drying steps. The liquid streams from the second-stage purification units are collected for furfural recovery. The aqueous stream discharged from the first-stage purification unit and the condensate of the steam jet associated with the furfural recovery unit are major waste water sources. The liquid pitch from tar distillation is cooled by direct contact with water and then dried to form the final product. The contact cooling water is another major waste water source.

The first step in naphthalene refining is extraction of topped carbolic oil with a caustic solution. The bottom layer in the extractors is the by-product of carbolate. The upper aqueous layer in the extractors is sent to a series of stills where naphthalene and intermediate products are generated. The only water pollution source is the condensate of the steam jets which are used to produce vacuum in the naphthalene stills.

End-of-pipe treatment and in-plant abatement have been achieved: segregation of clean water from process waste water, replacement of barometric condensers with indirect condensers, installation

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COAL TAR DISTILLATION

COAL TAR

DILUTE CAUSTIC

DEHYDRATION

C & W

L/L SEP.

STEAM

JETS

C & W

LIGHT OIL

SOLVENT

WASTEWATER

VACUUM DISTILLATION

TOPPED CARBOLIC OIL

FURNACE

TOPPED TAR MIXING

FLASH CHAMBER

FURNACE

FRACTIONAL DISTILLATION

LIGHT CREOSOTE

HEAVY CREOSOTE

PITCH STORAGE

PITCH

HEAVY CREOSOTE

STEAM

JETS

WATER

WASTEWATER

FIGURE IV-42
ANTHRACENE REFINING

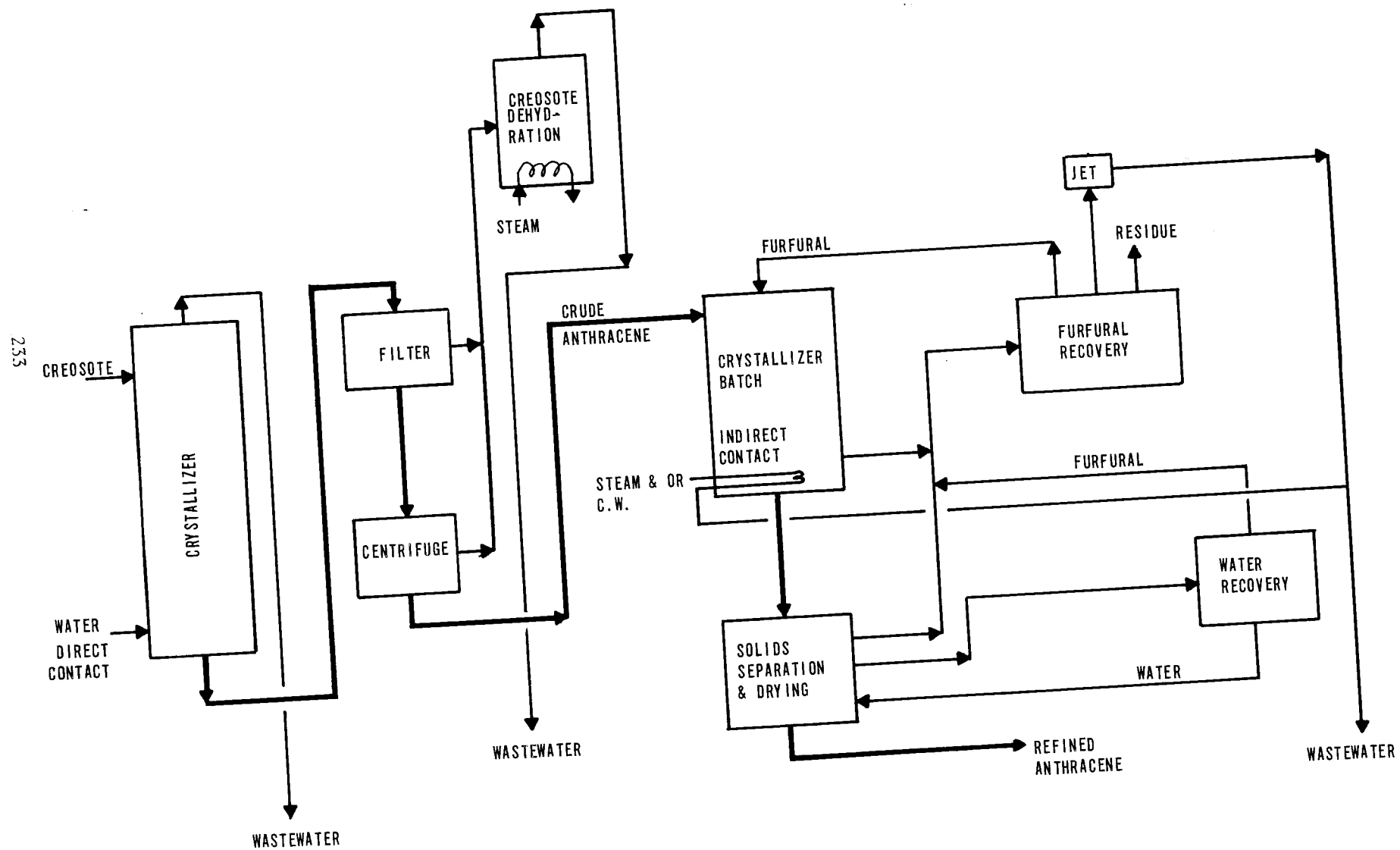


FIGURE IV-43
EXTRACTION AND NAPHTHALENE REFINING

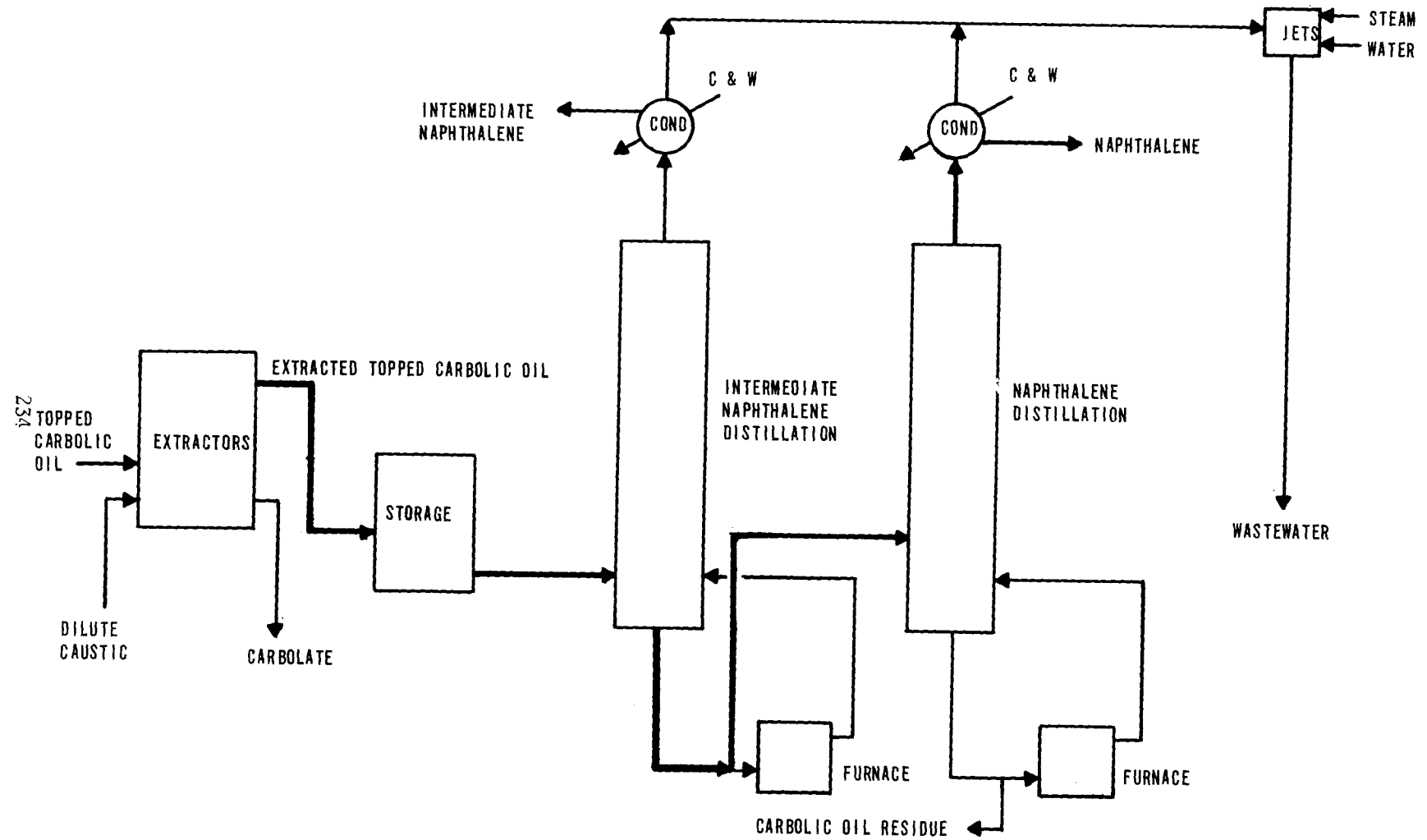
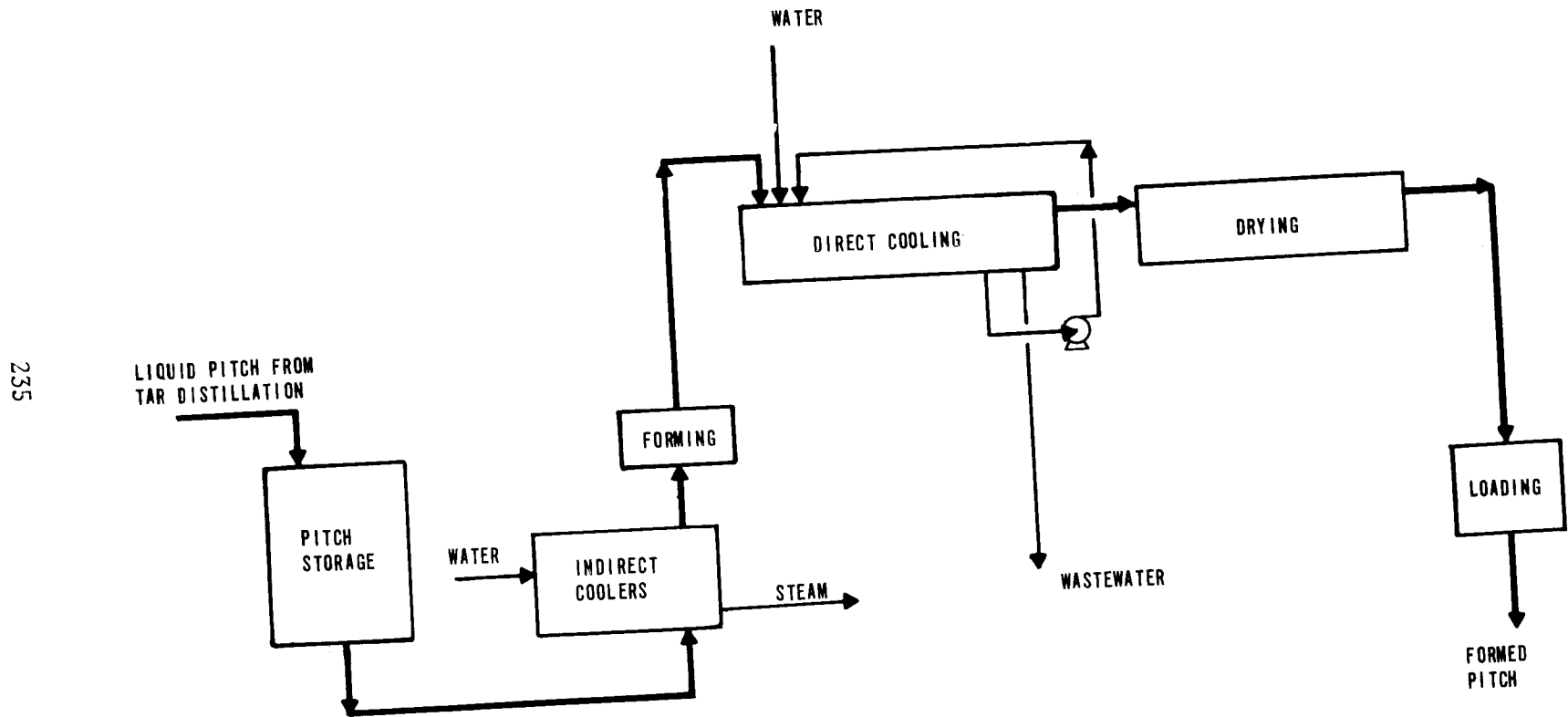


FIGURE IV-44
PITCH FORMING



of phenol recovery units, etc. These modification have resulted in a low RWL.

The characteristics of waste water obtained from the plant survey are shown in the following tabulation:

	Coal Tar Distillation	Pitch Forming
	405.3 gallons/1,000 gallons	126.1 gallons/1,000 lb
COD	2,570 mg/l 8.68 lb/1,000 gallons	61 mg/l 0.064 lb/1,000 lb
BOD ₅	833 mg/l 2.81 lb/1,000 gallons	N.A.
TOC	3,010 mg/l 10.16 lb/1,000 gallons	N.A.

The historical data provided by the plant indicate that pitch forming has a waste flow of 200 gal/1,000 lb of product, with 0.13 pounds of COD while the naphthalene refining has a waste flow of 408 gal/1,000 lb of product, with 0.86 pounds of COD.

Although there is a variation between the survey and the historical data, the raw waste loads derived from the above-mentioned abatements can be considered as representative of BPCTCA control technology of each individual process. However, standards for BATEA and BADCT should require that the remaining barometric condensers be converted to indirect condensers. Thus, the quantities of waste water from the processes of coal tar distillation and naphthalene refining can be reduced, although RWL may not be correspondingly reduced.

SUBCATEGORY D

Product

Dyes and Pigments

Process

Batch Manufacture

The manufacture and use of dyes and pigments constitute an important part of modern chemical technology. Because of the variety of products that require a particular material to give maximum coverage, economy, opacity, color, durability, and desired reflectance, manufacturers now offer many hundreds of distinctly different dyes and pigments. Usually dyes are classified according to both the chemical makeup and the method of application. The manufacturers look at dyes from the chemical aspect, and arrange and manufacture them in groups, usually of like chemical conversions, while the users of dyes group them according to the methods of application. Table IV-64 lists the principal types of dyes by application classification, and Table IV-65 by chemical arrangement. The selected pigments and their corresponding production figures are presented in Table IV-66.

The raw materials for the manufacture of dyes are mainly aromatic hydrocarbons, such as benzene, toluene, naphthalene, anthracene, pyrene, and others. These raw materials are almost never directly useful in dye synthesis. It is necessary to convert them to a variety of derivatives, which are in turn made into dyes. These derivatives are called intermediates. However, the industries which utilize either raw materials or intermediates to produce final-product dyes are all subcategorized as the dye industry.

Because of the large number of compounds that are required, often in limited amounts, most dyes, if not all, are manufactured in batches. Since the purpose of this project is to investigate process-related waste water generation sources rather than to examine detailed unit processes/operations of manufacturing processes for each class of dyes/ pigments, a typical manufacturing process for dyes is given to illustrate the waste water sources.

A typical process flow sheet for manufacture of azo dyes is presented in Figure IV-45. Raw materials (which include aromatic hydrocarbons, intermediates, various acids and alkalies, and solvents) are simultaneously or separately fed into the reactor, where the reaction is carried out ordinarily at atmospheric pressure. Because the reactions are exothermic, adequate temperature control is required to avoid side reactions. Temperature control is accomplished primarily by direct addition of ice to the reaction tank. When the reaction is complete, the dye particles salt out from the reaction mixture. The vent gases taken overheads from the reactor are continuously passed through a water scrubber before being discharged into the atmosphere. The liquid effluent from the reactor is then sent to a plate-and-frame filter press where the dye particles are separated from the mother liquor. The mother liquor is either directly discharged

FIGURE IV-45
DYES

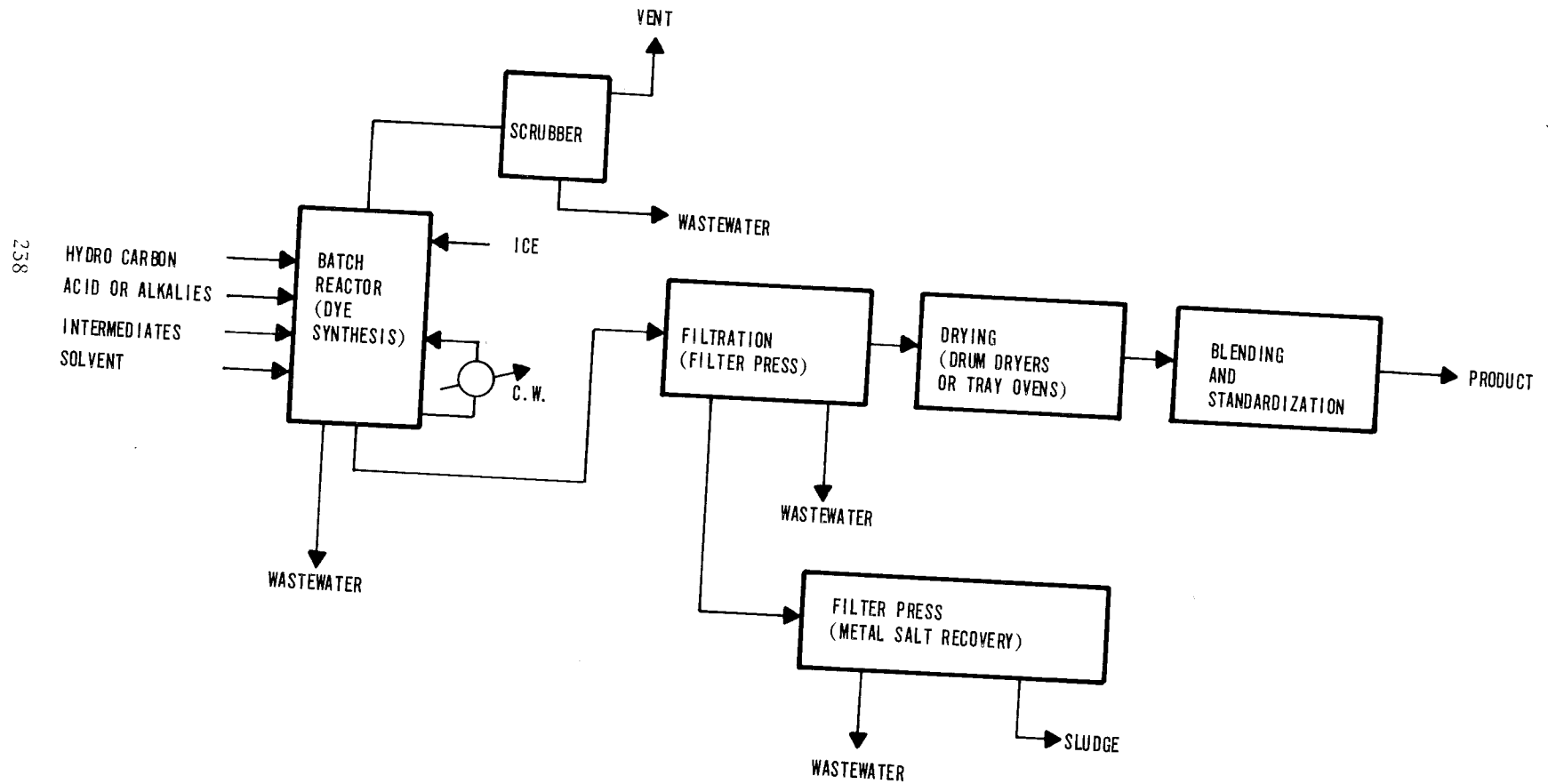


Table IV-64
U. S. Production of Dyes,
by Classes of Application, 1965

<u>Class of application</u>	<u>Production, 1,000 lb.</u>	<u>Sales</u>		<u>Unit value, Per lb.\$</u>
		<u>Quantity, 1,000 lb.</u>	<u>Value, \$1,000</u>	
Total	207,193	189,965	292,284	1.54
Acid	20,395	18,666	39,025	2.09
Azoic dyes and components:				
Azoic compositions	2,100	2,043	3,968	1.94
Azoic diazo components, bases (fast color bases)	1,558	1,310	2,057	1.57
Azoic diazo components, salts (fast color salts)	2,835	2,646	2,683	1.01
Azoic coupling components (naphthol AS and derivatives)	3,172	2,429	4,669	1.92
Basic	10,573	9,553	23,907	2.50
Direct	36,080	33,663	50,970	1.51
Disperse	15,514	13,522	32,878	2.43
Fiber-reactive	1,586	1,558	6,744	4.33
Fluorescent brightening agents	19,420	18,284	34,516	1.89
Food, drug, and cosmetic colors	2,923	2,736	10,238	3.74
Mordant	4,745	4,246	5,706	1.34
Solvent	9,837	8,930	15,351	1.72
Sulfur	18,648	17,471	9,960	0.57
Vat	57,511	52,439	48,728	0.93
All other	296	469	884	1.88

Source: Synthetic Organic Chemicals, U. S. Tariff Commission

Table IV-65

U.S. Production and Sales of Dyes,
by Chemical Classification, 1964

<u>Chemical class</u>	<u>Production, 1,000 lb.</u>	<u>Sales</u>		
		<u>Quantity, 1,000 lb.</u>	<u>Value, \$1,000</u>	<u>Unit value per lb.\$</u>
Total	184,387	178,273	264,023	1.48
Anthraquinone	41,661	40,675	66,889	1.64
Azo, total	57,897	57,367	96,579	1.68
Azoic	8,787	7,399	12,149	1.64
Cyanine	373	362	1,113	3.07
Indigoid	5,729	6,144	3,302	0.54
Ketone imine	731	782	1,614	2.06
Methine	1,074	974	3,367	3.46
Nitro	720	679	1,258	1.85
Oxazine	172	144	601	4.17
Phthalocyanine	1,987	1,868	4,800	2.57
Quinoline	637	519	1,658	3.19
Stilbene	18,488	17,640	29,166	1.65
Sulfur	17,776	17,268	9,798	0.57
Thiazole	462	480	1,043	2.17
Triarylmethane	5,607	5,312	12,682	2.39
Xanthene	1,312	737	3,473	4.71
All other	20,974	19,923	14,531	0.73

Source: Synthetic Organic Chemicals, U.S. Tariff Commission
 In 1965 total dye production increased 12.5% to
 207 million lb.

Table IV-66

Production or Shipment of Selected Pigments in the United States, 1958 and 1963

<u>Pigments</u>	<u>Short tons</u>	
	<u>1958</u>	<u>1963</u>
Titanium pigments, composite and pure (100%)	403,867	555,211*
White lead, except white lead in oil:		
Basic lead carbonate	} 14,527	
Basic lead sulfate		
Zinc oxide pigments:		
Lead-free zinc oxide	130,075	162,281*
Leaded zinc oxide	23,127	12,281*
Lithopone		
White extender pigments:		
Barites, etc. (excluding whiting)		823,625
Whiting (calcium carbonate)	28,393	158,773
Color pigments and toners (except lakes), chrome colors:		
Chrome green	3,907	2,867
Chromium oxide green	4,820	6,473*
Chrome yellow and orange	22,365	26,620*
Molybdate chrome orange	5,675	} 9,400*
Zinc yellow (zinc chromate)	6,005	
Iron oxide pigments	62,923	73,251
Colored lead pigments:		
Red lead	23,311	25,780
Litharge	121,698	93,958
Iron blues (Prussian blue, Milori blue, etc.)	4,265	5,030
Blacks:		
Bone black	11,471	
Other blacks (carbon black)		1,138,500*

Source: Chemical Statistics Handbook, 5th ed., Statistical Summary 4, Manufacturing Chemists' Association, Washington, D.C., August, 1961.

*1964

into sewers or sent to another filter press to recover some of the metal salts. The filter cake is first washed with compressed air while still in the press. The moist cake is discharged into shallow trays which are placed in a circulating air drier, wherein the moisture is removed at temperatures between 50 and 120°C. Vacuum driers and drum driers may also be used. The dried dye is ground and mixed with a diluent, such as salt, to make it equal in color strength to a predetermined standard. Dilution is necessary because batches differ in their content of pure dye. Uniformity is assured by dilution to a standard strength.

The great majority of dyes and pigments are manufactured by the typical process flow diagram described. However, the manufacture of some special dyes or pigments may require more or fewer processing steps. For example, in the manufacture of alkali-blue pigment, the process requires a steam ejector to produce vacuum for the batch reactors. The barometric condenser is then used to condense the exhaust steam. In the manufacture of Direct Blue 6 dye, the filter cake is not washed but merely freed from the adhering liquid by air drying.

The major water pollution sources of this process are the mother liquor from the filter press, the intermittent reactor clean-up waters, the draw-off from the vent gas scrubber, and the housekeeping cleaning waters. The data obtained from the plant survey are summarized in the following tabulation. Multiple data were collected at one of the plants, and these data were subjected to the analysis for probability of occurrence. The results of probability analysis are also shown in the tabulation.

Summary of Survey Wastewater Data

Product	Sample I.D.	Flow	COD	BOD5	TOC
		gal/1,000 lb	lb/1,000 lb (mg/l)	lb/1,000 lb (mg/l)	lb/1,000 lb (mg/l)
1; Dye	Sample 1	13,700	1,075 (9,400)	220 (1,920)	450 (3,945)
2; Dye	Sample 2	13,700	652 (5,700)	126 (1,100)	269 (2,350)
2; Dye		21,050	175 (997)	59 (337)	60 (360)
3; Dye	10% Occurrence	95,069	50 (63)	5 (6)	40 (51)
	50% Occurrence	95,069	1,850 (2,331)	79 (100)	790 (995)

90% Occurrence	95,069	3,700 (4,662)	156 (197)	1,580 (1,991)
4; Pigment	124,000	4,925 (4,764)	1,470 (1,422)	819 (792)

Because of frequent changing of feed materials and desired products, dyemaking requires large amounts of water and of cleaning aids (such as detergent and bleach) to clean up reactors and filter presses on each reaction cycle. Chemical reactions involved are often exothermic and require strict temperature control. Due to the necessity of rapid cooling in order to avoid side reactions, direct cooling with ice, in addition to jacket cooling, is commonly practiced, and this also contributes a significant amount of waste water. While the high organic loading in the waste water is primarily the result of incomplete crystallization and separation of dye products from the mother liquor, organic losses and cleaning aids from clean-up operations also contribute. Different from other organic chemical industries, jacket cooling water is required to be discharged into sewers to dilute the waste water to be treated.

Reuse or recycle of waste water from this type of process is deemed unfeasible, because the waste waters are contaminated with many different salts, metal ions, and a high intensity of color, which will in turn contaminate the product.

Phase I Subcategory D raw waste load data base for organic dyes and pigments is not considered to be adequate to support effluent limitations guidelines for this segment of the industry. Coverage of Subcategory D segment has been expanded in the Phase II study. Effluent limitations guidelines will be proposed in the Phase II proposed regulation for organic dyes and pigments.

SECTION V

WASTE CHARACTERIZATION

In order to develop production based effluent limitations and performance standards (expressed as unit weight of pollutant per unit weight of product), it is first necessary to define a raw waste load (RWL) for the process. Appropriate reduction factors can then be applied to the RWL to establish the desired production based restrictions.

The choice of the specific pollution parameters for which restrictions are to be recommended is to a large extent governed by existing conventions which have been established within the water pollution control field. Although it would be desirable to identify the specific chemicals which are present in the waste water streams associated with the organic chemicals industry, many of these would be present in the waste water from only a few processes so that the development of generalized restrictions which are applicable to large categories would not be possible. For this reason conventional general parameters related to oxygen demand, toxicity, turbidity, color, and taste were examined during the course of this study.

The waste water associated with each process was differentiated according to whether it was considered as contact waste water or non-contact waste water. It is impossible to equitably define production based RWL for the noncontact water streams. This is caused by the fact that these streams are always associated with a number of different processes with no equitable means available for allocating the pollutants which are present.

In a typical chemical process plant, utility functions such as the supply of steam and cooling water are set up to service several processes. Boiler feed water is prepared, and steam is generated in a single boiler house. Noncontact steam used for surface heating is circulated through a closed loop whereby varying quantities are made available for the specific requirements of the different processes. The condensate is nearly always recycled to the boiler house, where a certain portion is discharged as blowdown.

Noncontact cooling waters are also supplied to several processes. The system generally is either a closed loop utilizing one or more evaporative cooling towers, or a once-through system with direct discharge.

The amounts of blowdown from boilers and cooling towers are not directly related to individual processes but depend rather on the design of the particular plant utility system. Although noncontact steam and cooling water requirements were presented for the processes which have been examined, the quantities of blowdown associated with utility recycle loops cannot be correlated back to individual processes. Similarly, the amounts

of waste brine and sludge produced by ion exchange and water treatment systems cannot be allocated among the individual processes within a plant.

The quantities of pollutants such as dissolved solids, suspended solids, alkalinity, and other parameters which are associated with the noncontact streams and water treatment equipment were not included in the calculation of the production based RWL for each process. Subsequently, no production based limitations or standards are recommended for these parameters at this time. Studies currently underway will establish bases for development of effluent limitations for noncontact waste waters at a future date. Instead, contact process waste water streams formed the basis for all RWL calculations included in this study.

The RWL data to be presented in this section was based on past historical data supplied by some of the manufacturers surveyed as well as actual data obtained by sampling.

The RWL for each process was calculated by taking 24 hour composite samples of the contact process waste water streams. The pollutant concentrations obtained from the analysis of these samples were multiplied by the associated waste water flow during the same 24 hour period to give pollutant generation rate as lb per day. These generation rates were divided by the corresponding production to provide a series of production based RWL's.

It should be noted that many of the processes examined generate nonaqueous wastes. These may be liquid or semi-liquid materials, such as tars, or gaseous materials, such as by-product hydrocarbon vapors. As such, these wastes are normally burned as auxiliary fuel or are disposed of in some way that is unrelated to the contact process waste water. These materials were not included as part of the RWL calculated for the processes examined.

The RWL for a specific process module is based on the actual production rate of the principal product and the measured contact process waste water flow. Co-products are not included in the RWL calculation unless they have specific waste waters associated with their own purification or processing. An example of this situation is the RWL associated with butadiene as a co-product of ethylene manufacture. In this case, butadiene purification has a specific waste water flow and loading; therefore, a separate RWL has been defined.

Dissolved oxygen demanding material was found to be the major pollutant associated with production operations in this industry. Standard Raw Waste Loads (SWRL), expressed as average or median values, have been developed for the industrial subcategories. Four major parameters were considered:

1. Process Wastewater Flow Loading
(expressed as liters/kgg and

gal/1,000 lbs of product)

2. BOD₅ Raw Waste Loading
(expressed as kg BOD₅/kkg and
lb BOD₅/1,000 lb of product)
3. COD Raw Waste Loading
(expressed as kg COD/kkg and
lb COD/1,000 lb of product)
4. TOC Raw Waste Loading
(expressed as kg TOC/kkg and
lb TOC/1,000 lb of product)

The RWL data relating to individual manufacturing processes were first grouped according to the subcategory in which the process is assigned. The data for the processes within each subcategory were then plotted as pollutant raw waste loading versus contact process waste water flow loading. These plots are shown in the following figures:

Subcategory A

BOD ₅ vs. Flow	(Figure V-1)
COD vs. Flow	(Figure V-2)
TOC vs. Flow	(Figure V-3)

Subcategory B

BOD ₅ vs. Flow	(Figure V-4)
COD vs. Flow	(Figure V-5)
TOC vs. Flow	(Figure V-6)

Subcategory C

BOD ₅ vs. Flow	(Figure V-7)
COD vs. Flow	(Figure V-8)
TOC vs. Flow	(Figure V-9)

Subcategory D

BOD ₅ vs. Flow	(Figure V-10)
COD vs. Flow	(Figure V-11)

Since both the loading (ordinate) and flow (abscissa) are expressed on a production basis, dividing the loading by the flow gives a slope which may be expressed as a concentration. For orientation, reference lines of constant concentration have been drawn diagonally across each of the plots. Relating a specific data point to one of these lines provides a convenient estimate as to the raw waste concentration.

The five manufacturing processes examined in Subcategory A were described in the previous section. No clear range or SRWL can be defined for this category. This may partially be caused by the fact that external runoff, washings, and contaminated spray cooling water amount to a significant portion of the waste water flow in each case.

One of the major difficulties in obtaining meaningful RWL data for Subcategory A processes is the fact that a large portion of the waste water comes from sources which are difficult to sample or where pollutant loadings result from contact with chemicals on the ground. Unlike other process subcategories where specific process pipes or sewers can be used to sample and measure all process flows, Subcategory A waste waters are intermittently dumped directly into open ditches or common sewers within the process area. In some cases, Subcategory A waste waters flow by gravity to holding tanks where batch treatment is provided; in other cases, they are discharged directly into the overall plant treatment system.

There is also a question as to whether the continuous water washes are truly representative of the process or are necessitated by a specific feed impurity (ethyl benzene) or nonaqueous absorbent (Benzene, Toluene, Xylene recovered by solvent extraction) used by the particular manufacturers sampled.

When compared with the range of pollutant loadings presented for the other subcategories, it is apparent that those from Subcategory A are generally lower. The RWL for Subcategory A products-processes are summarized in Table V-1. The ethyl benzene process was determined to be a subcategory B type process due to the washing step in purifying the product.

The individual process RWL data for Subcategory B are plotted in Figures V-4 through V-6. General increasing trends between pollutant RWL and flow RWL appear to exist within the category.

The BOD₅ RWL for 13 Subcategory B processes generally falls in a concentration range of 100 to 500 mg/l. Loadings vary from 0.09 to 7.0 lb COD/1,000 lb of product. The corresponding range of flows increases from 50 to 3,000 gal/1,000 lb of product. It should be noted that two of the processes in Subcategory B ethylene dichloride (EDC) manufactured by the chlorination of ethylene, and vinyl chloride monomer (VCM) manufactured by the pyrolysis of EDC product contact process waste waters which are not amenable to the BOD₅ test. This was caused by objectionable conditions related to the high concentrations of wastes. In such cases, the wastes may still be degraded biologically, but require dilution with other less concentrated wastes or noncontact cooling water.

The COD RWL concentrations for 16 Subcategory B processes are between 100 and 5,000 mg/l. Loadings vary from 0.5 to 21.5 lb/COD/1,000 lb of product within the same range of flows as presented for the BOD₅ RWL.

The TOC RWL concentrations for 16 Subcategory B processes are generally between 100 and 2,000 mg/l. TOC loadings vary from a minimum of 0.2 to a maximum of 40 lbs TOC/1,000 lb of product.

Table V-1
Summary of Raw Waste Load Data
Subcategory A - Nonaqueous Processes

Product/Process	Flow		BOD5	COD
	L/kg	gal/1000 lb	kg/kg (lb/1000 lb)	kg/kg (lb/1000 lb)
BTX Aromatics (Hydrotreatment)	114.0	13.6	0.10	0.31
BTX Aromatics (Solvent Extractin)	504.0	60.4	-	-
Cyclohexane	No Discharge		-	-
Vinyl Chloride	2,004.0	240	-	0.12
Mean Value	873.0	105.0	0.10	0.22

FIGURE V-1

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR SUBCATEGORY A

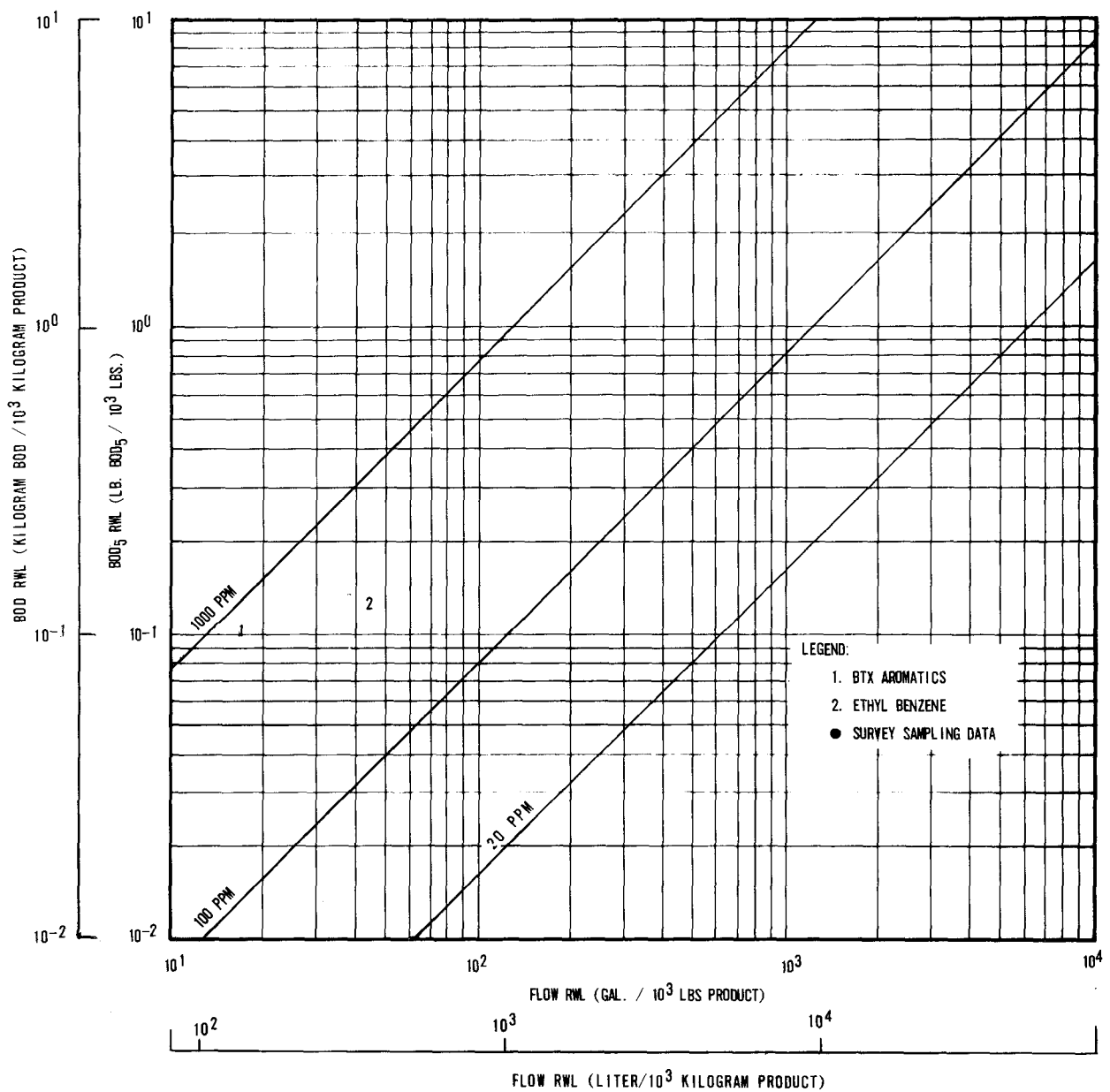


FIGURE V-2

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR SUBCATEGORY A

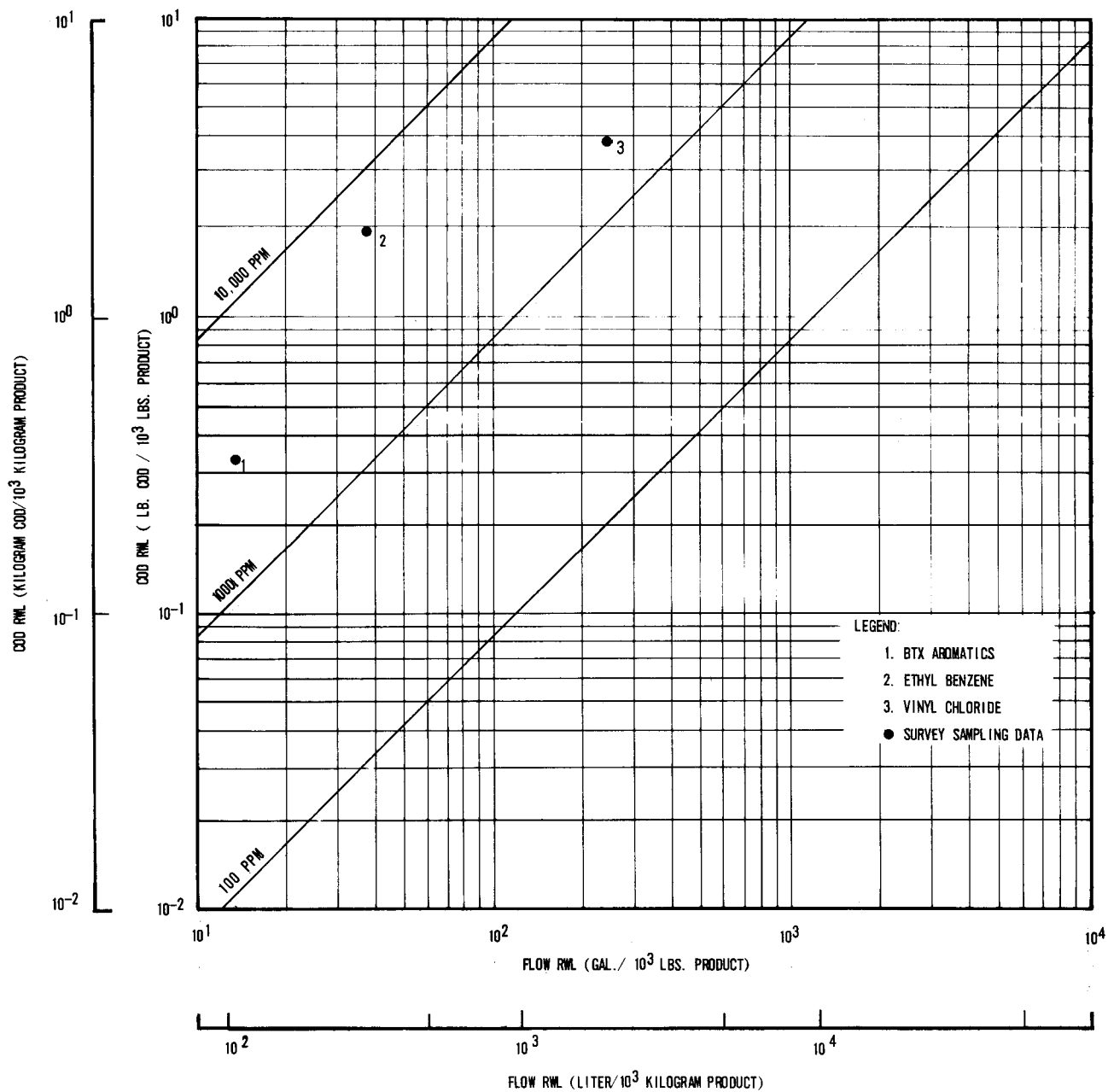
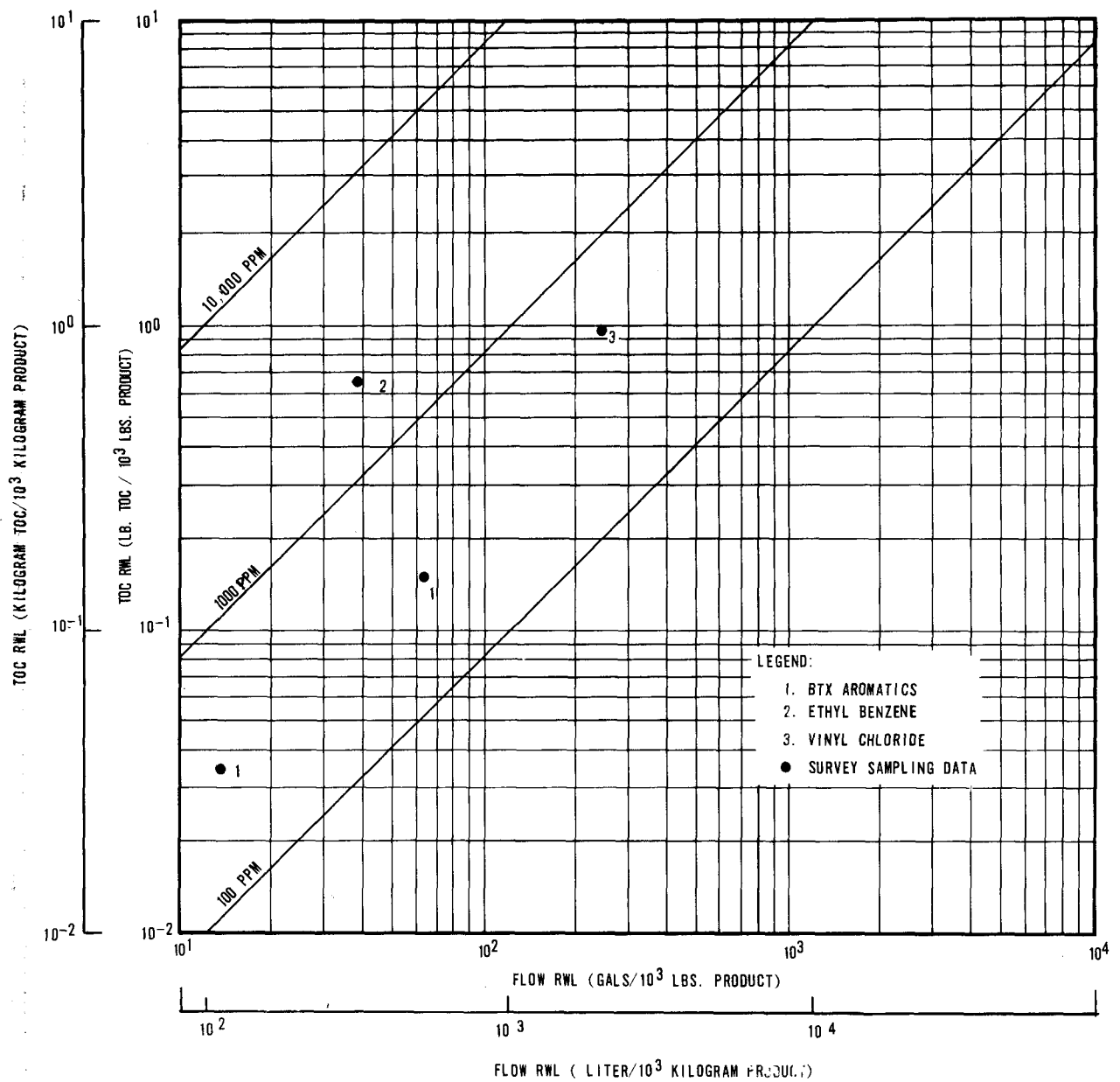


FIGURE V-3

RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR SUBCATEGORY A



There is no definite correlation between the BOD₅ and COD RWL within Subcategory B. COD/BOD₅ ratios generally vary between 2/1 and 10/1. This is understandable since there is still a wide variety of specific chemicals which may be present in the waste waters from this process category.

The wide spread in RWL data obtained for Subcategory B has led to the establishment of two subcategories designated as B₁ and B₂. The individual products, processes, and associated RWL allocated to each subcategory are indicated in Table V-2. It can be seen that the average flows and RWL for the two subcategories conform to the general relationship of increased loadings being associated with increased flows.

The individual process RWL data for Subcategory C are plotted in Figures V-7 through V-9.

As with Subcategory B, there appears to be an increasing trend between BOD₅ RWL and flow RWL. This relation is not nearly so definitive for the COD and TOC parameters.

The BOD₅ RWL for the Subcategory C processes generally fall in a concentration range of 3,000 to 10,000 mg/l. Loadings vary from 1.3 to 125 lb BOD₅/1,000 lb of product. The corresponding range of flows increases from 30 to 3,000 gal/1,000 lb of product.

The COD RWL data for the Subcategory C processes are between 10,000 and 50,000 mg/l. Loadings vary from 5.5 to 385 lb COD/1,000 lb of product within the same range of flows as presented for the BOD₅ RWL.

The TOC RWL concentrations for the Subcategory C processes are generally between 3,000 and 15,000 mg/l. TOC loadings vary between 1.5 and 150 lb/1,000 lb of product. An envelope drawn around the TOC data commensurate with the BPCTCA technology is shown in Figure 1-7.

As with Subcategory B, there is no definite correlation between the BOD₅ and COD RWL within this subcategory. COD/BOD₅ ratios generally vary between 3/1 and 5/1. However, some specific processes vary widely outside this range.

There is quite a wide spread in the RWL obtained for the processes surveyed within Subcategory C. For this reason, four subcategories designated as C₁, C₂, C₃ and C₄ have been established. The specific products, processes, and associated RWL assigned to each subcategory are indicated in Table V-3.

The individual process RWL data for the batch plants in Subcategory D are plotted in Figures V-10 and V-11. As with Subcategory A, the data are insufficient to establish any clear relationships between pollutant loading and flow. The ranges of loadings and flows are quite wide. This is caused mainly by the highly variable product mix and the inclusions of contact cooling and cleaning waters.

TABLE V-2
Summary of Raw Waste Load Data by Subcategory Group
Subcategory B - Processes with Process Water Contact as Steam Diluent
or Absorbent

	Flow gal/1000 lb.	Flow Liters/kg	BOD5 kg/kg (1b/1000 lb)	COD kg/kg (1b/1000lb)
<u>B₁ Product - Processes</u>				
Ethyl benzene	38	317	0.13	1.86
Ethylene and Propylene	355	2961	0.35	2.36
Butadiene (from ethylene	203	1693	0.63	2.04
Methanol	50	417	0.49	0.94
Acetone	175	1460	0.26	1.10
Vinyl Acetate	28	234	0.04	0.13
Formaldehyde	131	1093	-	-
Ethylene Oxide	74	617	0.7	6.48
Ethylene Dichloride	96	800	-	4.84
Vinyl Chloride (from ethylene dichloride)	336	2802	-	7.66
Methyl Amines	439	3661	0.48	12.8
B ₁ Mean Value	175	1460	0.38	4.0
<u>B₂ Product - Processes</u>				
Acetaldehyde (from ethanol)	1600	13,344	1.12	2.48
Butadiene (from n - butane)	1160	9,674	2.96	3.23
Acetylene	561	4,679	1.92	5.95
Styrene	1733	14,453	1.00	3.74
B ₂ Mean Value	1264	10,541	1.75	3.85

FIGURE V-4

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR **SUBCATEGORY B**

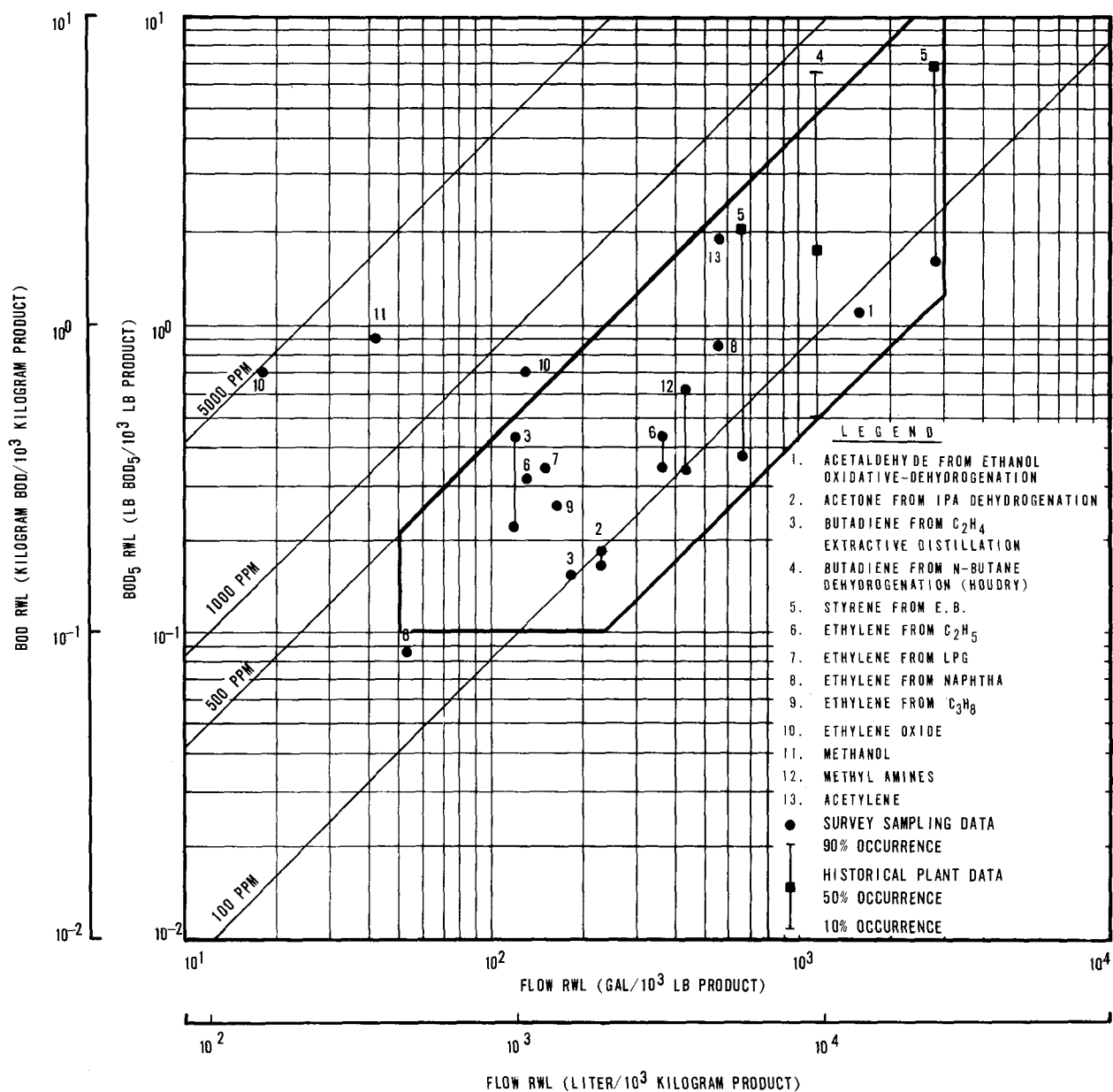


FIGURE V-5

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR **SUBCATEGORY B**

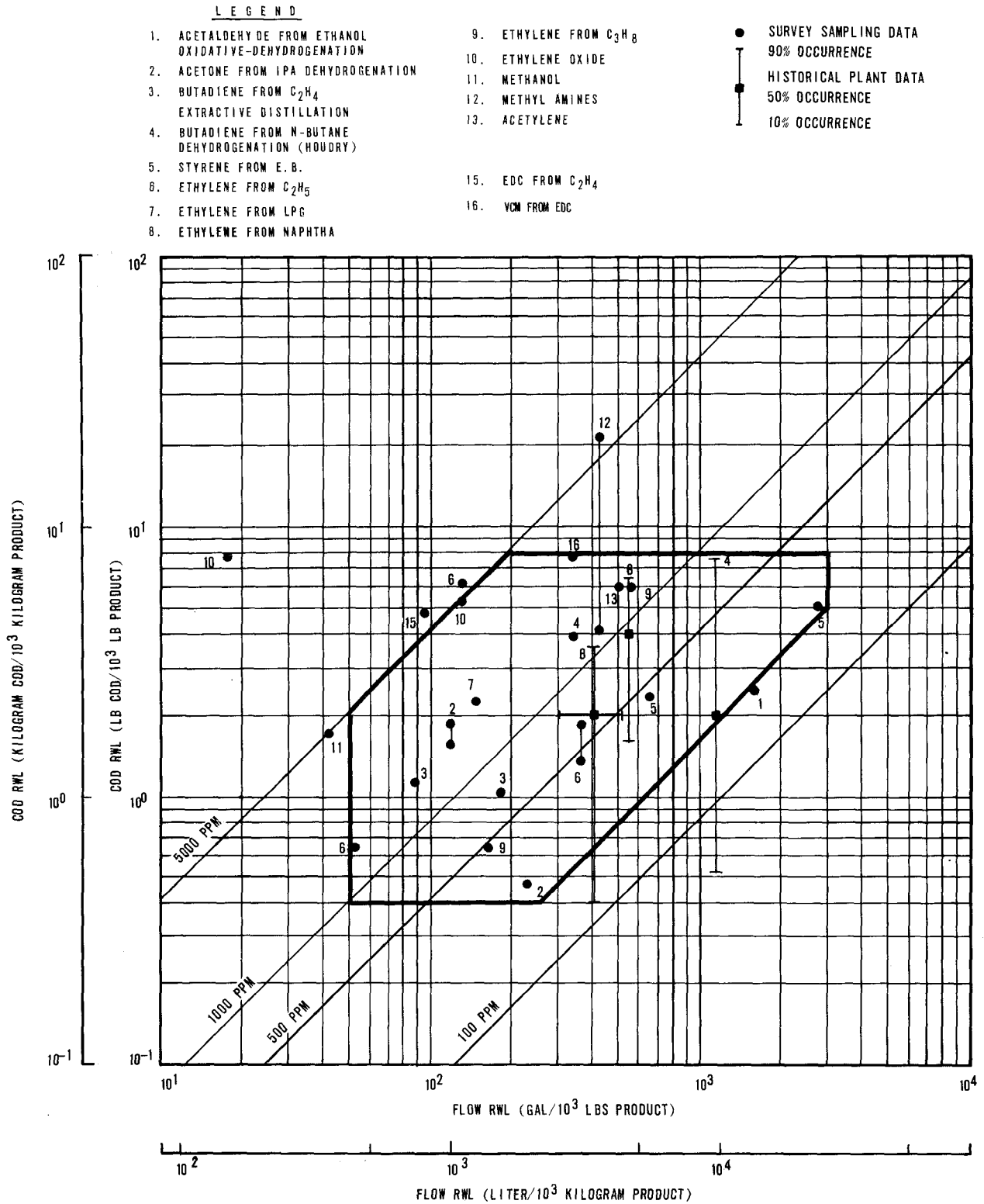


FIGURE V-6

RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR SUBCATEGORY B

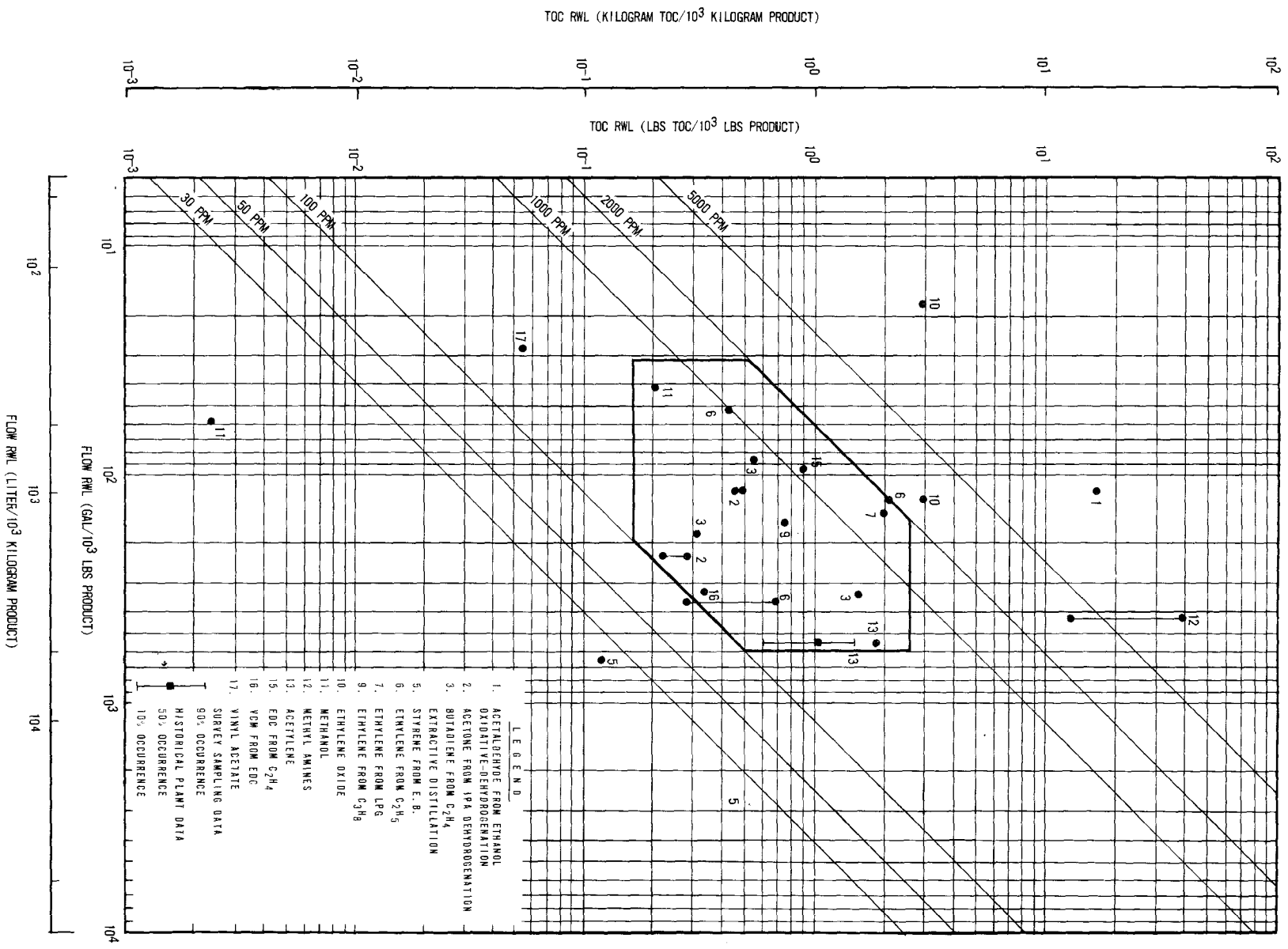


TABLE V-3
Summary of Raw Waste Load Data by Subcategory Group
Subcategory C - Aqueous Liquid Phase Reaction Systems

	Flow gal/1000 lb.	Flow liters/kg	BOD5 kg/kg (lb/1000 lb)	COD kg/kg (lb/1000 lb)
<u>C1 Product - Processes</u>				
Coal Tar (pitch Forming)	125	1,043	-	0.06
Acetic Acid	500	4,170	0.35	0.78
Acrylic Acid	475	3,962	0.74	1.64
Ethylene Glycol	584	4,871	0.34	8.76
Terephthalic Acid	186	1,551	0.82	1.72
C1 Mean Value	374	3,119	0.56	2.59
<u>C2 Product - Processes</u>				
Acetaldehyde (ethylene and oxygen)	61	509	1.9	5.8
Phenol and Acetane (cumene process) *	280	2,335	5.6	11.0
OXO Chemicals	420	3,503	3.2	4.25
Coal Tar (distillation)	400	3,336	2.8	8.7
Caprolactam	1,300	10,842	1.6	4.0
C2 Mean Value	492	4,103	3.03	6.75
<u>C3 Product - Process</u>				
Acetaldehyde (ethylene and air)	90	751	26.6	44
Aniline	190	1,585	-	21.2
Bisphenol A *	67	559	-	17.1
Dimethyl Terephthalate	270	2,252	24.4	38.2
C3 Mean Value	154	1,284	25.5	30.1
<u>C4 Product - Processes</u>				
Acrylates	2,856	23,819	47	118
P - Cresol *	1,291	10,767	123	256
Methyl Methacrylate	200	1,668	45	386
Terephthalic Acid (nitric acid Process)	659	5,496	59	104
Tetraethyl Lead	12,000	100,000	-	110
C4 Mean Value	3,401	28,366	68.5	195

* Phenol's raw waste load - 10 kg/1000 kkg (lb/1000 lb)

FIGURE V-7

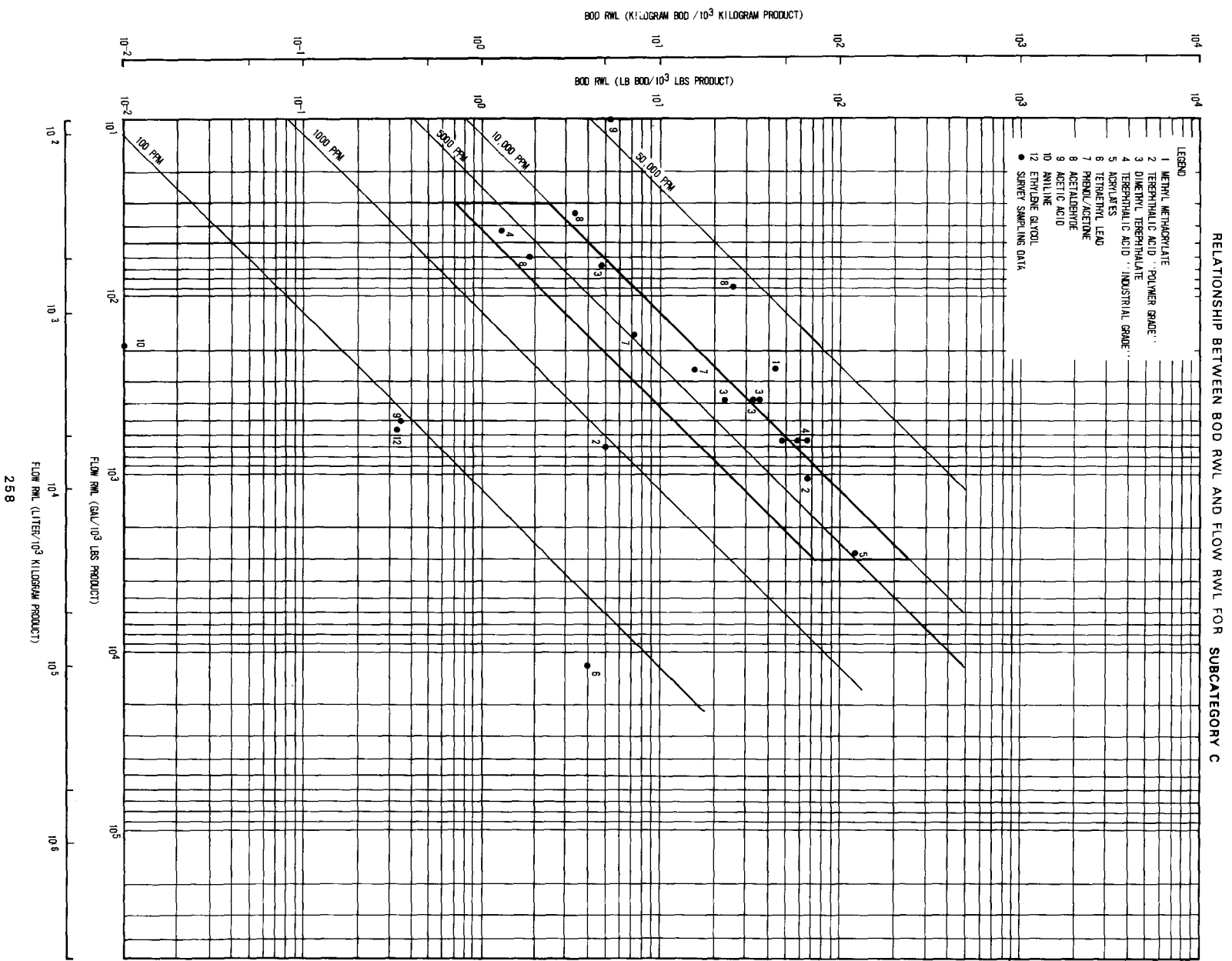


FIGURE V-8

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR SUBCATEGORY C

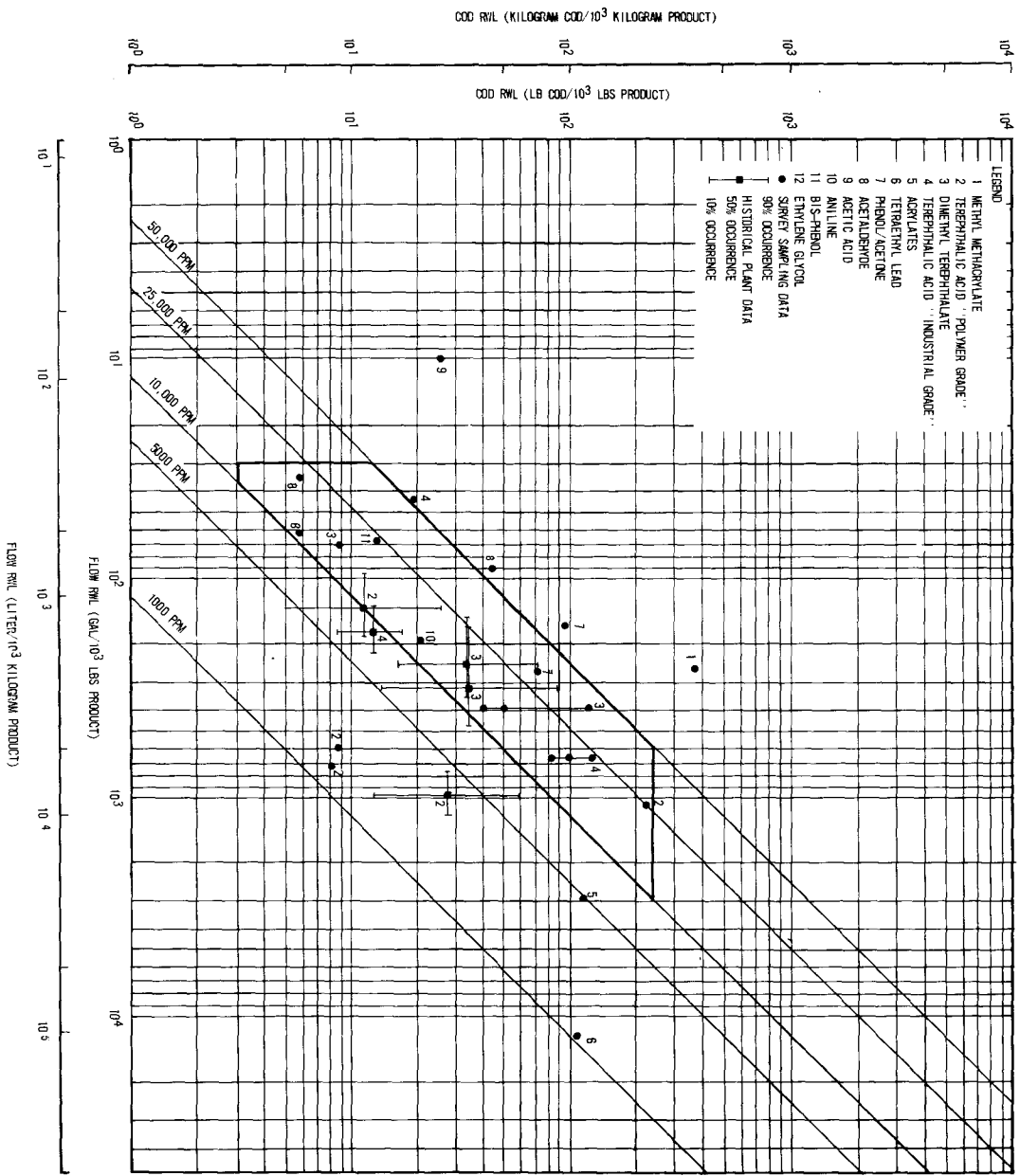
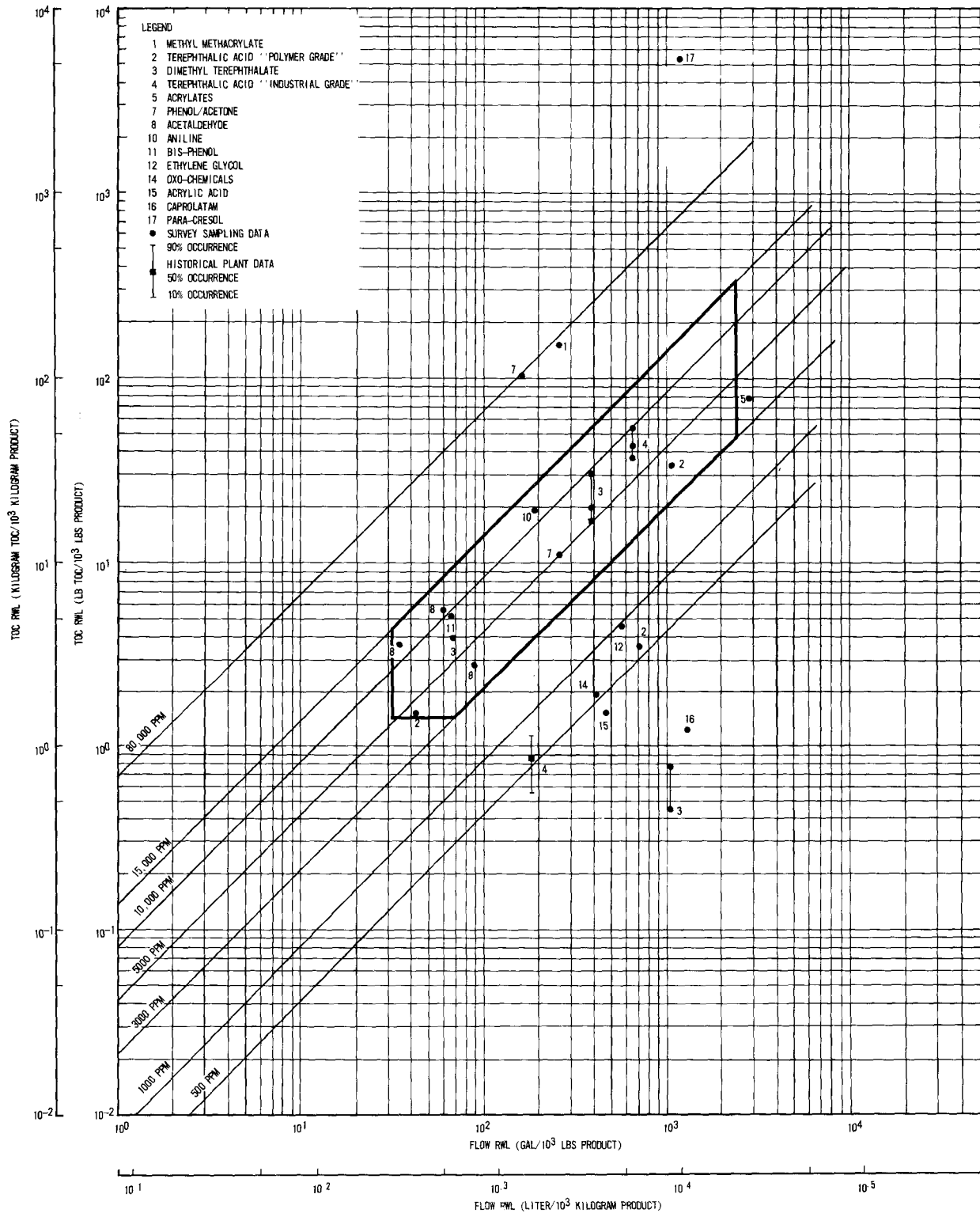


FIGURE V-9
RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR **SUBCATEGORY D**



It should be noted that the loadings shown for Subcategory D are based on the entire production from the batch plant. The RWL for Subcategory D were subjected to analysis for probability of occurrence and are summarized in Table V-4. Subcategory D (organic dyes and pigments) has been deleted from Phase I and included under Phase II coverage of the organic chemicals manufacturing industry.

Table V-4

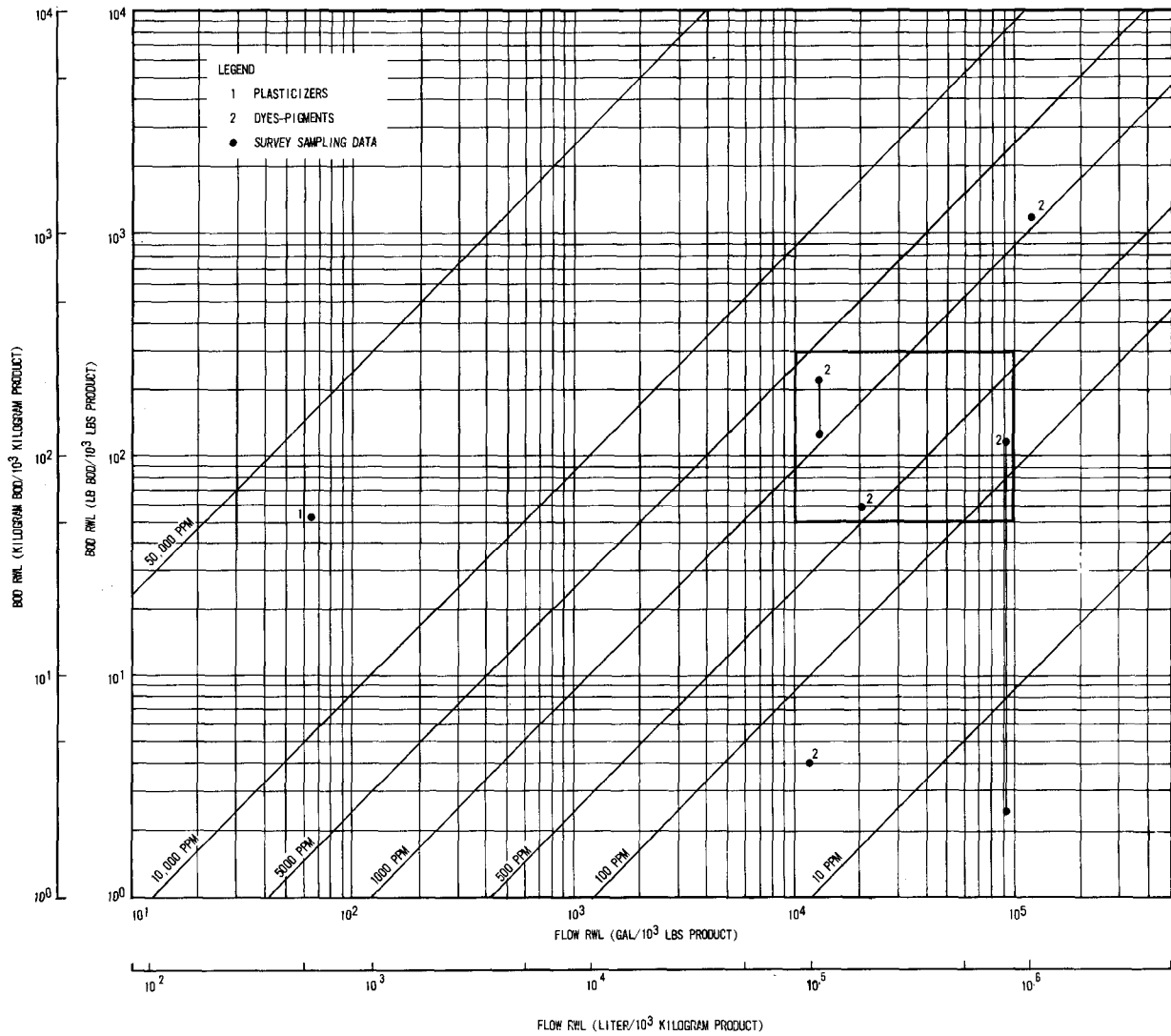
Subcategory D - Batch and Semi Continuous Processes

Summary of Raw Waste Load Data

<u>D₁</u> - Batch Organic Azo Dyes					
		<u>Flow</u>	<u>BOD</u>	<u>COD</u>	<u>TOC</u>
		liters/1000 kg (gal/1000 lb)	kg/1000 kg	or lb/1000 lb	
@50% occurrence		793,826	(95,069)	79	1,850
		114,395	(13,700)	220	1,075
		175,768	(21,050)	59	175
Mean Value		361,329	(43,273)	119	1,033
					433
					-0

FIGURE V-10

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR SUBCATEGORY D



RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR SUBCATEGORY D



SECTION VI

SELECTION OF POLLUTANT PARAMETERS

An extensive literature review resulted in the selection of twenty-five parameters which were examined during the field data collection program. These parameters are listed in Table VI-1, and all field data are summarized in Supplement B. Miscellaneous raw waste loads are also presented in Table VI-2 and Table VI-3.

The rationale and justification for pollutant subcategorization within the above groupings will be explored. This discussion will provide the basis for selection of parameters upon which the actual effluent limitations were postulated and prepared. In addition, particular parameters were selected for discussion in the light of current knowledge as to their limitations from an analytical as well as from an environmental standpoint.

Pollutants observed from the field data as present in sufficient concentrations to interfere with, be incompatible with, or pass thru inadequately treated in a publicly owned works are discussed in Section XII.

Pollutants of Significance

Parameters of pollutorial significance for which effluent limitations were developed in the organic chemicals industry are the major organic parameters of BOD₅, COD and TOC.

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is a measure of the oxygen consuming capabilities of organic matter. The BOD does not in itself cause direct harm to a water system, but it does exert an indirect effect by depressing the oxygen content of the water. Sewage and other organic effluents during their processes of decomposition exert a BOD, which can have a catastrophic effect on the ecosystem by depleting the oxygen supply. Conditions are reached frequently where all of the oxygen is used and the continuing decay process causes the production of noxious gases such as hydrogen sulfide and methane. Water with a high BOD indicates the presence of decomposing organic matter and subsequent high bacterial counts that degrade its quality and potential uses.

Dissolved oxygen (DO) is a water quality constituent that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at

reduced D.O. concentrations that make them less competitive and able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting, decreased tolerance to certain toxicants, reduced food efficiency and growth rate, and reduced maximum sustained swimming speed. Fish food organisms are likewise affected adversely in conditions with suppressed DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total lack of dissolved oxygen due to a high BOD can kill all inhabitants of the affected area.

If a high BOD is present, the quality of the water is usually visually degraded by the presence of decomposing materials and algae blooms due to the uptake of degraded materials that form the foodstuffs of the algal populations.

Table VI-1

List of Pollutants Surveyed for the Organic Chemicals Industry

Chemical Oxygen Demand (COD)	Total Dissolved (Filterable) Solids
Biochemical Oxygen Demand (BOD ₅)	Chloride
Total Organic Carbon (TOC)	Hardness - Total
Total Suspended (Nonfilterable) Solids (TSS)	Total Phosphorus
Oil and Grease	Calcium - Total
Ammonia Nitrogen	Magnesium - Total
Total Kjeldahl Nitrogen (TKN)	Zinc - Total
Phenols	Copper - Total
Cyanide, Total	Iron - Total
Color	Chromium - Total
Sulfate	Cadmium - Total
pH	Cobalt - Total
Acidity	Lead - Total
Alkalinity	

COD

Chemical oxygen demand (COD) provides a measure of the equivalent oxygen required to oxidize the organic material present in a waste water sample, under acid conditions with the aid of a strong chemical oxidant, such as potassium dichromate, and a catalyst (silver sulfate). One major advantage of the COD test is that the results are available normally in less than three hours. However, one major disadvantage is that the COD test does not differentiate between biodegradable and nonbiodegradable organic material. In addition, the presence of inorganic reducing chemicals (sulfides, etc.) and chlorides may interfere with the COD test.

8%Standards Methods for the Examination of Water and Wastewater, the principal reference for analytical work in this field, cautions that aromatic compounds and straight-chain aliphatic compounds, both prevalent in the organic chemicals industry, are not completely oxidized during the COD test. The addition of silver sulfate, a catalyst, aids in the oxidation of the straight-chain alcohols and acids but does not affect aromatic hydrocarbons. The exact extent of this partial oxidation has not been documented in the literature.

COD RWL data for the four subcategories is presented in Figures V-2, V-5, V-8, and V-11. A summary of the concentration range is presented below:

<u>Subcategory</u>	<u>COD RWL Range</u> mg/l
A	100-10,000
B	200-5,000
C	10,000-50,000
D	1,000-10,000

Typical COD values for municipal waste waters are between 200 mg/l and 400 mg/l.

Effluent limitations guidelines were not established for the COD pollutant parameter for BPCTCA and New Sources although its use is not precluded if a suitable correlation with BOD5 is established.

TOC

Total organic carbon (TOC) is a measure of the amount of carbon in the organic material in a waste water sample. The TOC analyzer withdraws a small volume of sample and thermally oxidizes it at 150°C. The water vapor and carbon dioxide is monitored. This carbon dioxide value corresponds to the total inorganic value. Another portion of the same sample is thermally oxidized at 950°C, which converts all the carbonaceous material; this value corresponds to the total carbon (carbonates and water vapor) from the total carbon value.

The TOC value is affected by any one or more of the following:

1. One possible interference in the measurement occurs when the water vapor is only partially condensed. Water vapor overlaps the infrared absorption band of carbon dioxide and can therefore inflate the reported value.
2. The sample volume involved in the TOC analyzer is so small (approximately 40 microliters) that it can easily become contaminated, with dust, for example.
3. Industrial wastes from the organic chemicals industry with low vaporization points may vaporize before 150C and therefore be reported as inorganic carbon.

TOC RWL data for Subcategories A, B, and C are shown in Figures V-3, V-6, and V-9. A summary of the concentration ranges are presented below:

<u>Subcategory</u>	<u>TOC RWL Range</u> mg/l
A	100-3,000
B	100-2,000
C	3,000-5,000

Typical values for municipal waste waters range between 50 and 250 mg/l.

Effluent limitations were not established for the TOC parameter, although its use is not precluded if a suitable correlation with BOD₅ or COD is established.

Other Significant Pollutants

Suspended solids, oil, ammonia nitrogen, total Kjeldahl nitrogen, phenols, dissolved solids, cyanide, sulfate, and color, in general were present in smaller concentrations. Effluent limitations are specified for TSS in all subcategories. Phenols are limited for the cumene process, bisphenol and p-cresol since concentration of phenols are considerably high for these process. Other pollutant parameters which are discussed in this section but no effluent limitations established are not present in all subcategories, and are generally controlled at the source. These may, however, present environmental problems where water quality standards dictate and may ultimately be limited.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and

various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

Oil and Grease

Oil and grease exhibit an oxygen demand. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified material ingested by fish may

taint the flavor of the fish flesh. Water soluble components may exert toxic action on fish. Floating oil may reduce the re-aeration of the water surface and in conjunction with emulsified oil may interfere with photosynthesis. Water insoluble components damage the plumage and costs of water animals and fowls. Oil and grease in a water can result in the formation of objectionable surface slicks preventing the full aesthetic enjoyment of the water.

Oil spills can damage the surface of boats and can destroy the aesthetic characteristics of beaches and shorelines.

Ammonia

Ammonia is a common product of the decomposition of organic matter. Dead and decaying animals and plants along with human and animal body wastes account for much of the ammonia entering the aquatic ecosystem. Ammonia exists in its non-ionized form only at higher pH levels and is the most toxic in this state. The lower the pH, the more ionized ammonia is formed and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other salts.

Nitrates are considered to be among the poisonous ingredients of mineralized waters, with potassium nitrate being more poisonous than sodium nitrate. Excess nitrates cause irritation of the mucous linings of the gastrointestinal tract and the bladder; the symptoms are diarrhea and diuresis, and drinking one liter of water containing 500 mg/l of nitrate can cause such symptoms.

Infant methemoglobinemia, a disease characterized by certain specific blood changes and cyanosis, may be caused by high nitrate concentrations in the water used for preparing feeding formulae. While it is still impossible to state precise concentration limits, it has been widely recommended that water containing more than 10 mg/l of nitrate nitrogen ($\text{NO}_3\text{-N}$) should not be used for infants. Nitrates are also harmful in fermentation processes and can cause disagreeable tastes in beer. In most natural water the pH range is such that ammonium ions (NH_4^+) predominate. In alkaline waters, however, high concentrations of un-ionized ammonia in undissociated ammonium hydroxide increase the toxicity of ammonia solutions. In streams polluted with sewage, up to one half of the nitrogen in the sewage may be in the form of free ammonia, and sewage may carry up to 35 mg/l of total nitrogen. It has been shown that at a level of 1.0 mg/l un-ionized ammonia, the ability of hemoglobin to combine with oxygen is impaired and fish may suffocate. Evidence indicates that ammonia exerts a considerable toxic effect on all aquatic life within a range of less than 1.0 mg/l

to 25 mg/l, depending on the pH and dissolved oxygen level present.

Ammonia can add to the problem of eutrophication by supplying nitrogen through its breakdown products. Some lakes in warmer climates, and others that are aging quickly are sometimes limited by the nitrogen available. Any increase will speed up the plant growth and decay process.

Phenols

Phenols and phenolic wastes are derived from petroleum, coke, and chemical industries; wood distillation; and domestic and animal wastes. Many phenolic compounds are more toxic than pure phenol; their toxicity varies with the combinations and general nature of total wastes. The effect of combinations of different phenolic compounds is cumulative.

Phenols and phenolic compounds are both acutely and chronically toxic to fish and other aquatic animals. Also, chlorophenols produce an unpleasant taste in fish flesh that destroys their recreational and commercial value.

It is necessary to limit phenolic compounds in raw water used for drinking water supplies, as conventional treatment methods used by water supply facilities do not remove phenols. The ingestion of concentrated solutions of phenols will result in severe pain, renal irritation, shock and possibly death.

Phenols also reduce the utility of water for certain industrial uses, notably food and beverage processing, where it creates unpleasant tastes and odors in the product.

Dissolved Solids

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances.

Many communities in the United States and in other countries use water supplies containing 2000 to 4000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated whereas they could not be in temperate climates. Waters containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh-water fish may range from 5,000 to 10,000 mg/l, according to species and

prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh-water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil-well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids over 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l water has little or no value for irrigation.

Dissolved solids in industrial waters can cause foaming in boilers and cause interference with cleanliness, color, or taste of many finished products. High contents of dissolved solids also tend to accelerate corrosion.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

Cyanide

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^- ; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to threefold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 ppm can have adverse effects. A single dose of 6, about 50-60 mg, is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as .1 part per million can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

Color

Color is objectionable from an aesthetic standpoint and also because it interferes with the transmission of sunlight into streams, thereby lessening photosynthetic action. Color is measured against a platinum cobalt standard which is basically a yellow-brown hue. This color shading was developed to simulate domestic waste waters. The use of the procedure on highly colored industrial waste waters is subject to question. During Phase II of this study, a more intensive investigation will be made as to the most appropriate procedure for reporting color.

Color RWL data for Subcategories B and C are generally not a major consideration. However, in Subcategory D color is as high as 50,000 Pt-Co-units for pigment and dye waste waters. There were two major reasons for not trying to set limitations for Subcategory D:

1. Sufficient RWL data were not collected during the sampling program. (This will be remedied during Phase II of this project).
2. Scarcity of treatment data on color removal presented major technological questions concerning levels of color removal for various types of dyes and pigments. This situation can be remedied during Phase II of our study by a concentrated study of the color removal of various waste water unit processes. However, there is recent evidence that carbon filters can be a satisfactory treatment agent for many color problems.

Many of the specific comments made previously regarding dissolved solids# are directly applicable to these parameters of minimal significance. Concentrations of calcium, magnesium, chlorides and hardness are generally higher for Subcategory C because of extensive recycling. In addition, particular processes in Subcategory C produce NaCl as a product of reaction, e.g. tetraethyl lead production. Subcategory D waste waters likewise have high concentrations as a result of inorganic chemical additions.

Phosphorus

During the past 30 years, a formidable case has developed for the belief that increasing standing crops of aquatic plant growths, which often interfere with water uses and are nuisances to man, frequently are caused by increasing supplies of phosphorus. Such phenomena are associated with a condition of accelerated eutrophication or aging of waters. It is generally recognized that phosphorus is not the sole cause of eutrophication, but there is evidence to substantiate that it is frequently the key element in all of the elements required by fresh water plants and is generally present in the least amount relative to need. Therefore, an increase in phosphorus allows use of other, already present, nutrients for plant growths. Phosphorus is usually described, for this reasons, as a "limiting factor."

When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities are immediately apparent. Dense populations of pond weeds make swimming dangerous. Boating and water skiing and sometimes fishing may be eliminated because of the mass of vegetation that serves as a physical impediment to such activities. Plant populations have been associated with stunted fish populations and with poor fishing. Plant nuisances emit vile stench, impart tastes and odors to water supplies, reduce the efficiency of industrial and municipal water treatment, impair aesthetic beauty, reduce or restrict resort trade, lower waterfront property values, cause skin rashes to man during water contact, and serve as a desired substrate and breeding ground for flies.

Phosphorus in the elemental form is particularly toxic, and subject to bioaccumulation in much the same way as mercury. Colloidal elemental phosphorus will poison marine fish (causing skin tissue breakdown and discoloration). Also, phosphorus is capable of being concentrated and will accumulate in organs and soft tissues. Experiments have shown that marine fish will concentrate phosphorus from water containing as little as 1 ug/l.

pH, Acidity and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stench are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic

life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Table VI-2
Miscellaneous RWL Loads for Subcategory B

Product	Flow gal/1000 lb	Phenol		NH ₃ -N		TKN		CN		Sulfate		Oil	
		mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb
Acetone via IPA	120	0.1815	1.815x10 ⁻⁴	11.2	1.12x10 ⁻²	12.6	0.0126	-	-	-	-	-	-
Butadiene via C ₄	1,742	18.5	0.2691	2.8	0.0404	5.0	0.0728	< 0.1	1.63x10 ⁻³	149	2.158	20.4	0.2965
Butadiene via C ₂ H ₄	183	0.01	1.6x10 ⁻⁵	0.97	1.47x10 ⁻³	2.6	4.02x10 ⁻³	0.19	3.0x10 ⁻⁴	15.8	0.024	8.6	0.013
	88	0.024	1.8x10 ⁻⁵	43.2	0.0317	235	0.172	< 0.04	< 3.0x10 ⁻⁵	190	0.0142	7.4	0.0053
	339	0.02	6.3x10 ⁻⁵	5907	16.6	12,200	34.4	< 0.04	1.2x10 ⁻⁴	64	0.18	93	0.261
Styrene via E.B.	657	2.0	0.011	4.2	0.023	7.0	0.0383	< 0.04	< 0.002	< 1	< 0.0055	38	0.208
EDC via Direct Chlorination	15.4	0.13	2.0x10 ⁻⁵	0.5	7.0x10 ⁻⁵	2.9	3.7x10 ⁻⁴	0.046	1.0x10 ⁻⁵	503	0.065	74	9.5x10 ⁻³
	336	0.006	1.7x10 ⁻⁵	1.7	4.62x10 ⁻³	4.6	0.0127	0.12	3.3x10 ⁻⁴	78	0.218	26	0.0712
Ethylene/Propylene via Pyrolysis	130	6.78	7.33x10 ⁻³	6.44	6.96x10 ⁻³	65.5	0.071	0.11	1.2x10 ⁻⁴	649	0.7013	483	0.522
	364	0.36	1.08x10 ⁻³	19.6	< 0.058	25.2	0.075	0.12	3.6x10 ⁻⁴	120	0.36	11.7	0.035
	52.5	2.36	1.03x10 ⁻³	< 0.5	< 2.2x10 ⁻⁴	< 0.5	< 2.2x10 ⁻⁴	< 0.04	2.0x10 ⁻⁵	73.6	0.032	172	0.075
	150	5.59	0.007	3.9	4.9x10 ⁻³	9.7	0.012	0.043	5.0x10 ⁻⁵	280	0.353	11	0.014
	554	8.25	0.038	2.2	1.02x10 ⁻²	9.0	0.041	0.055	2.6x10 ⁻⁴	0.98	4.5x10 ⁻³	188	0.87
	167	7.24	0.01	1.4	1.94x10 ⁻³	2.6	3.6x10 ⁻³	-	-	1.5	2.13x10 ⁻³	10.1	0.014
Ethylene Oxide	131	0.048	5.3x10 ⁻⁵	< 0.5	< 5.5x10 ⁻⁴	2.8	3.08x10 ⁻³	0.44	4.8x10 ⁻⁴	510	0.56	3.3	3.3x10 ⁻³
	17.8	0.154	2.3x10 ⁻⁵	5.6	3.7x10 ⁻⁴	14	2.1x10 ⁻³	< 0.04	< 6.0x10 ⁻⁶	5,400	0.81	1.8	3.2x10 ⁻⁴
Methyl Amines	429	0.031	1.12x10 ⁻⁴	7.9	2.82x10 ⁻²	26.3	0.0941	< 0.04	< 1.42x10 ⁻⁴	< 1		4.6	0.0163
Acetylene	560	0.76	3.55x10 ⁻³	5.6	0.0262	84	0.3927	0.312	1.46x10 ⁻³	280	1.309	1.4	6.55x10 ⁻³

Table VI-2
(continued)

Product	T-P		Zn		Cu		Fe		Cr		Cd	
	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb
Acetone via IPA	-	-	-	-	-	-	-	-	-	-	-	-
Butadiene via C ₄	1.93	0.02795	0.37	5.34x10 ⁻³	0.273	3.97x10 ⁻³	45.1	0.655	< 0.05	< 7.26x10 ⁻⁶	< 0.05	< 7.46x10 ⁻⁴
Butadiene via C ₂ H ₄	31.5	0.048	0.12	1.8x10 ⁻⁴	0.17	2.6x10 ⁻⁴	5.6	8.5x10 ⁻³	< 0.05	< 7.6x10 ⁻⁵	< 0.05	< 7.6x10 ⁻⁵
	0.77	5.6x10 ⁻⁴	-	-	0.17	1.28x10 ⁻⁴	0.65	4.8x10 ⁻⁴	< 0.05	< 4.0x10 ⁻⁵	< 0.05	< 4.0x10 ⁻⁵
	3.50	0.0098	-	-	0.36	0.001	0.5	1.52x10 ⁻³	< 0.05	< 1.5x10 ⁻⁴	< 0.05	< 1.5x10 ⁻⁴
Styrene via E.B.	0.66	0.0036	0.14	7.67x10 ⁻⁴	0.21	1.15x10 ⁻³	0.5	2.74x10 ⁻³	< 0.05	< 2.74x10 ⁻⁵	< 0.05	< 2.74x10 ⁻⁵
EDC via Direct Chlorination	0.544	7.0x10 ⁻⁵	0.62	8.0x10 ⁻⁵	0.24	3.0x10 ⁻⁵	1.06	1.4x10 ⁻⁴	< 0.05	< 1.0x10 ⁻⁵	< 0.05	< 1.0x10 ⁻⁵
	0.09	2.5x10 ⁻⁴	-	-	0.14	3.77x10 ⁻⁴	3.4	9.42x10 ⁻³	< 0.04	< 1.04x10 ⁻⁴	< 0.05	< 1.49x10 ⁻⁴
Ethylene/Propylene via Pyrolysis	1.30	1.41x10 ⁻³	< 0.05	< 5.6x10 ⁻⁵	0.14	1.48x10 ⁻⁴	1.22	1.32x10 ⁻³	< 0.05	< 5.44x10 ⁻⁵	< 0.05	< 5.56x10 ⁻⁵
	5.5	0.017	3.2	0.001	0.15	4.5x10 ⁻⁴	3.8	0.011	4.35	0.013	< 0.05	< 1.5x10 ⁻⁴
	1,469	0.64	0.671	2.9x10 ⁻⁴	0.08	3.0x10 ⁻⁵	1.17	5.1x10 ⁻⁴	1.86	8.2x10 ⁻⁵	< 0.021	< 1.07x10 ⁻⁵
	0.61	7.6x10 ⁻⁴	0.37	4.6x10 ⁻⁴	0.19	2.4x10 ⁻⁴	0.83	0.001	< 0.05	< 6.0x10 ⁻⁵	0.143	1.8x10 ⁻⁴
	0.196	9.1x10 ⁻⁴	0.153	7.1x10 ⁻⁴	0.1	4.6x10 ⁻⁴	0.64	2.95x10 ⁻³	0.197	9.1x10 ⁻⁵	0.051	2.4x10 ⁻⁴
	494	0.686	0.29	4.1x10 ⁻⁴	0.76	1.05x10 ⁻³	0.62	8.5x10 ⁻⁴	< 0.06	< 7.7x10 ⁻⁵	< 0.06	7.7x10 ⁻⁵
Ethylene Oxide	0.144	1.6x10 ⁻⁴	0.33	3.6x10 ⁻⁴	1.25	1.38x10 ⁻³	1.5	1.65x10 ⁻³	< 0.05	< 6.0x10 ⁻⁴	< 0.05	< 6.0x10 ⁻⁴
	1.2	1.8x10 ⁻⁴	0.14	2.1x10 ⁻⁵	0.41	6.0x10 ⁻⁵	1.33	2.0x10 ⁻⁴	0.07	1.1x10 ⁻⁵	< 0.05	< 8.0x10 ⁻⁶
Methyl Amines	0.066	2.37x10 ⁻⁴			0.25	9.0x10 ⁻⁴	3.38	0.0121				
Acetylene	0.25	1.17x10 ⁻³	0.2	9.35x10 ⁻⁴	< 0.05	< 2.3x10 ⁻⁴	0.4	1.87x10 ⁻³	< 0.05	< 2.34x10 ⁻⁴	< 0.05	< 2.34x10 ⁻⁴

Table VI-3
Miscellaneous RWL Loads for Subcategory C

Product	Flow		Phenol		NH ₃ -N		TKN-N		CN		Sulfate		Oil	
	gal/1000 lb	lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb
Acetaldehyde	90		1.81	1.36×10^{-3}	0.7	5.2×10^{-4}	1.7	1.3×10^{-3}	2.7	2.0×10^{-3}	373	0.23	105	0.079
	61		0.22	1.1×10^{-4}	0.7	3.6×10^{-4}	1.4	7.1×10^{-4}	< 0.04	2.0×10^{-5}	1.0	5.1×10^{-4}	1	5.6×10^{-3}
	35		5.3	1.6×10^{-3}	0.7	2.0×10^{-4}	1.4	4.1×10^{-4}	< 0.04	1.0×10^{-5}	1.0	2.9×10^{-4}	11	3.3×10^{-3}
Acetic Acid	10.22		2.7	2.3×10^{-4}	1.12	9.6×10^{-5}	2.2	1.85×10^{-4}	-	-	10.7	9.1×10^{-4}	1,294	0.11
Ethylene Glycol	584		0.14	6.8×10^{-4}	0.7	0.0034	3.5	0.017	0.056	2.7×10^{-4}	1,170	5.7	2	9.7×10^{-3}
Phenol/acetone	164		6,100	8.3	1.47	2.0×10^{-3}	2.2	3.0×10^{-3}	< 0.04	4.0×10^{-5}	154	0.21	1,230	1.67
Terephthalic Acid	1,090		0.23	2.1×10^{-3}	1.4	0.0127	4.2	0.038	0.80	7.4×10^{-3}	260	2.4	-	-
	43.4		0.13	4.7×10^{-5}	1.4	5.0×10^{-4}	2.8	1.0×10^{-3}	< 0.04	1.4×10^{-5}	300	0.110	29.4	0.011
	715		1.75	0.01	2.1	0.013	2.8	0.017	< 0.04	2.3×10^{-4}	896	5.3	-	-
	593		-	-	3.58	0.018	63	0.3117	-	-	-	-	-	-
Dimethyl Terephthalate	68.8		0.018	1.0×10^{-5}	0.7	4.0×10^{-4}	1.4	8.0×10^{-4}	< 0.04	2.3×10^{-5}	47	0.027	30	0.017
	325		-	-	4.2	9.47×10^{-3}	75	0.1905	-	-	-	-	-	-
Oxo-chemicals	420		0.093	3.2×10^{-4}	4.2	0.0147	9.1	0.032	0.05	1.74×10^{-4}	130	0.4535	151	0.5268
Acrylic Acid	475		0.36	1.43×10^{-3}	0.7	2.77×10^{-3}	3.5	1.39×10^{-2}	< 0.04	1.58×10^{-4}	90	0.3564	11.4	0.0451
Acrylates	2,895		0.17	3.98×10^{-3}	0.7	0.0167	42	1.015	< 0.04	9.55×10^{-4}	232	5.60	55	1.33
Caprolactam	1,334		0.229	2.55×10^{-3}	906	10.081	956	10.635	0.047	5.22×10^{-4}	89.5	0.9953	10.8	0.1203
Aniline	190		9.9	0.0156	3,607	5.7	3730	5.9	0.14	2.3×10^{-4}	10,200	16.1	17.1	0.027
Bisphenol-A	66.8		12,600	7.0	1.8	1.02×10^{-3}	15.5	8.59×10^{-3}	0.32	1.8×10^{-4}	138	0.077	-	-
Vinyl Acetate	28		17	4.1×10^{-3}	0.7	1.7×10^{-4}	2.1	$5. \times 10^{-4}$	< 0.04	1.0×10^{-5}	2500	0.6	0.7	1.7×10^{-4}
Tetraethyl Lead	12,000		0.301	0.0301	0.7	0.07	2.1	0.21	0.12	0.012	440	44	11.4	1.14
Methyl Methacrylate (with acid recovery)	213		0.06	1.06×10^{-5}	2.1	3.7×10^{-3}	2.8	4.96×10^{-3}	< 0.04	7.09×10^{-5}	4,400	7.80	0.2	3.55×10^{-4}
Methyl Methacrylate (without acid recovery)	260		2.38	0.0052	-	-	-	-	< 0.04	8.69×10^{-5}	-	-	703	1.52

Table VI-3
(continued)

Product	T-P		Zn		Cu		Fe		Cr		Cd	
	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb	mg/L	lb/1000 lb
Acetaldehyde	2.58	1.94×10^{-3}	0.36	2.7×10^{-4}	16	0.0124	2.3	1.73×10^{-3}	2.7	1.99×10^{-3}	< 0.05	$< 3.7 \times 10^{-5}$
	17.4	8.9×10^{-3}	0.05	3.0×10^{-5}	0.42	2.1×10^{-4}	0.5	2.6×10^{-4}	< 0.05	$< 3.0 \times 10^{-5}$	< 0.05	$< 3.0 \times 10^{-5}$
	7.6	2.2×10^{-3}	0.1	3.0×10^{-5}	1.7	5.0×10^{-4}	0.74	2.2×10^{-4}	< 0.05	$< 2.0 \times 10^{-5}$	< 0.05	$< 3.0 \times 10^{-5}$
Acetic Acid	0.55	4.7×10^{-5}	0.06	5.0×10^{-6}	0.11	9.0×10^{-6}	0.36	3.1×10^{-5}	< 0.05	$< 5.0 \times 10^{-6}$	< 0.05	$< 5.0 \times 10^{-6}$
Ethylene Glycol	0.194	9.5×10^{-4}	0.22	1.07×10^{-3}	0.3	1.46×10^{-3}	1.5	7.3×10^{-3}	< 0.05	$< 2.4 \times 10^{-4}$	< 0.05	$< 2.4 \times 10^{-4}$
Phenol/acetone	0.16	2.2×10^{-4}	0.22	3.1×10^{-4}	0.70	9.5×10^{-3}	0.7	9.56×10^{-4}	< 0.05	$< 4.6 \times 10^{-5}$	< 0.05	$< 9.1 \times 10^{-5}$
Terephthalic Acid	20	0.18	0.90	8.1×10^{-3}	0.40	3.6×10^{-3}	12.7	0.12	0.6	5.4×10^{-3}	< 0.05	$< 4.5 \times 10^{-4}$
	2.61	9.4×10^{-4}	1.57	5.6×10^{-4}	0.36	1.3×10^{-4}	5.4	1.9×10^{-3}	4.58	1.65×10^{-3}	< 0.05	$< 1.8 \times 10^{-5}$
	4.5	0.027	0.19	0.0013	0.23	0.0014	6.7	0.04	< 0.05	$< 3.0 \times 10^{-4}$	< 0.05	$< 3.0 \times 10^{-4}$
	-	-	-	-	24.6	0.1213	-	-	-	-	-	-
Dimethyl Terephthalate	0.854	4.8×10^{-4}	1.11	6.3×10^{-4}	0.25	1.4×10^{-4}	1.77	1.0×10^{-3}	3.51	2.0×10^{-3}	< 0.05	$< 2.8 \times 10^{-5}$
	-	-	-	-	29.7	0.081	-	-	-	-	-	-
Oxo-chemicals	0.65	2.27×10^{-3}	-	-	0.54	1.88×10^{-3}	3.5	0.0122	0.4	1.396×10^{-3}	0.05	1.74×10^{-4}
Acrylic Acid	0.32	1.27×10^{-3}	-	-	0.08	3.17×10^{-4}	0.5	1.98×10^{-3}	< 0.55	$< 2.18 \times 10^{-3}$	0.05	1.98×10^{-4}
Acrylates	0.064	1.45×10^{-3}	-	-	0.08	1.9×10^{-3}	0.73	0.0176	0.143	3.27×10^{-3}	0.05	1.19×10^{-3}
Caprolactam	0.11	1.26×10^{-3}	-	-	0.94	1.04×10^{-3}	2.22	2.47×10^{-2}	< 0.05	$< 5.52 \times 10^{-4}$	< 0.05	5.52×10^{-4}
Aniline	4.3	0.8×10^{-3}	0.35	5.6×10^{-4}	0.05	7.3×10^{-5}	0.28	4.4×10^{-4}	2.7	4.2×10^{-3}	< 0.02	$< 3.1 \times 10^{-4}$
Bisphenol-A	-	-	0.56	3.1×10^{-4}	0.31	1.7×10^{-4}	10	5.56×10^{-3}	< 0.05	$< 2.8 \times 10^{-5}$	< 0.05	$< 2.8 \times 10^{-5}$
Vinyl Acetate	2.43	5.8×10^{-4}	0.12	2.9×10^{-4}	0.07	1.7×10^{-5}	0.50	1.2×10^{-4}	0.07	1.7×10^{-5}	< 0.05	$< 1.2 \times 10^{-5}$
Tetraethyl Lead	1.024	0.1024	0.98	0.098	1.30	0.13	1.0	0.1	< 0.05	< 0.005	< 0.05	< 0.005
Methyl Methacrylate (with acid recovery)	-	-	-	-	52.2	0.0926	1.14	2.02×10^{-3}	-	-	-	-
Methyl Methacrylate (without acid recovery)	-	-	-	-	288	6.25×10^{-3}	500	1.085	-	-	-	-

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

It is the aim of this section to describe and present available data on the different pollution control and treatment technologies which are applicable to the organic chemicals industry. Based on that data available, conclusions have been drawn relative to the reduction of various pollutants which is commensurate with three distinct levels of technology. These levels are defined as:

BEST PRACTICABLE CONTROL TECHNOLOGY
CURRENTLY AVAILABLE (BPCTCA)

BEST AVAILABLE TECHNOLOGY ECONOMICALLY
ACHIEVABLE (BATEA)

BEST AVAILABLE DEMONSTRATED CONTROL
TECHNOLOGY (BADCT)

The conclusions relative to what combination of control and treatment technologies are consistent with these definitions are embodied in the reduction or removal of pollutants specified for each level. In later sections of this report specific reduction factors are applied to the process RWL developed for each industrial category to obtain numerical values for effluent limitations and new source performance standards. These reductions are general and are considered to be attainable by all of the processes considered within the category.

The costs associated with these effluent limitations and new source performance standards have been estimated based on 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 the economic models 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 effluent limitations and standards recommended in this report. These alternate choices include:

1. different types of end-of-pipe waste water treatment,
2. different in-process modifications and pollution control equipment,
3. different integrated combinations of end-of-pipe and in-process technologies.

It is the intent of this study 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 limitations and standards presented in this report.

In-Process Systems

It is not possible to recommend a general list of process modifications or control measures which are applicable to all of these processes within the organic chemicals industry or even to the processes within one industrial subcategory. The following discussions deal with individual techniques which may be applicable to groups of processes or to single processes. The techniques described are based on both the practices observed during the sampling visits as well as those which have been described in the literature. In most cases, they can both be implemented with existing processes or designed into new ones.

The general effect of these techniques is to reduce both the pollutant RWL and the volume of contact process water discharged for end-of-pipe treatment. This corresponds to moving the data shown in Figures V-1 through V-11 toward the lower left side of the RWL envelopes.

The control technology described in the following paragraphs starting on page VII-1 to page VII-4 comes from:

Thompson, S.J., "Techniques for Reducing Refinery Wastewater, "Oil and Gas Journal, Vol. 68, No.10, 1970, pp. 93-98.

Substitution of Surface Heat Exchangers for Contact Cooling Water Used in Barometric Condensers

Figure VII-1 illustrates the classic barometric condenser. In the typical example shown, the volume of water being contaminated can be decreased from 260,000 lb/hr to 10,000 lb/hr for a condensing duty of 10,000,000 BTU/hr. This can be accomplished by substituting an air exchanger for water sprays. This type of process modification can be sized to cover almost an infinite number of specific process cooling duties.

It should be noted that water cooled surface condensers can also be used in this application. However, these require the use of non-contact cooling water.

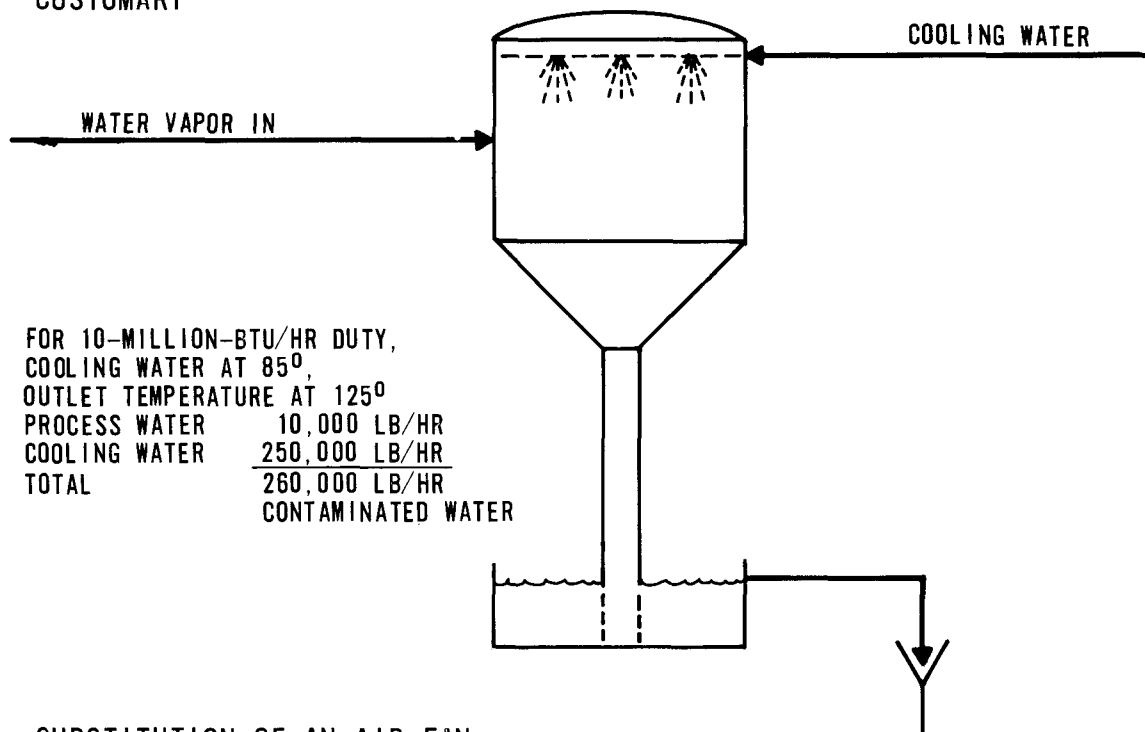
Regeneration of Contact Process Steam from Contaminated Condensate

Figures VII-2 illustrates the trade-off between contaminated contact process steam condensate and non-contact steam blowdown. The contact process waste water is reduced to a small amount of condensate. This scheme can be used to regenerate stripping steam in distillation towers or dilution steam in pyrolysis furnaces. Heat exchange is through a surface shell-and-tube heat exchanger, which can be sized for a wide variety of heat transfer duties. A system similar to this was described in detail for ethylene manufacture in Section IV.

FIGURE VII-1

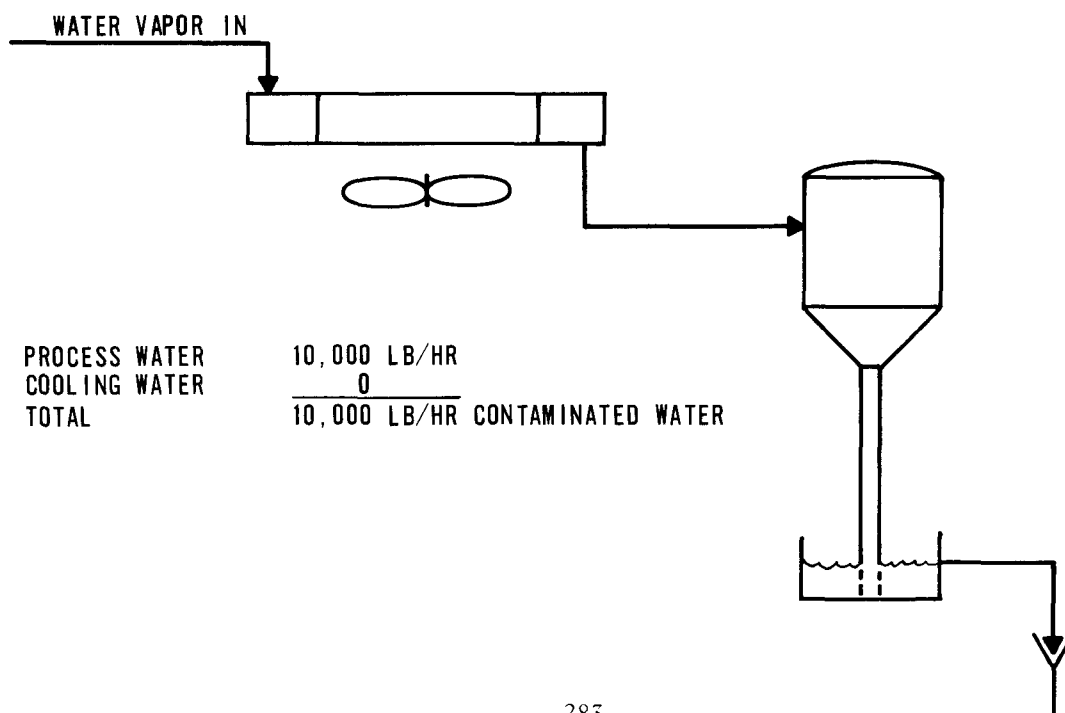
BAROMETRIC CONDENSER

CUSTOMARY



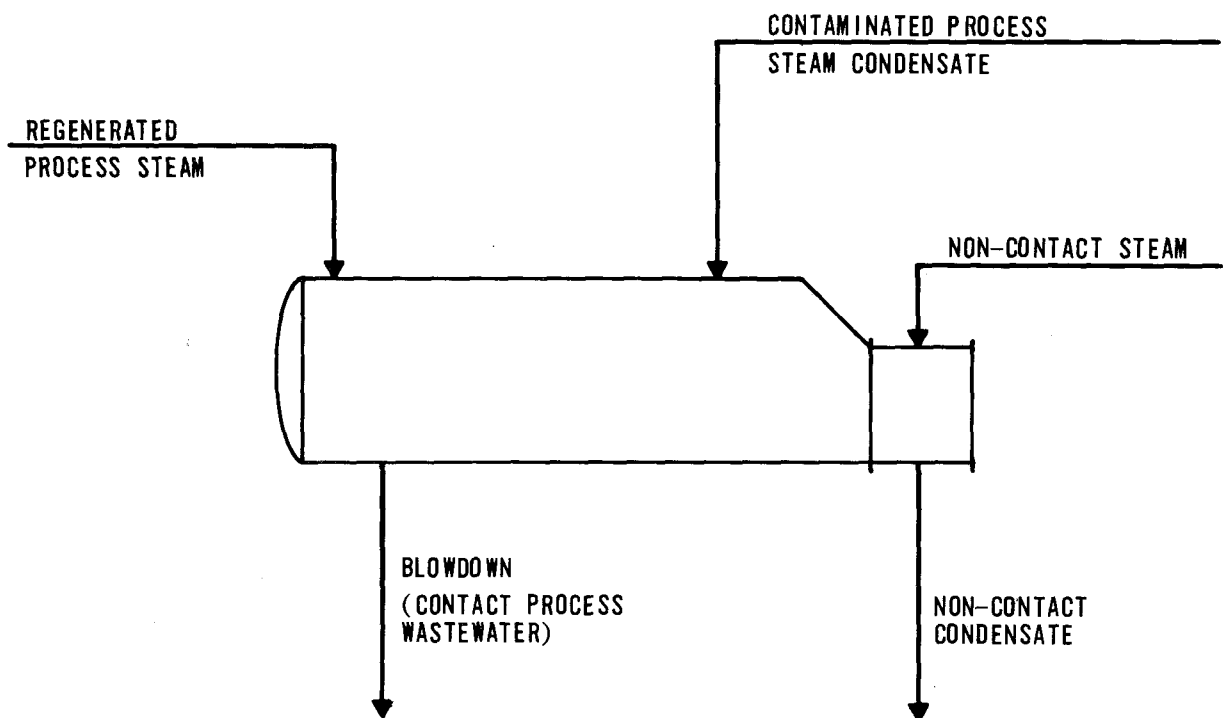
FOR 10-MILLION-BTU/HR DUTY,
 COOLING WATER AT 85°
 OUTLET TEMPERATURE AT 125°
 PROCESS WATER 10,000 LB/HR
 COOLING WATER 250,000 LB/HR
 TOTAL 260,000 LB/HR
 CONTAMINATED WATER

SUBSTITUTION OF AN AIR FAN



PROCESS WATER 10,000 LB/HR
 COOLING WATER 0
 TOTAL 10,000 LB/HR
 CONTAMINATED WATER

FIGURE VII-2
PROCESS STEAM CONDENSATE



Substitution of Vacuum Pumps for Steam Jet Ejectors

The use of vacuum pumps in place of steam jet ejectors is shown in Figure VII-3. This practice can be used to eliminate process RWL from the condensed steam used to draw a vacuum on the process. A specific vacuum pump system has been sized and priced for application in the process for manufacturing styrene by the dehydrogenation of ethyl benzene (Section IV). This same type of system is applicable to many other processes where operation under vacuum is necessary.

It should be noted that in many cases the steam jet ejector system may be coupled with a barometric condenser instead of the surface cooler shown in Figure VII-3. In this case, the volume reduction of contact process waste water will be quite substantial. It may also be possible to use the hydrocarbon vapors from the vacuum pump in the plant fuel-gas system (because of the reduced moisture content) rather than venting them to a flare.

The liquid compressant in a vacuum pump can protect it from corrosion. The manufacturers have accumulated operating data on performance of many liquids with different gas mixtures. It has been concluded that ordinary cast iron will often stand up well in resisting corrosive gases. More expensive materials for pump construction, such as monel or hastelloy C are available for particularly corrosive gases such as halogens.

Recycle of Scrubber Water

Figure VII-4 illustrates a method of concentrating contaminants in scrubber bottoms nearly to their saturation point. This is accomplished by recirculation of the scrubbing or wash water. Theoretically, the tower would require more trays or contacts, as dictated by the specific vapor-liquid equilibrium of the system. However, in many cases, existing towers can be modified to work in the manner illustrated.

Recovery of Insoluble Hydrocarbons

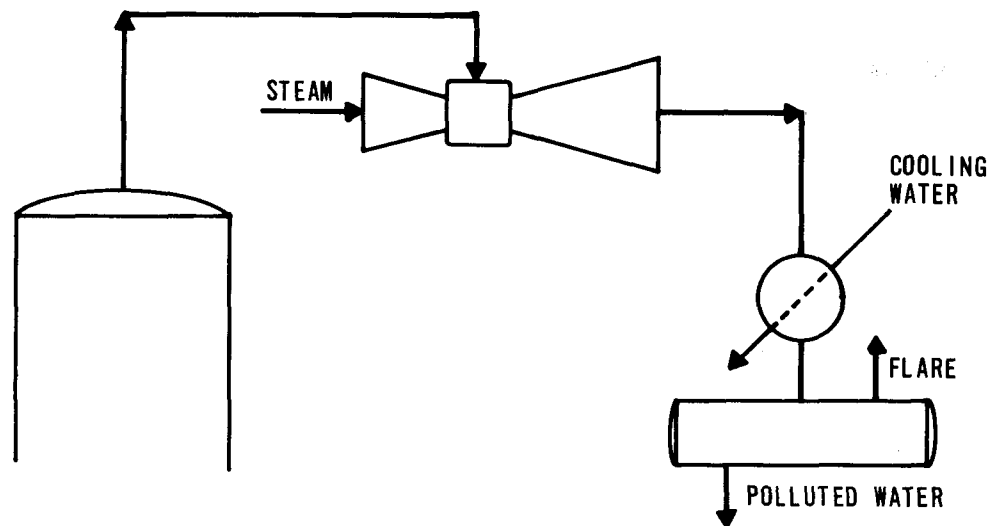
Two methods for improving the separation of insoluble hydrocarbons from water are shown in Figures VII-5 and 6. This type of separation is usually done by gravity in tanks which are similar to the oil/water separators used in refineries. The first technique involves the mixing of lighter oils to make the total hydrocarbon stream lighter and easier to separate. The second is the use of fuel gas to create an upward current in the separator. These techniques are widely used in ethylene plants to separate insoluble hydrocarbon by-products from the cracked gas quench water. Other systems such as filters and coalescers are also used for this type of separation.

The separation of oil by gravity is a common unit process in the cleanup of any oily waste water. The primary method of separation is to provide holding time so that the flow can be

FIGURE VII-3

NON-CONDENSIBLE REMOVAL

CUSTOMARY - VACUUM JETS



ALTERNATE - VACUUM PUMP

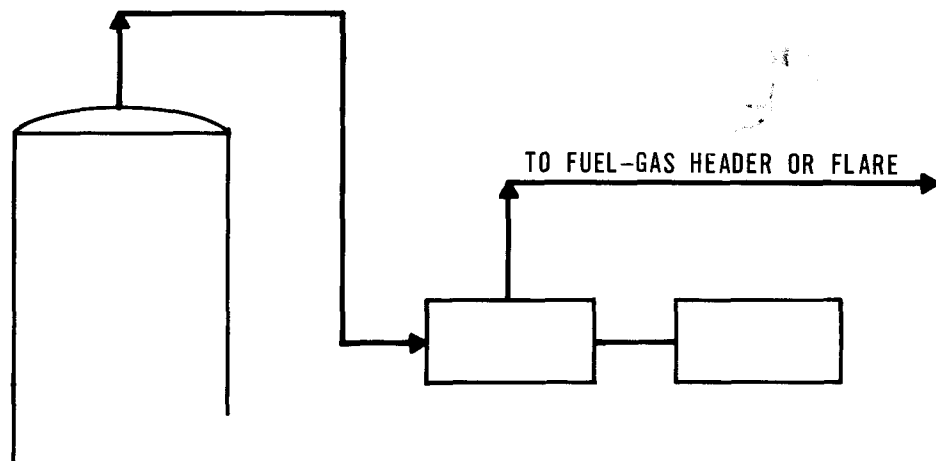
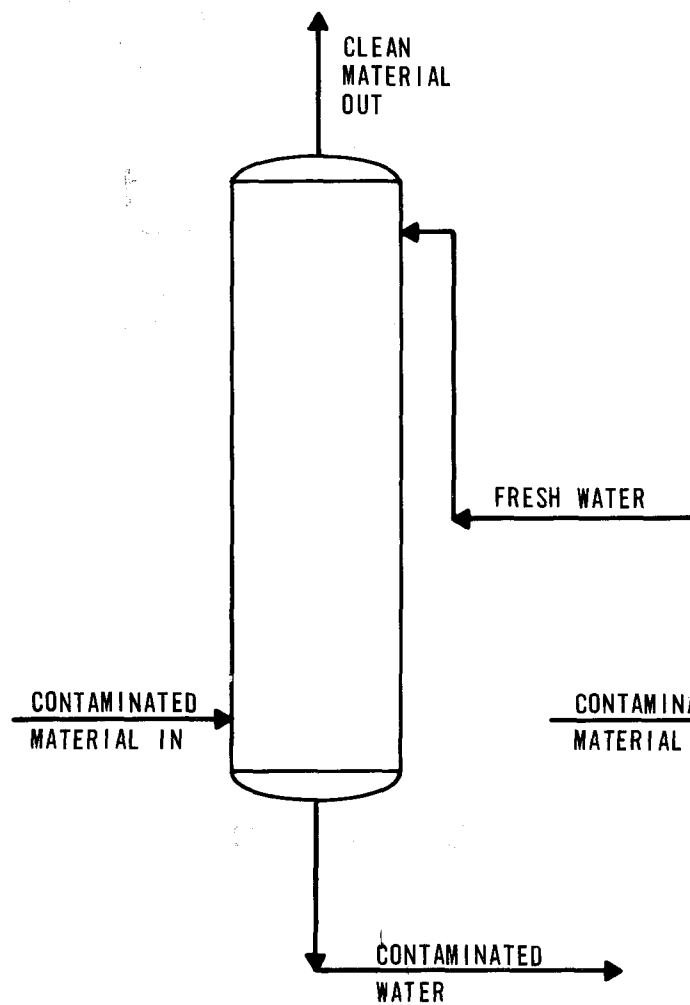


FIGURE VII-4
WATER SCRUBBING

CUSTOMARY



ALTERNATE

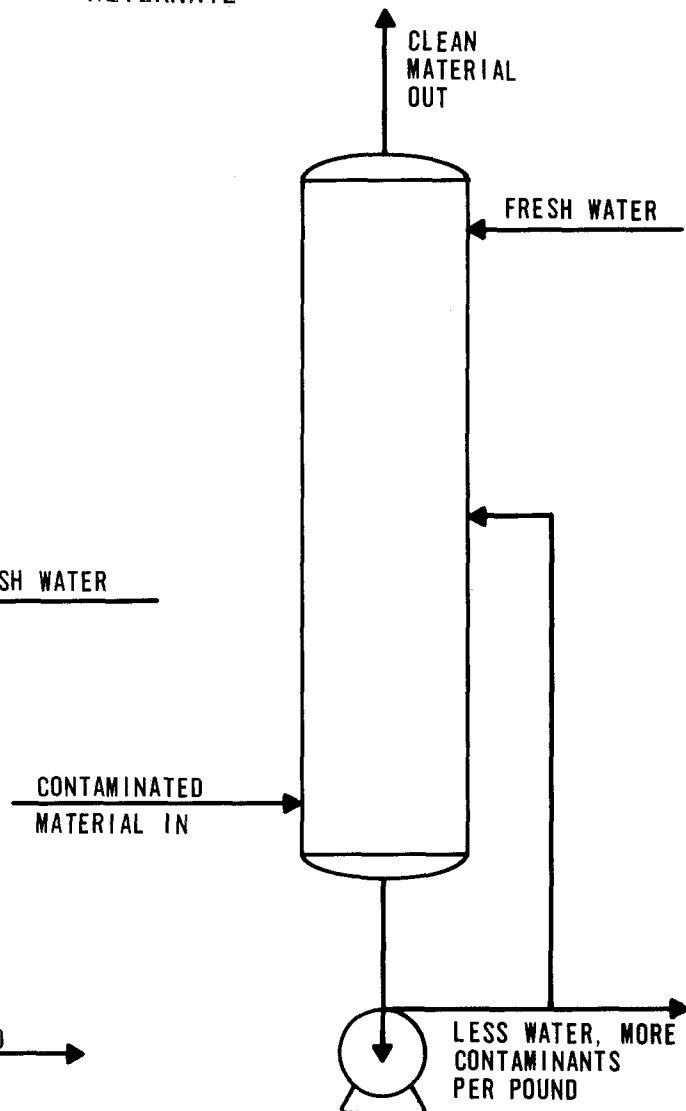


FIGURE VII-5
OIL AND WATER SEPARATION

LIGHT-OIL ADDITION

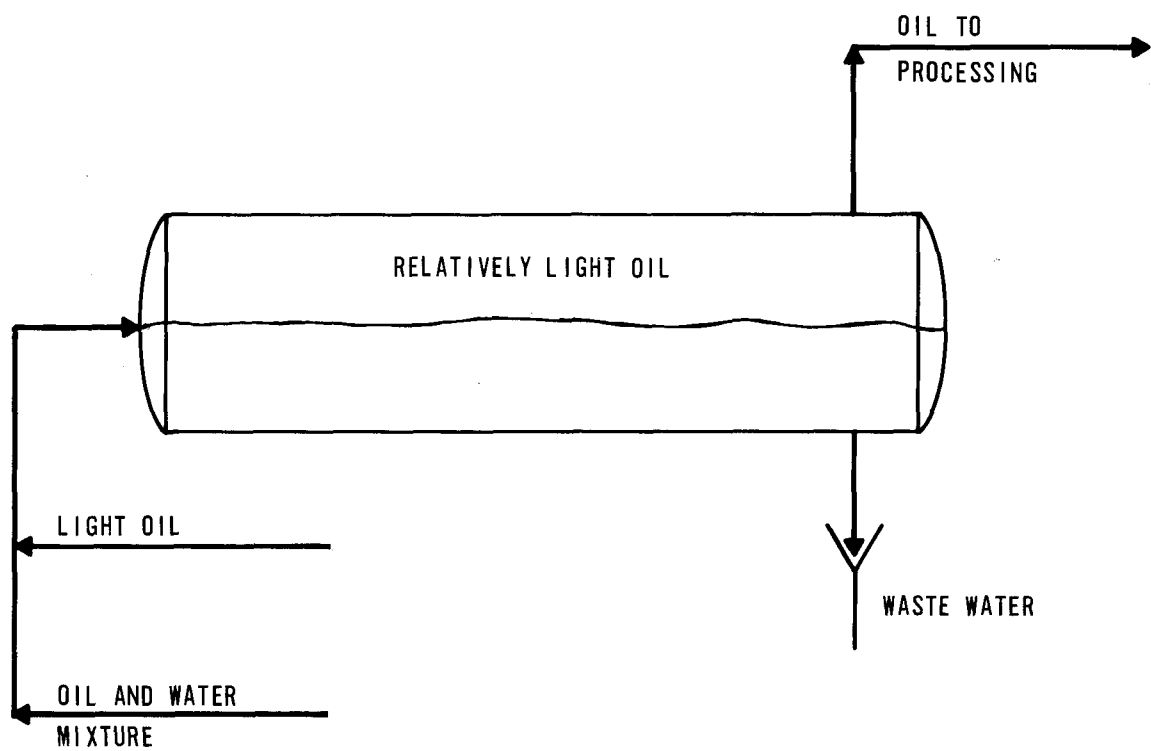
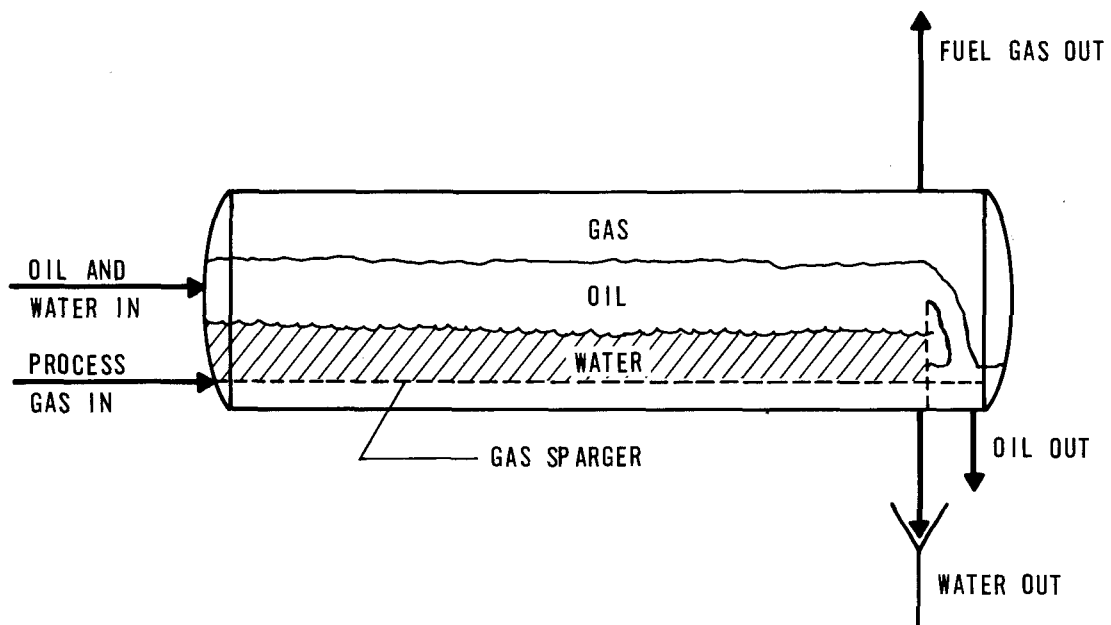


FIGURE VII-6
OIL AND WATER SEPARATION

FUEL-GAS ADDITION



maintained in a quiescent condition. Typical efficiencies of oil separation units are presented in Table VII-1.

Spent Caustic and Oily Sludge Incinerator

The final disposal of spent caustic and oily sludges has been successfully accomplished by using a fluid-bed incinerator. As the sludge is burned, the solids remain in the bed, while the gaseous products of combustion and water vapor discharge through the gas-cleaning system. When the operation on oily sludge has been stabilized, spent caustic is introduced. Water in the caustic solution is vaporized and the combustible material is oxidized; the solids accumulate in the fluid bed. The bed level is maintained by withdrawing ash as it accumulates from the deposition of solids. Solids removed from the process consist of iron oxide, sodium sulfate, sodium carbonate, and other inert solids, and have been used for landfill. Stack gases from the incinerator consists of water vapor, nitrogen, oxygen, carbon dioxide, and a few tenths of a part per million of sulfur dioxide.

Various phenol recovery systems using solvent extraction, carbon adsorption, and caustic precipitation are also described in Section IV. These recovery processes are all associated with phenol manufacturing processes.

Phenol Removal

Solvent Extraction

Solvent extraction has been used very effectively by the petroleum industry to remove phenols from various streams. Some of these solvents which have been used to extract phenols are aliphatic esters, benzene, light cycle oil, light oil, and tri-cresyl phosphates. Among those solvents, tri-cresyl phosphates are excellent solvents due to their low solubility in water and their high distribution coefficients for phenol but they are expensive and deteriorate at high distillation temperatures. However, it might be used when high phenol recoveries are desired for economic reasons. Most of the other solvents are considerably cheaper to use in waste treatment operations. Several types of extraction equipment such as centrifugal extractors, electrostatic extractors, etc., are available and the type of extraction equipment required for the use of a particular solvent is an important economic consideration. Reported efficiencies of some solvent extraction for phenol removal are given in the following tabulation.

TABLE VII-1

Typical Efficiencies of Oil Separation Units*

<u>Oil Content</u>		<u>Oil Removed</u> <u>%</u>	<u>Type of</u> <u>Separator</u>
<u>Influent</u> <u>(mg/L)</u>	<u>Effluent</u> <u>(mg/L)</u>		
7000-8000	125	98-99+	Circular
3200	10-50	98-99+	Impounding
400-200	10-40	90-95	Parallel Plate
220	49	78	API
108	20	81.5	Circular
108	50	54	Circular
90-98	40-44	55	API
50-100	20-40	60	API
42	20	52	API

*"Petrochemical Effluents Treatment Practices," Federal Water Pollution Control Administration, U.S. Department of the Interior, Program No. 12020--2/70.

Typical Efficiencies for Phenol Removal by Solvent Extraction*

<u>Solvent</u>	<u>Phenol</u>		<u>Phenol Removal (%)</u>
	<u>Influent, mg/l</u>	<u>Effluent, mg/l</u>	
Aromatics, 75%	200	0.2	99.9
Paraffins, 25%			
Aliphatic Esters	4,000	60	98.5
Benzene	750	34	95.5
Light Cycle Oil	7,300	30	90
Light Oil	3,000	35	99
Tri-cresyl Phosphates	3,000	300-150	90-95

*"Petrochemical Effluents Treatment Practices", Federal Water Pollution Control Administration, U.S. Department of the Interior, Program No. 12020, February 1970.

Steam Stripping

Steam stripping method has also been successfully used in removing phenol from waste streams. The method involves the continuous downward flow of the waste water through a packed or trayed tower while the stripping steam flows upward removing the desired constituent. The removed phenols are recycled back to the appropriate process. This stripping method can achieve at least a phenol reduction of 90 percent.

Chlorine Oxidation

Chlorine has been applied in oxidizing phenol in waste waters. The oxidation of phenol must be carried to completion to prevent the release of chlorophenols. An excess of chlorine is usually required because of the reaction with various other chemical compounds such as ammonia, sulfides, and various organics which can interfere with the chlorination process. Despite the potential for formation of chlorophenolics, chlorine can be used to completely (100%) oxidize phenolics under proper conditions.

Ammonia and Sulfide Stripper

Removal of hydrogen sulfide and ammonia from sour water can also be accomplished by stripping methods. Most of these stripping methods also involve the continuous downward flow of the waste water through a packed or trayed tower while the stripping gas or steam flows upward removing the desired constituent. Steam is considered to be the preferred heating and stripping agent, since hydrogen sulfide, which is concentrated in the steam condensate, may be further treated. Flue gases are frequently used because carbon dioxide produces a slightly stronger acid than hydrogen sulfide thus releasing hydrogen sulfide from the solution. The typical removal efficiencies are:

H₂S removal 98-99%

In many cases steam stripping may also remove as much as 20-40 percent of any phenols present.

Cyanide Removal

Cyanide can be oxidized to carbon dioxide and nitrogen by chlorination. The waste water must be kept at a pH value greater than 8.5 during treatment to prevent the release of toxic cyanogen chloride. The reaction time usually is one to two hours and the process is subject to the interference of various compounds such as ammonia, sulfides, and various organic substances.

Ozone Treatment

Ozone has been proposed as an oxidizing agent for phenols, cyanides, and unsaturated organic substances, since it is a considerably stronger oxidizing agent than chlorine. The chief disadvantages are the high initial cost of the equipment for energy needs and cooling water requirements for ozone generation. Ozone has several advantages, the most important being its ability to rapidly react with phenol and cyanide. The optimum pH for phenol destruction is 11 to 12. Thiocyanates, sulfates, sulfides, and unsaturated organic compounds will also exert an ozone demand which must be satisfied. This demand serves as the basis of design for an ozonation unit treating a waste water containing these compounds. Sulfides also can be removed from a waste water which is to be ozonated by air stripping them at low pH values, thus economically reducing the ozone demand. The pH of the waste water can then be raised to the appropriate level required for optimum ozonation.

Recent investigations have indicated the applicability of ozonating wastes from the manufacture of chlorinated hydrocarbons. The optimum pH for ozonation of this waste water was found to be 12.6, and as much as 90 percent of the waste COD was removed. This waste contains large quantities of unsaturated hydrocarbons, which are readily amenable to ozonation. Ozonation of a waste water can be either a batch or continuous operation, depending on the characteristics of the waste and the waste flow rate.

Incineration of Chlorinated Hydrocarbons

There are a limited number of devices currently available for burning waste chlorinated hydrocarbons with the recovery of by-product HCL. In the past, the traditional disposal routes for these waste materials have been ocean discharge, open-pit burning, drum burial, and deep-well injection. Recently, more stringent regulations have disallowed many of these methods. Subsequently, there has been an increase in activity by industry aimed at the development of systems for these hard-to-treat

wastes. The weight of these materials is estimated at 350,000 tons/year of chlorinated hydrocarbon residues generated during production of almost 10 million tons/year of chlorinated hydrocarbons by chemical companies. It should be noted that there are still serious drawbacks associated with most incineration systems. These relate to both the emissions from the systems as well as corrosion and other operating difficulties. The following paragraphs describe the systems currently utilized. It is not clear whether or not systems such as these truly represent a viable alternative for the disposal of hard-to-treat wastes. However, incineration is an alternative which will receive additional consideration by manufacturers whose processes generate concentrated reduced volume waste streams.

More chemical companies now incinerate wastes that cannot be treated. For example, one chemical company uses a high-temperature incinerator to dispose of polychlorinated biphenyls. Another chemical company has developed an efficient tar-burning unit. A system based on this technology was recently completed.

Some plants have also added scrubbers to clean emissions from incinerators. But for highly chlorinated hydrocarbon wastes--i.e., those containing more than 50% chlorine--the emission of gaseous hydrogen chloride is more than ordinary incinerator-scrubber units can cope with.

For example, a neoprene plant at one time operated a horizontal incinerator and vertical scrubber with a packed column in the stack. Maintenance costs were excessive (about \$40,000/year) and hydrogen chloride emissions were too high.

This plant has since turned to the only system for chlorinated hydrocarbon disposal and by-product recovery now operated in this country.

Four units are now operating at different chemical plants. In addition, another unit is scheduled to go on stream shortly. There is only one company which is not recovering by-product hydrogen chloride. The company decided against recovery because high-pressure operating conditions at the plant would have required the addition of equipment to compress the gas stream before stripping hydrochloric acid.

The system incinerates chlorinated liquid waste, cools the combustion gases, strips the aqueous product and turns out anhydrous HCl.

Hydrogen chloride gas is soluble in water. But, absorption is complicated by the heat generated in large quantities during combustion. For example, 36.4 million BTUs/hour must be removed from a 4,000 lbs/hr unit.

In the system, the sticky chlorinated hydrocarbon residue is atomized and incinerated in a combustion chamber that has a

vortex-type burner supplied by Thermal Research. The incinerated material is cooled from 2,500°F to 800°F in a graphite cooling chamber, where it is sprayed with 27% HCl.

The cooled gas passes through three falling-film acid absorbers made of impervious graphite. Stripped liquid is recycled through the absorbers in reverse order, removing heat of absorption and HCl from the gas stream.

Gas from the last absorber enters a final scrubber to reduce HCl emissions about 5 ppm. This scrubber is 5 ft. in diameter, contains 3 ft. of 1-inch-diameter plastic packing and includes a spray header and a demister made of polypropylene.

At some plants, the gas is released to the atmosphere through a stack designed for silencing the exhaust. It is a packed centrifugal unit with a diameter enlargement before the stack outlet to reduce gas velocity and permit entrained liquid particles larger than 100 microns to settle out.

The major problem with units has been the junction between the combustion and cooling chambers. The carbon blocks of the cooling chamber oxidize at 750°F and all parts of the chamber must be covered with liquid. If the spray is not properly adjusted, liquid HCl backs up into the combustion chamber and attacks the mortar joints and steel outer shell. A ceramic sleeve is now used to protect the furnace refractory at the joint from the HCl spray.

One company has also switched from field-erected to preassembled cooling chambers. Field-erected units were made of dense (100 lbs./cu.ft.) carbon blocks, keyed together by graphite rods, cemented with a special carbonaceous cement and reinforced by rubber-covered steel bands. The preassembled chambers have graphite wall units, eliminating the possibility of leaky joints.

From a pollution-control standpoint, the most significant change that can be made in process chemistry is from a "wet" process to a "dry" process, that is the substitution of some other solvent for water in which to carry out the reaction or to purify the product.

If any organic solvent can be used, the process can probably be worked out to produce an organic concentrate that will contain all the undesirable impurities and by-products. Their disposal in an organic concentrate is much simpler and cheaper than coping with them in an aqueous medium. Incineration costs for destruction of organic concentrates by contractors usually run between \$0.01/lb. and \$0.03/lb., depending on the halogen content and the presence of other inorganic compounds.

If water must be used in the process, its use should be restricted, and every opportunity for the replacement of fresh water with recycle water should be explored and implemented. (This is especially important in the inorganic chemical

processes.) Use of water can be restricted by countercurrent washing techniques. Discarding of waste water used for purifying a reaction product when fresh water is used for the reaction medium is also uncalled for. Similarly, another useful water-conservation practice is collection of vacuum-jet condensate, rain water, and floor water for reuse.

Another process change that can yield significant pollution-control benefits is the elimination of troublesome by-products by a change in the reactants, or a change in the catalyst. An example of the former is the emergency of oxychlorination processes (that generate by-product hydrochloric acid).

From these discussion it is apparent that significant reductions in the quantity of pollutants generated by a process are possible. Quantitative estimates for specific processes indicate that in some cases waste water flows can be reduced to approximately 10 gallons/1,000 lb of product, and corresponding COD loadings of 0.1 lb of COD/1,000 lbs of product. In some specific cases the discharge of pollutants can be reduced to near zero through the use of by-product recovery processes such as adsorption. Such systems generally take advantage of the specific characteristics of the chemicals in questions. It is not possible to specify a uniform restriction based on such systems that could be applied throughout the industry, or even one category.

End-of-Pipe Treatment System General Considerations

Raw Waste Load data from the Phase I field survey was handled as a separate report. However, because of the scarcity of treatment plant performance data, it was decided to combine the Phase I and Phase II data for this study. A summary of the types of treatment technology which were observed during both phases are listed in Table VII-2. During the Phase II study, 70 individual plants were surveyed however, 6 of the 70 plants were previously surveyed during the Phase I study. Table VII-2 has been prepared taking this duplication into consideration.

Biological Treatment

During the plant survey program, historic wastewater treatment plant performance data were obtained when possible. The data were statistically analyzed, and, when possible, the individual plant performance was evaluated with respect to the original design basis. Subsequent to this evaluation, a groups of plants were selected as being exemplary in performance. These particular exemplary plants are indicated in Table VII-3 which is a summary of all of the historic performance data made available by industry for the purposes of the study. The amount of analytical data used in the statistical analyses are indicated in the "data base column" of Table VII-3. The following is a summary of the average reductions capable of exemplary treatment plants:

Table VII-2

Organic Chemicals Study
Treatment Technology Survey

<u>Type of Treatment or Disposal Facility</u>	<u>Number of Plants Observed</u>	
	<u>Phase I</u>	<u>Phase II</u>
Activated Sludge	7	9
Activated Sludge-aerated lagoon	2	0
Activated Sludge-polishing pond	0	1
Activated Sludge-solar evaporation pond	0	1
Trickling Filter-activated sludge	1	0
Aerated lagoon-settling pond	3	1
Aerated lagoon-no solids separation	2	1
Facultative Anaerobic lagoon	4	4
Stripping Tower	1	1
No current treatment - system in planning stage	3	7
To Municipal Treatment Plant	5	23
Deep-well disposal	2	6
Physical Treatment, e.g. API Separator	4	3
Activated Carbon	0	6
Incineration	<u>0</u>	<u>1</u>
TOTAL	34	64

Table VII-3

Historic Treatment Plant Performance
50% Probability of Occurrence

Plant No.	Treatment System	Category	COD		BOD		TOC		SS		Data Base	
			% Removal	Effluent mg/l	% Removal	Effluent mg/l	% Removal	Effluent mg/l	% Removal	Effluent mg/l	Duration (months)	Performance Period
1 ¹	AL	D	75	320	97	10	--	--	--	--	6(Sept-Feb)	daily average
2 ^{1,2}	AS-AL	C	96.4	470	--	--	--	--	--	163	12	daily average
3 ¹	AS	D	63	200	93.5	16	--	--	--	55	12	monthly average
4 ¹	AS	B	64.2	120	--	15	--	--	--	--	14	monthly average
5 ^{1,2}	TF-AS	B	73.5	83	--	--	--	--	--	--	14	monthly average
6	AL	B-C	--	--	--	291	--	--	--	665	12	weekly average
7	AL	C	--	165	--	9.9	--	--	--	81	12	monthly average
8 ¹	AL	B	--	75	--	23.5	--	--	--	24.3	12	monthly average
9 ¹	AS	C	--	--	83	152	60	170	--	130	7(Aug-Feb)	daily average
10 ¹	AS	B	74.5	80	90.1	20	--	--	--	--	12	weekly average
11 ^{1,2}	AS-AL	C	--	--	99.7	20	97	100	--370	145	12	daily average
12	AS	A-B	85	97	--	59	--	--	--	--	12	monthly average
13	AS	B-C	--	610	--	294	--	295	--	189	14	monthly average
14	AS	B	--	--	73	410	42	780	--	280	14	monthly average
15	AL		--	226	--	63	--	--	--	--	6(July-Dec)	weekly average
16 ¹	AS	D	--	--	82.5	362	--	--	--	289	8(Aug-Mar)	monthly average
17 ¹	AS	D	67	1,760	--	--	--	--	--	--	6(June-Oct)	daily average
18	AS	D	25.4	1,520	63.6	303	--	--	--	480	12	weekly average
19 ¹	AS	D	--	--	97.6	157	--	--	--	--	5(June-Sept)	monthly average
20 ¹	AS	C	--	296	98.8	46.9	--	--	--	--	5(June-Sept)	weekly average
Exemplary Plant Average			74	378	93	82.2	79	135	--	134		
Exemplary Single Stage Plants - Average			69		92		60		--	65 ³		

¹Plants considered to be exemplary in performance.

²Multiple-stage biological treatment.

³Plant 16 is not included in average.

	COD <u>Removal</u> percent	BOD <u>Removal</u> percent	TOC <u>Removal</u> percent	Effluent <u>TSS</u> mg/l
Exemplary Single - and Multiple-Stage Plants	74	93	79	134
Exemplary Single-Stage Plants	69	92	60	65

The major differences observed in performance from the previous analyses are in the TOC removals. This is because only two historic TOC data points are available.

During the survey program, 24-hour composite samples were obtained in order to verify the plant's historic performance data, as well as to provide a more complete waste water analytical profile. These results are presented in Table VII-4. The following is a summary of the average reductions capable of being attained by exemplary treatment as verified by composite sampling:

	COD <u>Removal</u> percent	BOD <u>Removal</u> percent	TOC <u>Removal</u> percent
Exemplary Treatment Plants	72	87	58

Considering the variability associated with daily composite sample, testing and treatment plant performance, these efficiencies agree with the long term historical data.

The TOC removal of 58 percent would seem to substantiate the lower value of 60 percent as previously indicated for the historic values appearing in Table VII-3. As indicated by the TSS removal data, 9 of the 17 plants surveyed had negative TSS removal and over 75 percent of the plants had inadequate solids handling facilities.

The impact of TDS and oil on the TSS levels for the plants surveyed is indicated in Table VII-4. There is a trend indicating that high TDS and oils in the plant effluent contribute to high TSS levels, e.g. note the direct effect of TDS on the TSS is not clear from the sampling data, e.g. Plants 21 and 22 have high TDS and relatively low TSS, while Plant 19 has a high TDS as well as TSS in it effluent.

During the course of the plant surveys, three plants were observed to have multiple-stage biological treatment. Plant 5 (see Table VII-3) required two-stage treatment for phenol removal, while Plants 2 and 11 required it because of relatively high raw waste loads.

Filtration

Table VII-4

Treatment Plant Survey Data¹

Plant No.	Treatment System	Category	COD		Total BOD		TOC		TSS		TDS	Oil & Grease
			% Removal	Effluent mg/L	% Removal	Effluent mg/L	% Removal mg/L	Effluent mg/L	% Removal	Effluent mg/L	Effluent mg/L	Effluent mg/L
2 ²	AS-AL	C	64	2,300	90	427	32	2,710	Negative	4,700	2,300	-
3 ²	AS	D	71	284	73	74	71	132	Negative	62	3,100	1 ³
4 ²	AS	B	57	214	82	13	35	80	40	14	2,900	4 ³
5 ²	TF-AS	B	59	133	92	12	43	61	97	44	1,430	2 ³
6	AL	B-C	66	980	73	235	11	573	Negative	362	3,000	11 ³
8 ²	AL	B	69	92	84	6	26	52	99	3	690	-
9	AS	C	75	595	92	75	69	242	Negative	50	3,810	12 ³
11 ²	AS-AL	C	94	337	99	16	27	343	Negative	145	2,690	1 ³
13	AS	B-C	65	940	90	177	64	470	120	338	1,520	6 ³
16 ²	AS	D	54.8	1,650	82.1	300	80.8	280	43.6	552	10,990	226 ⁴
17 ²	AS	D	60.0	1,400	81.4	240	63.4	410	Negative	1,300	3,750	24 ⁴
			77.3	1,000	90.0	310	76.8	360		732	4,060	22 ⁴
18	AS	D	22.1	2,680	16.7	650	-	1,025	42.9	1,170	2,050	106 ⁴
19 ²	AS	D	59.5	5,100	69.8	1,800	55.8	1,700	Negative	2,500	8,360	-
20 ²	AS	C	96.2	317	99.5	19	96.6	114	Negative	100	1,950	19 ⁴
21	AL	C	62	600	78	27	66	47	89	30	9,800	-
22	AS	B	16.1	1,370	47.5	210	8.3	550	53.4	82	15,400	<.03 ⁴
23	AS	B	95.4	147	92.6	41	95.4	35	Negative	37	580	21 ⁴
Average ⁵			72		87		58					

¹Based on 24 hrs composite samples.²Plants considered to be exemplary in performance based on historical data.³Oil and grease are reported as carbon tetrachloride extractables.⁴Oil and grease are reported as Freon extractables.⁵Includes exemplary plants as well as Plant 23.

Supplement organics and solids removal is being practiced within the industry in one particular case using a polishing pond. One major problem during summer solids periods is algal blooms which, if unchecked, can drastically increase the TSS and COD of the polishing pond effluent. In addition, the acreage requirements of this system limits its potential uniform application.

In contrast, filtration has many of the advantages of polishing ponds and few of the disadvantages. In order to quantify the effectiveness of effluent filtration, samples of biological treatment plant effluents were collected and filtered using filter paper. The results are presented in Table VII-5. Average percent COD, BOD, and TOC removals associated with filtration are 20, 17, and 20 respectively,

Carbon Adsorption

Granular activated carbon technology is continuously being developed and is beginning to compete actively with biological treatment as a viable treatment alternative or as a biological treatment effluent polishing process for some industrial wastes. There exists a limited amenability of many low molecular weight, oxygenated chemicals to adsorption on activated carbon. In addition, experience has indicated that TSS in amounts exceeding 50 mg/l and oils above concentrations of 10 mg/l should not be applied directly to carbon beds. These materials tend to clog and coat the carbon particles, thereby reducing the adsorption effectiveness.

During the plant survey program, 6 activated carbon plants treating raw wastewaters were surveyed, and the results are presented in Table VII-6. The most interesting fact is that domestic wastewater treatment experience indicates that efficient treatment is provided with contact times between 10 and 50 minutes, while the design contact times in Table VII-6 vary between 22 and 660 minutes (calculated on an empty column basis. These higher contact times are required because of the much higher raw waste loads generated by industry.

The major problems encountered in trying to compare design criteria and present performance of carbon plants are as follows:

1. In most cases, design loadings, both organic and hydraulic, have not been attained. This means the new plants are sometimes grossly under-loaded.
2. Thermal carbon regeneration is presently an art which is acquired only with actual operating experience. For this reason, start-up problems are often extended, and it is not unusual for the pollutant concentrations of the activated carbon effluent to be higher than the design value. This situation continues until the carbon is regenerated thoroughly.

Table VII-5

Removal by Filtration
(Performed on Biological Treatment Plant Effluent)

<u>Plant</u>	<u>% COD</u>	<u>% BOD</u>	<u>% TOC</u>
3	9	4	3
15	87	56	78
15	85	--	82
14	24	28	14
9	11	--	5
9	10	--	17
13	32	36	8
4	--	--	--
24	8	2	20
12	21	--	7
21	3	--	8
16	84.3	57.8	75.9
25	39.3	--	39.4
20	8.5	17.2	33.0
35	51.4	--	27.7
26	26.2	71.4	41.2
27	--	12.5	25.0
18	86.8	72.1	90.6
17	88.4	55.6	91.6
19	<u>33.3</u>	<u>--</u>	<u>66.0</u>
Average¹	20	17	20

¹ Average does not include plants 15, 16, 17, 18, and 26, since these plants have excessively high effluent TSS and would bias the results.

Table VII-6
Activated Carbon Plants Treating Raw Wastewaters

Plant	Pretreatment	Removal Efficiencies-%		Flows-gpd		Hydraulic Loading gpm/sq.ft.		Contact Time-minutes		Carbon Exhaustion Rate	
		Design	Present	Design	Present	Design	Present	Design	Present	Design	Isotherm
28	Solids Removal and Equalization 9-hr detention time	----	Polyol-11	100,000	55,000	5.6	3.0	22	40	<u>0.4 lb. polyol</u> lb. carbon	----
29	Equalization 150-day detention time	T0C-94	T0C-89	20,000	7,000	0.49	0.17	540	1,550	<u>0.07 lb. T0C</u> lb. carbon	<u>0.19 lb. T0C</u> lb. carbon
30	Equalization, Neutralization and solids removal	Phenol-89	Phenol-94	750,000	500,000	4.6	3.1	69	104	<u>.028 lb. phenol</u> lb. carbon	----
31	Equalization and Neutralization	----	T0C-91	30,000	20,000	----	----	660	912	----	----
32	Equalization and Neutralization	Phenol-99.9	Phenol-95	72,000	22,000	2.0	0.6	215	75	----	----
33	Equalization, Neutralization and solids removal	Color-90	----	800,000	----	7.7	----	27	----	<u>5.4 lbs. color</u> lb. carbon	----

3. Plants with insufficient spill protection and/or inadequate housekeeping practices may discharge specific low molecular weight hydrocarbons which are not amenable to adsorption. This situation results in an erratic plant performance.

The carbon adsorption isotherm is widely used to screen the applicability of different activated carbons and to calculate theoretical exhaustion rates. The comparison of isotherm and design exhaustion rates for Plant 29 in Table VII-6 further substantiates the fact that isotherm data is preliminary and should not be used for design purposes. However, carbon isotherm data does indicate relative amenability of the particular wastewater to treatment and to fairly typical removal efficiencies.

To investigate the possibility of using activated carbon technology on the effluents from biological treatment plants treating organic chemical wastewaters, a series of carbon isotherms were run at standard conditions using a contact time of 30 minutes. The results of the isotherms are presented in Tables VII-7 through VII-9. Average performance values are presented as follows:

<u>Parameter</u>	<u>Carbon B Exhaustion Rate</u> Lbs removal/lb carbon	<u>Soluble Pollutant</u> <u>Removal</u> percent
COD	0.41	69
BOD	0.03	20
TOC	0.06	87

Inspection of the specific data in Tables VII-7 through VII-8 indicates that carbon adsorption has varying degrees of amenability with regard to cost effective wastewater treatment. However, the data does indicate that specific wastewaters are readily treatable using activated carbon.

BPCTCA Treatment Systems

The major purpose for the review of the historic treatment plant data was to be able to quantify BPCTCA reduction factors, which would then be applied to BPCTCA raw waste load figures for each subcategory in order to generate recommended effluent limitations guidelines. Based on the previous discussions of biological treatment, the following pollutant reduction factors are considered achievable with BPCTCA treatment technology:

Table VII-7

Summary COD Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

Plant No.	Carbon Exhaustion Rate		Max. Soluble COD Removal (%)	Category
	lbs COD Removed lb Carbon	lbs Carbon 1,000 gallons		
14	0.035	232	22	B
15	0.8	8.9	87	
15	0.2	28.6	87	
3	1.35	1.87	74	D
9	0.30	13.9	84	C
9	0.36	13.3	79	
13	0.42	10.6	75	
13	0.36	12.6	70	B-C
4	0.51	2.2	57	B
24	0.34	32.2	69	B
12	4.5	0.27	87	B
21	0.11	21.4	3	C
16	.12	29.5	50.2	D
25	-----	-----	57.8	
20	4.0	.25	41.6	C
35	-----	-----	42.4	B-C
26	.45	2.0	72.8	A
18	-----	-----	83.4	D
23	.069	3.9	63.6	B
27	-----	-----	20.4	B
17	0.094	44.3	93.9	D
Average ¹	.41	15.7	69.0	

¹The average does not include Plants No. 12, 14, 20 and 21.

Table VII-8
Summary BOD Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

Plant	Influent (soluble) mg/L	Effluent (soluble) mg/L	BOD Removal %	Carbon Exhaustion	
				<u>lbs BOD Removal</u> 1b Carbon	<u>lbs Carbon</u> 1,000 gal
16	165	82	50.3	-	-
25	12	1	91.6	.021	4.8
20	24	9	62.6	-	-
35	<1				
26	6.3	5.2	17.5	-	-
18	78	0	100	-	-
23	2	<1	>50	-	-
27	7	1	85.7	-	-
17	166	20	88.1	.039	35.5
19					
Averages ¹			89	.03	20.1

¹ Average includes only Plant No. 17 and 25

Table VII-9

Summary TOC Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

Plant	Influent TOC (soluble) mg/L	Effluent TOC (soluble) mg/L	TOC Removal %	Carbon Exhaustion	
				<u>lbs. TOC Removed</u> lb. carbon	<u>lbs. carbon</u> 1,000 gal.
16	87	58	33.4	---	---
25	43	5	88.4	.01	35.9
20	28	12	37.2	---	---
35	34	4	88.3	.13	2.25
26	20	2	90.0	1.35	.12
18	104	19	81.6	.0036	241
23					
27	6	3	50.0	---	---
17	148	20	86.6	.0485	25.4
19	—	—	—	—	—
Average ¹			87	.063	21.77

¹ Average includes Plant Nos. 17, 25, and 35.

	Percent Reduction Factors		Monthly Min. Average Effluent Concn. mg/l
	<u>Range</u>	<u>Average</u>	
BOD ¹	83-99	93	20
COD	63-96	74	-
TSS		65 mg/l ²	30

1. Controlling Parameters
2. Monthly Average

The BPCTCA effluent discharge recommendations will be made only for BOD. The major source of TSS in biological treatment plant effluents are biological solids which, in many cases, are intentionally not wasted for further sludge dewatering but rather are permitted to pass out in the plant effluent. This situation is further compounded in certain plants which have very high TDS, oil, and grease concentrations which tend to hinder settling and thereby contribute to the high effluent TSS.

The major justification for minimum effluent concentration is that a number of the BPCTCA BOD5 RWL data are in the vicinity of 100 mg/l. If BPCTCA reduction factors are applied without due consideration, the resulting effluent concentrations will be below what is achievable with BPCTCA technology. The recommended minimum effluent concentrations were selected based on EPA's preliminary definition of BPCTCA municipal secondary treatment. The minimum TSS concentration is specified for plants attaining the minimum BOD5 concentration. This insures that adequate solids handling facilities will be provided.

To evaluate the economic effects of the BPCTCA effluent limitations on the organic chemicals industry, it was necessary to formulate a BPCTCA treatment model. The model selected was single stage activated sludge. (See Figure VII-7). The BPCTCA design basis are described in Table II-10.

BATEA Treatment Systems

Based on the previous performance data from multiple-stage biological treatment plants, existing carbon treatment plants and various carbon isotherms, it has been possible to formulate waste reduction factors commensurate as BATEA treatment technology:

<u>Parameter</u>	Percent Reduction Factors Applied to BPCTCA	Minimum Monthly Average
	<u>Effluent Limitations</u>	<u>Effluent Concentration</u>
BOD	90	10
COD	69	50
TSS	15 mg/l	10

The BATEA effluent discharge limitations will have two controlling parameters, i.e., BOD and COD. The major emphasis, however, should be on COD removal since the major portion of the

carbonaceous oxygen demanding materials should have been removed with BPCTCA technology.

The BATEA treatment model used for economic evaluation of the proposed limitations included the BPCTCA treatment model followed by the dual media filtration and carbon adsorption. A typical flow diagram is shown in Figure VII-8. The BATEA design basis and the unit sizing criteria are discussed in Table VII-11. The carbon regeneration facilities were sized using 0.41 lb COD removed/lb carbon which is the average result as determined from the carbon isotherm data.

BADCT Treatment Systems

Based on the previous filtration data, it has been possible to formulate waste reduction factors commensurate as BADCT treatment technology:

<u>Parameter</u>	Percent Reduction Factors Applied to BBPCTCA <u>Effluent Limitation</u>	Minimum Monthly Average Average Effluent <u>Concentration</u> ----- mg/liter
BOD	17	10
COD	20	--
TSS	10 mg/l	10

The BADCT treatment model used for economic evaluation of the proposed limitations includes the BPCTCA treatment model followed by dual media filtration.

Figure VII-7
BPCTCA Waste Treatment Model

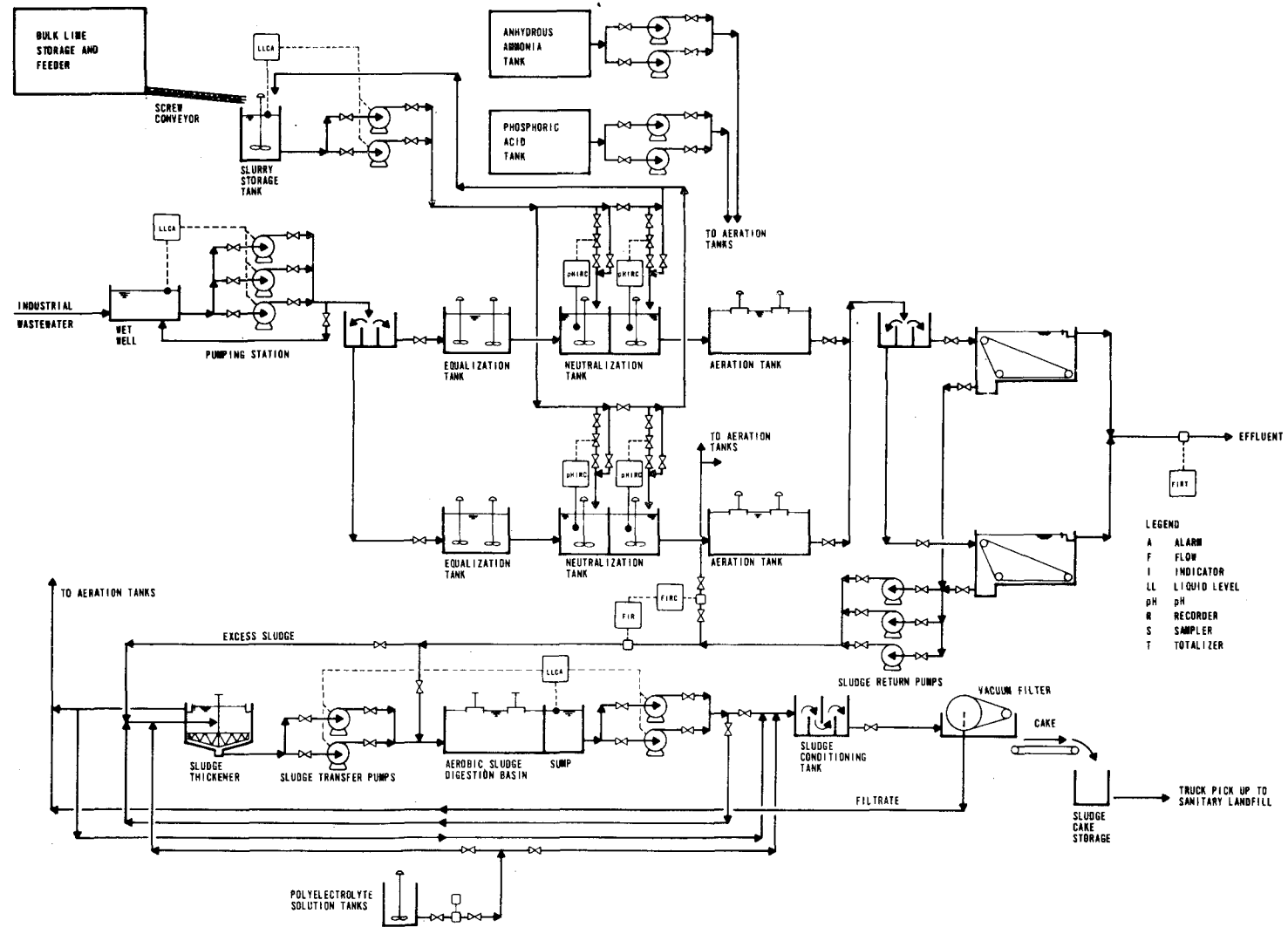


Figure V11-8

BATEA Waste Treatment Model

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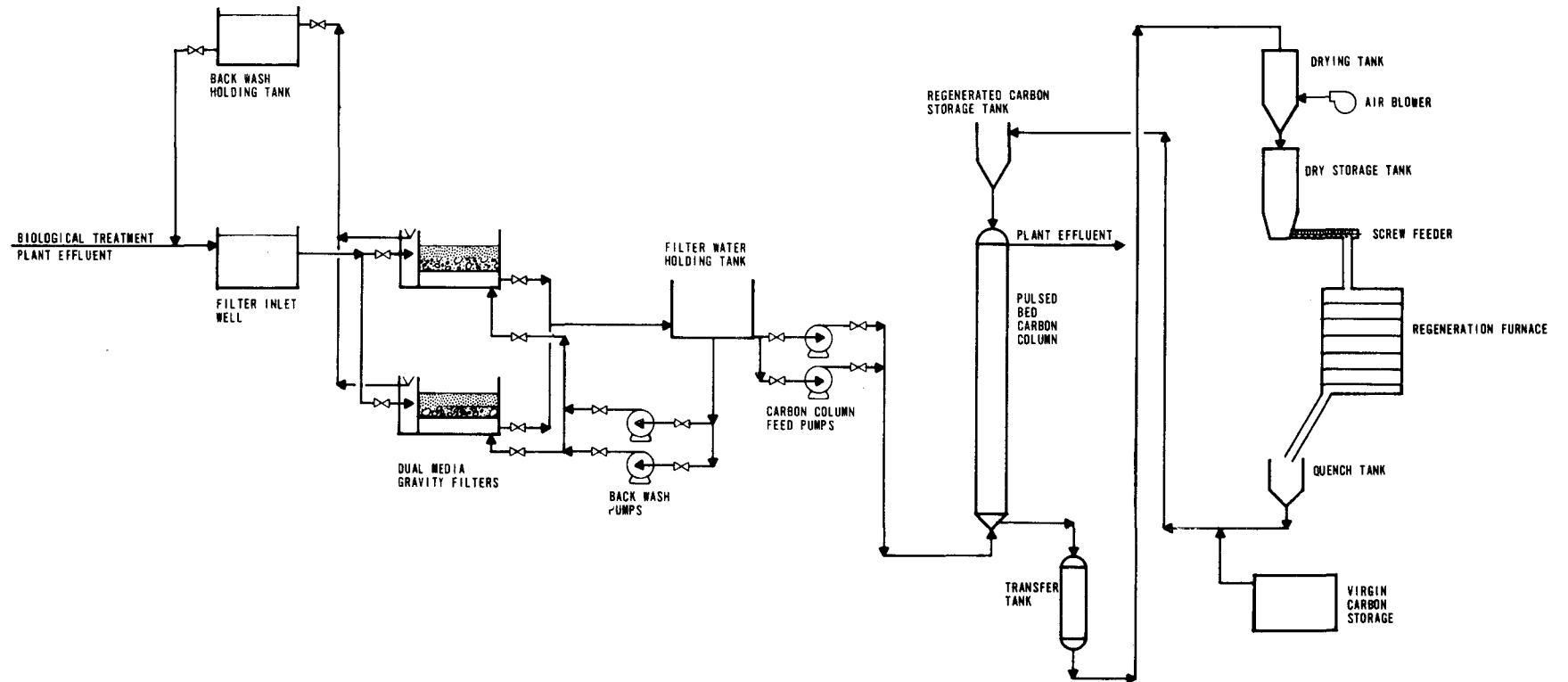


Table VII-10

BPCTCA Model Treatment System Design Summary

Treatment System Hydraulic Loading
(capacities covered, in gpd)

7,200	360,000
43,200	720,000
72,000	1,440,000
216,000	2,160,000

Pump Station

Capacity to handle 200% of the average hydraulic flow

Equalization

One day detention time is provided for Subcategories A, B, and C, and three days for Subcategory D. Floating mixers are provided to keep the content completely mixed.

Neutralization

The two-stage neutralization basin is sized on the basis of an average detention time of twenty minutes. The lime-handling facilities are sized to add 2,000 lb of hydrated lime per mgd of wastewater, to adjust the pH. Bulk-storage facilities (based on 15 days usage) or bag storage is provided, depending on plant size. Lime addition is controlled by two pH probes, one in each basin. The lime slurry is added to the neutralization basin from a lime slurry recirculation loop. The lime handling facilities are enclosed in a building.

Nutrient Addition

Facilities are provided for the addition of phosphoric acid and aqua ammonia to the biological system in order to maintain the ratio of BOD:N at 100:5:1/

Aeration Basin

Platform-mounted mechanical aerators are provided in the aeration basin. In addition, concrete walkways are provided to all aerators for access and maintenance. The following data were used in sizing the aerators:

Oxygen utilization	1.5 lb O ₂ /lb BOD removed
alpha factor	0.9
beta factor	0.9

Wastewater Temperature	20 C
Oxygen transfer	3.5 lb O ₂ /hr/shaft hp
	at 20 C and zero DO in tap water
Motor Efficiency	85%
Minimum Basin DO	1 mg/l

Oxygen is monitored in the basins using D.O. probes.

Secondary Clarifiers

All secondary clarifiers are rectangular units with a length-to-width ratio of 3 to 4. The side water depth is 10 ft. and the overflow rate varies between 100 and 500 gpd/sq ft depending on plant size. Sludge recycle pumps are sized to deliver 100% of the average flow.

Air Flotation

The air flotation units recommended for Subcategory C plants are sized on a solids loading of 20 lbs/sq/ft/day. In addition, liquid polymer facilities are provided to add up to 50 mg/l of polymer to enhance solids separation.

Sludge Holding Tank-Thickener

For the smaller plants, a sludge-holding tank is provided, with sufficient capacity to hold 5 days flow from the aerobic digester. The thickener provided for the large plants was designed on the basis of 6 lb/sq/ft/day and a side water depth of 10 ft.

Aerobic Digester

The aerobic digester is sized on the basis of a hydraulic detention time of 20 days. The sizing of the aerator-mixers was based on 1.25 hp/1,000 cu ft of digester volume.

Vacuum Filtration

The vacuum filters were sized on a cake yield of 2 lb/sq/ft/hr, and a maximum running time of 18 hr/day. The polymer system was sized to deliver up to 10 lb of polymer/ton dry solids.

Final Sludge Disposal

Sludge is disposed of at a sanitary landfill assumed to be 5 miles from the wastewater treatment facility.

Design Philosophy

The plant's forward flow units are designed for parallel flow, i.e., either half of the plant can be operated independently, thus providing reliability as well as flexibility in operation. The sludge facilities are designed on the basis of series flow. All outside tankage is reinforced concrete. The tops of all outside tanks are assumed to be 12" above grade.

Table VII-11

BATEA End of Pipe Treatment System

Design Summary

Gravity Dual-Media Filtration

The filters are sized on the basis of an average hydraulic loading of 3 gpm/sq ft. Backwash facilities are sized to provide rates up to 20 gpm/sq ft and for a total backwash cycle of up to 20 minutes in duration. The filter media are 24" of (No. 1 1/2) and 12" of sand (0.4-0.5 mm sand).

Granular Carbon Columns

The carbon columns are sized on a hydraulic loading of 4 gpm/sq ft and a column detention time of 40 minutes. A backwash rate of 20 gpm/sq ft was assumed for 40% bed expansion at 70°F.

Design Comments:

Subcategory A and B are fixed-bed downflow units, while the Subcategories C and D systems are pulsed-bed upflow unit, with the carbon being wasted over a prescribed time sequence, e.g., wasted for 15 minutes every two hours.

Filter-Column Decant Sump

Tanks are provided to hold the backwash water and decant it back to the treatment plant over a 24 -hour period. This will eliminate hydraulic surging of the treatment units.

Regeneration Furnace

The following exhaustion rates were used for the sizing of the regeneration facilities:

	<u>Influent COD</u>	<u>Exhaustion Capacity</u>
Subcategory	mg/l	lb COD/lb carbon
A	100	4.5
B	120	4.5
C and D	1200	0.35

These exhaustion capacities were selected, based on the carbon isotherm data previously presented in Table VII-8.

A multiple-hearth furnace is employed for regeneration of the carbon only for Subcategory D. The quantities of carbon exhausted based on the previous exhaustion capacities for Subcategories A and B are not sufficiently large to warrant the investment in a regeneration furnace.

Regenerated Exhausted Carbon Storage

Tanks are provided to handle the regenerated and exhausted carbon both before and after regeneration.

Section VIII

COST, ENERGY, AND NONWATER QUALITY ASPECTS

This section provides quantitative information relative to the suggested end-of-pipe treatment models.

The cost, energy, and nonwater quality aspects of in-plant controls are intimately related to the specific processes for which they are developed. Although there are general cost and energy requirements for equipment items (e.g. surface air coolers), these correlations are usually expressed in terms of specific design parameters, such as the required heat transfer area. Such parameters are related to the production rate and specific situations that exist at a particular production site.

Reference to the Tables in Section IV, which show plant sizes for specific process modules, indicates that even in the manufacture of a single product there is a wide variation between process plant sizes. When these production ranges are superimposed on the large number of processes within each subcategory, it is apparent that many detailed designs would be required to develop a meaningful understanding of the economic impact of process modifications. Such a development is really not necessary, because the end-of-pipe models are capable of attaining the recommended effluent limitations at even the highest RWL within any subcategory. The decision to attain the limitations through in-plant controls or by end-of-pipe treatment should be left up to individual manufacturers. Therefore, a series of designs for the end-of-pipe treatment models are provided. These can be related directly to the range of influent hydraulic and organic loadings within each subcategory.

The range of costs associated with these systems can then be divided by the range of production rates for any single process within any category. This will show the maximum range of impact on the required realization of any single product (i.e. the range of impact in terms of \$/lb of product). Total industry cost for BPCTCA is estimated at \$1,030 billion ("Economic Impact of Water Pollution Control in this Organic Chemicals Industry, "Arthur D. Little, Inc., Cambridge, Mass., 1973). It is estimated that this cost includes a substantial portion of capital investment as of 1973.

The major nonwater quality consideration which may be associated with in-process control measures is the use of alternative means of ultimate disposal. As the process RWL is reduced in volume, alternate disposal techniques such as incineration, ocean discharge, and deep-well injection may become feasible. Recent regulations are tending to limit the applicability of ocean discharge and deep-well injection because of the potential long-term detrimental effects associated with these disposal procedures. Incineration is a viable alternative for concentrated waste streams, particularly those associated with Subcategory C.

Associated air pollution and the need for auxiliary fuel, depending on the heating value of the waste, are considerations which must be evaluated on an individual basis for each use.

Other nonwater quality aspects, such as noise levels, will not be perceptibly affected. Most chemical plants generate fairly high noise levels (85-95 dB(A)) within the battery limits because of equipment such as pumps, compressors, steam jets, flare stacks, etc. Equipment associated with in-process or end-of-pipe control systems would not add significantly to these levels. In some cases, substituting vacuum pumps for steam jets would in fact reduce plant noise levels.

As discussed previously, design for the model treatment systems proposed in Section VII were costs estimated in order to evaluate the economic impact of the proposed effluent limitations. The design consideration (namely, the influent RWL) was selected so that it represented the highest expected RWL within each category. This resulted in the generation of cost data for each level of technology

Activated sludge was proposed in Section VII as the BPCTA model treatment system. The plant designs were varied to generate cost effectiveness data within each subcategory. Dual-media filtration and activated carbon adsorption were proposed in Section VII as best available technology economically achievable (BATEA) treatment for Categories A, B, and C. New source end-of-process treatment involves the addition of dual media filtration to biological waste treatment model processes.

Capital and annual cost data were prepared for each of the proposed treatment systems previously discussed in Chapter VII.

The capital costs were generated on a unit process basis, e.g. equalization, neutralization, etc. The following "percent add on" figures were applied to the total unit process costs in order to develop the total capital cost requirements:

<u>Item</u>	<u>Percent of Unit Process Capital Cost</u>
Electrical	12
Piping	15
Instrumentation	8
Site work	3
Engineering design and Construction supervision fees	15
Construction contingency	15

Land costs were computed independently and added directly to the total capital costs.

Annual costs were computed using the following cost basis:

<u>Item</u>	<u>Cost Allocation</u>
Amortization	20 years for capital recovery at 8 percent (10.2% of capital costs)
Operations and Maintenance	Includes labor and supervision, chemicals, sludge hauling and disposal, insurance and taxes (computed at 2 percent of the capital cost), and maintenance (computed at 4 percent of the capital cost).
Power	Based on \$0.02/kw hr for electrical power. Only BATEA Subcategory D (activated carbon regeneration) has a fuel oil allocation.

The following is a qualitative as well as a quantitative discussion of the possible effects that variations in treatment technology or design criteria could have on the total capital costs and annual costs:

<u>Technology or Design Criteria</u>	<u>Cost Differential</u>
1. Use aerated lagoons and sludge dewatering lagoons in place of the proposed treatment system.	1. The cost reduction could be 60 to 70 percent of the proposed figures.
2. Use earthen basins with a plastic liner in place of reinforced concrete construction, and floating aerators versus platform-mounted aerators with permanent-access walkways.	2. Cost reduction could be 10 to 15 percent of the total cost.
3. Place all treatment tanks above grade to minimize excavation, especially if a pumping station is required. Use all-steel tanks to minimize capital cost.	3. Cost savings would depend on the individual situation.
4. Minimize flow and maximize concentrations through extensive in-plant recovery and water conservation, so that other treatment technologies (e.g. incineration) may be economically competitive.	4. Cost differential would depend on a number of items, e.g. age of plant, accessibility to process piping, local air pollution standards, etc.

The recommendation of a level of treatment for BPCTCA comparable to biological treatment fixes the minimum organic removal (expressed as BOD₅) at approximately 90 percent.

The total cost requirements for implementing BPCTCA effluent standards are presented in Table VIII-1. Annual cost adjustment

factors are also shown for 95, 90, and 85 percent removal BOD₅. These factors are shown below:

<u>Percent Removal BOD₅</u>	<u>Subcategory</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
95	1.19	1.0	1.0
90	1.00	0.84	0.88
85	0.86	0.72	0.87

All cost data were computed in terms of August, 1971 dollars, which corresponds to an Engineering News Records Index (ENR) value of 1580. The model treatment system is activated sludge.

The following costs data were abstracted from the preceeding table for a flow of 720,000 gpd and the treatment system required to meet the recommended BPCTCA effluent criteria:

<u>Subcategory</u>	<u>Capital Cost</u> \$	<u>\$/year</u>	<u>Annual Costs</u>		
			<u>\$/1000 gal</u>	<u>\$/lb BOD₅ Removed</u>	<u>Percent BOD₅ Removed</u>
A	1,410,000	284,300	1.08	0.78	90
B	2,538,000	487,900	1.86	0.27	95
C	8,144,000	1,657,000	6.31	0.17	95

The following production capacities were selected for calculating the \$/lb BOD₅ removed: Subcategory A-10 million lb/day, Subcategory B-5 million lb/day, Category C-1 million lb/day,

Higher annual costs for Subcategory C reflect present technology in the industry toward water reuse, which tends to generate very concentrated waste waters. These waste waters require relatively longer aeration times and more extensive sludge handling facilities. As indicated above, any criterion (such as flow) which does not take into consideration the amount of organic removal (e.g. lb BOD₅ removed/day), will not be meaningful in describing the treatment system. The preceeding data on decreasing annual unit cost illustrate treatment system economies of scale.

Total costs as \$/year, \$/1000 gallons and \$/lb BOD₅ Annual costs and effectiveness data for BPCTCA are shown in Table VIII-2 for 95, 90, and 85 percent removal BOD₅. Effluent concentration BOD₅ is also shown for each removal efficiency and subcategory.

Depending on the particular production mix of the individual plant, floating oil could be a treatment consideration. For that reason, an API separator was sized for 720,000 gpd. The capital cost of the separator was then compared with the previously reported capital cost for the 720,000 gpd treatment system designed for each category. The following tabulation represents the percentage increase in capital costs if a separator were required:

Table VIII-1
TOTAL ESTIMATED CAPITAL AND ANNUAL WASTE TREATMENT
COSTS FOR BEST PRACTICABLE CONTROL TECHNOLOGY
CURRENTLY AVAILABLE BY PLANT SIZE AND SUBCATEGORY

ORGANIC CHEMICALS MANUFACTURING INDUSTRY
(Activated Sludge Treatment Model)

Production Capacity Million lb/day Product	Size of Treatment Plant Flow mgd	Costs (1971 Basis)				
		Capital \$	Annual* \$/year	\$/1000 gal	% Reduction BOD ₅	\$/lb BOD ₅ Removed
	<u>Subcategory A</u>					
10	0.072	588,000	107,600	4.09	90	0.29
10	0.72	1,410,000	284,300	1.08	90	0.78
	<u>Subcategory B</u>					
5	0.072	629,000	117,700	4.48	95	0.06
5	0.72	2,538,000	487,900	1.86	95	0.27
5	2.16	3,754,000	745,800	0.94	95	0.41
	<u>Subcategory C</u>					
1.0	0.072	2,895,000	527,000	20.05	95	0.05
1.0	0.72	8,144,000	1,657,000	6.31	95	0.17
1.0	2.16	13,290,000	2,917,300	3.70	95	0.30

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*Annual Cost Adjustment Factors:

<u>% Reduction BOD₅</u>	<u>Subcategory A</u>	<u>Subcategory B</u>	<u>Subcategory C</u>
95	1.19	1.00	1.00
90	1.00	0.84	0.88
85	0.86	0.72	0.87

Table VIII-2

TOTAL COSTS** AND EFFECTIVENESS DATA - BPCTCA
ORGANIC CHEMICALS MANUFACTURING INDUSTRY

SUBCATEGORY A NON-AQUEOUS PROCESSES

<u>Annual Costs</u>	<u>Percent Removal, BOD₅</u>	<u>Effluent Concentration, mg/liter BOD₅</u>	<u>Size of Treatment Plant, mgd</u>		
			<u>0.072 mgd</u>	<u>0.72 mgd</u>	<u>2.16 mgd</u>
<u>\$/year</u>	95	15	128,000	338,300	No Data
	*90	30	107,600	284,300	Available
	85	45	92,500	244,500	
<u>\$/1000 gallons</u>	95	15	4.87	1.28	
	*90	30	4.09	1.08	
	85	45	3.52	0.93	
<u>\$/lb BOD₅ Removed</u>	95	15	0.32	0.88	
	*90	30	0.28	0.78	
	85	45	0.25	0.71	

SUBCATEGORY B PROCESSES WITH PROCESS WATER CONTACT AS STEAM DILUENT OR ABSORBENT

<u>\$/year</u>	*95	30	117,700	487,900	745,200
	90	60	98,900	409,800	626,000
	85	90	84,700	351,300	536,500
<u>\$/1000 gallons</u>	*95	30	4.48	1.86	0.94
	90	60	3.76	1.56	0.79
	85	90	3.22	1.34	0.68
<u>\$/lb BOD₅ Removed</u>	*95	30	0.060	0.27	0.41
	90	60	0.059	0.27	0.41
	85	90	0.049	0.22	0.33

* Basis for recommended effluent limitations

SUBCATEGORY C AQUEOUS LIQUID PHASE REACTION SYSTEMS

<u>Annual Cost</u>	<u>Percent % Removal, BOD₅</u>	<u>Effluent Concentration, mg/liter BOD₅</u>	<u>Size of Treatment Plant, mgd</u>			
			<u>0.072 mgd</u>	<u>0.36 mgd</u>	<u>0.72 mgd</u>	<u>2.16 mgd</u>
<u>\$/year</u>	*95	45	527,000	No Data	1,657,000	2,917,300
	90	90	463,800	Available	1,458,000	2,567,200
	85	135	458,500		1,441,600	2,538,000
<u>\$/1000 gallons</u>	*95	45	20.05		6.31	3.70
	90	90	17.64		5.55	3.26
	85	135	17.44		5.48	3.22
<u>\$/lb BOD₅ Removed</u>	*95	45	0.050		0.17	0.30
	90	90	0.046		0.16	0.28
	85	135	0.048		0.17	0.29

<u>Subcategory</u>	<u>Percentage Increase In Capital Costs</u>
A	9
B	5
C	2

Sludge cake quantities from vacuum filtration corresponding to each treatment system design are presented in Supplement A. The following table summarizes the general ranges of sludge quantities generated by plants in each subcategory:

<u>Subcategory</u>	<u>Cu yd/year*</u>
A	30 - 200
B	30 - 2,000
C	1,500 - 44,000

*1% net-weight basis

Particular plants within Subcategory C may be amenable to sludge incineration because of the large quantities of sludge involved. For example, sludge incineration would reduce the previous quantities by about 90 percent. Sludge cake is 80 percent water, which is evaporated during incineration, and more than half of the remaining (20 percent) solids are thermally oxidized during incineration. Sludge incineration costs were not evaluated for those specific cases in Subcategory C, because the particular economics depend to a large degree on the accessibility of a sanitary landfill and the relative associated haul costs.

Before discussing the actual variations in costs within each category, the following discussion is presented to help visualize the complexities involved in evaluating cost effectiveness data. Every treatment system is composed of units whose design basis is primarily hydraulically dependent, organically dependent, or a combination of the two. The following is a list of the unit processes employed, and a breakdown of the design basis:

<u>Hydraulically Dependent</u>	<u>Organically Dependent</u>	<u>Hydraulically and Organically Dependent</u>
Pump station	Thickener	Aeration basin
API separator	Aerobic digester	Oxygen transfer eqpt.
Equalization	Vacuum filter	Air flotation unit
Neutralization		
Nutrient addition		
Sludge recycle pump		
Clarifier		

The annual cost associated with the hydraulically dependent unit processes is not a function of effluent level. On the other hand, the sizing of the organically dependent units should theoretically vary in direct proportion to the effluent level: e.g. reducing the BOD₅ removal from 95 to 85 percent should reduced the sizes of the sludge handling equipment by

approximately 10 percent. However, there are two complicating factors: 1) only a relatively few sizes of commercially available equipment; and 2) broad capacity ranges. These two factors, especially in regard to vacuum filters, tend to negate differentials in capital cost with decreasing treatment levels.

The relationship between design varying contaminant levels and the design of aeration basins and oxygen transfer equipment is somewhat more complex. The levels are dependent on the hydraulic flow, organic concentration, sludge settleability, and the relationship between mixing and oxygen requirements. For example, to reach a particular effluent level, the waste water's organic removal kinetics will require a particular detention time at a given mixed-liquor concentration. The oxygen transfer capacity of the aerators may or may not be sufficient to keep the mixed liquor suspended solids in suspension within the aeration basin. Therefore, the required horsepower would be increased merely to fulfill a solids mixing requirement. Alternatively, the oxygen requirements may be such that the manufacturer's recommended minimum spacing and water depth requirements would require that the basin volume be increased to accommodate oxygen transfer requirements.

Capital and annual costs for new sources are presented in Table VIII-3. The treatment model used, in developing the costs is activated sludge followed by dual media filtration. The same annual cost adjustment factors applicable to BPCTCA are also relevant to new sources due to the similarity of these systems. As expected, the end-of-pipe costs are not appreciably higher than those for BPCTCA. The following information was extracted from Table VII-3

<u>Subcategory</u>	<u>Capital Costs</u> \$	<u>Annual Costs</u>		
		<u>\$/year</u>	<u>\$/1000 gal</u>	<u>\$/lb BOD₅ Removal</u>
A	1,524,000	302,900	1.15	0.83
B	2,652,000	511,000	1.94	0.28
C	8,258,000	1,710,700	6.51	0.17

The following production capacities were selected for calculation of the \$/lb BOD₅ removed: Subcategory A-10 million lb/day, Subcategory B-5 million lb/day, Subcategory C-1 million lb/day and

Capital and annual costs are calculated for the best available technology economically achievable model treatment systems. These systems are described as follows: two stage biological treatment plus dual media filtration and activated carbon. Activated carbon treatment for Subcategories A and B consists of fixed bed columns. For Subcategories C pulsed bed columns with a carbon regeneration system are recommended. Costs are presented in Table VIII-4 for the BATEA model treatment system. The following information is extracted from this table for a 720,000 gallon per day facility.

Table VIII-3
TOTAL CAPITAL AND ANNUAL WASTE TREATMENT COSTS FOR
NEW SOURCES WITH BEST AVAILABLE DEMONSTRATED
CONTROL TECHNOLOGY BY PLANT SIZE AND SUBCATEGORY

ORGANIC CHEMICALS MANUFACTURING INDUSTRY
(Activated Sludge and Filtration Treatment Model)

Production Capacity Million lb/day Product	Size of Treatment Plant Flow mgd		Costs (1971 Basis)					
			Capital	Annual	*			
			\$	\$/year		\$/1000 gal	% Reduction BOD ₅	\$/lb BOD ₅ Removed
	<u>Subcategory A</u>							
10	0.072	632,000	114,300	4.34	90	0.31		
10	0.72	1,524,000	302,900	1.15	90	0.83		
	<u>Subcategory B</u>							
5	0.072	673,000	124,800	4.75	95	0.07		
5	0.72	2,652,000	511,000	1.94	95	0.28		
5	2.16	3,934,000	781,800	0.99	95	0.43		
	<u>Subcategory C</u>							
1	0.072	2,939,000	543,000	20.66	95	0.055		
1	0.72	8,258,000	1,710,700	6.51	95	0.17		
1	2.16	13,470,000	3,013,000	3.82	95	0.31		

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*Annual Cost Adjustment Factors:

<u>% Reduction BOD₅</u>	<u>Subcategory A</u>	<u>Subcategory B</u>	<u>Subcategory C</u>
95	1.19	1.00	1.00
90	1.00	1.84	0.08
85	0.86	0.72	0.87

<u>Subcategory</u>	<u>Capital Cost</u> \$	<u>Annual Costs</u>		
		<u>\$/year</u>	<u>\$/1000 gal</u>	<u>\$/lb COD Removal</u>
A	2,498,000	477,100	1.82	0.47
B	3,626,000	682,500	2.60	0.11
C	10,410,000	2,110,500	8.03	0.10

The following production capacities were selected for calculation of the \$/lb COD removal: Subcategory A-10 million lb/day, Subcategory B-5 million lb/day, Subcategory C-1 million lb/day

Table VIII-4
TOTAL ESTIMATED CAPITAL AND ANNUAL WASTE TREATMENT COSTS FOR
BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE
(1983 STANDARD) BY SIZE OF PLANT AND SUBCATEGORY

ORGANIC CHEMICALS MANUFACTURING INDUSTRY
(Biological Treatment, Filtration, and Activated Sludge Treatment Model)

Production Capacity Million lb/day Product	Size of Treatment Plant Flow mgd	Costs (1971 Basis)				
		Capital \$	Annual \$/year	\$/1000 gal	Overall % Removed COD	\$/lb COD Removed
<u>Subcategory A</u>						
10	0.072	861,000	143,500	5.46	90	0.14
10	0.720	2,498,000	477,100	1.82	90	0.47
<u>Subcategory B</u>						
5	0.072	902,100	153,900	5.86	94	0.025
5	0.72	3,626,000	682,500	2.60	94	0.11
5	2.16	5,853,000	1,210,500	1.53	94	0.19
<u>Subcategory C</u>						
1	0.072	3,466,100	607,300	23.10	94	0.029
1	0.72	10,410,000	2,110,500	8.03	94	0.10
1	2.16	17,663,000	4,028,700	5.11	94	0.19

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE - EFFLUENT LIMITATIONS

Best practicable control technology currently available (BPCTCA) for the organic chemical industry is based on the utilizations of both in process controls and end-of-process treatment technologies.

Alternative in-process controls commensurate with BPCTCA include the implementation of process observation and sampling to determine the quantity, compositions, concentration, and flow of the process waste streams. Such waste characterization studies logically lead to the selection of various process waste sources for segregation. Exemplary plants within the industry segregate contaminated contact process water streams from non-contaminated streams such as cooling water. This practice appreciably reduces the waste volume to be treated in a centralized waste treatment plant. In addition process water streams are segregated on the basis of the ease with which certain constituents can be recovered as well as the ease with which the wastes can ultimately be treated.

Process modification consistant with BPCTCA include the substitution of nonaqueous media in which to carry out the reaction or to purify the products. In some cases aqueous waste by-products are eliminated by changes in the reactants, reactant purity, or catalyst system. Where waste is used in the process, its use should be restricted and the possibility of using recycled or reused water should be investigated. Examples of this practice include recycle between an absorber and a steam stripper, countercurrent washing techniques, and the collection of vacuum-jet condensate, rain water and floor water for reuse.

Equipment associated with the separation of an organic phase from an aqueous phase, such as decanters, are provided with backup coalescers or polishing filters for the aqueous phase. Direct vacuum-jet condensers are replaced with indirect condensers or vacuum pumps.

In addition to waste reductions obtained through segregations and process change, exemplary plants using BPCTCA combine recovery of products and by-products with waste water purifications. The recovery of chemicals from the waste waters includes both the physical separation of chemicals from the waste water as well as subjecting the waste water to additional chemical reactions that will render them more amenable to recovery and purification.

Physical separation processes utilized by exemplary plants include adsorption, solvent extration, and distillation. Adsorbents in use include activated carbon, zeolites, and synthetic resins. The adsorbed chemicals are recovered by desorption which also serves to regenerate the saturated adsorbent. One system for the non-destructive, inplace,

regeneration of activated carbon is the use of pH change to cause the adsorbed chemicals to desorb. Such a system has been used successfully to recover phenol and acetic acid by the addition of caustic.

Solvent extraction is used for the recovery of phenol from the waste water of the cumene process for phenol manufacture. Solvent extraction is practiced when the chemical can be extracted into a solvent already in use in the process. Excess solvent is steam stripped from the effluent. Effluent phenol concentration is expected to average less than 1 mg/liter from the treatment system.

Distillation is used to recover by-products from reduced volume waste water streams by steam stripping. This concentration step produces an overhead condensate containing the strippable organic substances and water. This condensate is then reused in the process. Exemplary plants utilizing either solvent extraction or steam distillation of waste waters usually apply additional polishing treatment to the effluent to remove the small remaining quantities of organic substances.

Chemical reactions such as chlorination, hydrolysis, cracking, dechlorination and dealkylation have been used to convert impurities into forms suitable for subsequent physical separations. A typical example is the hydrolysis of aromatic tars with caustic with subsequent acidification and physical separation of the organic and aqueous phases.

It is not possible to delineate a specific sequence or combination of in-process controls which could be considered as an across the board definition of BPCTCA. However, methods taken from those previously described and end-of-process treatment systems should enable all processes within each category to attain the BPCTCA effluent limitations. Mean raw waste loads were calculated for each subcategory group and are shown in Table IX-1. These raw waste loads were the basis for determining the BPCTCA effluent limitations. This data is also presented in Sections IV and V (Tables V-1, V-2 and V-3).

End-of-pipe treatment technologies commensurate with BPCTCA are based on the utilization of biological systems including the activated sludge process, extended aeration, aerated lagoons, trickling filters, and anaerobic and facultative lagoons. These systems include additional treatment operations such as equalization, neutralization, primary clarification with oil removal, and nutrient addition. Because the removal of certain organic materials may require the utilization of high concentrations of biological solids, effluent polishing steps such as coagulation, sedimentation, and filtration are considered as commensurate with BPCTCA. Effluent suspended solids are expected to be maintained below 60 mg/liter for the maximum 30 average limitation and 135 mg/liter for the maximum daily limitation.

Phenols limitations are based upon an average effluent 0.01 kg/kg production for three product-process segments: cumene process, bisphenol A and p-cresol manufacturing. This represents 99.9 percent reduction of the standard raw waste load of phenols for these processes (10 kg/kg production).

Effluent limitations for BPCTCA have been listed in Table II-2. Table IX-1 contains a summary of the raw waste load data for each subcategory group. Detailed summaries have been presented in Tables V-1, V-2 and V-3. Table IX-1 shows the method utilized in deriving BPCTCA effluent limitation guidelines.

It should be noted that because biological systems have been proposed as the mode of treatment consistent with BPCTCA, the BOD₅ parameter is controlling and is the only one for which the effluent limitations are to be applied. It may be desirable in certain cases to establish limitations for COD or TOC instead of the BOD₅ parameter. The feasibility of such a substitution can only be determined on an individual basis after adequate correlation has been established.

Effluent limitations are specified on the bases of the maximum for any one day and the maximum average of daily values for any period of 30 consecutive days. The rationale and basis for determining the daily and monthly maximum variations are presented in Section XIII.

TABLE IX - 1
Summary of Mean Raw Waste Load Data (RWL) and Bases
for Effluent Limitations
BPCTCA

Subcategory	Mean Process Waste Flow, liter/kg	-BOD- (4)			COD			Mean TSS 30mg/liter)
		Mean RWL kg/kg	Reduction Factor	Mean BPCTCA Effluent kg/kg (1)	Mean RWL, kg/kg	Reduction Factor	Mean BPCTCA Effluent kg/kg (2)	
A	500 (5)	0.1	N.S.	0.01 (3)	0.22	0.74	0.057	0.015
B ₁	1,460	0.38	N.S.	0.029 (3)	4.0	0.74	1.04	0.044
B ₂	10,550	1.75	N.S.	0.21 (3)	3.85	0.74	1.00	0.32
C ₁	3,119	0.56	N.S.	0.062 (3)	2.59	0.74	0.67	0.094
C ₂	4,103	3.03	0.96	0.12	6.75	0.74	1.75	0.12
C ₃	1,284	25.5	0.99	0.25	30.1	0.74	7.83	0.034
C ₄	23,819 (5)	68.5	0.99	0.68	195	0.74	50.7	0.63

N.S. indicates value not specified (less than 93 percent removal BOD₅ required for 20 mg/liter BOD₅ effluent).

(1) BOD₅ is the control oxygen demand parameter for which effluent limits are calculated on the daily maximum basis (X 4.5) and maximum 30 day average basis (X 2.0).

(2) COD guidelines are calculated on basis of average performance of exemplary plants (74 percent removal COD) and variability factors for daily maximum (X 3.4) and maximum 30 day average (X 2.0).

(3) Value derived by the mean flow X 20 mg/liter BOD₅

(4) BOD₅ is the control oxygen demand parameter.

(5) Median value

Effluent limits for phenols are applicable to the cumene process (Subcategory C₂), bisphenol A (Subcategory C₃) and p - cresol (Subcategory C₄) at average effluent concentration <1 mg/liter (0.01 kg/kg). Effluent limitations are based on daily maximum (X 4.5) and maximum 30 day average (X 2.0).

SECTION X
Best Available Technology Economically
Achievable (BATEA)

The best available technology economically achievable is based upon the most exemplary combination of in-process and end-of-process treatment and control technologies.

The full range of treatment and control technologies which are applicable to the major organic chemicals segment of the organic chemicals manufacturing industry has been described in Section VII. This level of technology is primarily based upon significant reductions in the chemical oxygen demand (COD), as well as the biochemical oxygen demand pollutant parameters.

The model end-of-process treatment system has been determined to be biological plus additional activated carbon treatment. It must be noted that this does not preclude the use of activated carbon as an in-process treatment in lieu of its use at the end-of-process. This may be desirable when product can be recovered or when harmful pollutants must be removed prior to treatment.

Two model systems are presented for cost estimation purposes:

1. Activated sludge treatment followed by filtration and activated carbon adsorption in fixed-bed columns (applied to Subcategories A and B)
2. Activated sludge treatment followed by carbon adsorption in pulsed bed columns (applied to Subcategory C).

The performance of these treatment systems has been discussed in Section VII - Control and Treatment Technologies.

These systems or equivalent combinations can provide the reduction in BOD₅ and COD pollutant parameters as listed below:

BOD 90 percent reduction (BATEA is
 10 percent of BPCTCA effluent)

COD 69 percent reduction (BATEA is
 31 percent of BPCTCA effluent)

Effluent limitations guidelines for BATEA were calculated by applying these reduction factors to average effluent for BPCTCA.

These are specific subcategories where the direct use of these reduction factors will still result in effluent concentrations which are below the capabilities of the control systems considered as BATEA. In the case of Subcategories A, B1, B2, C1, C2, and C4, effluent limitations guidelines for BATEA were obtained by applying minimum concentrations of 10 mg/liter BOD₅ to the mean waste water flow for each subcategory group. COD effluent limitations were derived in a similar manner for Subcategories A and B2 with a mean COD effluent concentration of 50 mg/liter.

It is noted that the BATEA requires suspended solids removal to an average concentration of 15 mg/liter through the use of filtration. This concentration limitation should again be applied to the total effluent from any multi process facility.

Effluent limitations for phenolic compounds are based upon an achievable concentration of 0.1 mg/liter phenolic compounds by the model BATEA treatment system. These limitations apply to the following product-process segments: cumene process, bisphenol A and p-cresol manufacturing. Effluent limitation for phenols also assure an achievable reduction of 99.99 percent of the initial raw waste values.

Effluent limitations are based on the daily maximum and maximum 30 day average basis. Variability factors applicable to the model system were based upon engineering judgements of the variability associated with the 99/50 ratio of probability of occurrence. For the COD parameter the following factors apply to the daily maximum limitation and the maximum 30 day average limitations: 2.5 and 1.8 respectively. For BOD5, TSS and phenols the applicable ratios are 3.0 and 1.7 respectively.

Table X-1
Summary of Basis for BATEA Effluent Limitations

Subcategory	-BOD5-			-COD-			TSS
	Average BPCTCA Effluent	Reduction Factor	Average (3) BATEA Effluent	Average BPCTCA Effluent	Reduction Factor	Average (4) BATEA Effluent	BATEA Effluent (3) @ 15 mg/liter
A	0.01	N.S.	0.005 (1)	0.057	N.S. (2)	0.025	0.0075
B ₁	0.029	N.S.	0.014 (1)	1.04	0.69	0.32	0.022
B ₂	0.21	N.S.	0.10 (1)	1.00	N.S. (2)	0.53	0.16
C ₁	0.062	N.S.	0.03 (1)	0.67	0.69	0.21	0.047
C ₂	0.12	N.S.	0.04 (1)	1.75	0.69	0.54	0.062
C ₃	0.25	0.90	0.025	7.83	0.69	2.43	0.017
C ₄	0.68	N.S.	0.21 (1)	50.7	0.69	15.7	.32

N.S. indicates value not specified (less than 90% removal BOD5 and 69% removal COD).

(1) Value derived by minimum achievable effluent concentration of 10 mg/liter BOD5.

(2) Value derived by minimum achievable effluent concentration of 50 mg/liter COD.

(3) Variability factors for daily maximum limit (X 3.0) and maximum 30 day average limit (X 1.7) are used to derive limitations.

(4) Variability factors for daily maximum limit (X 2.5) and maximum 30 day average limit (X 1.8) are used to derive limitations.

Phenols limits for cumene process (Subcategory C₂), bisphenol A (Subcategory C₃) and p cresol (Subcategory C₄) based on average concentration of 0.1 mg/liter (0.001 kg/kg) and variability factors for daily maximum (3.0) and maximum 30 day average (1.7)

SECTION XI

New Source Performance Standards

Determination of the best available demonstrated control technology (BADCT) for new major organic sources involves the evaluation of the most exemplary in-process control measures with exemplary end of process treatment. Some major in-process controls which were fully described in Section VII are applicable to new sources as follows:

- (1) The substitution of non-contact heat exchangers using air, water or refrigerants for direct contact water cooling equipment (barometric condensers);
- (2) The use of nonaqueous quench media, e.g. hydrocarbons such as furnace oil, as a substitute for water, where direct contact quench is required;
- (3) The recycle of process water, such as between absorber and stripper;
- (4) The reuse of process water (after treatment) as make-up to evaporative cooling towers through which noncontact cooling water is circulated;
- (5) The reuse of process water to produce low pressure steam by non-contact heat exchangers in reflex condensers or distillation columns;
- (6) The recovery or spent acid or caustic solutions for reuse;
- (7) The recovery and reuse of spent catalyst solutions;
- (8) The use of nonaqueous solvents for extraction of products.

Although these control measures are generally applicable, no attempt was made to identify all of these or any single one as universally applicable.

The end of process treatment model has been determined to be biological treatment with the additional suspended solids removal by clarification, sedimentation, sand and/or dual media filtration. The following system is proposed for cost estimating purposes and does not limit the use of equivalent systems: two stage activated sludge plus dual medium filtration. These costs are presented in Section VIII.

Although biological treatment has been described as the basis for the BADCT, it is recognized that chemical-physical systems such as activated carbon may also be employed as an end-of-process technology or as an in-process or by-product recovery system. It may also be necessary to remove certain wastes which are toxic to or interfere with biological waste treatment systems by in-process chemical-physical control processes.

Reductions in the BOD5 and COD parameters were obtained through laboratory evaluations of the effluent from activated sludge treatment systems sampled during the Phase II study. These

results have been incorporated in the Phase I report and are indicated in Section VII, Control and Treatment Technology. These reductions were applied to the effluent obtained from BPCTCA and are listed in as follows:

BOD5 17% reduction (BADCT effluent is 83% of BPCTCA effluent).

COD 20% reduction (BADCT effluent is 80% of BPCTCA effluent).

As with BPCTCA, the major oxygen demand pollutant parameter is BOD5 for which effluent limitations guidelines are established. TSS limitations are based upon an achievable concentration of 15 mg/liter. Phenolic compounds are limited for the cumene process, bisphenol A and p-cresol manufacturing. These limits were established on the same basis as BPCTCA with an achievable effluent concentration of less than 1 mg/liters. This represents a 99.9 percent reduction of the average raw waste load for phenolics in each of these product-process segments.

The variability associates with the BADCT model treatment process was determined to be the same as that for BPCTCA since both systems are identical except for filtration which is added to the biological system for BADCT. The factors which represent the 99/50 ratio of probability of occurrence for daily maximum and maximum 30 day average limitations are 4.5 and 2.0 respectively and apply to the average limitations for BOD5, phenols, and TSS.

TABLE XI -1
Summary of Basis for New Source Standard (BADCT)

Subcategory	-BOD- (3)			COD			Average (1) TSS 15 mg/liter
	Average BPCTCA Effluent, kg/kg	Reduction Factor	Average BADCT (1) Effluent, kg/kg	Average BPCTCA Effluent, kg/kg	Reduction Factor	Average BADCT (2) Effluent kg/kg	
A	0.01	0.17	0.008	0.057	0.20	0.046	0.0075
B ₁	0.029	0.17	0.024	1.04	0.20	0.83	0.022
B ₂	0.21	0.17	0.17	1.00	0.20	0.80	0.16
C ₁	0.062	0.17	0.05	0.67	0.20	0.54	0.047
C ₂	0.12	0.17	0.10	1.75	0.20	1.4	0.062
C ₃	0.25	0.17	0.21	7.83	0.20	6.26	0.017
C ₄	0.68	0.17	0.57	50.7	0.20	40.56	0.32

(1) Variability factors for the daily maximum (X 4.5) and maximum 30 day average (X 2.0) are used to derive effluent limitations.

(2) Variability factors for daily maximum guideline (X 3.4) and maximum 30 day average guideline (X 2.0) were employed.

(3) BOD5 is the control oxygen demand parameter.

Phenols limits for cumene process (Subcategory C₂), bisphenol A (Subcategory C₃) and p cresol (Subcategory C₄) are based upon an average concentration of 1 mg/liter 10.01 kg/kg in the effluent and variability factors for daily max (X 4.5) and maximum 30 day average (X 2.0).

SECTION XII

PRETREATMENT GUIDELINES

Pollutants from specific processes within the organic chemicals industry may interfere with, pass through, or otherwise be incompatible with a publically owned treatment works. The following section examines the general waste water characteristics of the industry and the pretreatment unit operations which may be applicable.

A review of the waste water characteristics indicated that certain products can be grouped together on the basis of pollutants requiring pretreatment. Accordingly, the previously determined subcategories were divided into two Sub-groups as follows:

Subgroup 1

Subcategory A
Subcategory B

Subgroup 2

Subcategory C

The principal difference in the general characteristics of the process waste waters from the manufacture of chemicals in these two Sub-Groups is that the waste waters of Subgroup 1 are more likely to include significant amounts of free and emulsified oils, whereas the wastewaters of Subgroup 2 are more likely to include significant amounts of heavy metals.

Detailed analyses for specific products in the industry are presented in Supplement B.

The types and amounts of heavy metals in the waste water depend primarily on the manufacturing process and on the amounts and types of catalysts lost from the process. Most catalysts are expensive and, therefore, recovered for reuse. Only unrecoverable catalysts (metals), generally in small concentrations, appear in the waste water. The products and processes in Subgroup 2 are most likely to have metals in their waste water.

The manufacture of acrylonitrile (Subcategory C) produces a harmful waste water which is difficult to treat biologically. The harmful characteristics have been attributed to the presence of hydrogen cyanide in excessive quantities (500 to 1,800 mg/l). In addition, the waste water is generally acidic (pH 4 to 6) and contains high concentrations of organic carbon. These waste waters are generally segregated from other process wastes and disposed of by other means (e.g. incineration), and they are not generally discharged to municipal collection systems. For these reasons, the pretreatment unit operations developed in the following section do not include the process waste waters from the manufacture of acrylonitrile.

Table XII-I shows the pretreatment unit operations which may be necessary to protect joint waste water treatment processes.

Oil separation may be required when the oil content of the waste water exceeds 10 to 15 mg/l.

The heavy metals present in organic chemical wastes are in many cases so low in concentration that metals removal is not required from the standpoint of treatability characteristics. However the effluent limitations for metals and harmful pollutants may require additional pretreatment (chemical precipitation) for removal of these materials.

The pretreatment unit operations generally consist of equalization, neutralization, and oil separation. In addition, phenol recovery (to reduce the phenol concentration) and spill protection for spent acids and spent caustics may be required in some cases.

Biological Treatment Inhibition

The survey data collected during the sampling program were examined from the standpoint of the occurrence of specific pollutants which may inhibit biological treatment. This review indicated agreement with the results of the comprehensive study of biological treatment in EPA's Federal Guidelines-Pretreatment of Discharges to Publicly Owned Treatment Works, and no changes in the lists of inhibitory pollutants are warranted.

The following is a brief discussion of the reference material used to determine the phenol and iron values. Phenol is biologically degradable in an acclimated system. McKinney, for example, reports that concentrations as high as 2,000 to 3,000 mg/l of mixed phenolic substances are degradable in a properly designed system. However, concentrations as low as 50 mg/l can inhibit biological treatment if the organisms are not properly acclimated. Nemerow has reported in his literature review that concentrations of iron on the order of 5 mg/l can be inhibitory to anaerobic sludge digestion.

Concentrations of iron on the order of 5 mg/l have been reported by Nemerow to be inhibitory to anaerobic sludge.

SECTION XIII

ALLOWANCE FOR VARIABILITY IN TREATMENT PLANT PERFORMANCE

As previously discussed in End-of-Pipe Treatment in Section VII, the historic treatment plant data were analyzed on the basis of monthly averages. Subsequent effluent limitations for BPCTCA, BADCT, and BATEA were based on both the maximum for any one day (daily maximum) and maximum average of daily values for any period of thirty consecutive days.

Daily historic data from two biological treatment plants treating Subcategory C waste waters were reviewed; weekly and consecutive thirty day averages were calculated, and then the data were analyzed statistically. The results of these analyses are summarized in Table XIII-1.

The significance of the data is that a biological treatment plant on the average (50% of the time) is producing an effluent with a BOD₅ concentration of 20 mg/l, will also produce an effluent with 90 mg/l of BOD₅ 5% of the time.

Variations in the performance of a treatment plant are attributable to one or more of the following:

1. Seasonal variations in waste water temperature which either accelerate or depress the biological kinetics.
2. Variations in the sampling technique or in the analytical procedures.
3. Variations in one or more operating parameters, e.g., amount of sludge recycle, dissolved oxygen in the aeration basin, etc., which can affect performance.
4. The relationship of the plant's hydraulic and organic loading to the plant's design values. The degree of underloading or overloading could be reflected in performance.
5. In-plant process bottle necking which can be responsible for degrading the effluent when seasonal loadings strain these particular facilities. For example, inadequate sludge handling facilities during peak periods of sludge production may require modified wasting of the sludges. The overall effect would manifest itself in an increase in TSS and BOD₅ in the plant effluent.

These variations are purely a function of the treatment plant design and performance. They will still occur even if the treatment plant has provisions for equalization of variations in the influent raw waste load which it receives.

Table XIII-1

Effluent Variation of Biological
Treatment Plant Effluent

	Probability of Occurrence % less than or equal to	BOD			COD			TOC		
		Daily mg/L	Weekly mg/L	Monthly mg/L	Daily mg/L	Weekly mg/L	Monthly mg/L	Daily mg/L	Weekly mg/L	Monthly mg/L
340	10	6	10	12	180	270	400	55	65	67
	20	9	13	14	250	350	590	67	74	76
	30	13	16	16	320	415	560	78	82	82
	40	16	17	18	390	485	630	88	90	89
	50	20	20	20	470	555	700	100	98	96
	60	25	26	22	570	640	780	110	105	103
	70	30	26	25	690	740	880	130	115	111
	80	40	30	29	870	880	1000	150	130	122
	90	60	40	35	1200	1130	1230	180	150	140
	95	90	50	40	1600	1400	1430	220	170	150
	99	160	70	55	2500	2000	1940	300	210	185

Selected statistical data in Table XIII-1 were examined to compare the ratios of the 99% probability of occurrence to the 50% probability of occurrence, the 95% to the 50% value, and the 90% to the 50% value, as shown below:

<u>Ratio of Probability</u>	<u>Daily</u>	<u>BOD5</u>	<u>Weekly</u>	<u>Thirty Consecutive Day Period</u>
99/50	8.0		3.5	2.7
95/50	4.5		2.5	2.0
90/50	3.0		2.0	1.7
		<u>COD</u>		
99/50	5.3		3.6	2.8
95/50	3.4		2.5	2.0
90/50	2.5		2.0	1.8
		<u>TOC</u>		
99/502	3.0		2.2	1.9
95/50	2.2		1.7	1.6
90/50	1.8		1.5	1.4

Plants A and B have primary settling and nutrient addition. In Plant A, there are four parallel trains of 3 aeration basins each for a total of 12 basins. Flow from each of the parallel trains goes to a clarifier. Additional organic and solids removal is accomplished by using an aerated polishing lagoon.

Plant B has two parallel trains of 3 aeration basins each for a total of 6 basins. Clarification and air flotation are provided in order to reduce the aeration basin mixed liquor (MLSS) which average about 7-8,000 mg/l of organics components and solids. Plant A is located in the southern United States and not subject to extreme seasonal temperature fluctuations. Plant B is in the Midwest and it has been found necessary to add steam to the aeration basin during the winter to maintain the basin temperature above 45°F.

Daily analyses of TOC and BOD were available from Plant A and only COD data were available from Plant B. Weekly and thirty consecutive day period averages were calculated and then the data were analyzed statistically. The results of the analyses were summarized in Table XIII-2.

Treatment plant variability factors were used in deriving time based limitations for the following pollutant parameters: BOD5, TSS, and phenols. These variability factors are 4.5 and 2.0 respectively, for the daily maximum and maximum 30 average limitations. Although these factors represent the apparent 95/50 ratio of probability of occurrence, it is assumed that an effectively higher probability, 99/50 ratio is actually representative of these factors. The reasons for this are as follows:

1. Data used in calculating the variability of BOD5 contain three weeks of unstabilized conditions for the model treatment system. Excluding these data will provide an effectively higher probability of occurrence for the variability factors associated with the apparent 95/50 ratio.

2. The variability factors selected closely agree with the factors associated with the 99/50 ratio of probability of occurrence for other chemical industry treatment plants in the plastics and synthetic products and petrochemical segments.

SECTION XIV

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SECTION XV

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- (28) EPA Research Study No. 21 ABK 16, "Treatability of Organic
- (29) EPA Research Study No. 21 ACP 09, "Removal of Toxic Metals in Physical Chemical Pilot Plant," EPA NERC Cincinnati, Ohio January 1, 1972.
- (30) EPA Research Study No. 16 ACG-05, "Identify Pollutants in Physical Chemical Treated Wastes," EPA NERC Corvallis, Oregon, January 8, 1971.
- (31) EPA Advanced Waste Treatment Demonstration Grant No. 800685, "A Demonstration of Enhancement of Effluent from Trickling Filter Plant," City of Richardson, Texas, December 24, 1971.
- (32) EPA Advanced Waste Treatment Demonstration Grant No. 801026, "Removal of Heavy Metals by Waste Water Treatment Processes," City of Dallas, Texas, January 2, 1972.
- (33) EPA Advanced Waste Treatment Demonstration Grant No. 801401,

"Piscataway Model advanced Waste Treatment Plant," Washington Suburban Sanitary Commission, Hyattsville, Maryland, January 1, 1967.

- (34) EPA Research Grant No. 800661, "Oxidation Mechanisms on Supported Chromia Catalysts," Purdue Research Foundation, Lafayette, Indiana, January 6, 1970.
- (35) EPA Research Grant No. 12130 DR0, "Deep Water Pilot Plant Treatability Study," Delaware River Basin Commission, Trenton, New Jersey, July, 1971.

SECTION XVI

GLOSSARY

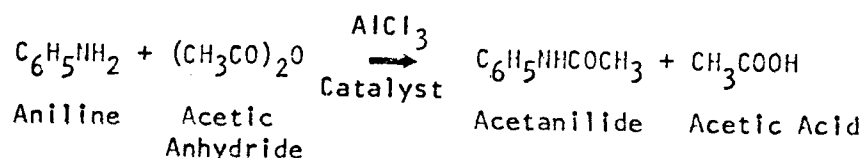
The terms defined here relate to common chemical conversions utilized extensively in the organic chemicals industry.

Acylation

Subcategory A

The acylation reaction introduces an acyl group, RCO-, into an aromatic ring. The product is an aryl ketone. The arylating reagents commonly used are acid halides, RCOCl, or anhydrides, (RCO)₂O. The catalyst is aluminum chloride. The reaction is usually carried out in an organic solvent, commonly carbon disulfide or nitrobenzene.

Acylation is utilized in the manufacture of dye intermediates such as acetanilide, and acetyl-p-toluidine. The reaction for acetanilide is shown below:

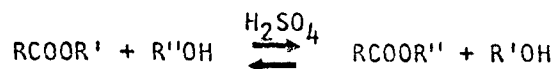


Although the reaction itself is nonaqueous (Subcategory A), water may be used in the subsequent separation of the reaction products. When carried out batchwise the reaction may fall within the context of an overall Subcategory D system.

Alcoholysis (Transesterification)

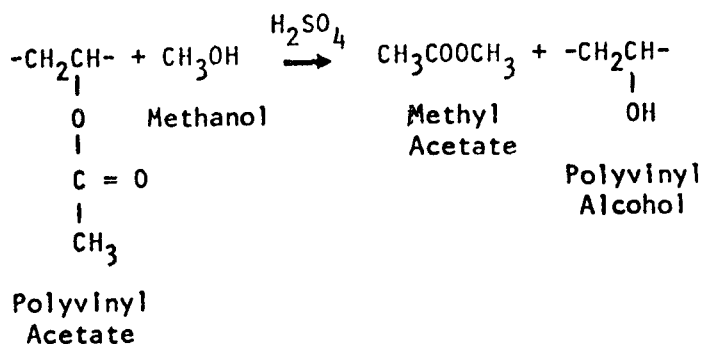
Subcategory C

Alcoholysis is the cleavage of an ester by an alcohol. It is also called transesterification. The reaction is usually catalyzed by aqueous sulfuric acid. A generalized equation for the reactions is shown below:



Transesterification is an equilibrium reaction. To shift the equilibrium to the right it is necessary to use a large excess of the alcohol whose ester is desired, or else remove one of the products from the reaction mixture. The second approach is used in most industrial applications, since in this way the reaction can be driven to completion.

An excellent example of the application of transesterification is found in the synthesis of the polymer, polyvinyl alcohol.



Although there are hundreds of acetate groups in every molecule of polyvinyl acetate, each of them undergoes the reactions typical of any ester. In the presence of aqueous sulfuric acid, polyvinyl acetate and methyl alcohol can exist in equilibrium with methyl acetate and polyvinyl alcohol. The reaction mixture is heated so that the lowest boiling compound, methyl acetate, distills out and the reaction proceeds to completion.

Ammonolysis

Subcategory C

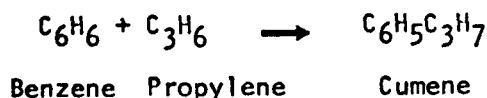
The reaction is classified within Subcategory C as it is conducted with an aqueous catalyst system.

Alkylation

Subcategories A and B

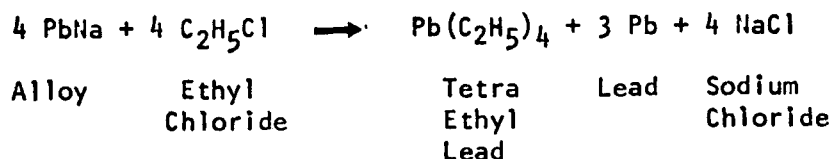
Alkylation refers to the addition of an aliphatic group to another molecule. The media in which this reaction is accomplished can be vapor or liquid phase, as well as aqueous or nonaqueous.

Benzene is alkylated in the vapor phase over a solid catalyst (silicaalumina impregnated with phosphoric acid) with propylene to produce cumene.



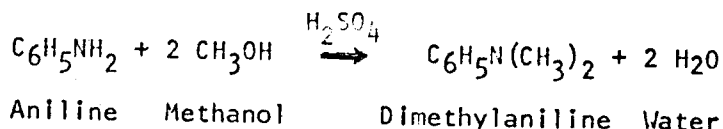
This reaction is nonaqueous and is considered within Subcategory A.

Tetraethyl lead (the principal antiknock compound for gasolines) is also a very important alkylated product. It is prepared by the action of ethyl chloride on a lead-sodium alloy.



The reaction is carried out in an autoclave equipped with a heating jacket, a stirrer to agitate the lead alloy, and a reflux condenser. The mixture is heated at the start and then cooled. After 6 hours, the excess ethyl chloride is distilled off, and the tetraethyl lead is steam stripped from the reaction mixture. This type of staged batch reaction with direct contact steam is considered typical of Subcategory D.

The alkylation reaction is also utilized in the manufacture of dyestuffs and intermediates. Dimethylaniline is employed intensively in the manufacture of triarylmethane dyes. It is prepared according to the following reaction:



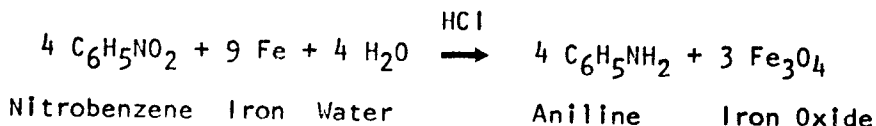
Aniline, with an excess of methanol and aqueous sulfuric acid, is heated in an autoclave. The dealkylated product is discharged through a cooling coil, neutralized, and vacuum distilled. This is again typical of the chemical conversions with Subcategory D.

Amination by Reduction

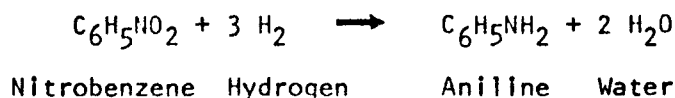
Subcategories B and D

Amination by reduction involves the formation of an amino group (-NH₂) through the reduction of a nitro group (-NO₂). The reaction can be carried out batchwise in an aqueous liquid phase (Subcategory D) or continuously in the vapor phase (Subcategory B).

The reducing agents in the batch conversion are iron and an aqueous acid catalyst (such as hydrochloric acid). Aniline is produced by the reaction as follows:



This batch reaction for reducing nitrobenzene with iron to aniline is being replaced by the continuous vapor phase reduction shown below:



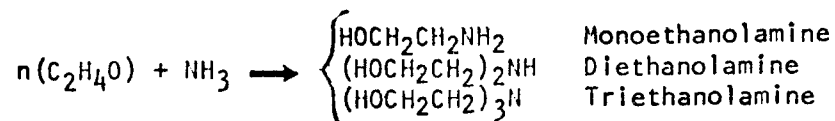
The reaction is conducted with a very short contact time in a tube packed with copper on SiO₂ as the catalyst. The hydrogen is adsorbed to the catalyst surface. Molecules of nitrobenzene are next adsorbed on the hydrogenated surface. The reaction products, aniline and water vapor, then desorb from the catalyst. This type of vapor phase reaction is typical of Subcategory B.

Ammonolysis

Subcategory C

Amination by ammonolysis relates to those reactions in which an amino compound is formed using aqueous ammonia. Industrial applications include the production of ethanolamines and methylamines.

A mixture of mono-, di-, and triethanolamine is obtained when ethylene oxide is bubbled through aqueous ammonia as shown by the following equation:

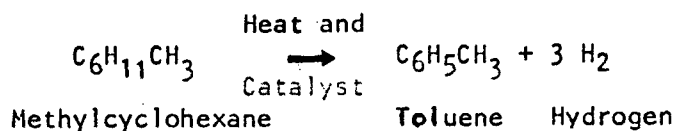


Methylamines are formed similarly by the ammonolysis of methanol. These continuous reactions are also considered within Subcategory C.

Aromatization (Reforming)

Subcategory A

Aromatization is the conversion of saturated cyclic compounds to aromatic compounds. The reaction is illustrated by the following equation:



The reaction is carried out in the vapor phase with or without catalysts. It is nonaqueous and considered within Subcategory A.

Condensation

Subcategory D

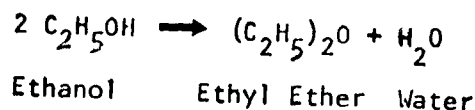
Condensation reactions involve the closure of structural rings in aromatic compounds. They are carried out batchwise in aqueous acid solutions and are of great importance in the manufacture of dye intermediates.

Dehydration

Subcategories B and C

Ethers are commonly produced by the dehydration of alcohols. When carried out in the liquid phase using sulfuric acid as a catalyst, the reaction is considered within Subcategory C. However, it can also be accomplished in the vapor phase over solid alumina catalysts within Subcategory B.

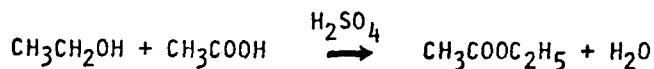
The following reaction for the production of ethyl ether from ethanol can be accomplished by either route:



Esterification

Subcategory C

Esterification generally involves the combination of an alcohol and an organic acid to produce an ester and water. The reaction is carried out in the liquid phase with aqueous sulfuric acid as the catalyst. The use of sulfuric acid has in the past caused this type of reaction to be called sulfation. The equation for producing ethyl acetate from acetic acid and ethanol is shown below:



Ethanol Acetic Acid Ethyl Acetate Water

Continuous esterification reactions are considered within Subcategory C.

Friedel-Crafts Reactions

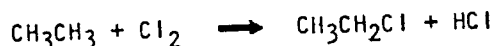
Subcategory A

Friedel-Crafts reactions involve the alkylation or acylation of an aromatic ring in the presence of such catalysts as AlCl_3 , BF_3 , SnCl_4 , I_2 . These addition reactions are sensitive to trace quantities of moisture and must be carried out under anhydrous conditions.

Halogenation and Hydrohalogenation

Subcategory A

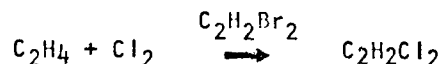
These reactions refer to the addition of a halogen (Cl_2 , Br_2 , I_2 , F_2) to an organic molecule. The various products are obtained through both liquid and vapor phase reactions with or without catalysts. Aliphatic compounds such as methane and ethane can both be chlorinated in the vapor phase with the cocurrent production of HCl gas.



Ethane Chlorine Ethyl Hydrogen
 Chloride Chloride

The by-product HCl can also be reacted with ethylene to form ethyl chloride by hydrohalogenation. This later reaction is carried out over an anhydrous aluminum chloride catalyst.

The addition of halogens to unsaturates (alkenes) serves to give many other derivatives such as ethylene dichloride, ethylene dibromide, dichloroethylene, trichloroethylene, and tetrachloroethane. The preparation of ethylene dichloride is typical:



Ethylene Chlorine Ethylene Dichloride

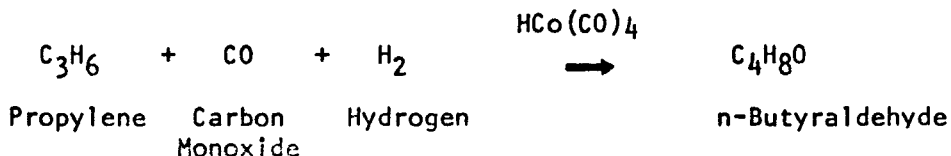
The chlorine gas is bubbled through a tank of liquid ethylene dibromide (catalyst), and the mixed vapors are sent to a chlorinating tower where they meet a stream of ethylene. The products from the tower pass through a partial condenser, followed by a separator, with the crude ethylene dichloride passing off as a gas and the liquid ethylene dibromide being returned to the systems.

These reactions are all non-aqueous and are within Subcategory A. However, it should be noted that some of these reactions may also be carried out batchwise in dye manufacture and as such may fall within the context of a Subcategory D system.

Hydroformylation (CXO Process)

Subcategory C

The oxo process is a method of converting olefins to aldehydes containing one additional carbon atom. The olefin is reacted in the liquid phase with a mixture of hydrogen and carbon monoxide in the presence of a soluble cobalt catalyst to produce the aldehyde. A typical reaction follows, in which propylene is converted to n-butyraldehyde:



The reaction itself is nonaqueous. However, the regeneration of the cobalt carbonyl catalyst complex requires extensive usage of aqueous solutions of sodium carbonate and sulfuric acid. This aqueous catalyst regeneration causes the hydroformylation reaction to be classified in Subcategory C.

Hydrogenation and Dehydrogenation

Subcategory B

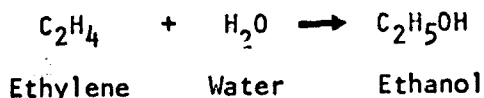
The hydrogenation reaction involves the addition, while dehydrogenation involves the removal of hydrogen from an organic molecule. Both types of reaction are carried out in the vapor phase, at elevated temperatures, over solid catalysts such as platinum, palladium, nickel, copper, or iron oxides. Steam is added in many cases as a diluent to reduce the partial pressure of hydrocarbons in the reactor and prevent the formation of coke on the catalyst. These reactions are considered within Subcategory B.

Typical hydrogenation products include methanol produced from carbon monoxide and hydrogen as well as other alcohols produced from aldehydes. Dehydrogenation products include ketones, such as acetone, produced from alcohols, such as isopropanol.

Hydration (Hydrolysis)

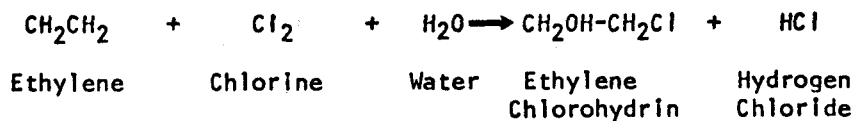
Subcategories B and C

These reactions can be either liquid or vapor phase. Liquid phase systems include the production of ethanol from ethylene with aqueous sulfuric acid or isopropanol from propylene. The corresponding vapor phase routes are carried out over solid H_3PO_4 catalysts. The equation shown for ethanol can be done either way:

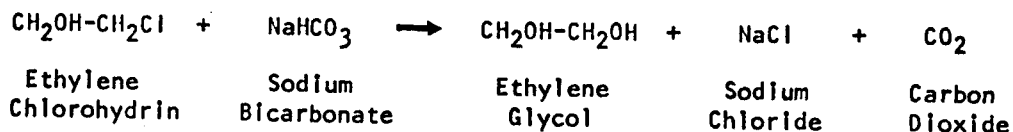


Ethylene glycol and ethylene oxide can also be produced by either a liquid or vapor phase route. The liquid reaction involves the

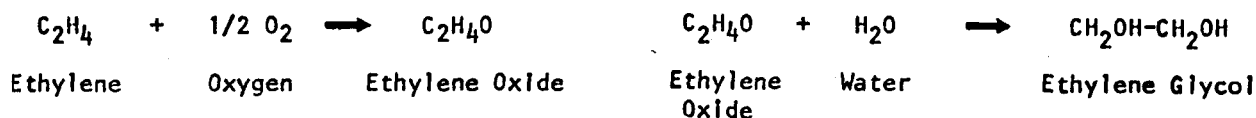
formation of ethylene chlorohydrin, which is produced by the reaction of aqueous chlorine with ethylene.



The ethylene chlorohydrin is treated with aqueous sodium bicarbonate solution to produce ethylene glycol.



More recently the chlorohydrin route to ethylene oxide and glycol has been replaced by the reaction of ethylene with oxygen and water:



Ethylene and oxygen are charged to a tubular reactor which is filled with silver catalyst (vapor phase) or sulfuric acid (liquid phase). Ethylene oxide is recovered from the gaseous reactor effluent by absorption in water. The wet ethylene oxide is then reacted with water in the presence of sulfuric acid to produce ethylene glycol.

Depending on whether these reactions are aqueous liquid phase or vapor phase they may be considered in either Subcategory B or C.

Neutralization

Subcategory C

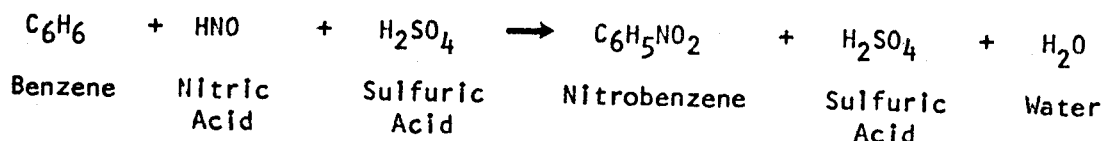
The treatment of reactor effluents with either caustic or acid is a necessary part of many reaction systems. The neutralizing reagents normally used are sulfuric acid or sodium hydroxide. Gaseous effluents are normally treated in an absorber while

liquid effluents are treated in a liquid- liquid contactor. Both types of treatment are considered within Subcategory C.

Nitration

Subcategories C and D

This reaction involves the introduction of nitrogen onto a hydrocarbon by the use of nitric acid. It is usually carried out in the liquid phase and may be either continuous or batch. Nitrobenzene is produced as a dye intermediate by the direct nitration of benzene, using a mixture of nitric and sulfuric acids according to the following equation:



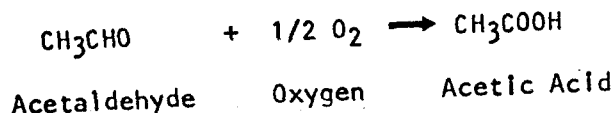
This type of reaction is considered either in Subcategory C or D.

Oxidation

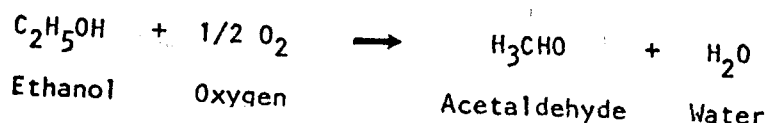
Subcategories B and C

This family of reactions may be carried out either in aqueous solutions or in the vapor phase. The oxidant may be either air or oxygen.

The liquid phase systems all utilize dissolved mineral salts such as cobalt acetate. A typical reaction is the oxidation of acetaldehyde to give acetic acid in an aqueous mixture of cobalt acetate and acetic acid.



Alternatively, acetaldehyde can be produced by the vapor phase oxidation of ethanol over a silver gauze catalyst.



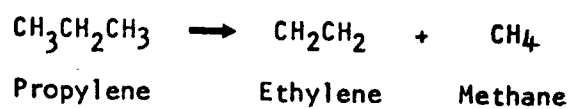
Depending on whether the reaction is vapor or liquid phase it may be considered within Subcategory B or C.

Pyrolysis (Cracking)

Subcategory B

These reactions involve the breaking of carbon chains in alkanes with the subsequent formation of alkanes and alkenes of lower molecular weight. The equation below illustrates the cracking reaction by which ethylene is produced:

The reactions are all carried out in the vapor phase at very high temperature. Steam is usually added as a diluent to prevent the formation of coke. For this reason, the reactions are considered within Subcategory B.



METRIC UNITS
CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectafes
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram-calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/ kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	kilowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	ton	0.907	kkg	metric tons (1000 kilograms)
yard	yd	0.9144	m	meters

* Actual conversion, not a multiplier

