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

MAJOR ORGANIC PRODUCTS

Segment of the Organic Chemicals
Manufacturing Point Source Category

U.S. ENVIRONMENTAL PROTECTION AGENCY

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DEVELOPMENT DOCUMENT

for

PROPOSED EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

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

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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 perfromance were then developed 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.

During Phase I of the study, general groups of products within the broad ranges of the two SIC groups were established, on the basis of similarity of chemical structure. The specific chemicals in each group are listed in Table I-3. In this table, those chemicals covered in Phase I of this study are identified by the designation I and those proposed for coverage in Phase II by the designation II. Total production of the chemicals covered, as a fraction of the aggregate output, is indicated by Coverage I for Phase I and Coverage II for Phases I and II combined. Approximately 75 percent of the organic chemicals manufacturing industry's aggregate production capacity is covered by Phase I product-processes. Phase II will cover an additional 88 to 100 significant product-processes and increase the total coverage to approximately 98 percent of the aggregate production capacity.

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.

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Subcategory B: Processes 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-4 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-5. The raw waste load (RWL) data obtained in the field surveys are summarized in Table I-6. Subcategories B, C, and D were further subcategorized on the basis of raw waste loads. For subcategories B and C, product-processes were classified above and below the median raw waste load (BOD_5 and COD) for the subcategory. Those product-processes with raw waste loads above the median subcategory raw waste load were designated B2 and C2, respectively, and those product-processes with raw waste loads below the median value were designated B1 and C1, respectively, for each subcategory. Subcategory D includes one subcategory, azoic dyes and components.

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 non-contact 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 non-contact waters be segregated from process waste waters. Oterwise, combined waste waters are subject to effluent limitations.

Separate limitations are presented for each of the four subcategories. 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 were based upon three significant pollutant parameters: BOD5, total suspended solids (TSS) and phenols. The application of alternate oxygen demand parameters such as COD or TOC in lieu of the BOD5 parameter may be possible, in siturations where a direct correlation with BOD5 has been satisfactorily established. For both New Source Performance Standards (BADCT) and 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. Suspended solids are maintained at an average concentration of 30 mg/l. 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 biotoxic to the biological waste treatment system. Phenolic compounds are expected to be maintained at an average of 0.5 mg/l in the effluent by suitable combinations of in-process controls, (i.e. activated carbon, solvent extraction) and end-of-process treatment systems.

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 recyle 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-proces or end-of-process treatment. This may be advantageous in areas where land availability is limited.

Substantial reductions of $BOD\underline{5}$ are expected from new sources as well as significant removals of dissolved organic compounds as measured by COD. Suspended solids and phenolic compounds are also maintained at average levels of 15 mg/l and 0.1 mg/l respectively.

Effluent limitations for BPCTCA, BATEA, and New Sources (BADCT) were developed on the basis of major subcategory median raw waste loads. 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 B$\underline{1}$, B$\underline{2}$, C$\underline{1}$ and C$\underline{2}$.

Subcategory D includes a single group, organic dyes and organic pigments.

Finally, effluent effluent limitations were derived on the basis of the *maximum of any one day* and the *maximum average of daily values* for any 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 conseder the normal variations of exemplary designed and operated waste treatment systems.

Table I-I
Chemicals Listed Under SIC Code 2815

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

Acid dyes, synthetic
Acids, coal tar: derived from coal
    tar distillation
Alkylated diphenylamines, mixed
Alkylated phenol, mixed
Aminoanthraquinone
Aminoazobenzene
Aminoazotoluene
Aminophenol
Aniline
Aniline oil
Anthracene
Anthraquinone dyes
Azine dyes
Azobenzene
Azo dyes
Azoic dyes
Benzaldehyde
Benzene, product of coal tar dis-
    tillation
Benzoic acid
Benzol, product of coal tar distilla-
    tion
Biological stains
Chemical indicators
Chips and flakes, naphthalene
Chlorobenzene
Chloronaphthalene
Chlorophenol
Chlorotoluene
Coal tar acids, derived from coal
    tar distillation
Coal tar crudes, derived from coal
    tar distillation
Coal tar distillates
Coal tar intermediates
Color lakes and toners
Color pigments, organic: except
    animal black and bone black
Colors, dry: lakes, toners, or full
    strength organic colors
Colors, extended (color lakes)
Cosmetic dyes, synthetic
Cresols, product of coal tar distilla-
    tion
Creosote oil, product of coal tar dis-
    tillation
Cresylic acid, product of coal tar
    distillation
Cyclic crudes, coal tar: product of
    coal tar distillation
Cyclic intermediates
Cyclohexane
Diphenylamine
Drug dyes, synthetic
Dyes, synthetic organic
Eosine toners
Ethylbenzene

Food dyes and colors, synthetic
Hydroquinone
Isocyanates
Lake red C toners
Lithol rubine lakes and toners
Maleic anhydride
Methyl violet toners
Naphtha, solvent: product of coal
    tar distillation
Naphthalene, product of coal tar
    distillation
Naphthol, alpha and beta
Naphtholsulfonic acids
Nitroaniline
Nitrobenzene
Nitro dyes
Nitrophenol
Nitroso dyes
Oils: light, medium, and heavy--
    product of coal tar distillation
Orthodichlorobenzene
Paint pigments, organic
Peacock blue lake
Pentachlorophenol
Persian orange lake
Phenol
Phloxine toners
Phosphomolybdic acid lakes and
    toners
Phosphotungstic acid lakes and
    toners
Phthalic anhydride
Phthalocyanine toners
Pigment scarlet lake
Pigments, organic: except animal
    black and bone black
Pitch, product of coal tar distilla-
    tion
Pulp colors, organic
Quinoline dyes
Resorcinol
Scarlet 2 R lake
Stilbene dyes
Styrene
Styrene monomer
Tar, product of coal tar distillation
Toluene, product of coal tar distilla-
    tion
Toluol, product of coal tar distil-
    lation
Toluidines
Toners (reduced or full strength
    organic colors)
Vat dyes, synthetic
Xylene, product of coal tar distil-
    lation
Xylol, product of coal tar distilla-
    tion

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

Accelerators, rubber processing:
  cyclic and acyclic
Acetaldehyde
Acetates, except natural acetate of
  clime
Acetic acid, synthetic
Acetic anhydride
Acetin
Acetone, synthetic
Acids, organic
Acrolein
Acrylonitrile
Adipic acid
Adiponitrile
Alcohol, aromatic
Alcohol, fatty: powdered
Alcohols, industrial: denatured
  (nonbeverage)
Algin products
Amines of polyhydric alcohols, and
  of fatty and other acids
Amyl acetate and alcohol
Antioxidants, rubber processing:
  cyclic and acyclic
Bromochloromethane
Butadiene, from alcohol
Butyl acetate, alcohol, and pro-
  pionate
Butyl ester solution of 2, 4-D
Calcium oxalate
Camphor, synthetic
Carbon bisulfide (disulfide)
Carbon tetrachloride
Casing fluids, for curing fruits,
  spices, tobacco, etc.
Cellulose acetate, unplasticized
Chemical warfare gases
Chloral
Chlorinated solvents
Chloroacetic acid and metallic salts
Chloroform
Chloropierin
Citral

Citrates
Citric acid
Citronellol
Coumarin
C-eam of tartar
Cyclopropane
DDT, technical
Decahydronaphthalene
Dichlorodiflouromethane
Diethylcyclohexane (mixed isomers)
Diethylene glycol ether
Dimethyl divinyl acetylene (di-
  isopropenyl acetylene)
Dimethylhydrazine, unsymmetrical
Enzymes
Esters of phthalic anhydride: and
  of phosphoric, adipic, lauric,
  oleic, sebacic, and stearic acids
Esters of polyhydric alcohols
Ethanol, industrial
Ether
Ethyl acetate, synthetic
Ethyl alcohol, industrial (non-
  beverage)
Ethyl butyrate
Ethyl cellulose, unplasticized
Ethyl chloride
Ethyl ether
Ethyl formate
Ethyl nitrite
Ethyl perhydrophenanthrene
Ethylene
Ethylene glycol
Ethylene glycol ether
Ethylene glycol, inhibited
Ethylene oxide
Ferric ammonium oxalate
Flavors and flavoring materials,
  synthetic
Fluorinated hydrocarbon gases
Formaldehyde (formalin)
Formic acid and metallic salts
Freon

Table I-2
(continued)

Fuel propellants, solid organic
Fuels, high energy, organic
Gases, fluorinated hydrocarbon
Geraniol, synthetic
Glycerin, except from fats (synthetic)
Grain alcohol, industrial
Hexamethylenediamine
Hexamethylenetetramine
High purity grade chemicals, organic: refined from technical grades
Hydraulic fluids, synthetic base
Hydrazine
Industrial organic cyclic compounds
Ionone
Isopropyl alcohol
Ketone, methyl ethyl
Ketone, methyl isobutyl
Laboratory chemicals, organic
Lauric acid esters
Lime citrate
Malononitrile, technical grade
Metallic salts of acyclic organic chemicals
Metallic stearate
Methanol, synthetic (methyl alcohol)
Methyl chloride
Methyl perhydrofluorine
Methyl salicylate
Methylamine
Methylene chloride
Monochlorodifluoromethane
Monomethylparaminophenol sulfate
Monosodium glutamate
Mustard gas
Nitrous ether
Normal hexyl decalin
Nuclear fuels, organic
Oleic acid esters
Organic acids, except cyclic
Organic chemicals, acyclic
Oxalates
Oxalic acid and metallic salts
Pentaerythritol
Perchloroethylene
Perfume materials, synthetic
Phosgene
Phthalates
Plasticizers, organic: cyclic and acyclic
Polyhydric alcohols

Potassium bitartrate
Propellants for missiles, solid, organic
Propylene
Propylene glycol
Quinuclidinol ester of benzylic acid
Reagent grade chemicals, organic: refined from technical grades
Rocket engine fuel, organic
Rubber processing chemicals, organic: accelerators and antioxidants--cyclic and acyclic
Saccharin
Sebacic acid
Silicones
Soaps, naphthenic acid
Sodium acetate
Sodium alginate
Sodium benzoate
Sodium glutamate
Sodium pentachlorophenate
Sodium sulfoxalate formaldehyde
Solvents, organic
Sorbitol
Stearic acid esters
Stearic acid salts
Sulfonated naphthalene
Tackifiers, organic
Tannic acid
Tanning agents, synthetic organic
Tartaric acid and metallic slats
Tartrates
Tear gas
Terpineol
Tert-butylated bis (p-phenoxyphenyl) ether fluid
Tetrachloroethylene
Tetraethyl lead
Thioglycolic acid, for permanent wave lotions
Trichloroethylene
Trichloroethylene stabilized, degreasing
Trichlorophenoxyacetic acid
Trichlorotrifluoroethane terachlorodifluoroethane isopropyl alcohol
Tricresyl phosphate
Tridecyl alcohol
Trimethyltrithiophosphite (rocket propellants)
Triphenyl phosphate
Urea
Vanillin, synthetic
Vinyl acetate

Table I-5

Major Organic Chemicals from SIC Codes 2815 and 2818 Listed by Chemical Functional Groupings

NOTE: (I) denotes coverage during Phase I field data collection program.
(II) denotes proposed coverage during Phase II field data collection program.
Numbers shown indicate annual production for industry in millions of pounds.

Acids	Alcohols	Aldehydes	Amines	Anhydrides	Cyclic Crudes	Cyclic Intermediates
Acetic Acid (I) 2,150	Methanol (I) 5,960	Formaldehyde (II) 5,500	Analine (I) 553	Acetic Anhydride (II) 1,560	Benzene (I,II) 8,950	Ethylbenzene (I) 6,650
Terephthalic Acid (I) 1,500	Ethanol (I) 1,870	Acetaldehyde (I) 1,610	Ethanol Amines 255	Phthalic Anhydride (II) 776	Toluene (I,II) 5,960	Styrene (I,II) 5,870
Adipic Acid 1,350	Isopropanol (II) 1,850	Crotonaldehyde 80	Methyl Amines 120	Maleic Anhydride (II) 227	Xylenes (I,II) 5,810	Cumene (II) 2,750
Acrylic Acid (I) 500	Oxo-Alcohols (I) 1,400	Benzaldehyde (II) 4	Fatty Amines (II) 20		Cyclohexane (I) 2,290	Phenol (I) 1,930
Fatty Acids (II) 900	Sec-butyl Alcohol (II) 260		Hexamethylene Tetramine (II) 100		Naphthalene (II) 663	Caprolactam (I) 500
Benzoic Acid (II) 34	Diacetone Alcohol (II) 400		Hexamethylamine Diamine (II) 130		Dodecylbenzene 516	Toluene Di-isocyanate (I,II) 270
Cresylic Acid (II) 203			Diphenyl Amine (II) 25		Pyridines (I,II) 24	Cresol (I,II) 203
Oxalic Acid (II) 22			Alkylamines (II) 30		Bio-phenol (I) 160	Pitch (II) 500
Formic Acid (II) 25			Alkanol Amines (II) 70			Tar (II) 8,000
Tannic Acid (II) 100						Tricresol Phosphate (II) 200
Naphthenic Acid (II) 25						Creosote Oil (II) 500
Lauric Acid (II) -						
Citric Acid (II)						
Amino Acids (II) 5,945						
Estimated Aggregate Production 12,789	19,570	7,194	1,343	2,563	24,373	27,373
Coverage I, % 32	40	32	32	0	95	56
Coverage I and II, % 89	100	75	71	100	98	100

Table 1-3
(Continued)

Dyes and Intermediates	Esters	Ethers	Food Additives	Glycols	Halogenated Hydrocarbons	Ketones
Anthraquinone 551	Dimethyl Terephthalate (1) 2,000	Glycol Ethers (11) 380	Flavors (11) 90	Ethylene Glycol (1) 3,300	Ethylene Dichloride (1) 7,120	Acetone (1) 1,760
Phthalocyanine 23	Vinyl Acetate (1) 922		Vanillin (11) 2	Propylene Glycol 300	Vinyl Chloride (1,11) 5,180	Methyl-ethyl Ketone (1,11) 450
Xanthine 14	Acrylates (1) 303		Enzymes (11) 100	Synthetic Glycerine (11) 300	Carbon Tetrachloride (11) 1,009	Methyl-Isobutyl Ketone 230
Beta-Naphthol 30	Methyl Methacrylate (1) 450		Sodium Glutamate (11) 30	Pentaerythritol (11) 100	Perchloroethylene 703	
Acid Dyes (1,11) 234	Dioctyl Phthalates 432		Geraniol (11) 1	Hexylene Glycol (11) 10	Trichloroethylene (11) 573	
Basic Dyes (1,11) 14	Ethyl Acetate (11) 128		Potassium Bitartrate (11) 15		Methyl Chloride 412	
Direct Dyes (11) 32	Propyl Acetate (11) 35		Ionone (11) 1		Chloroprene 370	
Disperse Dye (1,11) 29	Butyl Acetate (11) 90		Saccharin (11) 26		Methyl Bromide 21	
Vat Dyes (11) 56	Calcium Stearate (11) 150		Sorbitol (11) 1		Tetrachloroethylene (11) 225	
Metallized Dyes (11) 40	Sodium Acetate (11) 16		Methyl Salicylate (11) 6		1,1,2-Trichloro 1,2,2-Trifluoro ethane (11) 372	
Chrome Dyes (11) 35			Citral (11) 1		Methylene Chloride (11) 175	
Amino Anthraquinone Dyes (11) 4			Sodium Alginate (11) 10		Chloroform (11) 175	
Amino Phenol (11) 5			Citronellol (11) 1		Chlorobenzene (11) 500	
Nitroaniline (11) 20					Dichlorobenzene (11) 29	
					Pentachloroethane (11) 225	
Estimated Aggregate Production 1,057	4,526	380	258	4,010	17,083	2,440
Coverage 1, % 26	82	0	0	82	72	91
Coverage 1 and 11, % 42	91	100	100	92	89	91

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Table I-3
(Continued)

Metallo Organics	Nitriles	Olefins	Oxides	Miscellaneous
Tetraethyl Lead (I) 325	Acrylonitrile (II) 572	Ethylene (I) 20,530	Ethylene Oxide (I) 4,080	Acetylene 844
Tetramethyl Lead 76	Malonitriles (II) 100	Propylene (I) 7,960	Propylene Oxide (II) 1,170	Nitrotoluene 320
		Butadiene (I)		Acrolein 50
				Morpholine 20
				Tetrahydro Naphthalene 20
				Camphor (II) 20
				Resorcinol (II) 150
				Nitrophenols (II) 16
				Terpineol (II) 10
Estimated Aggregate Production				
401	1,072	32,300	5,250	1,450
Coverage I, %				
62	0	100	78	0
Coverage I and II, %				
81	100	100	100	14

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Table I-4

Products and Manufacturing Processes Listed By Category

Product   Manufacturing Process

CATEGORY A (CONTINUOUS NON-AQUEOUS PROCESSES)

Product	Manufacturing Process
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 hydrodealkvlation
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

CATEGORY B (CONTINUOUS VAPOR PHASE PROCESSES WHERE WATER IS USED AS DILUENT OR ABSORBENT)

Product	Manufacturing Process
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

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Table 1-4
(continued)

Product	Manufacturing Process
CATEGORY 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	Ammoxidation 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 Isoamylene
Vinyl acetate	Acetylene and acetic acid process Vapor phase ethylene and acetic acid process
Mixed cresols and xylenols	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

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Table I-4
(continued)

Product	Manufacturing Process

CATEGORY B (CONTINUED)

Product	Manufacturing Process
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 actimic light

Table I-4 ()
(continued)

Product   Manufacturing Process

CATEGORY C (CONTINUED)

Product	Manufacturing Process
Acetophenone	By-product of phenol by cumene peroxidation
Acrolein	Condensation of acetaldehyde with formaldegyde
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 propionaldhyde
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 cf acetic acid
Sodium Chloroacetate	Esterification of chloroacetic acid
Chloropicrin (nitrotrichloro- methane-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 I-4
(continued)

Product	Manufacturing Process

CATEGORY C (CONTINUED)

Product	Manufacturing Process
Isocyanates	Phosgene and Amines
Coal tar cyclic intermediates	Coal tar distillation

CATEGORY D (BATCH PROCESSES)

Product	Manufacturing Process
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 B-naphthol
Lithol rubine	Diazotization of p-toluidine meta sulfonic acid followed by coupling with 3-hydropy-2-naphthic acid
Eosin toners	Bromination of fluorescin
Amino anthraquinone	Reduction of nitroanthraquinone Substitution of sulfonate with amino group
Amino azobenzene (para)	Catalytic heating of diazoaminobenzene 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_2S reduction of O-nitrophenol and aqueous ammonia (para) Reduction of p-nitrophenol by Fe and HCl Electrolytic reduction of nitrobenzene in sulfuric acid
Anthraquinone (dyes)	Heating phthalic anhydride and benzene in presence of $AlCl_3$ catalyst and dehydrating
Azine dyes	From phenazine

Table I-4
(continued)

Product   Manufacturing Process

CATEGORY C (LIQUID PHASE REACTION SYSTEMS)

Product	Manufacturing Process
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 I-4
(continued)

Product   Manufacturing Process

CATEGORY 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 hydro-
  chlorination
  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
  agueous calcium hypochlorite
  Liquid phase oxidation of isobutane
  followed by liquid phase epoxi-
  dation

Propylene glycol
: Hydration of propylene oxide
  catalyzed by dilute H_2SO_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 nitrification, toluene
  diamine production, HCl
  electrolysis, phosgene production,
  TDI production, purification

Silicones
: Reaction of silicon metal
  with methyl chloride

Table 1-4
(Continued)

Product	Manufacturing Process
CATEGORY C (CONTINUED)	

Product	Manufacturing Process
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 alkalin 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 I-4
(continued)

Product   Manufacturing Process

CATEGORY 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_2SO4
                                              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

20

Product	Manufacturing Process
CATEGORY D (CONTINUED)	

Azobenzene — Reduction of nitrobenzene with sodium stannite

Azo dyes (generic) — Diazotation and coupling

Monosodium glutamates — Ferementation 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 sufuric 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 1-4
(continued)

Product   Manufacturing Process

CATEGORY D (CONTINUED)

Product	Manufacturing Process
Alkylated phenols	Alkylation with lewis acid catalyst
Acetamide	Distillation of ammonium acetate
Organic esters	Steam distillation of naturally occuring 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 dimethyl-amine and ammonia
Nitrophenol	Nitrochlorobenzene and caustic soda

Table I-5

Products and Processes Covered in Raw Waste Load Sampling

CATEGORY A (CONTINUOUS NON-AQUEOUS PROCESSES)

Product	Process	Phase I Survey Visits
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.	1
	Fractional Distillation	1
4 Products	5 Manufacturing Processes	6 Visits

Table I-5

Products and Processes Covered in Raw Waste Load Sampling

CATEGORY B (CONTINUOUS VAPOR PHASE PROCESSES WHERE WATER IS USED AS DILUENT OR ABSORBENT)

Product	Process	Phase I Survey Visits
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
12 Products	12 Manufacturing Processes	25 Visits

Table 1-5

Products and Processes Covered in Raw Waste Load Sampling

CATEGORY C (LIQUID PHASE REACTION SYSTEMS)

Product	Process	Phase 1 Survey Visits
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 Catalytic Oxidation of Para-Xylene	1 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
20 Products	**20 Manufacturing Processes**	**31 Visits**

CATEGORY D (BATCH PROCESSES)

Product	Process	Phase 1 Survey Visits
Dyes/Pigments	Batch Mfg.	5

25

Table I-6

Major RWL's of Pollutants Based on
Process Wastewater

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

FIGURE 1—1

SUBCATEGORY A

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

27
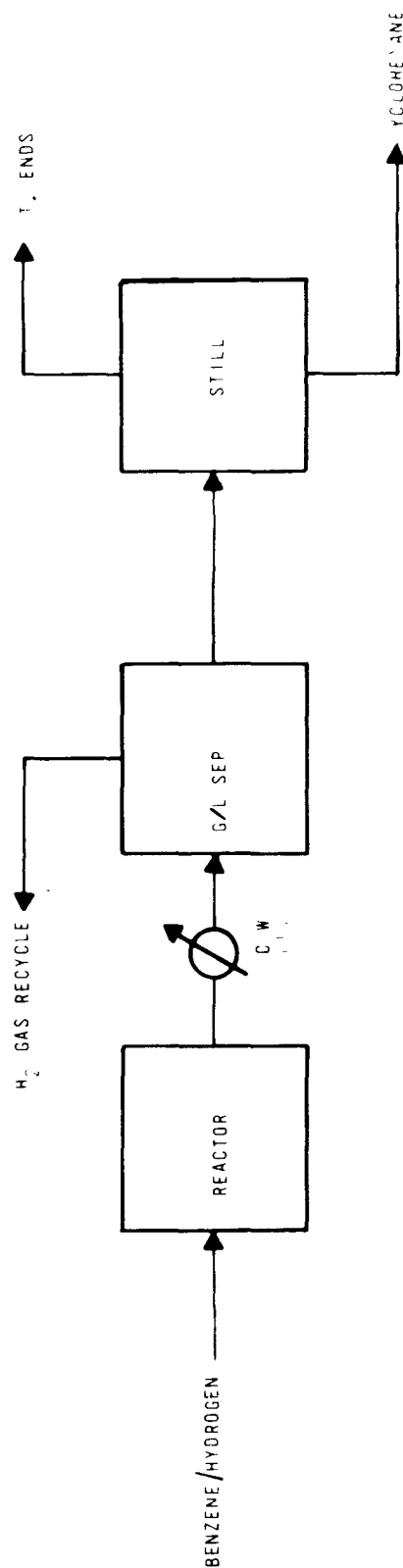
FIGURE 1—2

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.
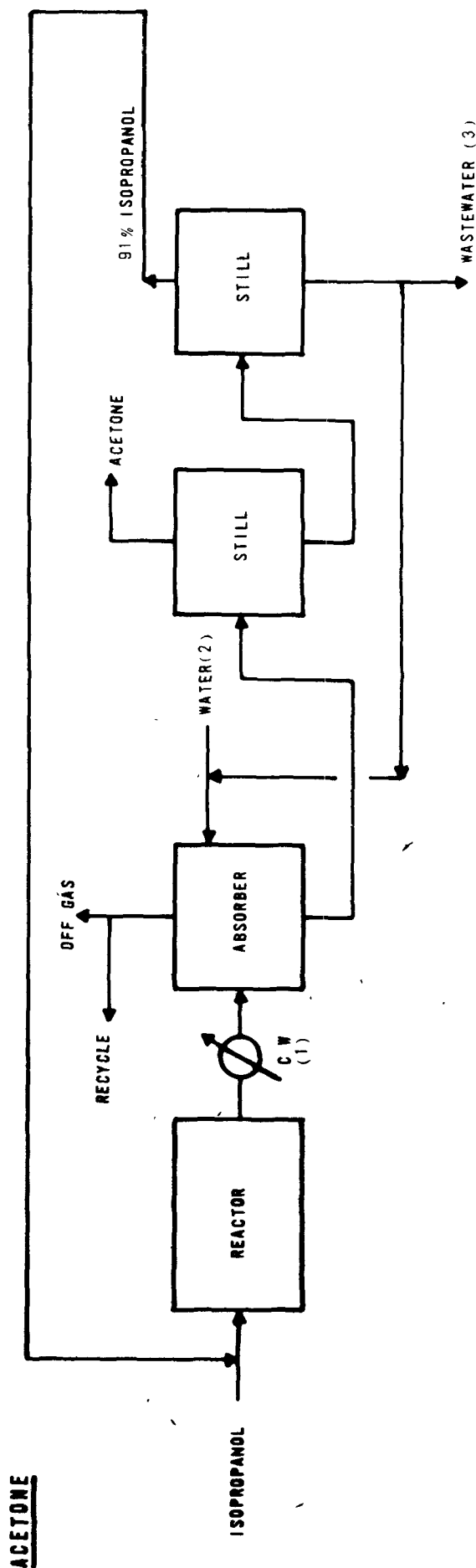
ACETONE

28

(43)

FIGURE I-3

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.

PHENOL
ACETONE

29
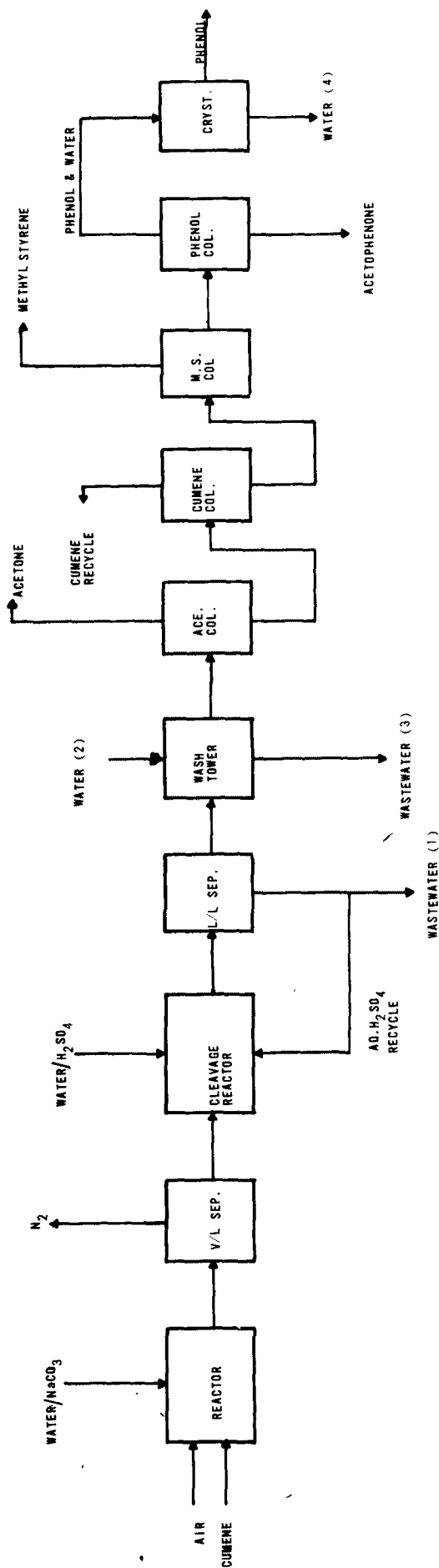
SUBCATEGORY D

PROCESSES ARE CARRIED OUT IN REACTION [unclear]
DEPENDING ON THE NATURE OF THE OPERATION [unclear]
REACTANTS AND PRODUCTS ARE TRANSFERRED [unclear]
OR PRESSURIZATION WITH AIR OR INERT GAS [unclear]
AUTOMATIC PROCESS CONTROL. FILTER [unclear]
REQUIRED. AIR OR VACUUM OVENS ARE USED [unclear]
MAJOR SOURCE OF WASTEWATER. ANTICIPATED [unclear]
LEAST TEN TIMES THOSE FROM CONTINUOUS PROCE[unclear]

CONTINUOUS AND BATCH PROCESSES

[unclear] REFLUX CONDENSERS, ETC.
[unclear] AQUEOUS CATALYST SYSTEMS.
[unclear] BY GRAVITY FLOW, PUMPING,
[unclear] WITH LIMITED USE OF
[unclear] LIQUID. WHERE DRYING IS
[unclear] EQUIPMENT CONSTITUTES
[unclear] AND PURIFICATION WILL BE AT

BATCH PROCESSES
(DYE SYNTHESIS)

RAW MATERIAL

COOLING WATER
& PROCESS WATER

BLENDING

PRODUCT

CITY SEWER

BLEACH

SECTION II

RECOMMENDATIONS

Effluent limitations commensurate with the best practicable control technology currently available are presented for each industrial subcategory of the organic chemicals manufacturing industry. Major product-process segments of the industry 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 auxilary 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 to control suspended solids levels.

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 chemicalphysical 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. 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 systems for removal of suspended solids. Effluent limitations for the major product-process segments are presented in Table II-4. The most exemplary performance of the biological treatment system is assumed in terms of BOD_5 and COD reductions since in-process controls substantially reduce biotoxic polluants.

TABLE II-1

SUBCATEGORIES OF THE ORGANIC CHEMICALS MANUFACTURING INDUSTRY (PHASE I - MAJOR PRODUCT-PROCESSES)

Subcategory A	Process Descriptions
Cyclohexane	Hydrogenation of Benzene
Ethyl Benzene	Alkylation of Benzene with Ethylene
Vinyl Chloride	Addition of HCl to Acetylene
BTX Aromatics	Hydrotreating Pyrolysis Gasoline
BTX Aromatics	Solvent Extraction of Reformate

Subcategory B
B1 Products

Ethylene and Propylene	Pyrolysis of Naptha or liquid Petroleum Gas (LPG)
Butadiene	Co-product of Ethylene
Methanol	Steam Reforming of Natural Gas
Acetone	Dehydrogenation of Isopropanol
Acetaldehyde	Dehydrogenation of Ethanol
Vinyl Acetate	Synthesis of Ethylene and Acetic Acid

B2 Products

Butadiene	Dehydrogenation of n-Butane
Butadiene	Oxidative dehydrogenation on n-Butane
Acetylene	Partial Oxidation of Methane
Ethylene Oxide	Oxidation of Ethylene
Formaldehyde	Oxidation of Methanol
Ethylene Dichloride	Direct Chlorination of Ethylene
Vinyl Chloride	Cracking of Ethylene Dichloride
Styrene	Dehydrogenation of Ethyl Benzene
Methyl Amines	Addition of Ammonia to Methanol

Subcategory C
C1 Products

Acetaldehyde	Oxidation of Ethylene
Acetic Acid	Oxidation of Acetaldehyde
Acrylic Acid	Synthesis with CO and Acetylene
Aniline	Nitration and Hydrogenation of Benzene
Bisphenol A	Condensation of Phenol and Acetane
Caprolactam	Oxidation of Cyclohexane
Coal Tar	Pitch forming and Distillation
Ethylene Glycol	Hydrogenation of Ethylene Oxide

32

| Dimethyl Terephthalate | Esterification of Terephthalic acid (TPA) |
| Oxo Chemicals | Carbonylation and Condensation |

Phenol	Oxidation of Cumene
Terephthalic Acid	Oxidation of p-Xylene
Terephthalic Acid (Polymer grade)	Purification of Crude Terephthalic Acid

C2 Products

Acrylates	Esterification of Acrylic Acid
P-Cresol	Sulfonation of Toluene
Methy methacrylate	Acetone Cyanohydrin Process
Terephthalic Acid	Nitric Acid Process
Tetraethyl Lead	Addition of Ethyl Chloride to Lead Amalgam

Subcategory D

| Organic Dyes: | Batch Processes |
| Azoic Dyes and Components | |

TABLE II-2

EFFLUENT LIMITATIONS FOR THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPCTCA) ORGANIC CHEMICAL MANUFACTURING INDUSTRY MAJOR PRODUCT-PROCESSES BY SUBCATEGORY

Effluent Characteristics	Effluent Limitations* kg/kkg Production	
Subcategory A	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days
BOD5	0.045	0.025
TSS	0.038	0.023
Phenols	0.00050	0.00025
Subcategory B **B1 Product-Processes**		
BOD5	0.10	0.06
TSS	0.10	0.06
Phenols	0.0013	0.00066
B2 Product-Processes		
BOD5	0.30	0.17
TSS	0.27	0.16
Phenol	0.0034	0.0017
Subcategory C **C1 Product-Processes**		
BOD5	0.30	0.17
TSS	0.27	0.16
Phenol	0.0034	0.0017
C2 Product-Processes		
BOD5	1.5	0.9
TSS	0.80	0.49
Phenols	0.011	0.0050
Subcategory D		
BOD5	15.0	9.0
TSS	13.0	7.88
Phenols	0.17	0.088

*kg/kkg production is equivalent to lb/1000 lb production.

TABLE II-3

EFFLUENT LIMITATIONS FOR THE BEST AVAILABLE
TECHNOLOGY ECONOMICALLY ACHIEVALBE (BATEA)
ORGANIC CHEMICALS MANUFACTURING INDUSTRY
MAJOR PRODUCT-PROCESSES BY SUBCATEGORY

Effluent Characteristics	Effluent Limitations* kg/kkg Production	
Subcategory A	Maximum for Any One Day	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days
COD	0.04	0.02
BOD5	0.004	0.002
TSS	0.006	0.004
Phenols	0.00005	0.000025
Subcategory B **B1 Product-Processes**		
COD	0.130	0.065
BOD5	0.008	0.004
TSS	0.017	0.010
Phenols	0.00013	0.000065
B2 Product-Processes		
COD	0.74	0.37
BOD5	0.02	0.01
TSS	0.0042	0.0025
Phenols	0.00034	0.00017
Subcategory C **C1 Products-Processes**		
COD	0.78	0.39
BOD5	0.02	0.01
TSS	0.0083	0.005
Phenols	0.00068	0.00034
C2 Products-Processes		
COD	14.4	7.2
BOD5	0.4	0.2
TSS	0.27	0.16
Phenols	0.0022	0.0011
Subcategory D		
COD	130.0	65.0
BOD5	0.8	0.4
TSS	2.19	1.30
Phenols	0.017	0.0085

*kg/kkg production is equivalent to lb/1000 lb production.

TABLE II-4

STANDARDS OF PERFORMANCE FOR NEW ORGANIC CHEMICALS MANUFACTURING SOURCES
MAJOR PRODUCT-PROCESSES BY SUBCATEGORY

Effluent Characteristics	Effluent Limitations* kg/kkg Production	
Subcategory A	Maximum for any One Day	Maximum Average of Daily Values for any Period of thirty Consecutive Days
BOD5	0.02	0.012
COD	0.15	0.10
TSS	0.012	0.0075
Phenol	0.0001	0.0005
Subcategory B **B1 Product-Processes**		
BOD5	0.06	0.035
COD	0.55	0.4
TSS	0.033	0.02
Phenol	0.00026	0.00013
B2 Product-Processes		
BOD5	0.15	0.085
COD	3.0	2.2
TSS	0.083	0.05
Phenol	0.00068	0.00034
Subcategory C **C1 Product-Processes**		
BOD5	0.15	0.085
COD	3.3	2.3
TSS	0.083	0.05
Phenol	0.00068	0.00034
C2 Product Processes		
BOD5	0.75	0.40
COD	60.0	40.0
TSS	0.27	0.16
Phenol	0.0022	0.0011
Subcategory D		
BOD5	1.5	0.85
COD	540.0	390.0
TSS	4.38	2.60
Phenol	0.034	0.017

*kg/kkg production is equivalent to lb/1000 lb production.

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 for 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 endof-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 requirments 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

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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 position 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.

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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 off-gas, 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 exlusively a source of aliphatic chemicals. The next step was the development of processes for extracting

aromatic hydrocarbons from catalytic reformate. 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:

Petrochemical	Current Cost	Cost Increase Associated with 50¢/bbl Increase in Crude Oil
Ethylene	3.0¢/lb	+0.3¢/lb
Butadiene	5.0¢/lb	+0.8¢/lb
Benzene	23.0¢/lb	+1.7¢/lb
p-Xylene	5.5¢/lb	+0.7¢/lb

The 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 naphatha).
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 solid 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 positon 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.

Table III-I

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

Raw Materials By Distillation	Precursors (Basic Chemicals) By Conversion	Intermediates By Conversion	Finished Products By Conversion
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.).

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FIGURE III-1

PETROCHEMICALS FROM METHANE

FIGURE III-2

PETROCHEMICALS FROM ETHYLENE

FIGURE III-3

PETROCHEMICALS FROM PROPYLENE AND BUTYLENES

ACETONE

SULFURIC ACID OR SULFUR DIOXIDE

GLYCEROL

ISOOCTYL ALCOHOL

PHENOL

METHYL ETHYL KETONE

HYDROGEN

POLYMERS (AND COPOLYMERS WITH
STYRENE AND ACRYLONITRILE)

ADIPONITRILE THEN
HEXAMETHLENEDIAMINE

COPOLYMER WITH 2
(ISOPRENE (BUTYL RUBBER))

POLYISOBUTYLENE

OXIDATION OR DEHYDROGENATION

NONYLPHENOL

DODECYLBENZENE

BENZENE

CUMENE HYDROPEROXIDE

EPICHLORHYDRIN

ALLYL ALCOHOL

ALDEHYDES CONTAINING
8 CARBON ATOMS

DEHYDROGENATION

SODIUM CYANIDE HYDROLYSIS

POLYPROPYLENE

ISOPROPYL ALCOHOL

TRIMER

TETRAMER

CUMENE

ALLYL CHLORIDE

PROPYLENE OXIDE

HEPTENES

SEC BUTYL ALCOHOL

BUTADIENE

CHLOROBUTENES

BUTYL ALCOHOL

DI- AND TRIISOBUTYLENE

CARBON MONOXIDE
HYDROGEN

CHLORINE

(CATALYST)

WATER
(SULFURIC ACID)

ACID

BENZENE

CHLORINE
(HIGH TEMPERATURE)

CHLORINE
WATER

ACID

WATER
(SULFURIC ACID)

DEHYDRO-
GENATION

WATER
(SULFURIC ACID)

SULFURIC ACID

BORON TRIFLUORIDE LOW TEMPERATURE

PROPYLENE

n-BUTYLENES

ISOBUTYLENE

REFINERY-
CRACKED
GAS

AIR

FIGURE III-4

CYCLIC PETROCHEMICALS

XYLENES

O-XYLENE — AIR → PHTHALIC ANHYDRIDE

M-XYLENE — AIR → ISOPHTHALIC ACID*

P-XYLENE — AIR → TEREPHTHALIC ACID*

*OR METHYL ESTERS

BENZENE TOLUENE XYLENES ETHYL-BENZENE

TOLUENE — NITRIC ACID → NITROTOLUENES — REDUCTIONS → TOLUENEDIAMINE — PHOSGENE → TOLUENE DIISOCYANATE

ACETYLENES → DITOLYLETHANE → VINYLTOLUENE

PROPYLENE

CUMENE — AIR → HYDRO-PEROXIDE

ACID

ACETONE

PHENOL

BISPHENOL → EPOXY RESINS

EPICHLOROHYDRIN, FORMALDEHYDE, UREA → PHENOLIC RESINS

PROPYLENE TRIMER

NONYLPHENOL → DETERGENTS

SULFONATION AND ALKALI FUSION OR CHLORINATION AND HYDROLYSIS

PROPYLENE TETRAMER

DODECYLBENZENE → DETERGENTS

BENZENE

ETHYLENE → ETHYL-BENZENE — DEHYDRO-GENATION → STYRENE → POLYMERS

EXISTING AROMATICS

REFORMING OF CYCLOPENTANES, CYCLOHEXONES, AND PARAFFINS

(MINOR)

REFINERY NAPHTHAS → CYCLOHEXANE — AIR → CYCLOHEXANOL CYCLOHEXANONE — HYDROXYL-AMINE, ACID / NITRIC ACID → ADIPIC ACID

AIR

HEXAMETHYLENE-DIAMINE

CAPROLACTAM → NYLONS

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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.

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 I: 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,

Table III - 2

Fifty Largest Chemical Producers in the United States

Rank 1972	Rank 1971	Company	Chemical Sales $ Millions	Net Sales $ Millions	Chemical Sales as Per Cent of Total Sales	SIC Class
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)	SIC 2815	SIC 2818	Total No.	Total %
< 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
> 2,500	0	7	665	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

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 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.

FIGURE III-5

PLOT PLAN FOR CHEMICAL PLANT
ILLUSTRATING FOUR-AREA LAYOUT
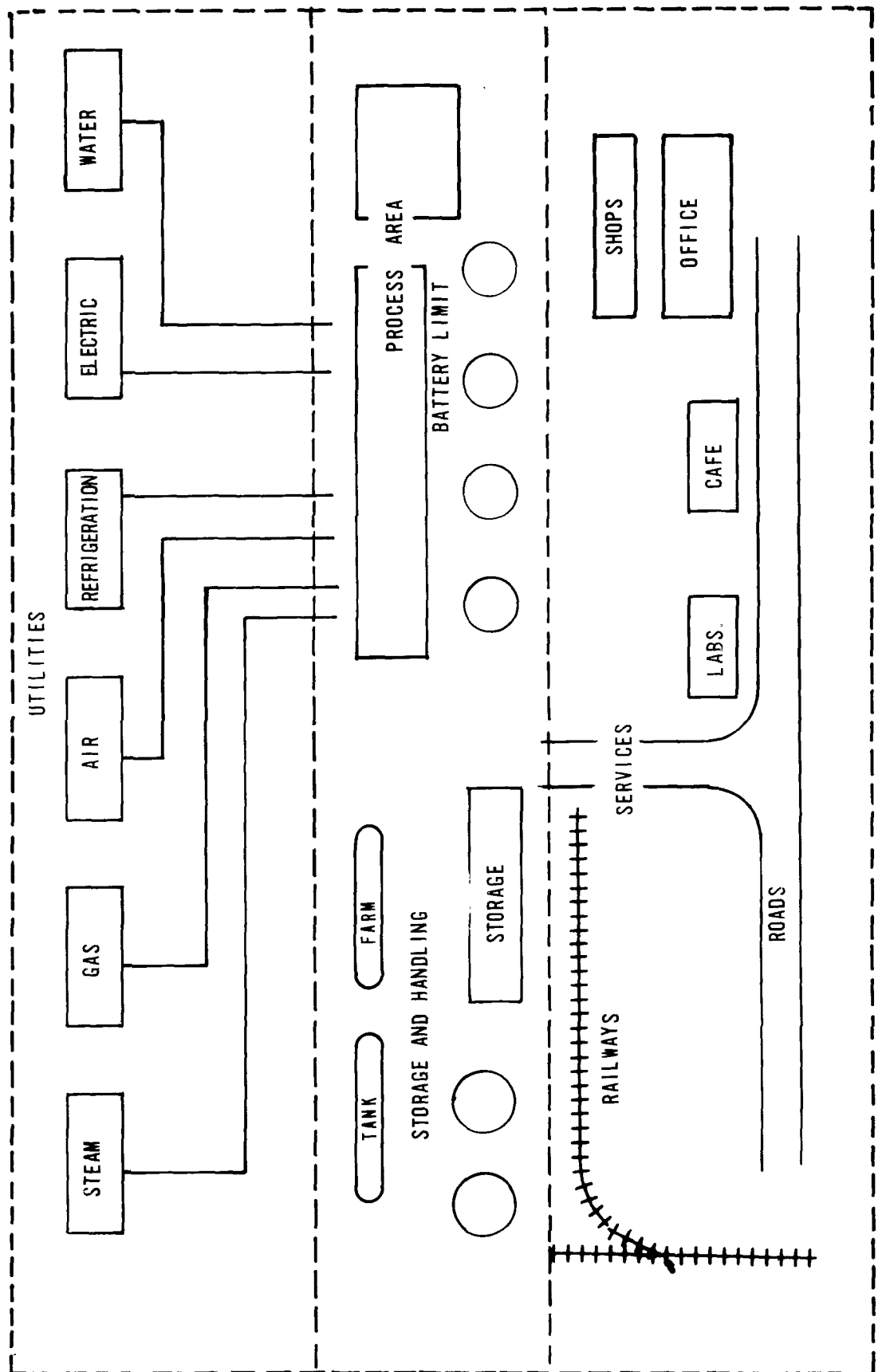
Steam is supplied to the different users throughout the plant either by natural-circulation, vapor-phase systems, or by forced-circulation liquid heat-transfer systems. Both types of system discharge some condensate as blowdown and require the addition of boiler makeup water. The main areas of consideration 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 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.

Parameters	Boiler Pressure, Psig			
	0-300	301-450	451-600	601-750
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 standarized 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

FIGURE III-6
CLOSED SYSTEM
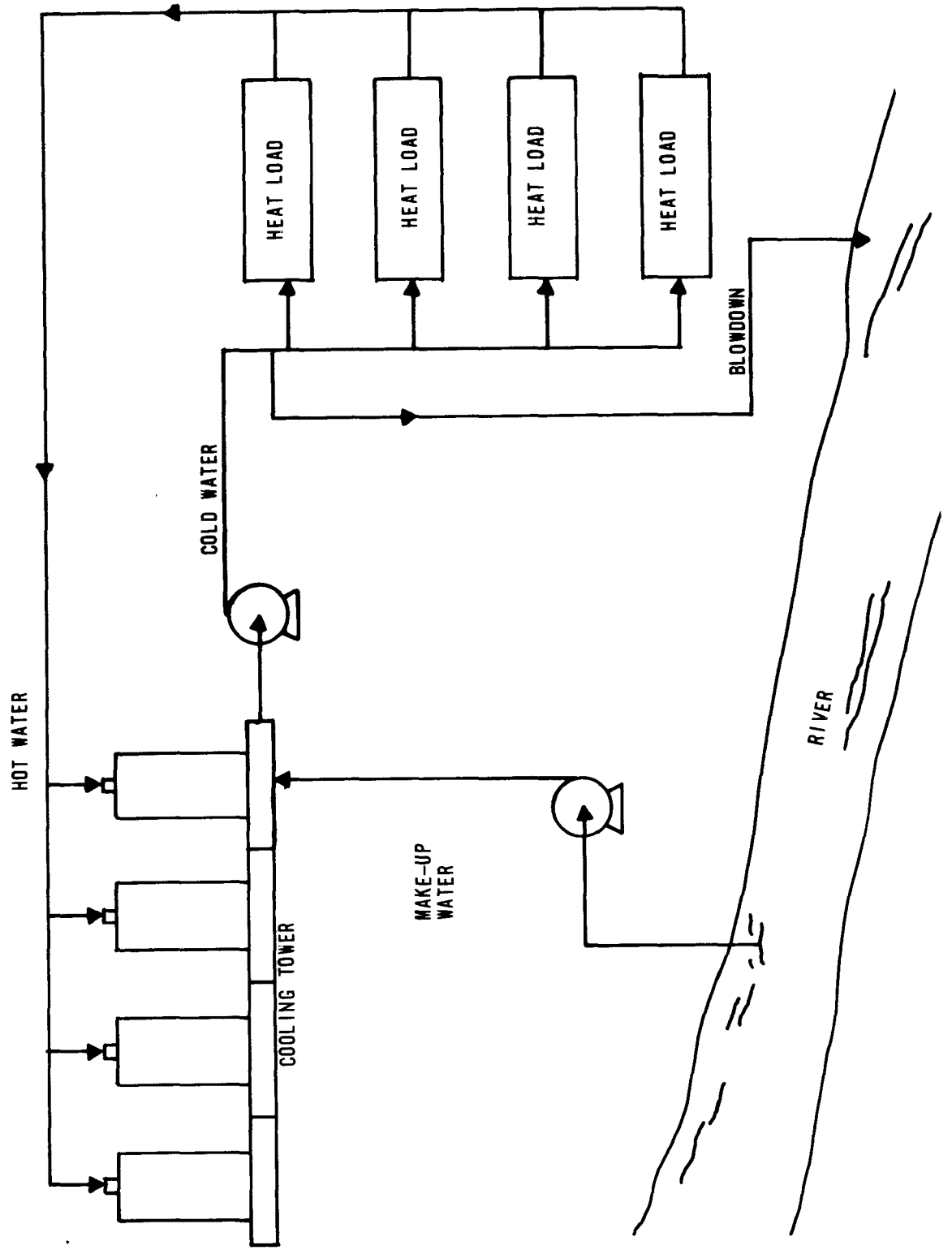
the Service area normally are combined with the wastes from the process area prior to treatment.

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.

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 con-

trolled 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, efficans 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 surface 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 by-products. 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.

FIGURE III-7

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:

```
RAW  ⎫          CONTACT ⎫        NATURE  ⎫              UNIT OPERATIONS
WASTE⎬ ──▶      PROCESS ⎬        OF      ⎬        ↗(PHYSICAL SEPARATIONS)
LOAD ⎭          WATER   ⎬ ═▶     PROCESS ⎬ ──▶
                USAGE   ⎭        MODULE  ⎭        ↘      CHEMICAL
                                                        CONVERSIONS
                                                        (REACTIONS)
```
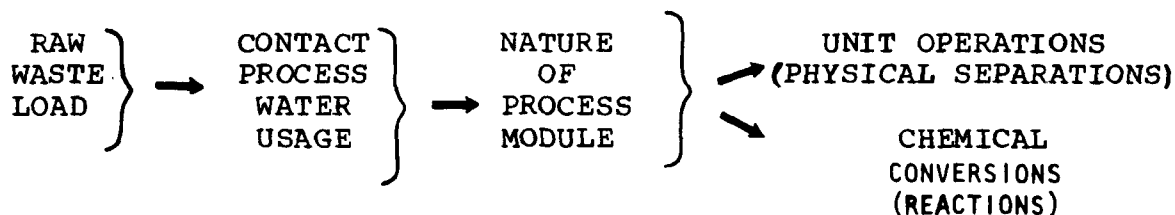
Manufacturing processes have been examined for type of process water usage associated with each. Process water is defined to be all water which comes in contact with chemicals within the process and includes:

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.

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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:

Subcategory A	Subcategory B	Subcategory C	Subcategory D
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.

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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

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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 soltion, 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.

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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.

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Product___   _____Process_____
Cyclohexane   Hydrogenation of Benzene

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

C6H6   +   3H2   ➝   C6H12

Benzene   Hydrogen   Cyclohexane
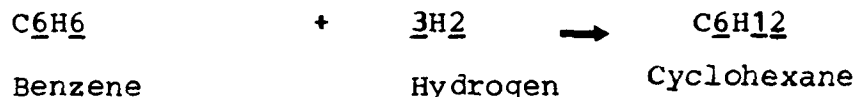
The reaction is usually carried out in the liquid phase with a nickel-palladium or platinum catalyst at elevated temperature and pressure. Fresh feed (benzene) is combined with makeup and recycle hydrogen and preheated to reaction temperature by heat exchange first with reactor effluent and then with 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
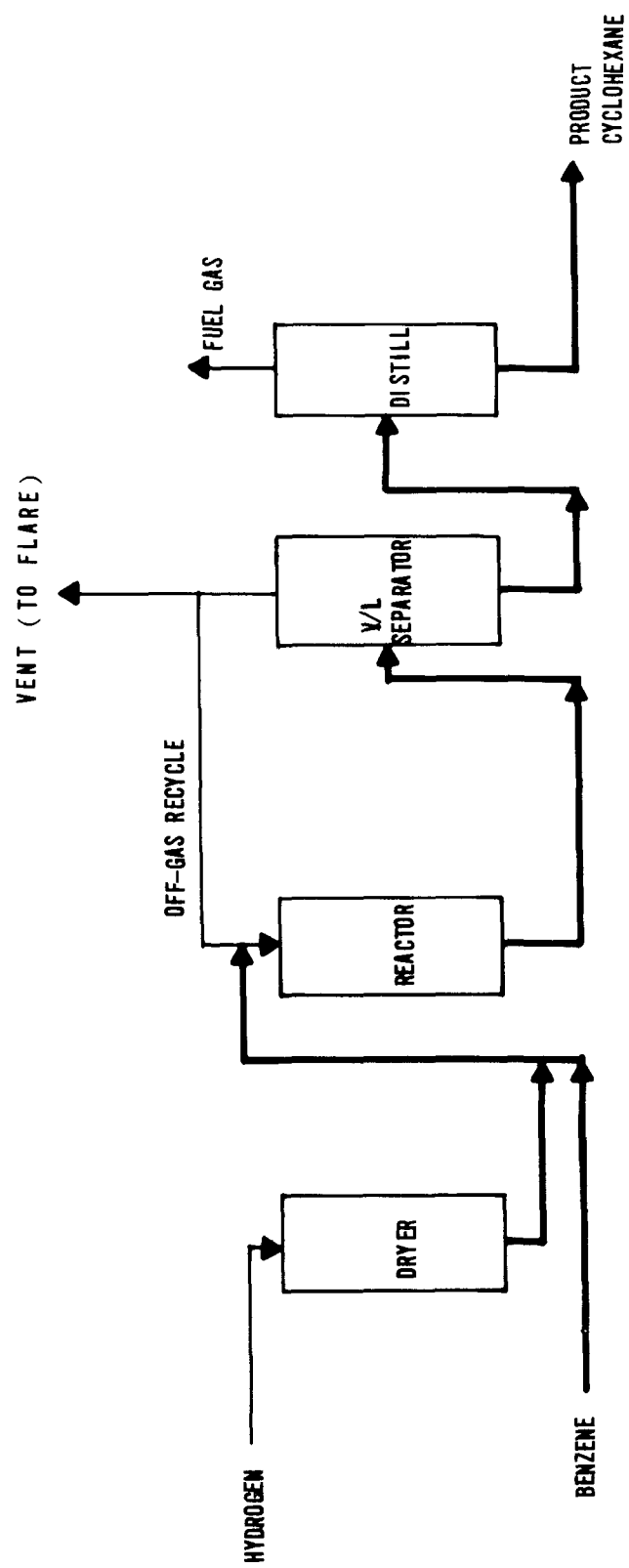
Table IV-I

U.S. Cyclohexane Capacity
(MM gal)

Company	1967[1]	1972[2]	Process
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	434	387	
Total[3] (MM lb)	2,820	2,520	

[1] 82% based on benzene hydrogenation.
[2] 74% based on benzene hydrogenation.
[3] 6.5 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

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

SUBCATEGORY A

Product   Process
Ethyl benzene   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:

$$C_6H_6 \quad + \quad C_2H_2 \quad \longrightarrow \quad C_6H_5C_2H_5$$
Benzene   Ethylene   Ethyl Benzene

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 recyled 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

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
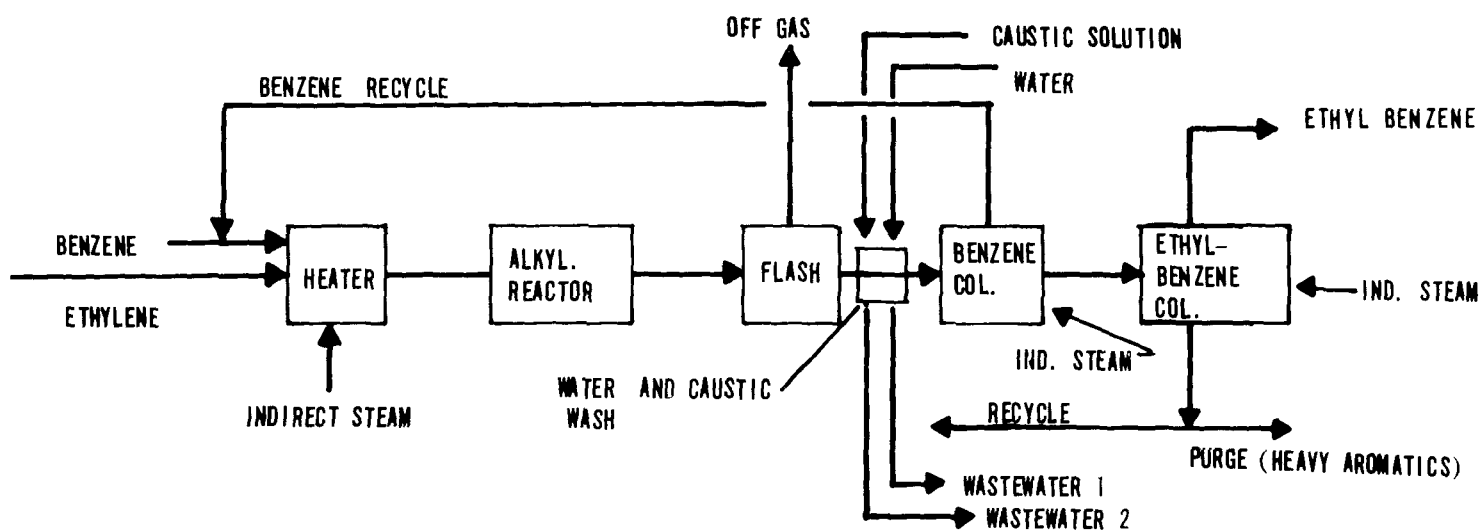
Table IV-3

U.S. Ethyl Benzene Capacity

Producer	Plant Location	Estimated Mid-1970 Capacity** Alkylation	Recovery
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	350	-
TOTAL		6,250	465

* Plant not currently operating but not dismantled.
  Not included in total.
** MM lbs/yr.

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SUBCATEGORY A

_____Product_____   _____Process_____
Vinyl Chloride   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:

$$C_2H_2 \quad + \quad HCl \quad \longrightarrow \quad C_2H_3Cl$$

Acetylene   Hydrogen   Vinyl Chloride
                   Chloride
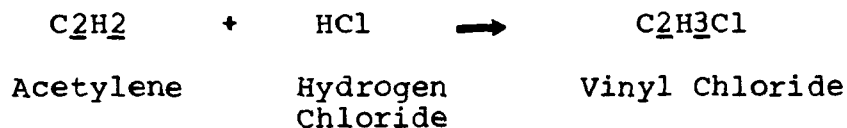
A process flow sheet is shown in Figure IV-3. The feed stocks,
acetylene and anhydrous hydrogen chloride, are fed into tubular reactors
which are packed with mercuric chloride impregenated on granular
activated carbon. The reactor effluent is sent to a three column
distillation system for purification, 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.

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The analytical results for a single batch are presented below:

	Before Treatment	After Treatment
COD (mg/l)	1,836	1,306
TOC (mg/l)	448	33
SS (mg/l)	1,124	24
Hg (micrograms/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
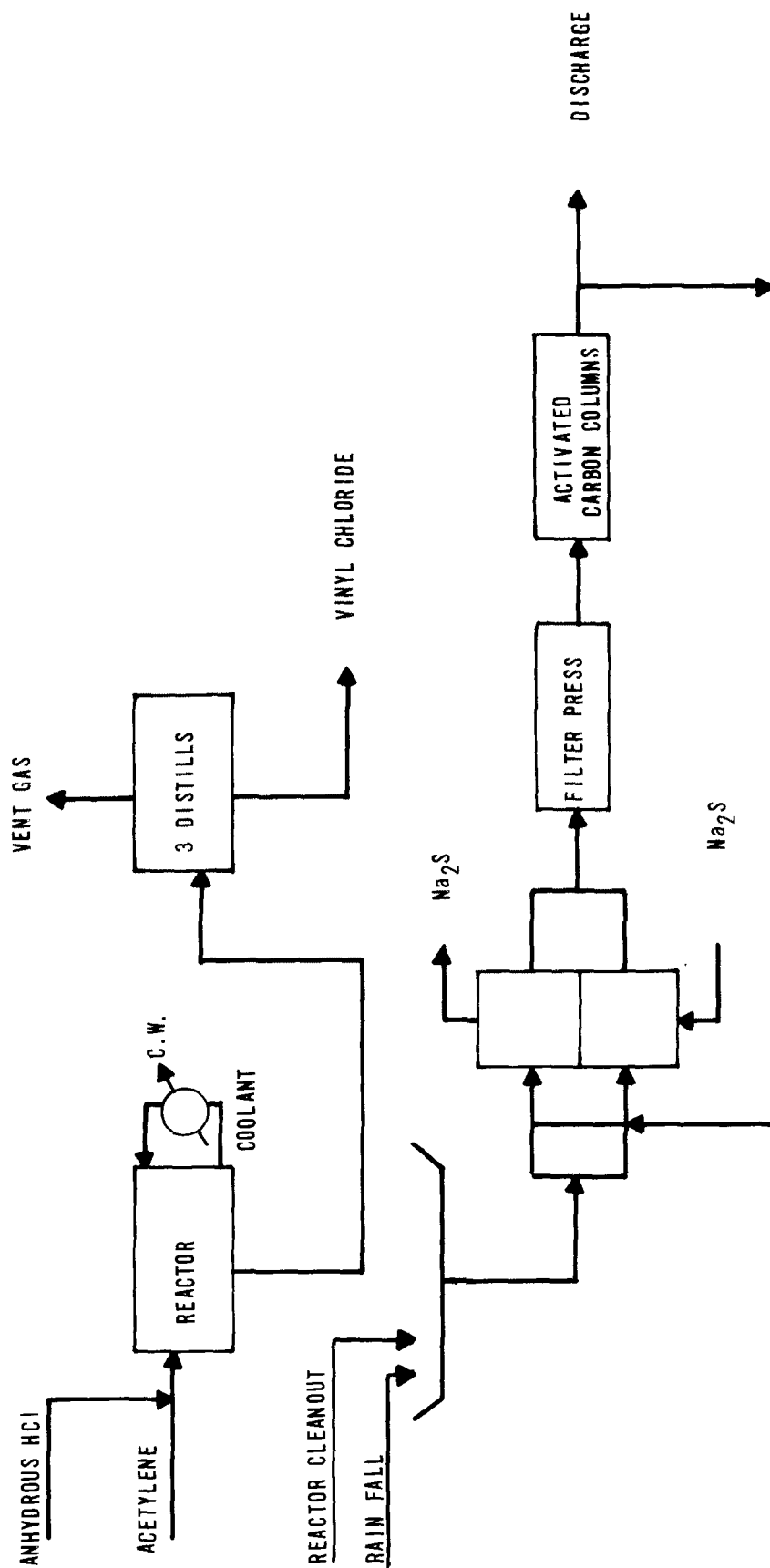
Product   Processes

Benzene, Toluene and Xylene(BTX) Aromatics   1.   Hydrogenation Pyrolisis
                                                   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 naptha 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 nable 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

FIGURE IV - 4

BTX PRODUCED BY HYDROTREATING PYROLYSIS GASOLINE
WITH SUBSEQUENT SOLVENT EXTRACTION
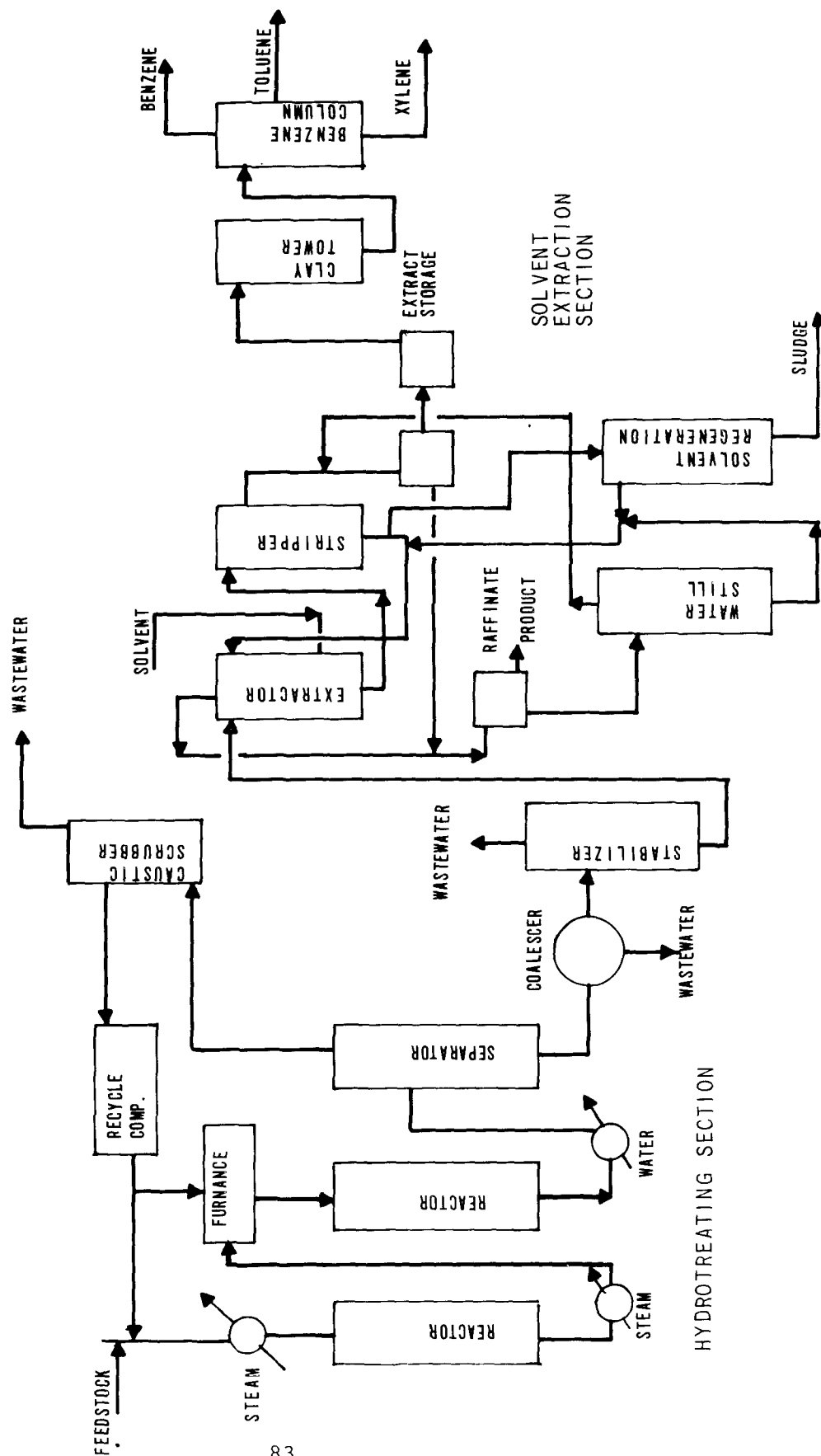
from the reactor is passed through a coalescer (where water is used to trap coke particles formed in the pyrolysis reactor) and a stabilizer (where light hydrocarbons are removed).

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
BOD5	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 napthas 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

Producer	Location	Benzene from petroleum — Extraction	Benzene from petroleum — Dealkylation	Toluene
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.

Product	Process
BTX Aromatics	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 digylcloamine 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 etraction. With this argument, solvent extraction will only be used on reformate 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	73
TOTAL			1,225

*From reformate and pyrolysis gasoline.
 Does not include coke oven operations.

a = Reformate
b = Pyrolysis gasoline
c = Toluene Disproportionation

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Product   Process
Ethlyene and Propylene   Pyrolysis of Hydrocarbons

Ethylene and proylene 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:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$
Ethane   Ethylene   Hydrogen

$$2\ C_3H_8 \longrightarrow C_3H_6 + H_2 + C_2H_4 + CH_4$$
Propane   Propylene   Hydrogen Ethylene Methane
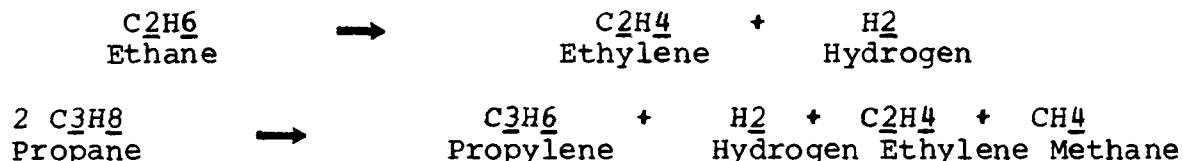
A process flow sheet is shown in Figure IV-5. The hydrocarbon feedstock is diluted with steam and passed thourgh a pyrolysis furnace, where cracking takes place. Normal temperatures in the cracking section of the furnace are 1,500 to 1,600 F, and residence time is one second or less. The purpose of steaqm 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 hydorgen 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 hydeogenated 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 sepatated. 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
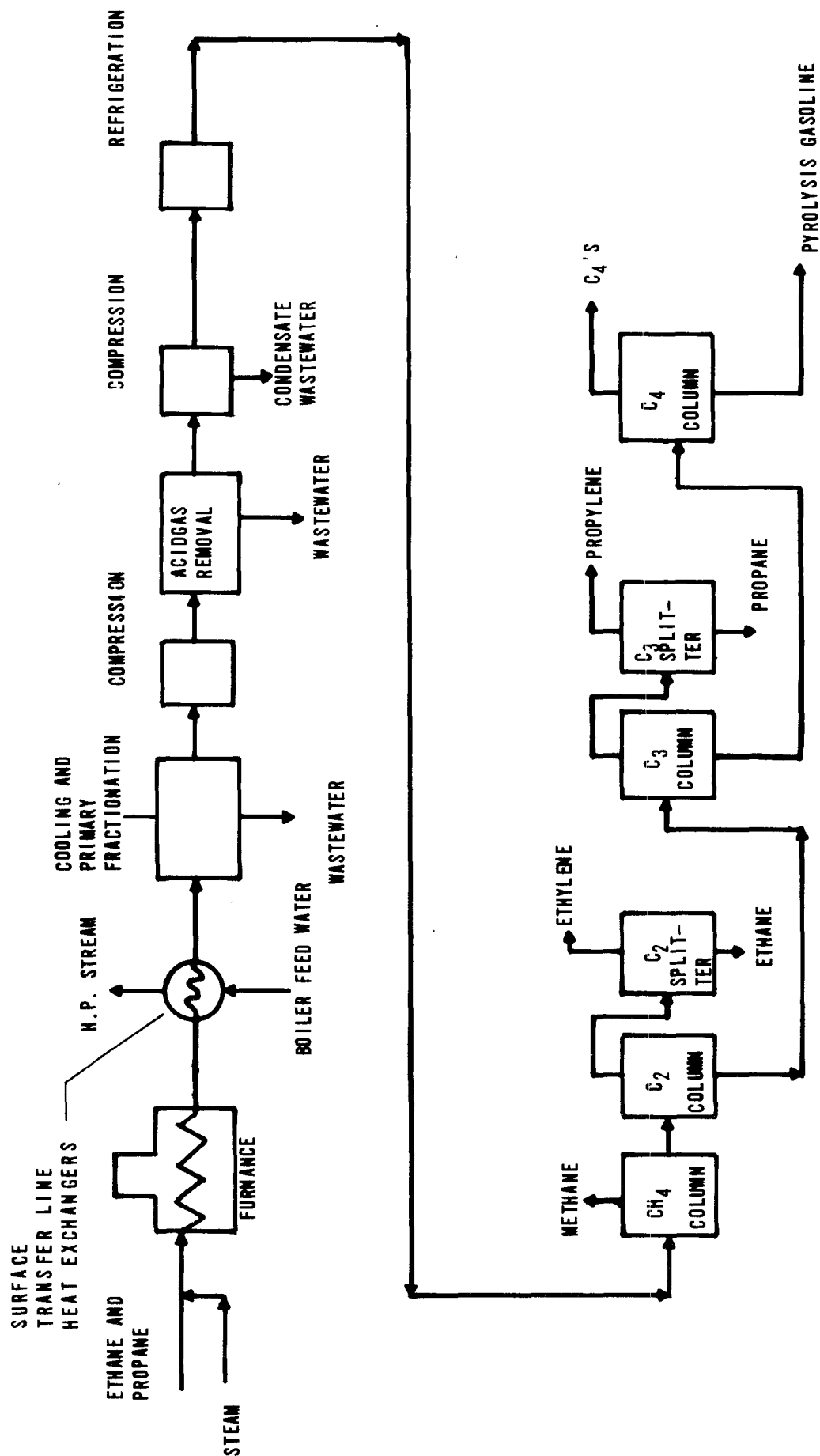
The C4 + depropanizer bottoms are sent to the debutanizer, and the over-head is selectively hydrogenated in the heavy acetylene splitter in order to remove trace amounts of methyl acetylene and propadiene. The de-propanizer overhead goes to the C3 splitter where the propane and propylene are separated. 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 amy 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 reduct the hydeocarbon 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 the 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 hudeocarbon 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 palnt 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 pases to a tray section where cooling to approximately 105°F (40°C) takes place, the exact temperature being a function of the available cooling water temperature. Fractionation

Table IV-6

U.S. Ethylene Capacity (1972)

Company	Feedstock	MM lb
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 (Penuelas, 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
		21,630

Source: Informations Chiemie, May, 1970 p. 157

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 sepatated int he quench tower, ferquently 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 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 rpoduce an additional vacuum distillate; this additional product would notmally 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.

Plant No.	Flow gal/1,000 lb	COD lb/1,000 lb (mg/l)	BOD5 lb/1,000 lb (mg/l)	TOC 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.

Plant	Occurrence	Flow gal/1,000 lb	COD lb/1,000 lb	TOC 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 wastwater 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 wastwater 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 requied 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 guage 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 palnt 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 strippper and steam dilution. In addition, 2 pumps, and a steam reboiler are required. Investments for these facitities for a 5×10^8 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 operting 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

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 $ 80,000

                          TOTAL $240,000

*For a 500 MM lb/yr ethylene plant using C_2/C_3 feed,
totally installed, U.S. Gulf Coast location,[3] 1973.

FIGURE IV-6

WATER QUENCH WITHOUT CONDENSATE STRIPPER
(500MM LB./YR. ETHYLENE PLANT WITH C_2 / C_3 FEEDSTOCK)

100^0F COOLED GAS TO COMPRESSION
153,500 #/HR.

105^0F 430,000 #/HR.

$\emptyset$ 12'-4''

LOW LEVEL
HEAT REMOVAL

C.W.

130^0F 1,182,250 #/HR.

$\emptyset$ 16'-8''

HIGH LEVEL
HEAT
RECOVERY

FURNACE EFFLUENT FROM
TRANSFER LINE HEAT

EXCHANGERS
187,000 #/HR.
600^0F

8 PSIG

1,645,750 #/HR.

CONDENSED OIL
2850 #/HR.

180^0F

43,000 #/HR.
WATER

WATER MAKE-UP
12,350 #/HR.

CIRCULATING WATER
1,599,900 #/HR.
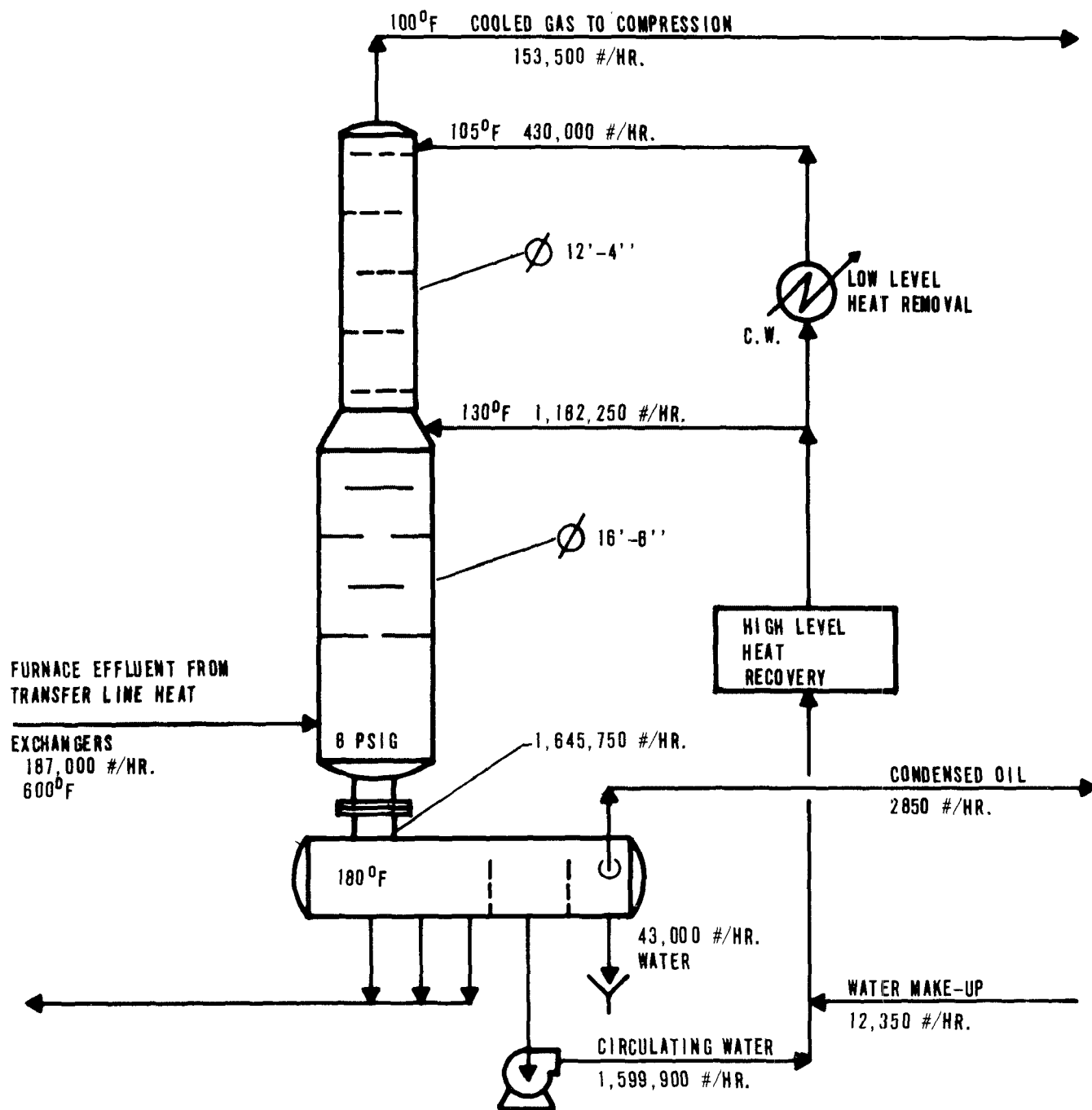
FIGURE IV-7

WATER QUENCH WITH CONDENSATE STRIPPER
(500 MM LB./YR. ETHYLENE PLANT WITH C_2/C_3 FEEDSTOCK)

110 °F COOLED GAS TO COMPRESSION

153,500 #/HR.

105°F 430,000 #/HR.

LOW LEVEL
HEAT REMOVAL
C.W.

∅ 12'-4''

130°F 1,182,250 #/HR.

∅ 16'-6''

HIGH LEVEL
HEAT
RECOVERY

3260 #/HR.

FURNACE EFFLUENT
FROM TRANSFER LINE HEAT

600°F

EXCHANGERS 187,000 #/HR.

8 PSIG

CONDENSED OIL
2850 #/HR.

180°F

MAKE-UP
WATER
12,250 #/HR

TAR TO DISPOSAL
(NORMALLY ZERO)

CIRCULATING
WATER
1,600,000 #/HR.

DILUTION STEAM
43,000 #/HR.
110 PSIG
TO FURNACE

46,160 #/HR.

344°F

7' ∅ X 20'

4' & 8 ∅ X 38'

30%
VAP.

40 PSIG

STEAM
STEAM
6100 #/HR.
3000 #/HR.
9200
#/HR.

C.W.

11 PSIG
240°F

130°F

49,000 #/HR.

6000 #/HR BLOWDOWN

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

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

Investment Items:

Depreciation	24,000
Maintenance, Insurance and Other	11,000
	$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.

other handling problems. This water would probably be returned to the quench tower for re-processing.

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:

Plant No.	Flow gal/1,000 lb	COD lb/1,000 lb (mg/l)	BOD5 lb/1,000 lb (mg/l)	TOC 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

Product	Processes
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:

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_2 = CHCH = CH_2 + 2H_2$$
$$\text{n-butane} \qquad \text{1-3 butadiene} \qquad \text{Hydrogen}$$
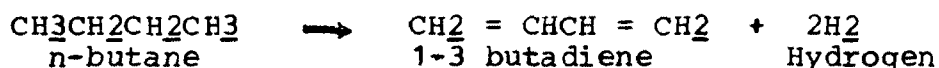
A process flowsheet is shown in Figure IV-8. The feedstock (n-butane) and recycled butane and butenes are fed into a battery of fixed-bed reactors. The reactor effluent is oil-quenched, compressed, and sent to an absorption column, where hydrocarbon vapor is absorbed with light oil. The effluent from 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:

$$C_4H_8 + 1/2 \ O_2 \longrightarrow C_4H_6 + H_2O$$
$$\text{Butylene} \qquad \text{Oxygen} \qquad \text{Butadiene} \qquad \text{Water}$$
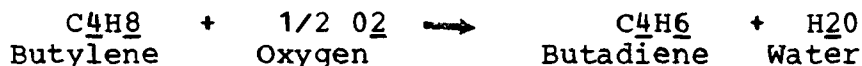
2. **Co-product of ethylene manufacture**

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

FIGURE IV-8

BUTADIENE, DEHYDROGENATION OF n-BUTANES
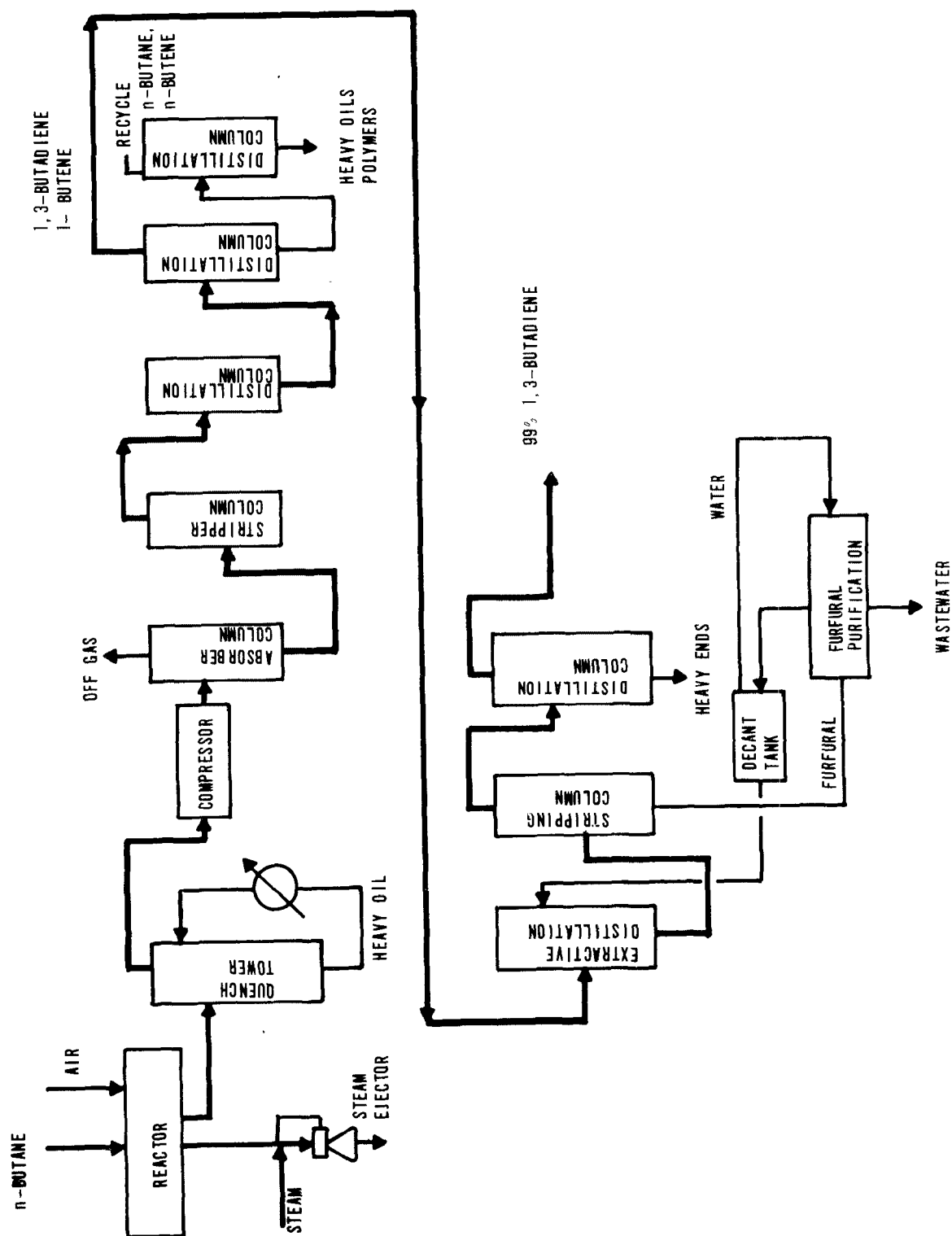
cuprous ammonium acetate (CAA) extraction. The effluent is then sent to a steam stripper and fractionator, where heavy ends are removed. The stream taken overhead from the fractionator is further washed with water to remove solvents.

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 gal/1,000 lb (mg/l)	COD lb/1,000 lb (mg/l)	BOD5 lb/1,000 lb (mg/l)	TOC 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
BOD5	0.18 lb/1,000 lb
TOC	0.21 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 barmetric 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 C_4-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)

Company	Location	MM lbs/yr.
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 C4		
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

	Cost ¢/lb. butadiene
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

Product
Methanol

Process
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:

1. CH_4 + H_2O $\longrightarrow$ CO + $3H_2$ (synthesis)
   Methane   Water   Carbon   Hydrogen   gas)
                                    Monoxide

2. CO + $2H_2$ $\longrightarrow$ CH_3OH
   Carbon   Hydrogen   Methanol
   Monoxide

3. CO_2 + $3H_2$ $\longrightarrow$ CH_3OH + H_2O
   Carbon   Hydrogen   Methanol   Water
   Dioxide
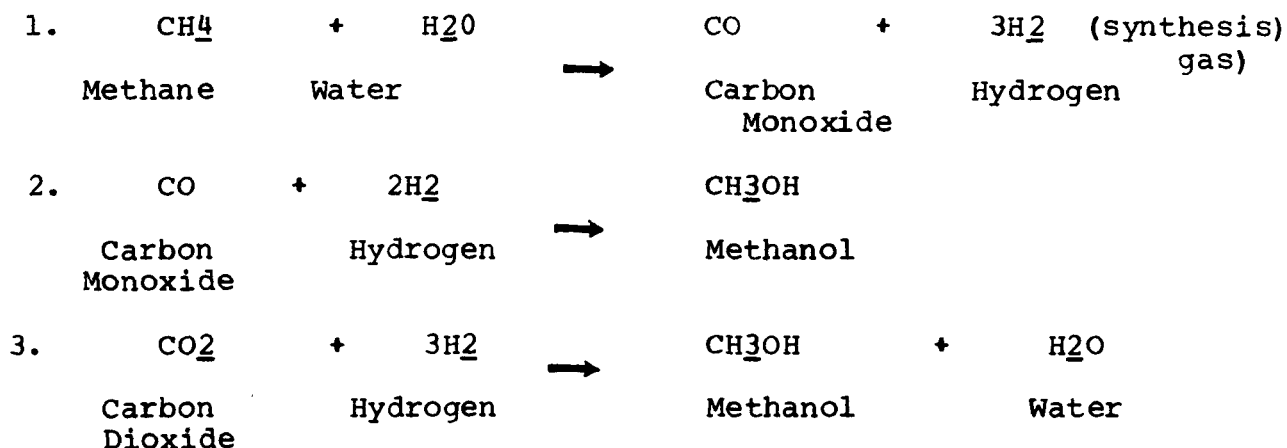
The optimum atomic ratio for C/H in methanol synthesis is 1/4 as indicated above. However, carbon dioxide is added to take care of extra hydrogen resulting from steam reforming of natural gas.

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.

FIGURE IV-9

METHANOL
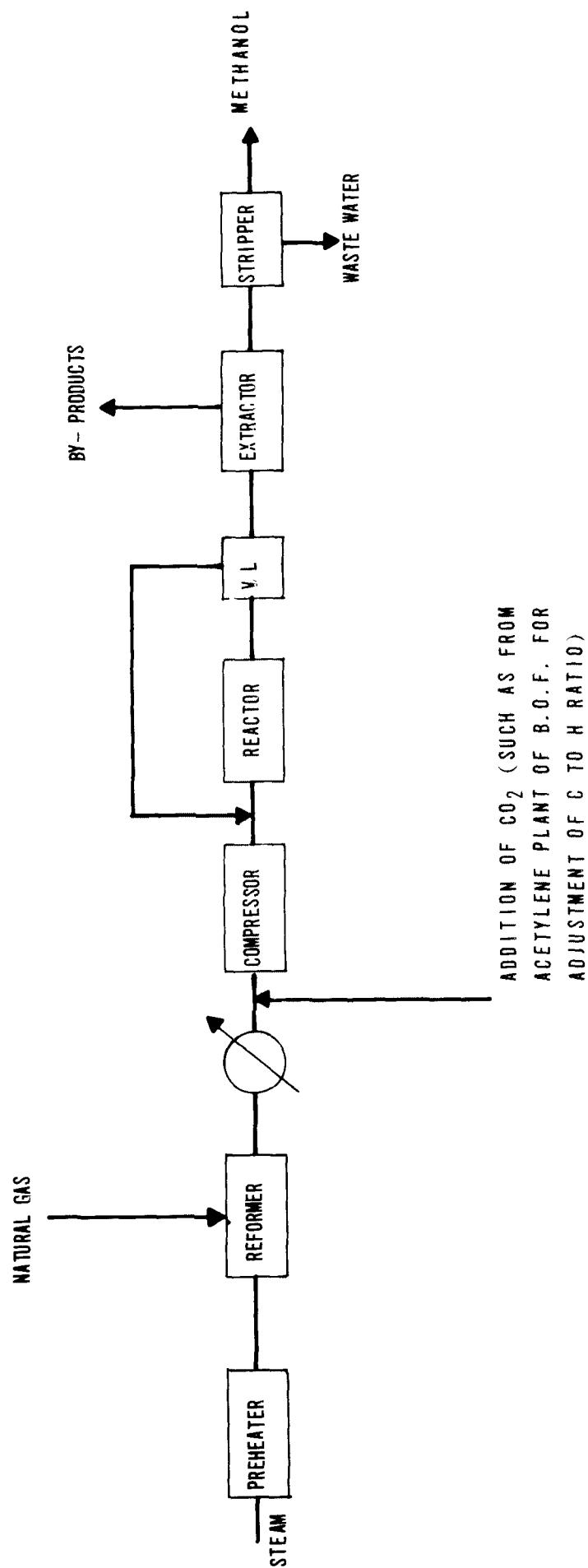
The only waste water stream from methanol plants using 100% natural gas feedstock is the aqueous stream from the final methanol distillation column. Processes which utilize off-gases from acetylene manufacture as feedstock introduce impurities into the system. These impurities must be removed before 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$\underline{5}$	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)

Company	Location	MM gallons
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	42
	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.

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:

$$CH_3 CHOHCH_3 \longrightarrow CH_3COCH_3 \quad + \quad H_2$$

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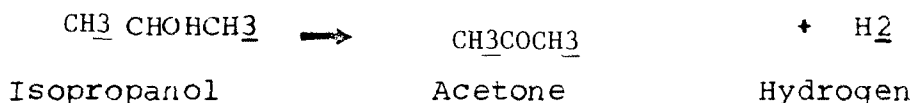
In this process, water is used to absorb product acetone and unreacted isopropanol from the hydrogen produced. After fractionation, one or two waste water streams are produced as bottoms from the isopropanol stripping still or as bottoms from the intermediate flash column. The waste water contains acetone,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

	Plant 1	Plant 2
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
BOD5	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

FIGURE IV.-10
ACETONE, DEHYDROGENATION OF ISOPROPANOL

concentration in the intermediate flash column waste water is a function of the column design; recycle of the above mentioned streams will not 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$\underline{5}$	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)

Company	Location	1967	1968	1970	1972	Process
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	

	1967	1968	1970	1972
% 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

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

Product	Processes
Acetaldehyde	1. Oxidative-Dehydrogenation of Ethyl Alchohol
	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:

Feedstock	Process	Percent of 1970 U.S. Capacity
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:

$$C_2H_5OH \quad + 1/2\ O_2 \longrightarrow CH_3CHO \ + \ H_2O$$

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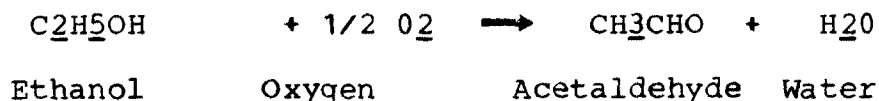
The reaction is vapor-phase and is carried out over a solid silver gauze catalyst at about 1,000°F. The reactor effluent is condensed and is passed to a phase separator. The gaseous phase is absorbed in refrigerated water. Off-gases pass from the system, and the wash is combined with the liquid stream.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

Dehydrogenation of ethanol is based on the chemical reaction:

$$C_2H_5)OH \longrightarrow CH_3CHO \ + \ H_2$$

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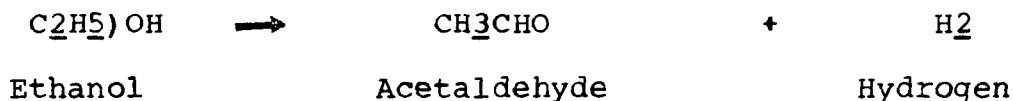
This reaction is also vapor phase and is carried out over a solid copper catalyst promoted by cobalt or chromium on an asbestos support at 500°F.

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

FIGURE IV-11

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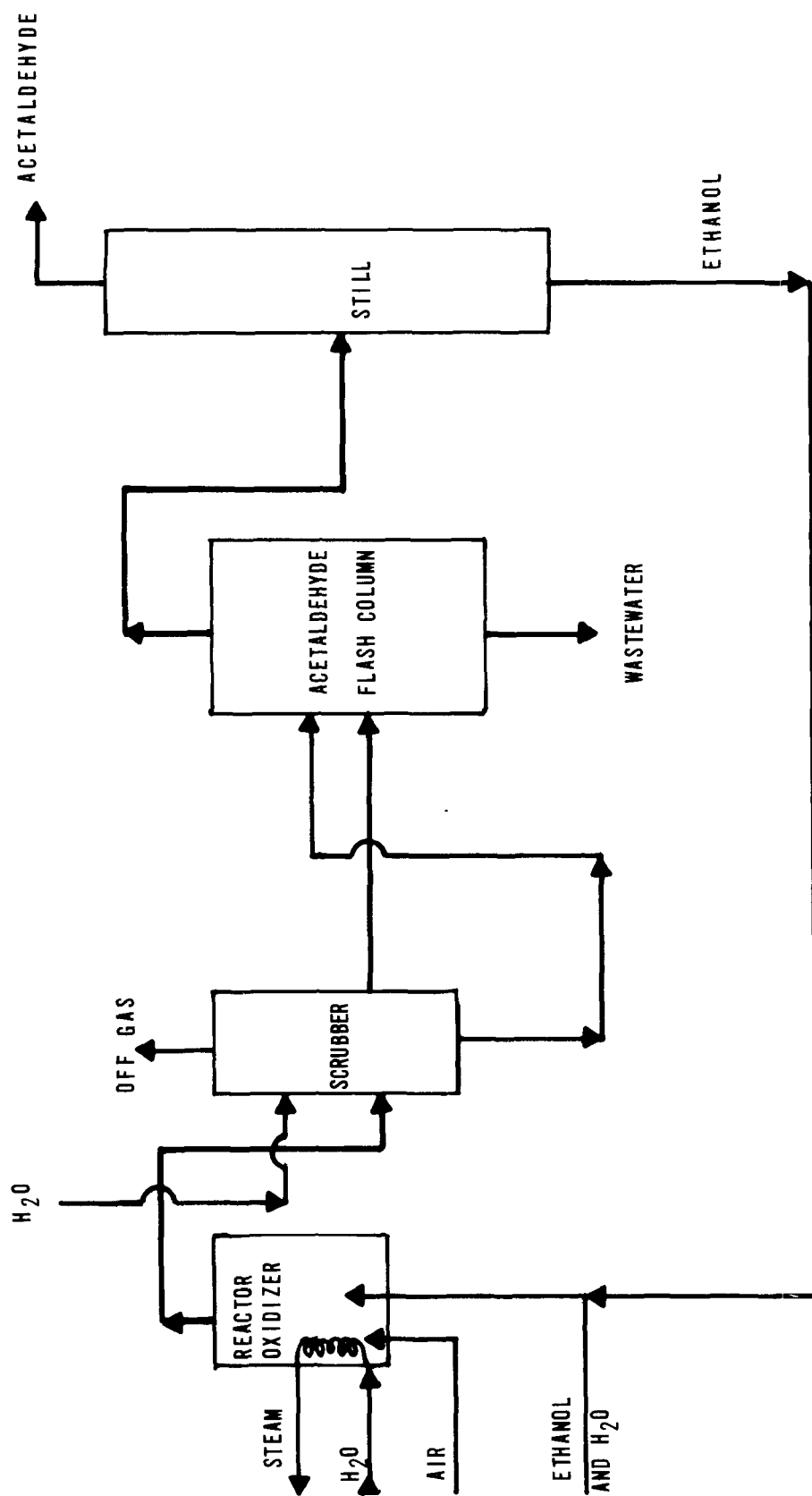
These processes yield from 85 to 95 percent of the stoichiometric amount of acetaldehyde. The only waste water stream generated in these processes is either from the acetaldehyde flash column or the ethanol recovery still, and contains liquid by-products such as acetic acid. The survey data are shown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

	Plant 1	Plant 2
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.
BOD5	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:

Plant	Process Water lb/lb product	Cooling Water lb/lb product
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.

Table IV-16

Acetaldehyde Capacity

(MM lb)

Company		1967	1972	Process
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	Process
Acetylene	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.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Methane   Oxygen   Carbon Dioxide   Steam

$$2CH_4 \longrightarrow C_2H_2 + 3H_2$$

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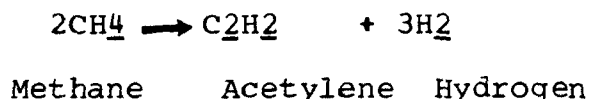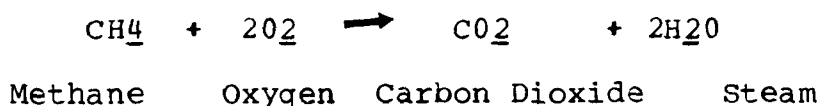
Cracking occurs at 1,500°C with a residence time of 0.01 to 0.1 seconds. The resulting gases are rapidly quenched with water to prevent acetylene decomposition. A gas cooler and a series of distillation columns are then used to separate acetylene from by-products.

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
BOD5	410 mg/l 1.92 lb/1,000 lb
TOC	393 mg/l

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FIGURE IV-12
ACETYLENE

NATURAL GAS

OXYGEN

BURNER

GAS COOLER

WATER

DISTILLATION COLUMN

PRODUCT ACETYLENE

BY-PRODUCTS

DAF

VACUUM FILTER

INCINERATION

HOT QUENCH WATER

COLD QUENCH WATER

COOLING TOWER

DRAW-OFF
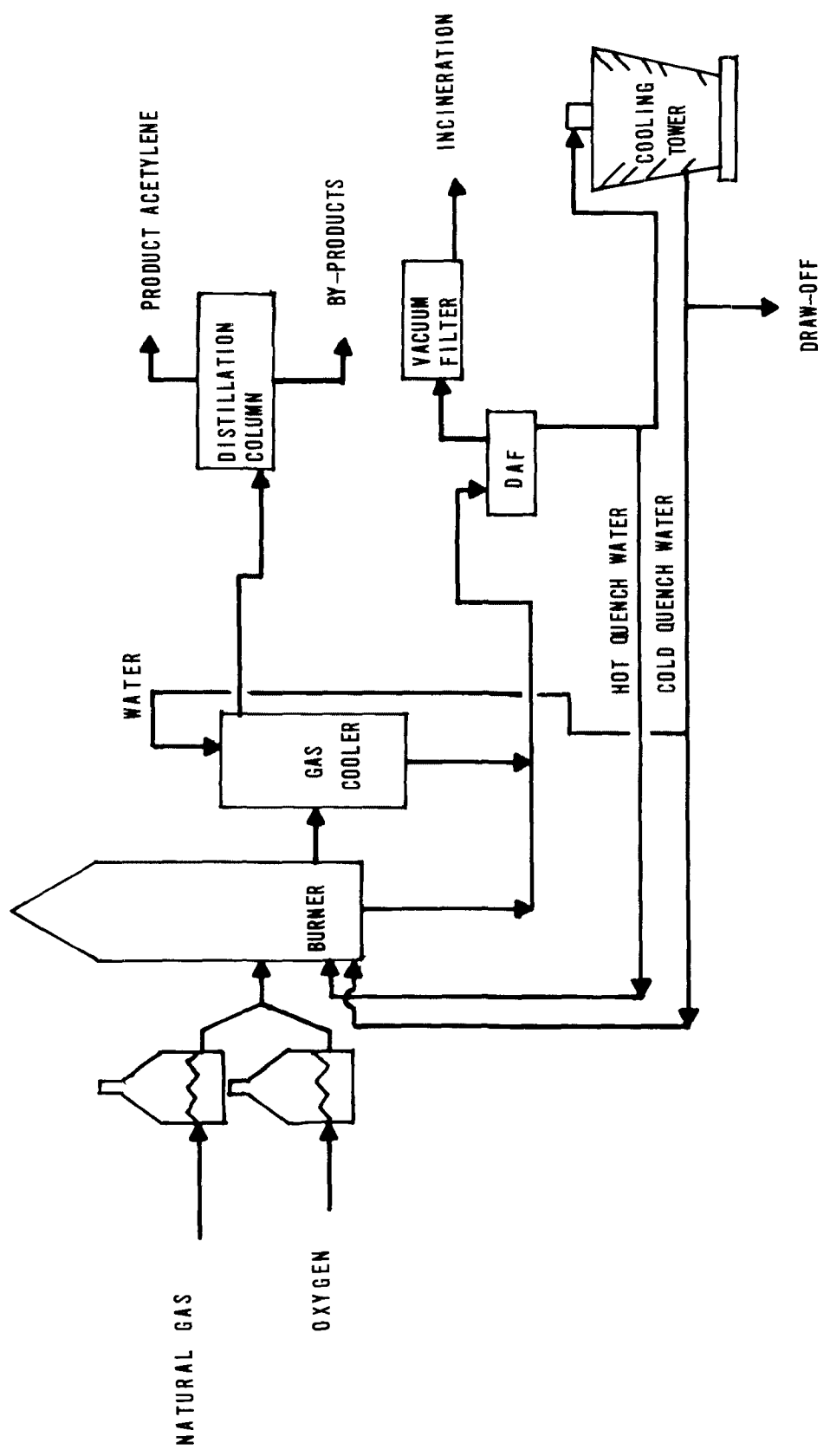
Comparing these data with those for the cooling water just prior to being discharged to the cooling tower inlet indicates that a significant amount of hydrocarbons are evaporated into atmosphere. In order to further reduce the RWL and not sacrifice ambient air quality, a steam stripper can be installed 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)

Company	MM lb	Process
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	Parial oxidation
Other	735	Calcium carbide
Total	1,203	

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

Product	Process
Ethylene Oxide	Catalytic Oxidation of Ethylene

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

$$C_2H_4 \quad + \quad 1/2\ O_2 \quad \longrightarrow \quad H_2COCH_2$$

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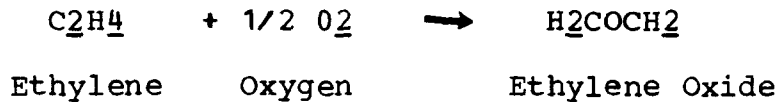
Oxidation takes place in the main reactor. Partial oxidation of ethylene to ethylene oxide and total oxidation to carbon dioxide and water are the two primary reactions. Ethylene oxide is recovered from the reactor effluent by absorption in a dilute aqueous solution.

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
BOD5	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

FIGURE IV-13

ETHYLENE OXIDE
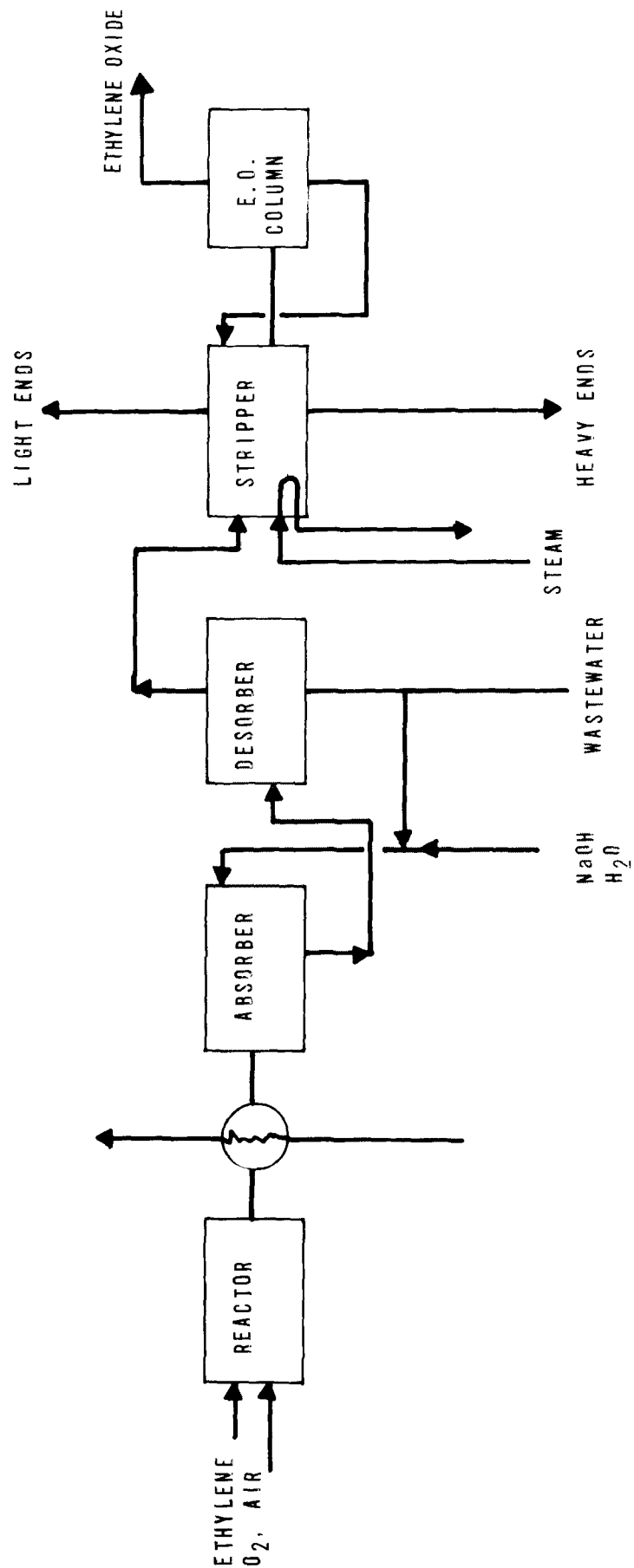
operates more effectively and, consequently, generates a lesser volume of wastewater. Further reduction of RWL of Plant 1 is deemed unfeasible, and it should be considered as a representative RWL of this process in BPCTCA standards.

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)

Company	Location	1970	1972
Calcasieu Chemical	Lake Charles, La.	150	150
Celanese	Clear Lake, Texas	300	300
Dow	Freeport, Texas	425	425
	Placequemine, 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
	Texas City, Texas	700	500[1]
	Torrance, Calif.	50	50
	Whiting, Ind.	150	150
	Ponce, P.R.	100	100
	Taft, La.	350	450
	TOTAL	4,280	4,215

[1]One 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

Process	$ MM
Chlorohydrin	15.20
Catalytic air oxidation	38.60

Estimated Operation Cost

	Cost	
	¢/lb ethylene oxide	
	Chlorohydrin	Air Oxidation
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)	0.50	1.32
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.

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___Product__   _____Process_____
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:

$$CH_3OH \quad + \; 1/2 \; O_2 \quad \longrightarrow \quad HCHO \quad + \quad H_2O$$

Methanol   Oxygen   Formaldehyde   Water
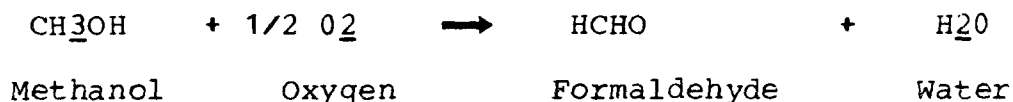
A flow sheet for the methanol oxidation process is shown in Figure IV-14. A mixture of methanol and water is vaporized by a closed steam loop, which circulates between the reactor and feed vaporizer. The reactants, mixed with air, flow through a thin layer of catalyst crystals in the reactor. The product 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.

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FIGURE IV-14
FORMALDEHYDE, METHANOL OXIDATION
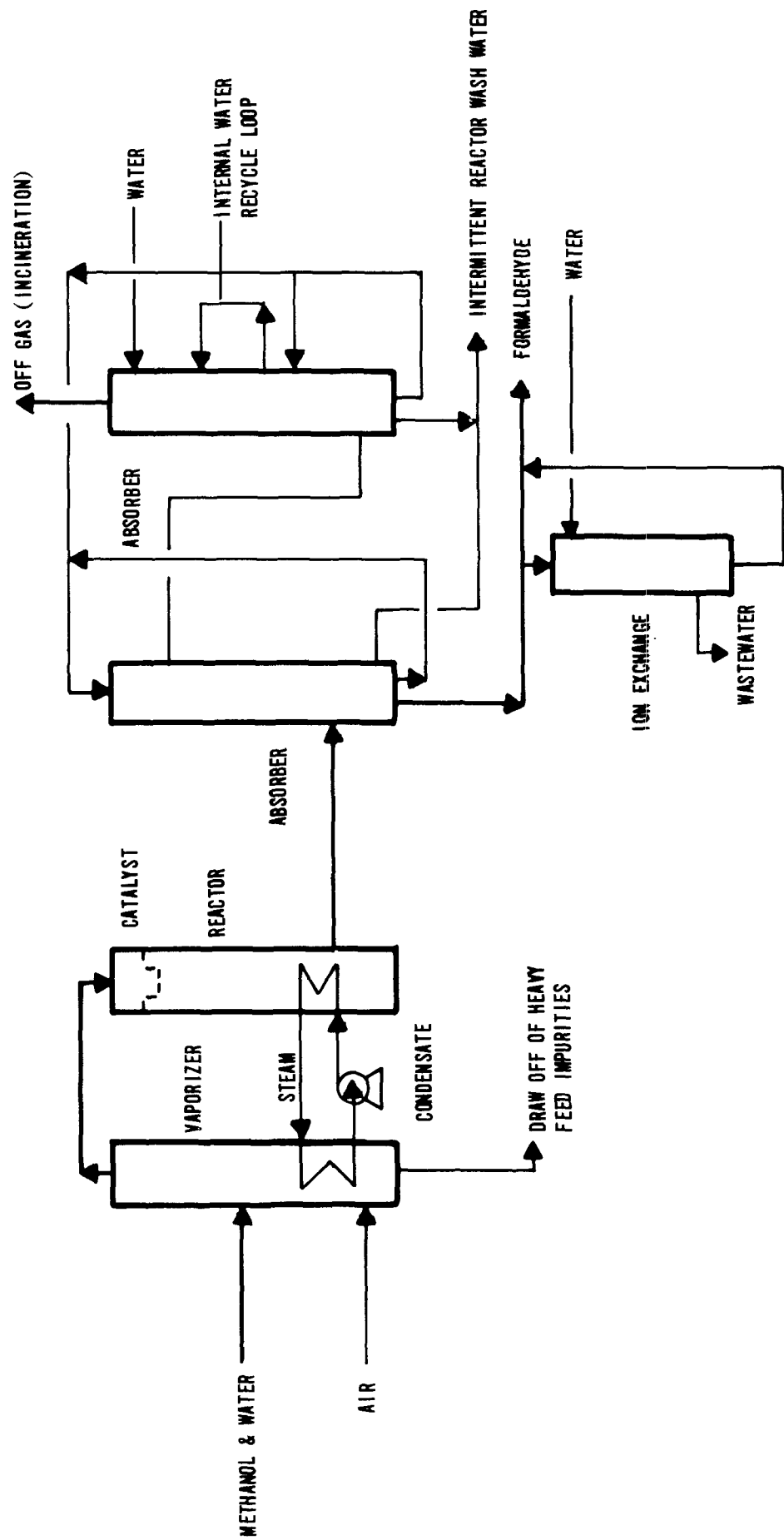
About 90 percent of the formaldehyde produced in the U.S. is based on methanol as a raw material. The balance of the formaldehyde production is as a co-product of butane oxidation. The basic chemical reaction is summarized as follows:

$$2C_3H_8 + 2C_4H_{10} + 9O_2 \longrightarrow 14HCHO + 4H_2O$$

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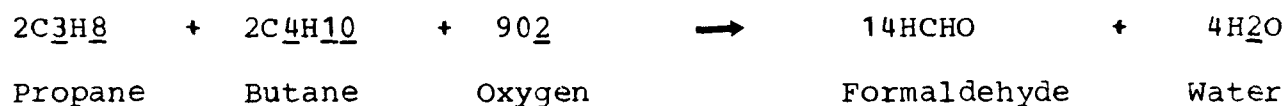
The U.S. formaldehyde capacity and the estimated economics for formaldehyde production of a 100 million pounds per year (100 percent) unit based on iron-molybdenum catalyst process are shown in Tables IV-20 and IV-21.

Table IV-20

U. S. Formaldehyde Capacity

Producer	Plant Location	Estimated Capacity* (MM lbs. 37% Soln./Yr.)
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)

Producer	Plant Location	Estimated Capacity* (MM lbs. 37% Soln. /Yr.)
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.	100
TOTAL		6,570

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

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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	1.5	1.5
TOTAL	6.5	8.2

SUBCATEGORY B

Product	Process
Ethylene Dichloride	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.

$$C_2H_4 \quad + \quad Cl_2 \quad \longrightarrow \quad ClCH_2\,CHCl$$

Ethylene   Chlorine   Ethylene Dichloride
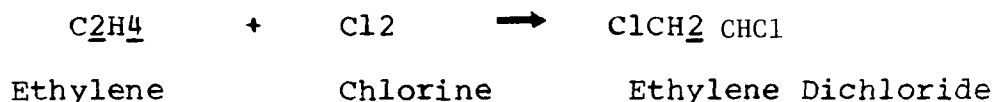
The gas stream from the reactor is passed through a caustic scrubber, where the unreacted gases and a trace amount of hydrogen chloride are removed by a caustic solution. The liquid stream from the reactor is first sent to a distillation column to remove heavy ends and then to a wash tower, where a caustic 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 off-gas 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.

FIGURE IV-15

ETHYLENE DICHLORIDE (EDC) BY OXYCHLORINATION AND DIRECT CHLORINATION
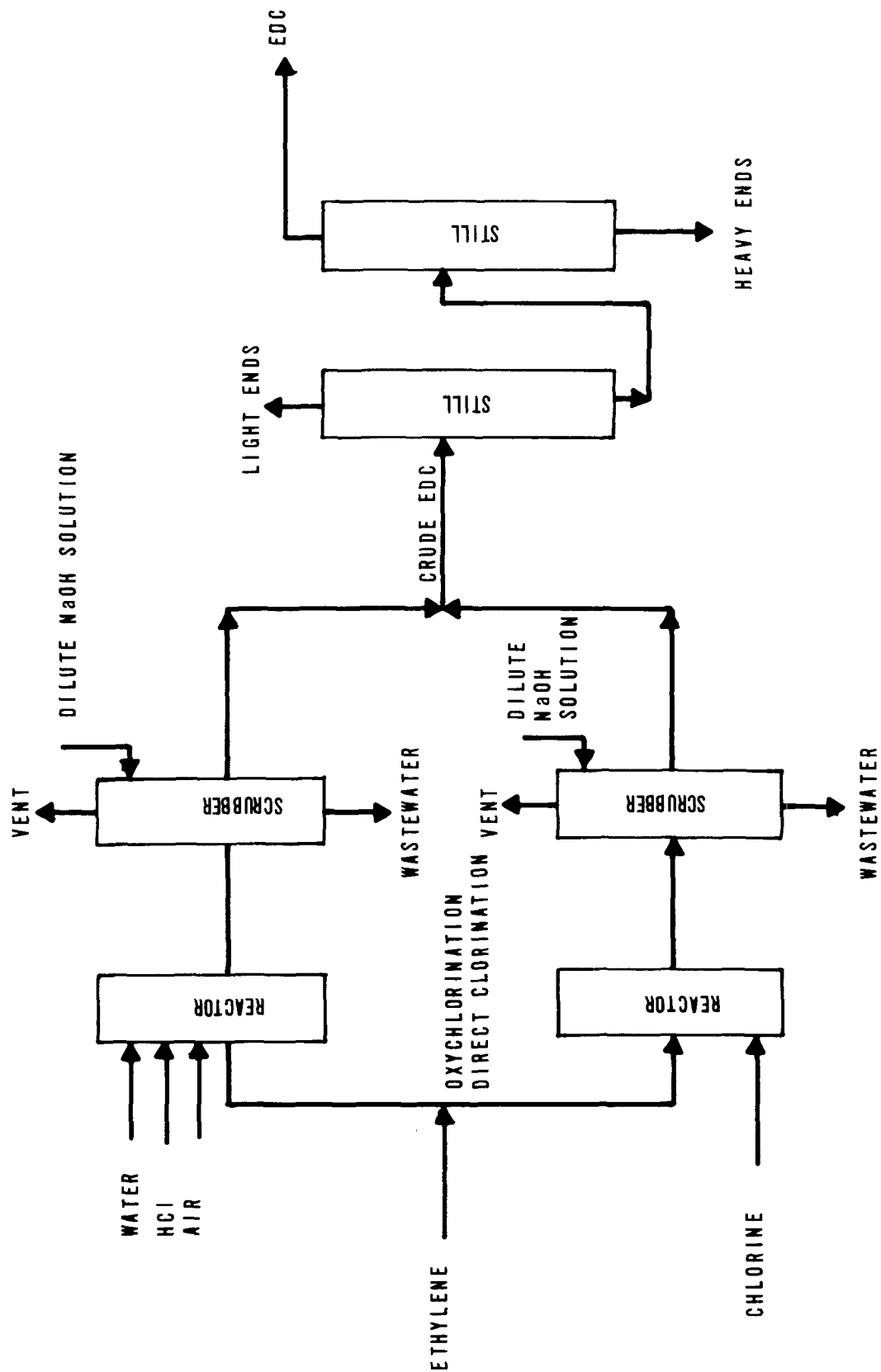
An alternate route in manufacturing EDC is oxychlorination of ethylene with hydrochloric acid and air over a supported copper chloride catalyst. The characteristic waste water stream from this process will contain most of the same impurities found in the direct chlorination process.

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)

Company		MM lb.
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

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

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Product	Process
Vinyl Chloride	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:

$$C_2H_4Cl_2 \longrightarrow C_2H_3Cl + HCl$$

EDC	Vinyl Chloride	Hydrochloric Acid
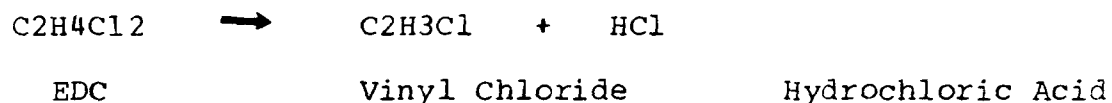
After quenching by direct contact cooling, the furnace products are separated into HCl and high-purity vinyl chloride monomer. The liquid streams from the quencher are fractionated to separate the vinyl chloride product from unreacted EDC, which is then recycled. A flow sheet for this process is shown 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
BOD5	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
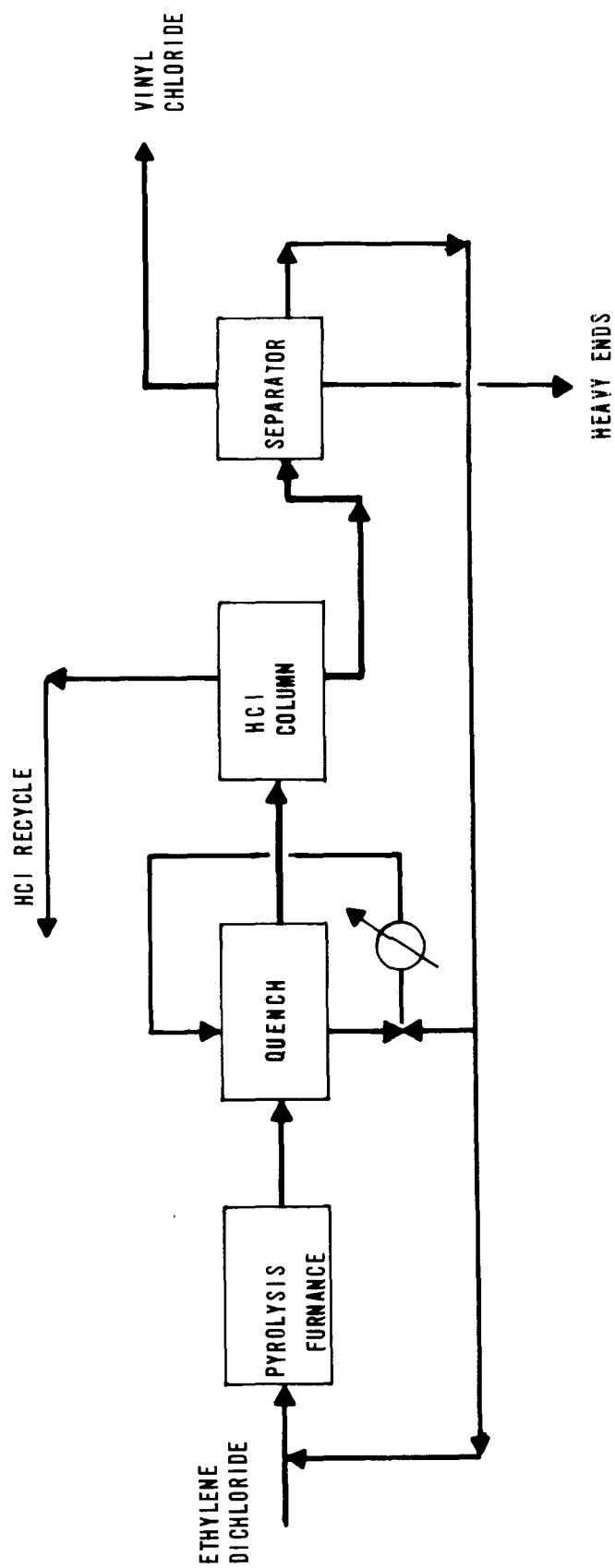
An alternate route in manufacturing of vinyl chloride is the classical acetylene addition reaction. This has been covered under the discussion in Category A.

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 capacity[1]
(MM lb)

Company	1967	1969	1972	Process
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:	Ethylene	Acetylene	Ethane
Raw materials			
Ethane (0.59 lb/lb at 0.9¢/lb)	-	-	0.53
Ethylene (0.49 lb/lb at 3.0¢/lb)	1.46	-	-[1]
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

[1] 0.58 lb/lb at 2.5c/lb.

Product	Process
Styrene	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.

$$C_6H_5\ C_2H_5 \longrightarrow C_6H_5\ C_2H_3\ +\ H_2$$
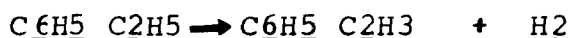
$$\text{Ethyl Benzene} \qquad \text{Styrene} \qquad \text{Hydrogen}$$

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 benzeneconversion, 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:

	Plant 1	Plant 2
Flow	2,810 gallons/1,000 lb	657 gallons/1,000 lb
COD	219 mg/l	426 mg/l
	5.13 lb/1,000 lb	2.34 lb/1,000 lb
BOD5	69 mg/l	70 mg/l
	1.62 lb/1,000 lb	0.381 lb/1,000 lb
TOC	22 mg/l	22 mg/l
	0.53 lb/1,000 lb	0.12 lb/1,000 lb

FIGURE IV-17
STYRENE, DEHYDROGENATION OF ETHYL BENZENE
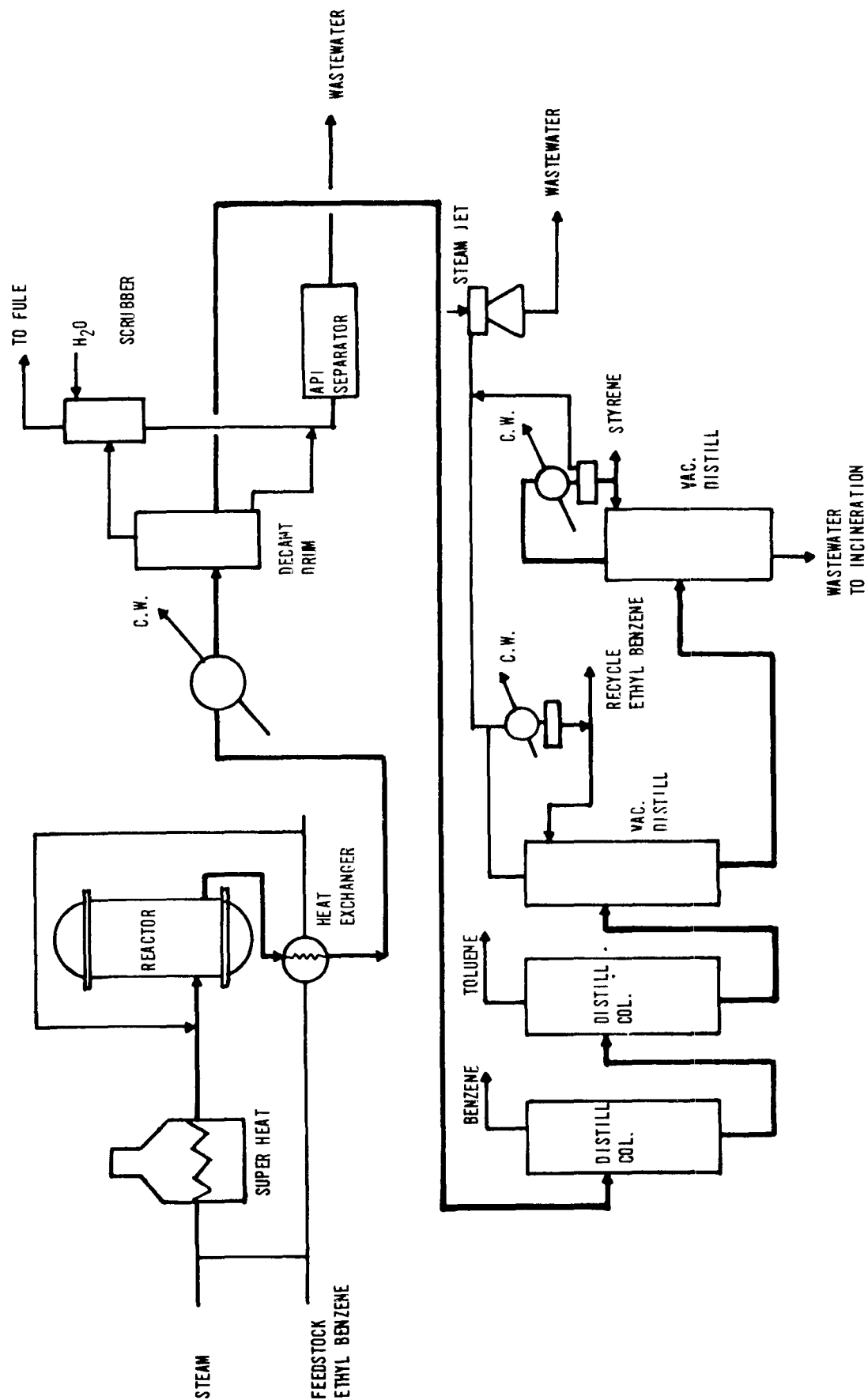
The smaller amount of waste water in Plant 2 is attributed to its use of steam jets with surface heat exchangers in contrast to the steam jets with barometric condensers used in Plant 1, and also to effective operation of the scrubber system. Use of untreated river water as quenching water for the barometric condensers at Plant 1 introduces some contaminants into the waste water stream. Plant 2 discharges uncondensible 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 x 10^8 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 srream 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

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FIGURE IV.18

STYRENE- ETHYLBENZENE DISTILLATION, VACUUM VIA TWO-STAGE STEAM EJECTORS
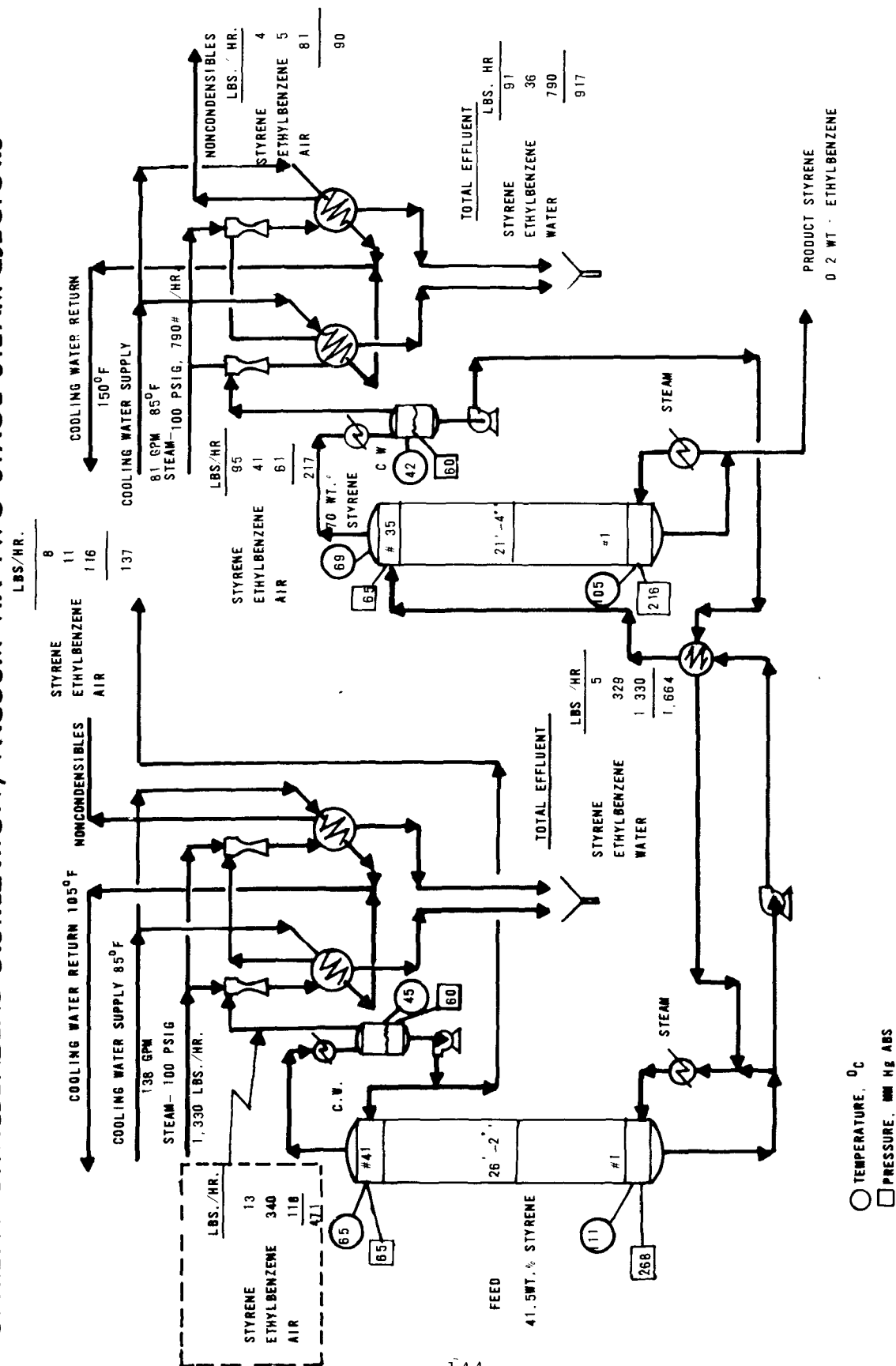
FIGURE IV-19

STYRENE - ETHYLBENZENE DISTILLATION, VACUUM VIA VACUUM PUMPS
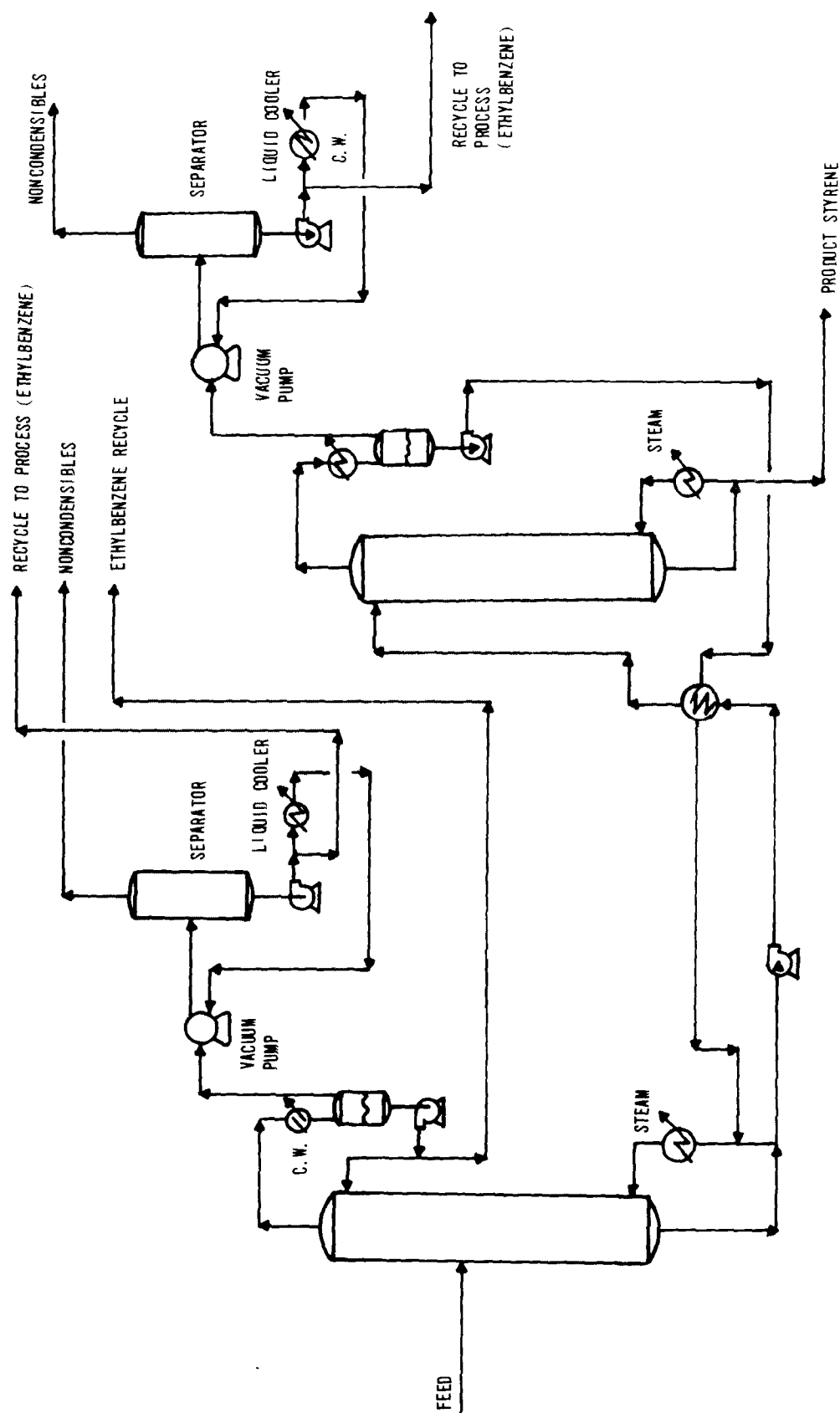
Table IV-26

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	
Utilities	Lb/Hr	$/Yr	Lb/Hr	$/Yr
Steam, x 55¢/M lb	1,330	6,000	790	3,600
Cooling Water, 2.5¢/M gal	GPM	$/Yr	GPM	$/Yr
$\Delta T = 20°F$	150	1,800	89	1,100
Total Utilities, $/Yr		7,800		4,700
Investment Related		$/Yr		$/Yr
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		1,000		740
Total Investment Related Expenses, $/Yr.		1,480		1,100
Product Losses	Lb/Hr	$/Yr	Lb/Hr	$/Yr
Styrene, 7.0 ¢/lb	13	7,500	95	54,500
Ethylbenzene, 3.5 ¢/lb	340	97,600	41	11,800
Total Product Losses, $/Yr		105,100		66,300
Total Operating Costs, $/Yr		114,380		72,100
		186,480		
Total Operating Costs, ¢/lb styrene produced			0.037	

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Table IV-27

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

Two-Tower System

	Tower No. 1	Tower No. 2
Styrene		
In	13	95
Out In Exhaust	8	4
Amount Recycled	5	91
Ethylbenzene		
In	340	41
Out In Exhaust	11	5
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	

Utilities

	kwh	$/yr	kwh	$/yr
Power, 0.800 ¢/kwh	51	3,350	29	1,900
	GPM	$/yr	GPM	$/yr
Cooling Water, 2.5 ¢/Mgal ΔT=20°F.	13	160	7	90
Total Utilities, $/yr		3,510		1,990

Investment Related Expenses

	$/yr	$/yr
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	3,000	2,300
Total Investment Related Expenses, $/yr	5,430	4,830

Product Losses

	Lbs/yr	$/yr	Lbs/yr	$/yr
Styrene, 7¢/lb.	8	4,600	4	2,300
Ethylbenzene, 3.5¢/lb.	11	3,160	5	1,440
Total Product Losses, $/yr		7,760		3,740
Total Operating Costs, $/yr		16,700		10,560
			27,260	
Total Operating Cost, ¢/lb styrene product			0.005	

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

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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 presented in Table IV-29, and estimated economics for a competitive 5 x 10^8 lb plant are shown in Table IV-30.

Table IV-29

U.S. Styrene Capacity[1]
(MM lb)

Company		1967[1]	1970[1]	1972
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

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

Table IV-30

Estimated Economics For Styrene[1]
(500 MM-lb plant; 1972 construction period)

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

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

[1] Dehydrogenation process.
[2] 1.10 lb ethybenzene at 3.50¢/lb + catalyst and chemicals.

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Product	Process
Methyl Amines	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.

$$CH_3OH \quad + \quad NH_3 \quad \longrightarrow \quad CH_3NH_2 \quad + \quad H_2O$$

Methanol   Ammonia   Monomethylamine   Water

$$2C_3OH \quad + \quad NH_3 \quad \longrightarrow \quad (CH_3)_2NH \quad + \quad H_2O$$

Dimethylamine

$$3CH_3OH \quad + \quad NH_3 \quad \longrightarrow \quad (CH_3)_3N \quad + \quad H_2O$$

Trimethylamine
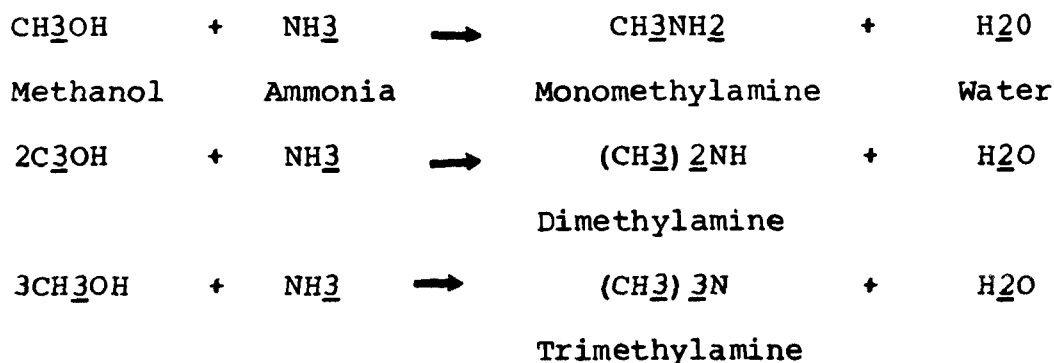
Reactants are first preheated by the converter effluent, thereby recovering some of the exothermic reaction heat. The product stream is then flashed to remove the noncondensibles and is sent to the recovery system. First, ammonia is taken overhead and recycled, together with some trimethylamine. Next, 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.

	Sample No. 1	Sample No. 2
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	174 mg/l

FIGURE IV-20
METHYLAMINES
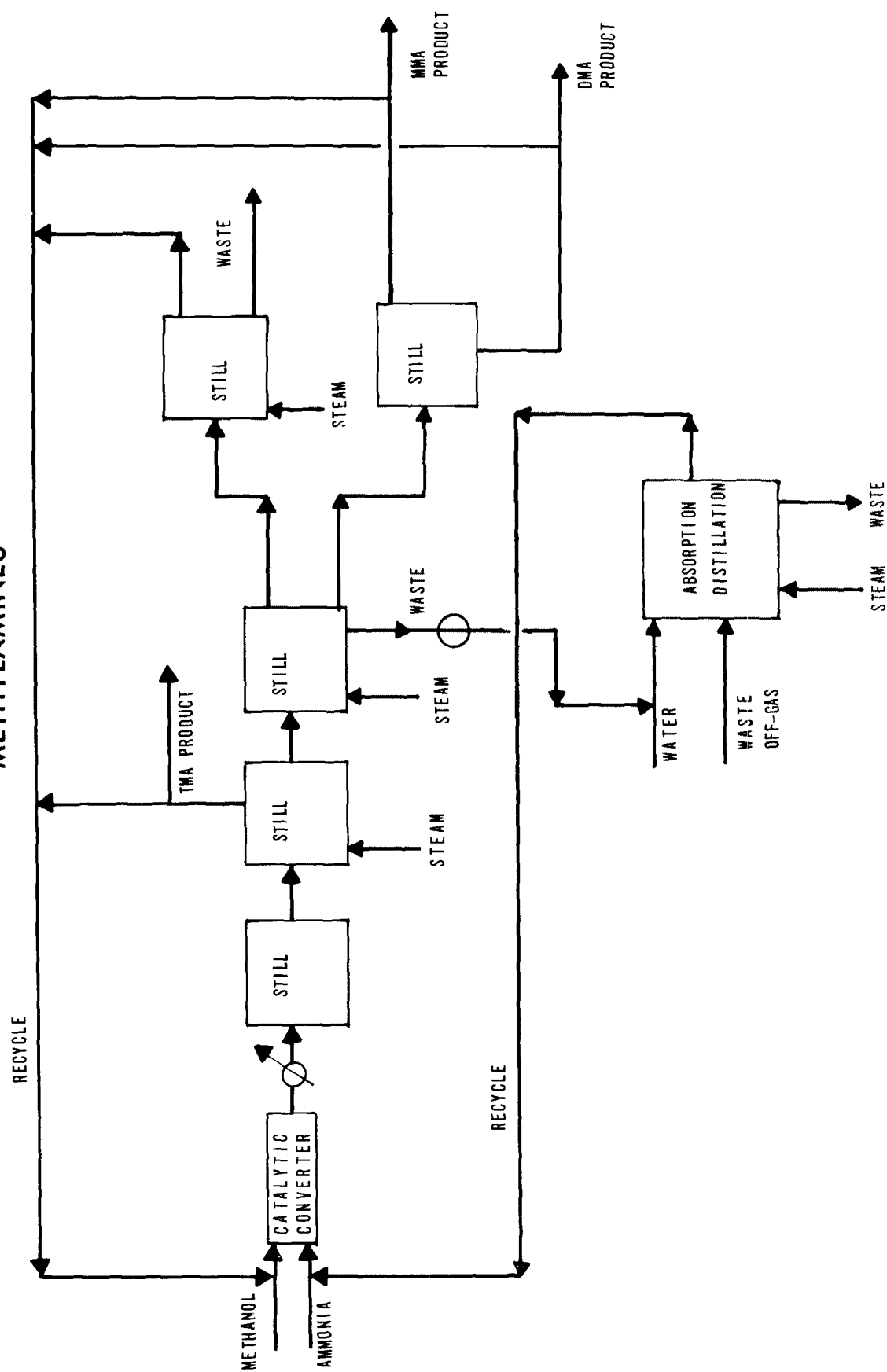
	0.351 lb/1,000 lb	0.62 lb/1,000 lb
TOC	11,634 mg/1	3,808 mg/1
	41.65 lb/1,000 lb	13.63 lb/1,000 lb

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)

Company	Location	Capacity 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.	10
TOTAL		189

Table IV-32

Estimated Economics for Methylamines
(10 MM lb. Plant)

Total Fixed Capital =$1.5 MM

Estimated Production Cost

	Cost ¢/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	5.0
Total	13.9

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Product
Vinyl Acetate

Process
Synthesis with Ethylene and Acetic Acid

Fresh ethylene, oxygen, and acetic acid are combined with their respecttive 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 alummina. 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$\underline{5}$	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 if 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 slectivity. Acetaldehyde co-product yield is controlled by suitable

FIGURE IV-21

VINYL ACETATE, FROM ETHYLENE AND ACETIC ACID
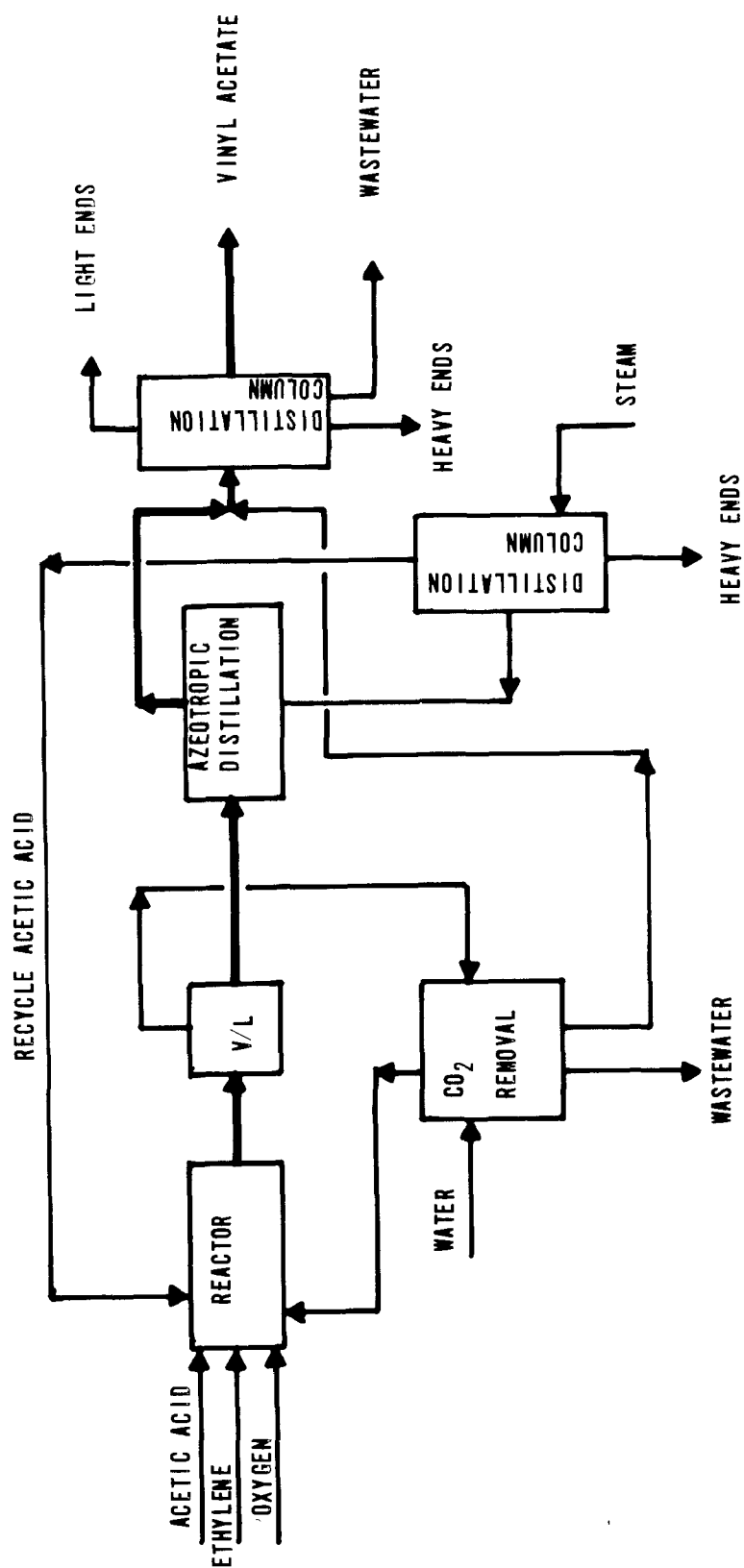
adjustment of the water content, and this co-product is oxidized in-situ to form acetic acid, which is used for the main reaction. The literature indicates that this route produces the best economics.

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

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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	0.32	0.29
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)	0.42	0.57
Total	8.51	7.57

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Product

Phenol

<u>Process</u>
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.

$$C_6H_5CH (CH_3) \quad 2O_2 \longrightarrow C_6H_5C (CH_3)2OOH$$
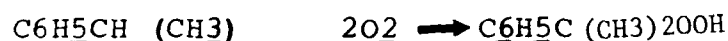
Cumene   Oxygen   Cumene Hydroperoxide

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

$$C_6H_5C (CH_3) 2OOH \longrightarrow C_6H_5OH + CH_3 COCH_3$$

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 if 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:

$$C_6 H_5Cl + 2NaOH (Excess) \longrightarrow C_6H_5 ONa + NaCl + H_2O$$

Chlorobenzene   Sodium Hydroxide   Sodium Phenate   Sodium Chloride   Water
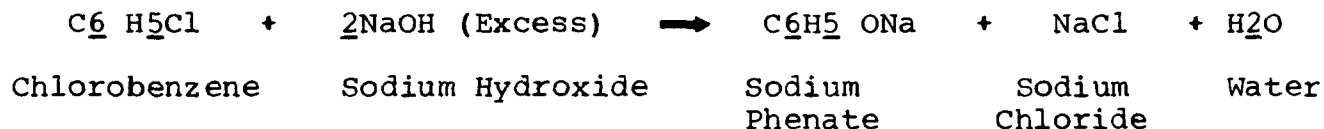
FIGURE IV-22

PHENOL, VIA CUMENE
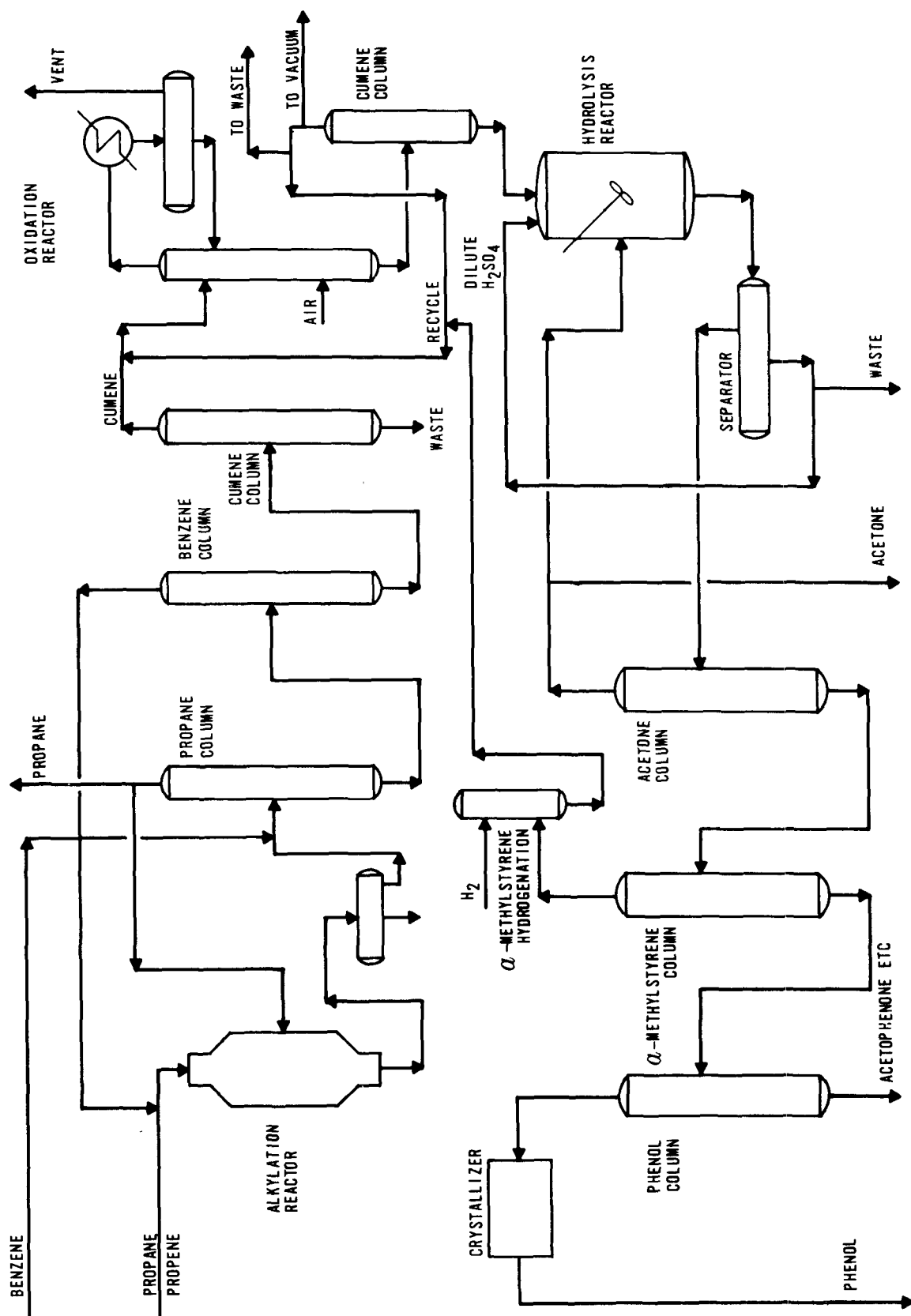
FIGURE IV-23

PHENOL, FROM MONO-CHLOROBENZENE

$$C\underline{6}H\ \underline{5}ONa \quad + HCl \quad \longrightarrow \quad C\underline{6H5O}H \quad + \quad NaCl$$

Sodium Phenate   Hydrochloric Acid   Phenol   Sodium Chloride
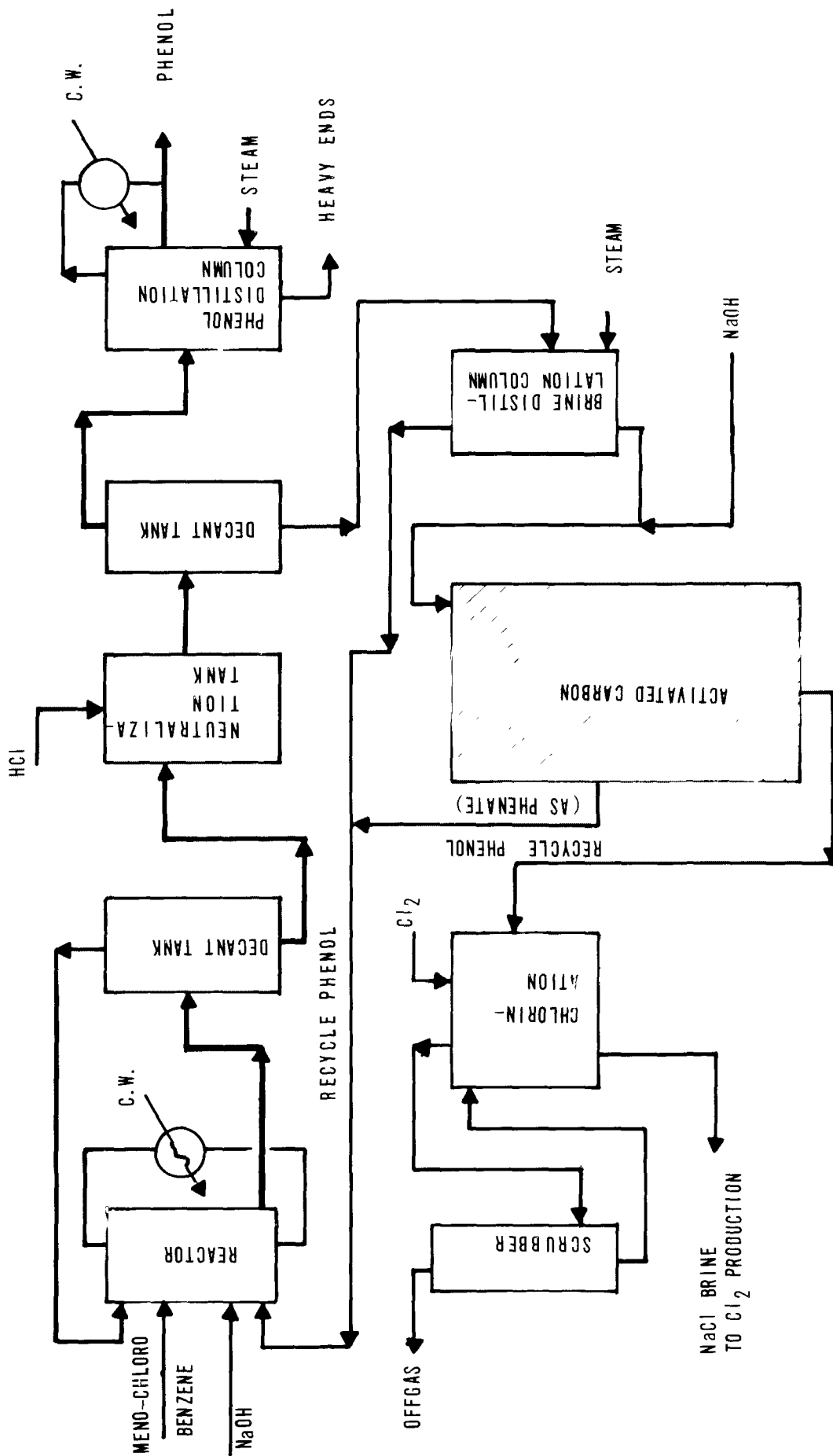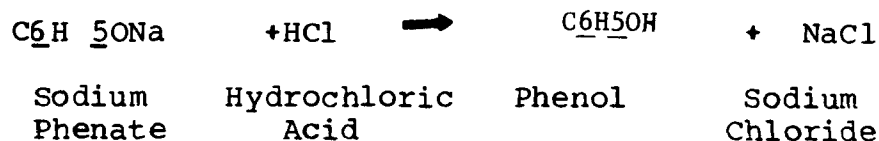
The feed materials (chlorobenzene and excess caustic solution) are fed into a liquid-phase reactor, and the effluent is discharged into a decanter. The upper layer of unreacted chlorobenzene is recycled back to the reactor. The bottom layer of sodium phenate is neutralized to produce a mixture of phenol 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 reamining 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 paramters 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.

	Plant 1	Plant 2
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

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BOD5	2,410 mg/l	17,575 mg/l
	5.6 lb/1,000 lb	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 clorobenzene 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 convereted 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*

Producer	Plant Location	Estimated Capacity MM lbs/yr	Process Route
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		90	
	TOTAL	2,085	

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

**Reported shut down.

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Table IV-36

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

FIXED INVESTMENT COSTS

Process	$MM
Cumene	26.6
Toluene	30.0
Raschig	36.1

PRODUCTION COSTS

	Cumene ¢/lb	Toluene ¢/lb	Raschig ¢/lb
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%)	0.67	0.76	0.91
TOTAL	8.38	5.98	6.53
By-product credit[4]	2.74	–	–
NET	5.64	5.98	6.53

[1] 1.45 lb cumene/lb at 3.7¢/lb + catalyst and chemicals.

[2] Includes 1.3 lb toluene at 2.5¢/lb.

[3] 0.94 lb benzene/lb at 3.4¢/lb + catalyst and chemicals.

[4] 0.60 lb acetone/lb phenol at 4.6¢/lb.

Product   Process
Oxo Chemicals   Carbonylation and Condensation

The oxo process is a broadly applicable technology which is used to pro-
duce 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:

$$C_3H_6 + CO + H_2 \longrightarrow CH_3CH_2CH_2CHO + CH_3 \overset{CH_3}{\underset{}{CHCHO}}$$

Propylene   Carbon   Hydrogen   n-butyraldehyde   iso-butyraldehyde
              Monoxide

$$2CH_3 CH_2 CH_2 CHO \longrightarrow CH_3 CH_2 CH_2 \underset{CH_2H_5}{CH=C-CHO} + H_2O$$

n-butyraldehyde   2-ethylhexanal   Water

$$CH_3 CH_2 CH_2 \underset{C_2H_5}{CH=C-CHO} + H_2 \longrightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 - \overset{H}{\underset{CH_2H_5}{C}} - CH_2OH$$

2-ethylhexenal   Hydrogen   2-ethylhenanol
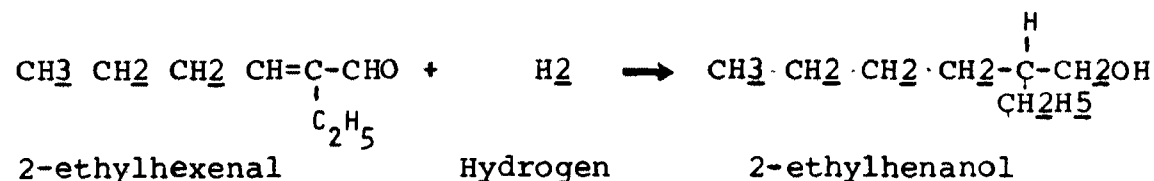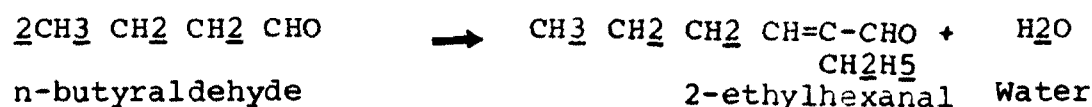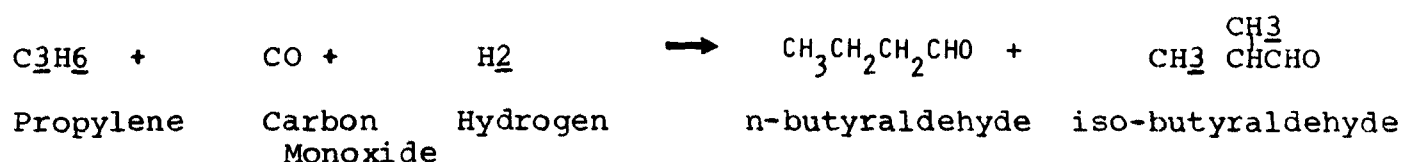
Carbon dioxide, natural gas, and steam are passed into a synthesis gas
reactor to produce water gas (1:1 ratio of H_2O and CO) which is then
mixed with propylene in a liquid-phase reactor in the presence of a
cobalt solution. The reaction is carried out under pressure and the
reactor is maintained approximately 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 subse-
quent reaction is carried out at moderate temperature and atmospheric
pressure in the presence of strong base such as sodium or potassium hy-

FIGURE IV-24
OXO - CHEMICALS
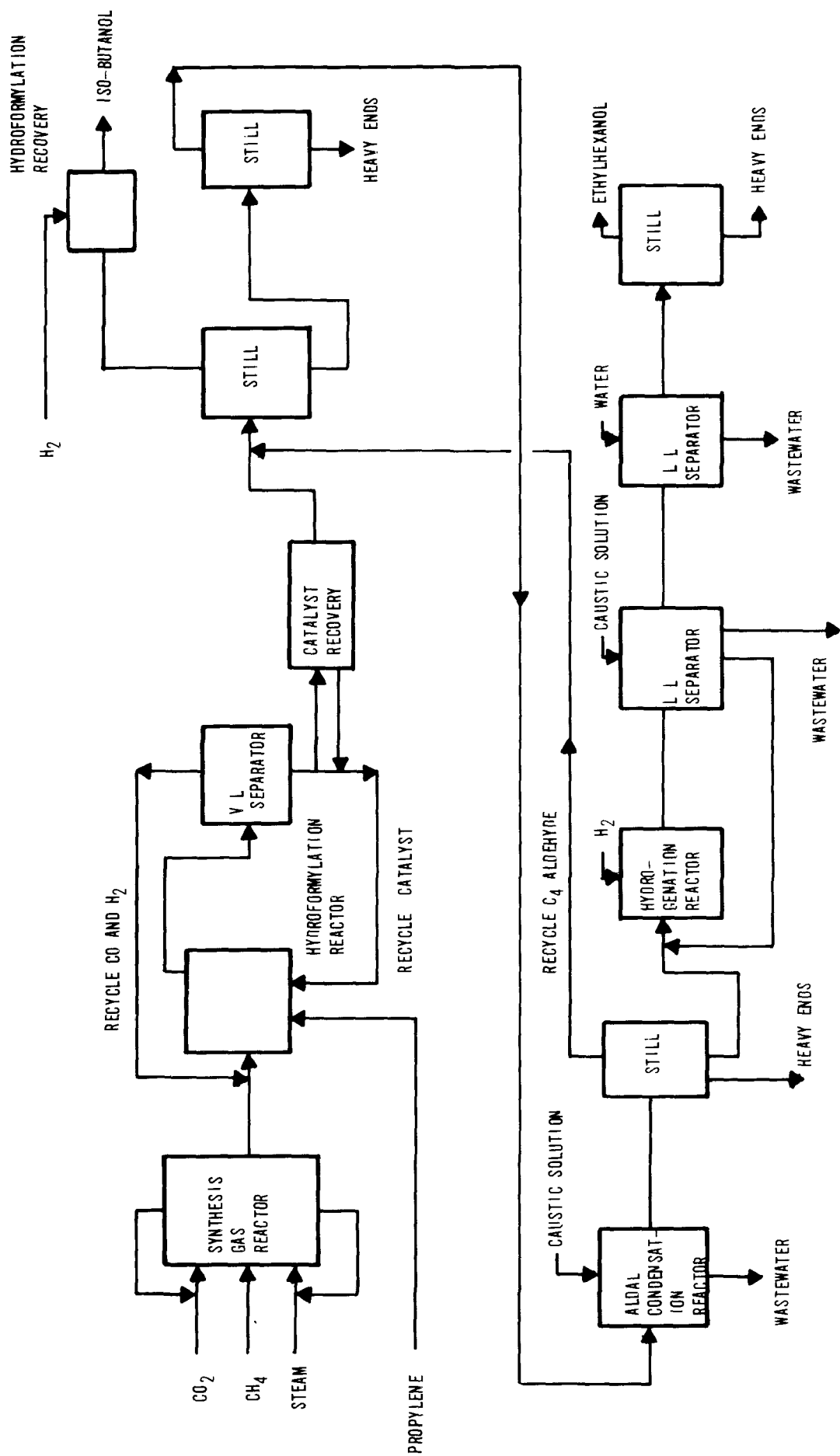
droxide. Continuous removal of the water produced during reaction drives the aldol condensation to completion. The unreacted C^o4^o aldehyde is separated from the product 2-ethylhexenal by distillation and is recycled to the condensation reactor.

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
BOD5	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 (H_2/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

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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)

Company	Location	Capacity
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	70
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

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

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SUBCATEGORY C

Product	Process
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:

$$C_2H_4 \quad + \quad 1/2 \; O_2 \quad \longrightarrow \quad CH_3CHO \quad + \quad Heat$$

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:

Reaction:

$$C_2H_4 \quad + \quad 2CuCl_2 \quad + \quad H_2O \quad \xrightarrow{PdCl} \quad CH_3CHO \quad + \quad 2HCl \quad + \quad 2CuCl$$

Ethylene   Cupric Chloride   Water   Acetaldehyde   Hydrochloric Acid   Cuprous Chloride

Regeneration:

$$2CuCl \quad + \quad 2HCl \quad + \quad 1/2 \; O_2 \quad \longrightarrow \quad 2CuCl_2 \quad + \quad H_2O$$

Cuprous Chloride   Hydrochloric Acid   Oxygen or Air   Cupric Chloride   Water
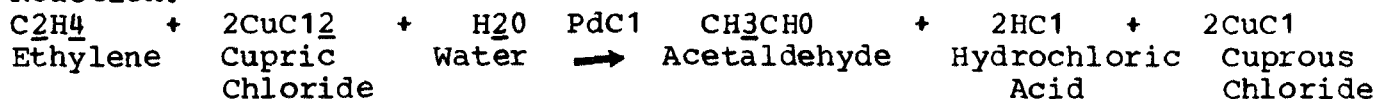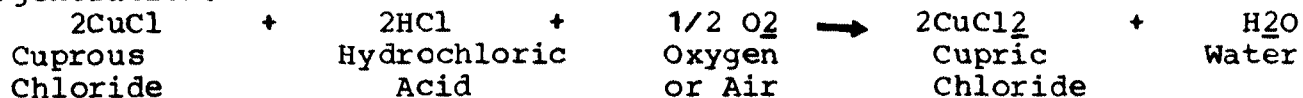
There are two basic process variations, and choice depends upon such factors as oxygen cost, utilities prices, and available ethylene purity. In the single-stage process, pure oxygen is employed as the oxidant. The reactor effluent is condensed and water-scrubbed. Unreacted gas is recycled into the reactor. 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

FIGURE IV - 25

ACETALDEHYDE (SINGLE-STAGE WACKER PROCESS)
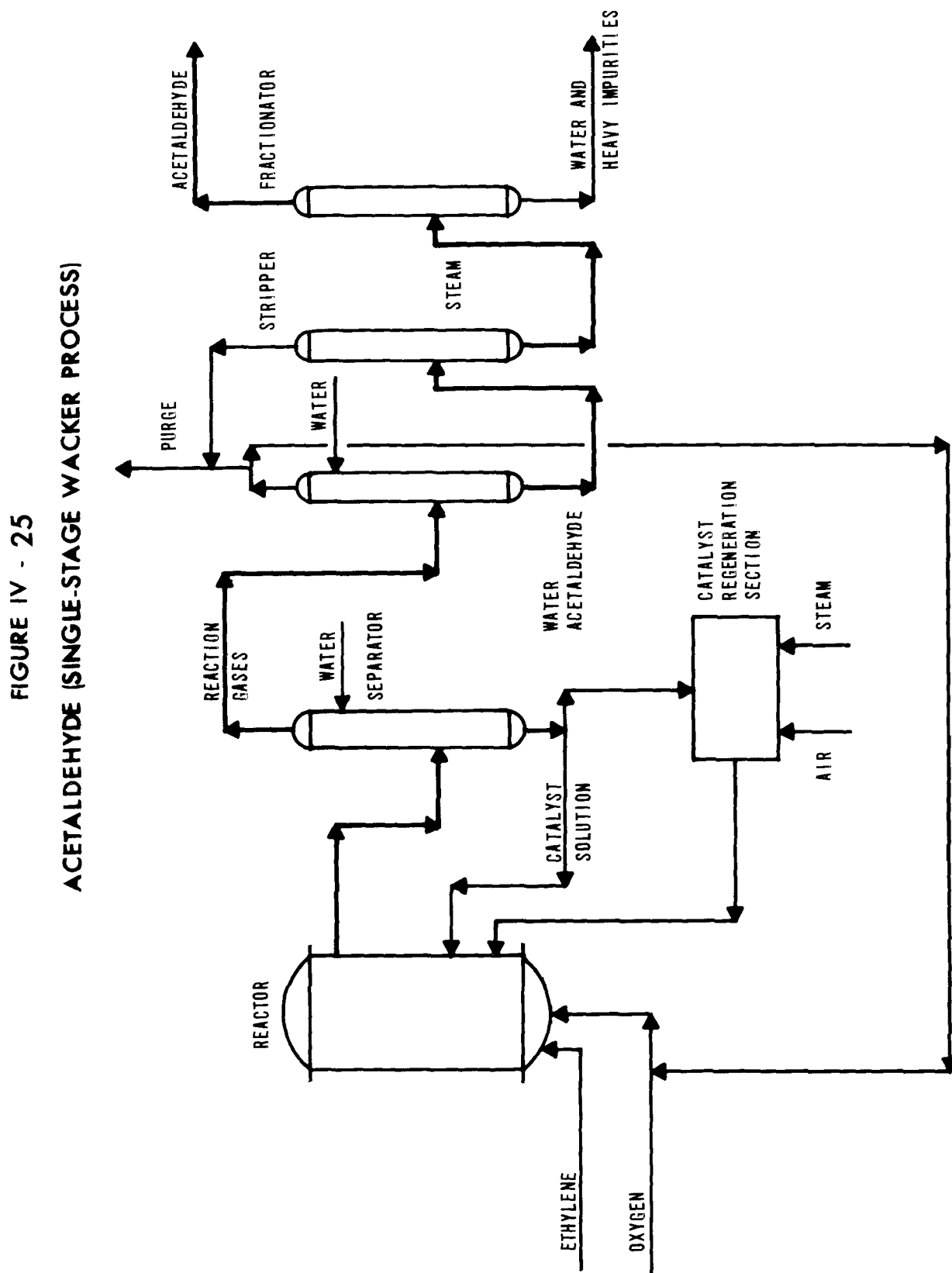
acetaldehyde still. The characteristics of the wastewater are shown in the following tabulation.

	Plant I	Plant 2	Plant 3
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$\underline{5}$		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

Process	$ MM
Ethylene	14.80

Estimated Operation Cost

	Cost ¢/lb ethylene
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)	0.75
TOTAL	4.99

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

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Product   Process
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:

$$CH_3CHO \quad + \quad 1/2\ O_2 \quad \longrightarrow \quad CH_3COOH$$
Acetaldehyde   Oxygen   Acetic Acid
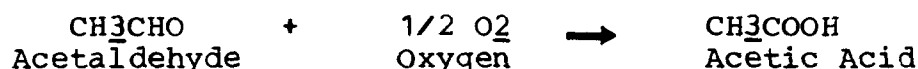
The reaction is carried out in the liquid phase at 150°F and 60 psig, with manganese acetate dissolved in aqueous solvent as catalyst.

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:

	Plant 1	Plant 2
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
BOD5	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

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FIGURE IV.26

ACETIC ACID, ACETALDEHYDE OXIDATION

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ends and heavy ends from distillation columns 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$\underline{5}$	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 waste-flow.

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 un-reacted 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.

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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 off-gases, which contain catalyst in the form of methyl iodide vapor.

Table IV-40

Acetic Acid Capacity (1972)

Producer	Location	MM lb	Process
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		100	
	TOTAL	2,800	

Product   Process
Methyl Methacrylate   Acetone Cyanohydrin Process

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

$$CH_3COCH_3 \quad + \quad HCN \quad \longrightarrow \quad (CH_3)_2OHC(CN)$$
acetone Hydrogen Cyanide Acetone Cyanohydrin

$$\overset{H_2SO_4}{}$$

$$(CH_3)_2OHC(CN) \quad \longrightarrow \quad CH_CH_2CONH_3HSO_4$$
Acetone Cyanohydrin   Methacrylamide Sulfate

$$\overset{CH_3OH}{}$$

$$CH_3CH_2CONH_3HSO_4 \quad \longrightarrow \quad CH_3CH_2CCOOCH_3 \quad + \quad NH_4HSO_4$$
Methacrylamide Sulfate Methyl Methacrylate Ammonium Bisulfate
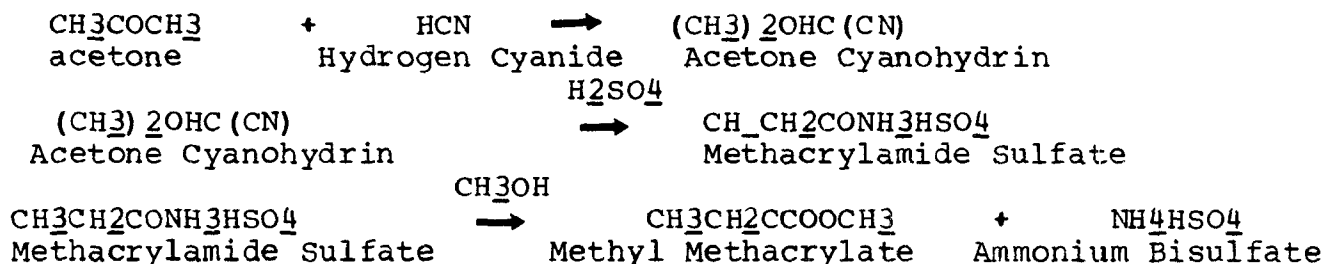
A process flow diagram is shown in Figure IV-27. Acetone cyanohydrin is produced by the reaction of hydrogen cyanide and acetone with an alkaline catalyst in a cooled reaction kettle. The excess catalyst is neutralized, and crude acetone cyanohydrin passes to holding tanks. The salt formed by neutralization 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

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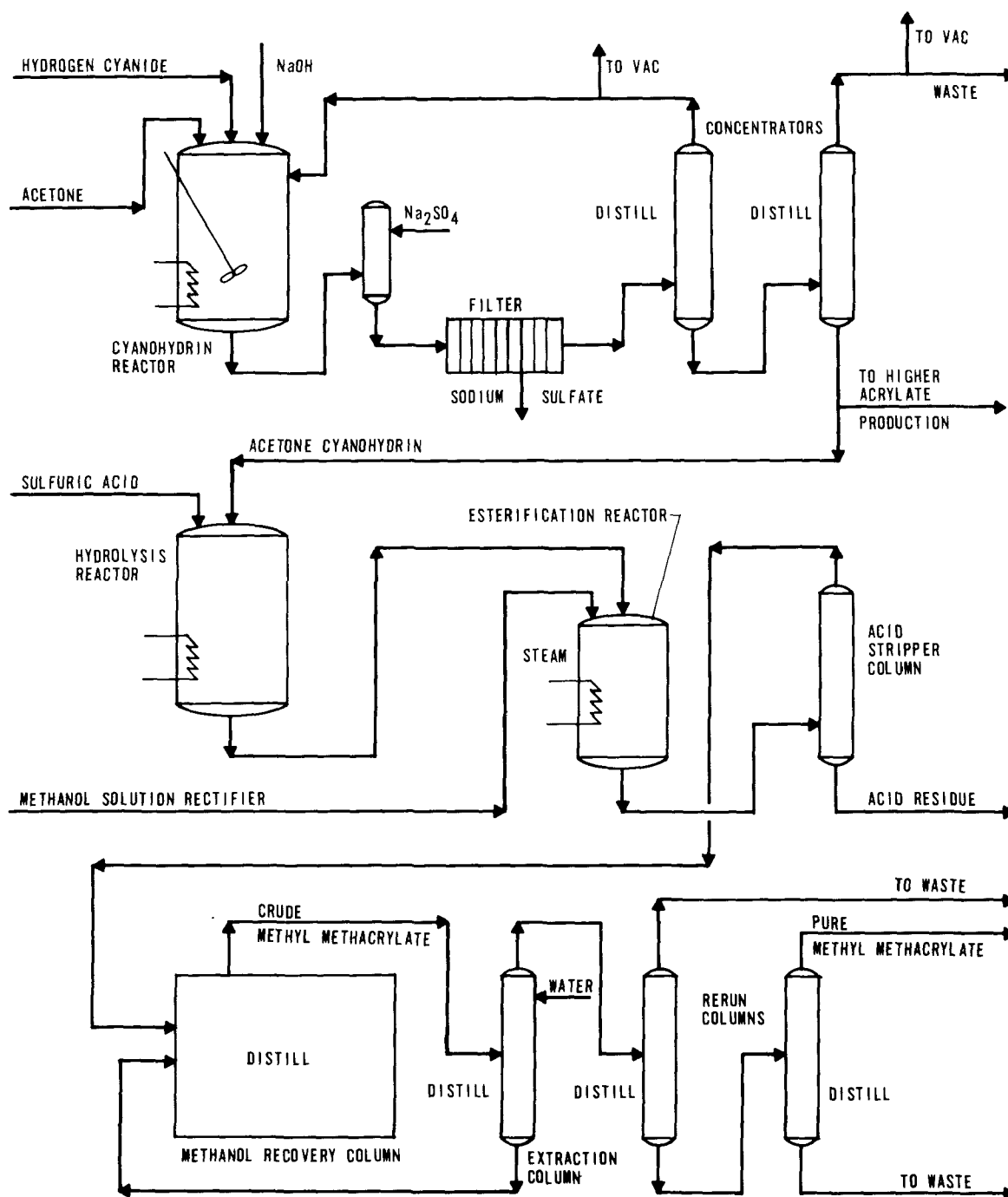
	Into SAR	From SAR
Flow	260 gallons/1,000 lb	213 gallons/1,000 lb
COD	178,000 mg/1	110 mg/1
BOD5	20,700 mg/1	15 mg/1
TOC	69,998 mg/1	18 mg/1

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 SO_2, O_2, and water vapor. Simultaneously, the organic substances are oxidized, and the contained

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FIGURE IV-28

SPENT ACID RECOVERY UNITS

1 NEUTRALIZATION

HN₃ 68 MM LB/HR.

SPENT ACID

2 COMPLETE COMBUSTION

FUEL

OXYGEN

SPENT ACID

COMBUSTION

DEHYDROGENATION SO₂ OXIDATION

WASTEWATER

ABSORPTION

FRESH WATER

98% SULFURIC ACID
288 MM LB/HR

NEUTRALIZATION

CRYSTALIZATION FILTRATION

AQUEOUS OVERHEAD

AQUEOUS PURGE

AMMONIA SULFATE
390 MM LB/HR.
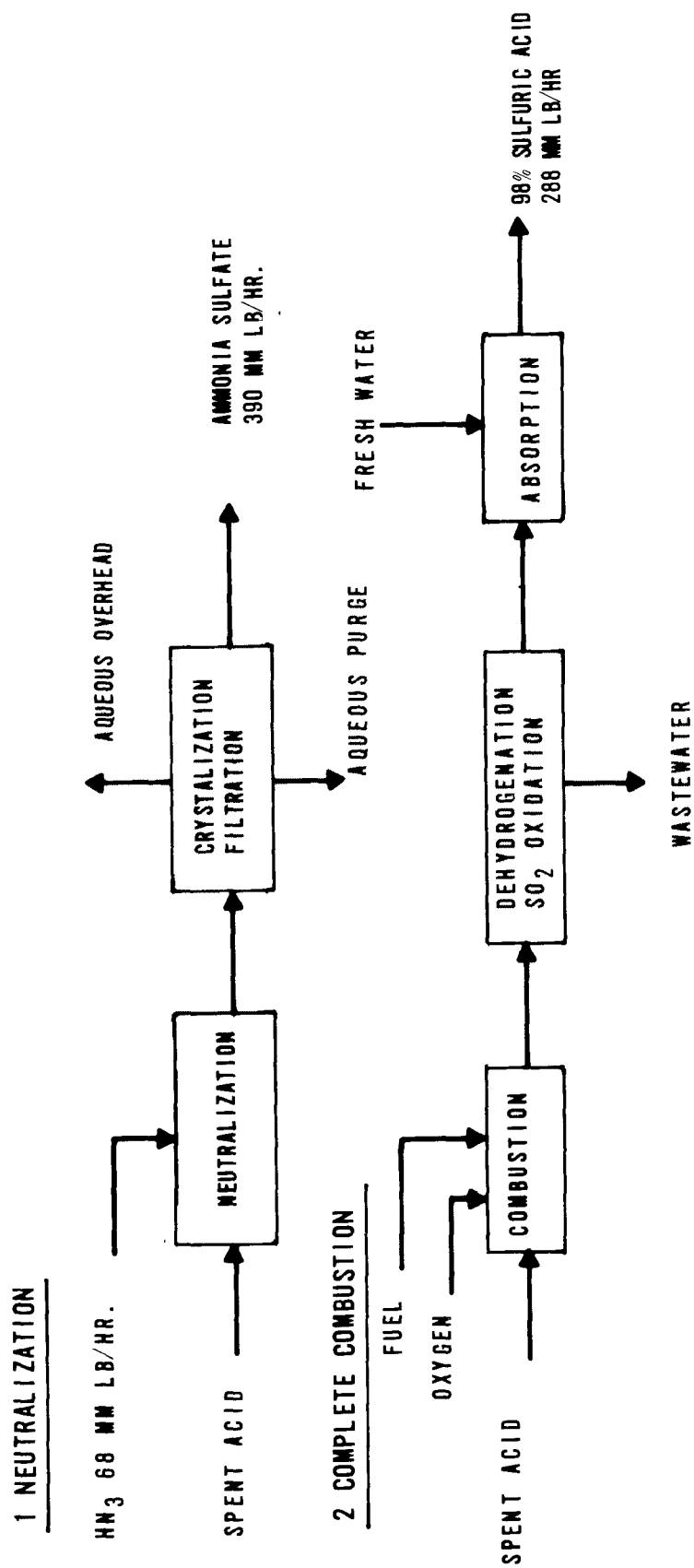
Table IV-41

Economics of Spent Acid Recovery by Neutralization[*]

Investment

Battery Limits	= $2,200,000
Off-site	= 800,000
Total Investment	$3,000,000

Operating Costs

Utilities	$/yr
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	= 60,000
	$ 570,000

Chemicals

NH_3: 68,000,000 lb @ 2¢/lb	= $1,360,000
Amortization	= 440,000
Labor	= 200,000
Sub-total	$2,000,000
Return on Total Investment @ 20%	= $ 600,000
Total Annual Cost	= $3,170,000

Net Revenue from Recovered Ammonium Sulfate 390 MM lbs/yr @ 0.70¢/lb	= $2,730,000

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

ammonia converted to N_2 and water. The SO_2 gas stream is passed over a catalytic converter to oxidize the SO_2 to SO_3, which is then absorbed to form 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_2SO_4	=	245,000 lb/hr
$(NH_4)_2SO_4$	=	16,500 lb/hr
H_2O	=	13,500 lb/hr
Organic substances	=	6,150 lb/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

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Table IV-42

Economics of Spent Acid Recovery by Complete Combustion[*]

Investment

Battery Limits	= $3,000,000
Off-site	= 1,000,000
Total Investment	$4,000,000

Operating Costs

Utilities

$/yr

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	= 22,500
	$ 446,500

Amortization	= $ 600,000
Labor	= 100,000
	$ 700,000

Return on Total Investment @ 20% = $ 800,000

Total Annual Cost = $1,946,500

Net Revenue on Recovered H_2SO_4
144,000 tons/yr @ $20/ton = $2,880,000

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

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Table IV-43

U.S. Methyl Methacrylate Capacity

Producer	Location	Capacity MM lbs/yr.	Route
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.	20.0	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	2.6
TOTAL	16.6

II. Isobutylene Process

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

Product   Process
Ethylene Glycol   Hydration of Ethylene Oxide

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

$$H_2COCH_2 \quad + \quad H_2O \quad \longrightarrow \quad HOCH_2CH_2OH$$
Ethylene Oxide   Water   Ethylene Glycol
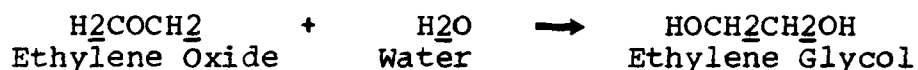
Ethylene oxide and water are reacted at about 300 psig and 180°C in the presence of sulfuric acid solution. By selection of the oxide-to-water ratio, it is possible to control the production of the mono-, di-, and higher glycols produced. Excess water is required for temperature control and to prevent 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
BOD5	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 multiple-effect 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.

FIGURE IV-29

ETHYLENE GLYCOLS, FROM ETHYLENE OXIDE

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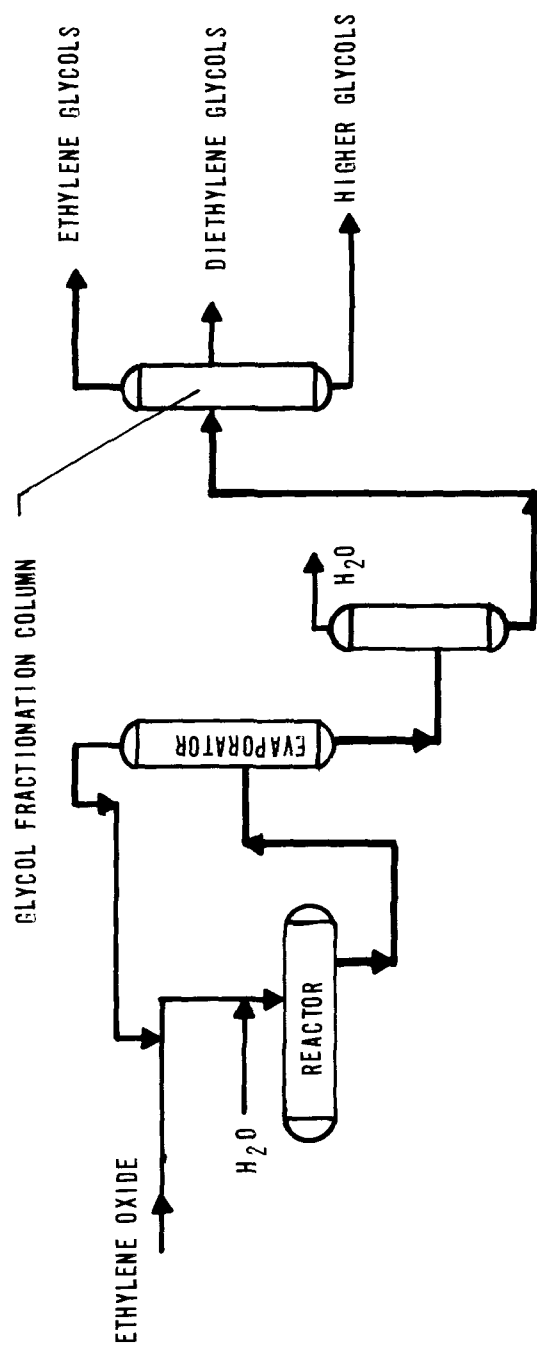
The manufacture of ethylene glycol is invariably associated with ethylene oxide production, and glycol growth rates are moderate. The U.S. ethylene glycol capacity is presented in Table IV-45.

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

Producer	Location	Mid-1970 Estimated Capacity MM lb/yr
Allied	Orange, Texas	60
Calcasieu	Lake Charles, La.	180
Celanese	Clear Lake, Texas	300
Dow	Freeport, Texas	500
	Plaquemine, La.	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.	150
	TOTAL	3,045

Table IV-46

Estimated Economics for Ethylene Glycol
(80 MM lb plant)

Total Fixed Capital = $0.8 MM

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

Product	Process
Acrylic Acid	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:

$$C_2H_2 \quad + \quad H_2O \quad + \quad CO \quad \longrightarrow \quad C_2H_3COOH$$

Acetylene   Water   Carbon Monoxide   Acrylic Acid
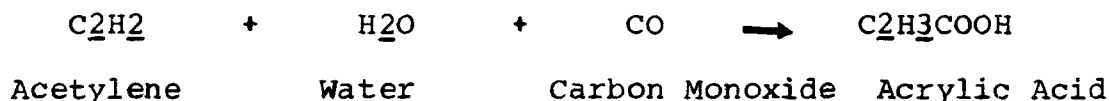
The acetylene feedstock is first dissolved in THF (tetrahydrofuran) in an absorption tower. This solution and carbon monoxide are then mixed in a reactor, and the reaction is carried out at approximately 450°F and 1,500 psig in the presence of a nickel bromide and cupric bromide solution. The off-gas 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 separtion 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
BOD5	186 mg/l 0.737 lb/1,000 lb
TOC	387 mg/l 1.53 lb/1,000 lb

FIGURE IV-30
ACRYLIC ACID, FROM ACETYLENE

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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.

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, BOD_5, 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

Producer	Plant Location	Est. Capacity [*] (MM lbs./yr.)	Process Used
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
Union Carbide	Houston, Texas Institute, W. Va.	70	Ethylene oxide-HCN
	Taft, La.	200	Propylene
TOTAL		660	

[*]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)

Total Investment Cost

Process	$MM
Acetylene	10.0
Propylene	16.9

Production Cost

	Route:	¢/lb.	
		Acetylene	Propylene
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		0.67	1.14
TOTAL		9.28	6.93

[1] 0.42 lb./lb. at 8.0¢/lb.

[2] 0.88 lb./lb. at 3.0¢/lb.

Product   Process
Acrylates   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 purfied 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:

C_2H_3COOH + $R-OH$ H_2SO_4 C_2H_3COOR H_2O
                                    $\longrightarrow$

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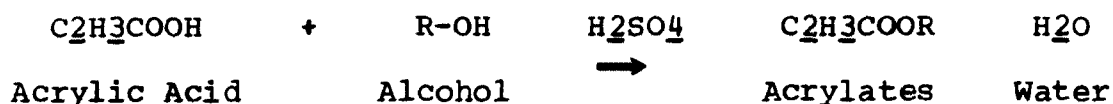
The two main sources of water pollution in acrylate manufacture are the
bottoms of the alcohol recovery still and the effluent of the saponifi-
cation kettle. The possible contaminants in the waste stream are
acrylic acids, alcohols, and sodium salts of various acids. The results
of the plant survey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

Flow	2,856 gallons/1,000 lb
COD	4,870 mg/l
	117.5 lb/1,000 lb
BOD5	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 pro-
duct.

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).

Product	Processes
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 HNO_3 (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

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FIGURE IV-32

TEREPHTHALIC ACID, P-XYLENE TO POLYMER GRADE TPA
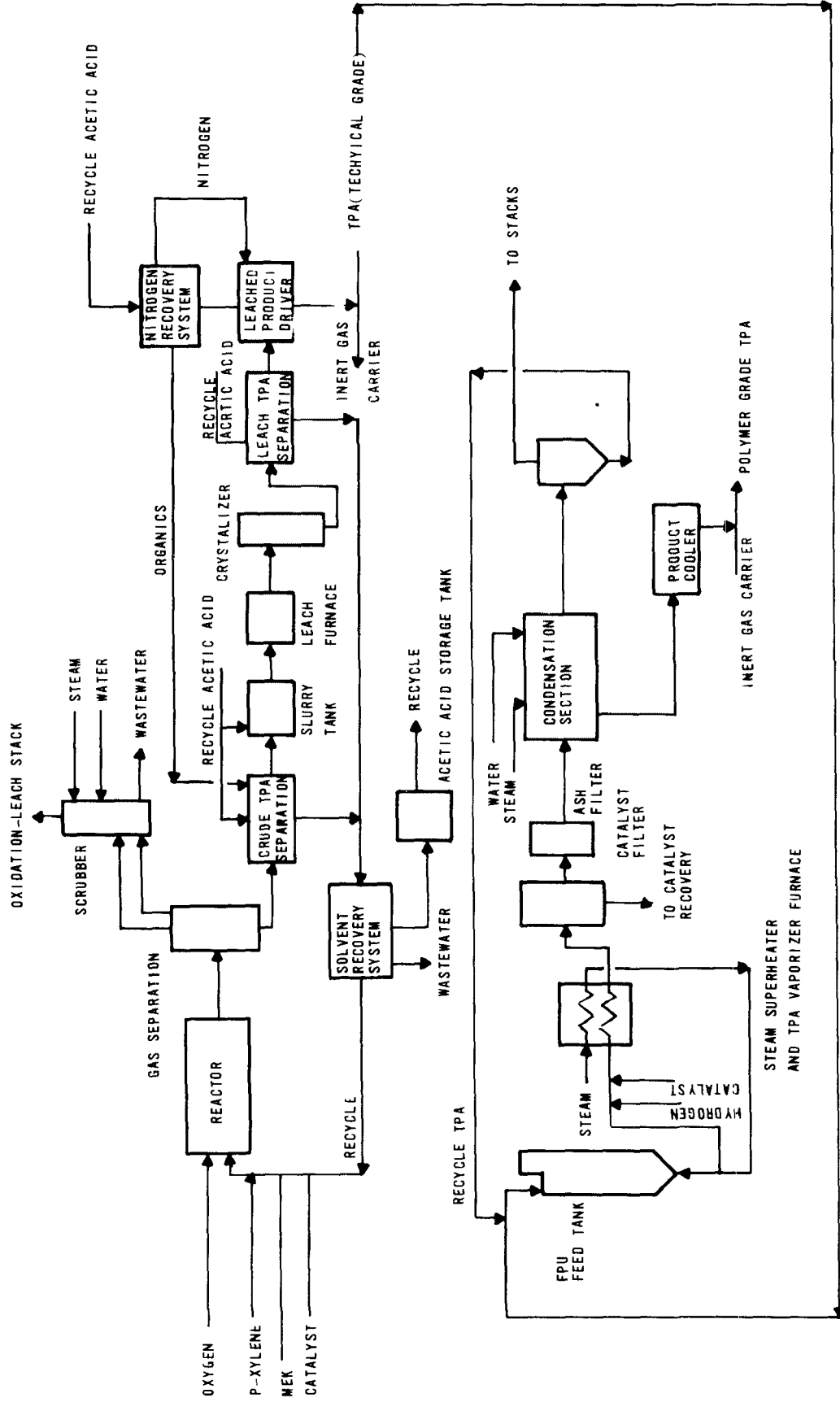
more than 99 weight percent TPA in contrast to 93 weight percent TPA of the other process.

At some plants, the TPA product is further purified to produce fiber-grade 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 fiber-grade 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 waste-water obtained from plant visits are summarized in the following tabulation.

Plant	Process	Flow gal/1,000 lb	COD	BOD5 lb/1,000 lb (mg/l)	TOC
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 indentical 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:

	Probability of Occurrence			Ratio
	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.

Plant	Process Water Usage lb/lb product	Cooling Water Usage 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

Producer	Plant Location	Est. Crude TPA Capacity (MM Lbs./Yr.)
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		1475

*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)

Investment cost

Process	$ MM
Oxidation (Bromine compound)	52.9
Oxidation (Methylethyl Ketone)	58.6

Production costs

	¢/lb	
	Amoco[1]	Mobil[2]
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

[1] Includes 0.67 lb p-xylene at 6.5¢/lb.
[2] P-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.

Product   Process
Dimethyl Terephthalate   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 manu-
facture 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 con-
ventional 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 reac-
tor to prevent the methanol from vaporizing too rapidly are the major
water pollution sources. The waste water may contain some alcohol, ben-
zene, 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:

	Plant 1	Plant 2	Plant 3
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
BOD5,			
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 anal-
ysis for probability of occurrence are summarized in the following tabu-
lation:

FIGURE IV.33

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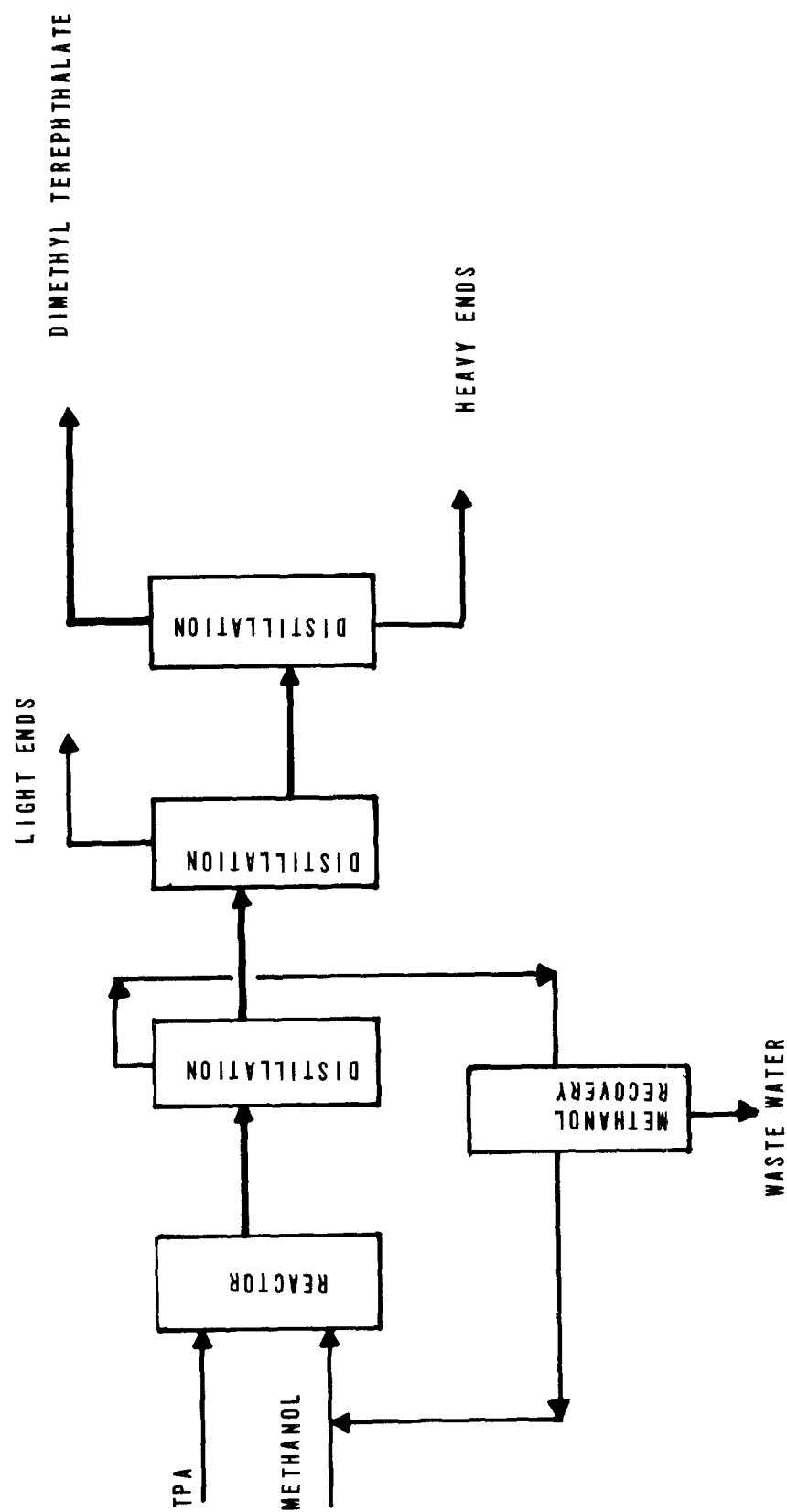
	Flow RWL (gal/1,000 lb)		COD RWL (lb/1,000 lb)	
	Unit A	Unit B	Unit A	Unit B
10% Occurrence	167	150	13.5	16.1
50% Occurrence	313	248	34.	33.7
90% Occurrence	461	344	86.5	70.5
Ratio 90%/50%	1.47	1.39	2.54	2.06

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:

Plant	Process Water Usage lb/lb product	Cooling Water Usage 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 p-toluic 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.)

		Estimated Capacity		
Producer	Plant Location	p-Xylene	Crude TPA	Total
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.	400	--	400
Total		600	1100	1700

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Product ___   _____Process_____
Para-Cresol   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:

$$C_6H_5CH_3 \; + \; H_2SO_4 \; \longrightarrow \; (SO_3H)C_6H_4CH_3$$
$$\text{Toluene} \qquad \text{Sulfuric Acid}$$

$$(SO_3H)C_6H_4CH_3 \; + \; NaOH \; \longrightarrow \; (OH)C_6H_4CH_3 \; + \; Na_2SO_3$$
$$\text{P-Cresol}$$
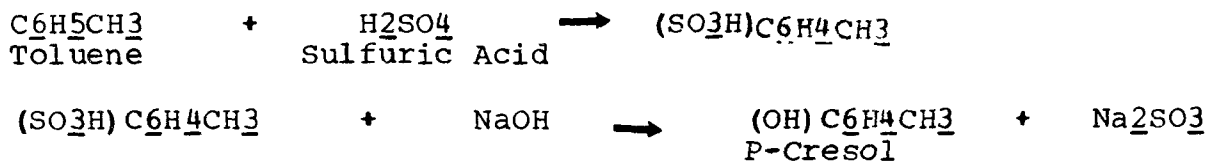
A process flow sheet is shown in Figure IV-34. Toluene and a gas mixture of sulfur dioxide and sulfur trioxide are fed into a sulfonation reactor. The reactor effluent gas is passed through a caustic scrubber to remove unreacted sulfur dioxide. The liquid effluent from the reactor is first diluted with 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
BOD5	11,400 mg/l 123 lb/1,000 lb
TOC	5,020 mg/l 54 lb/1,000 lb

FIGURE IV-34
PARA-CRESOL

208
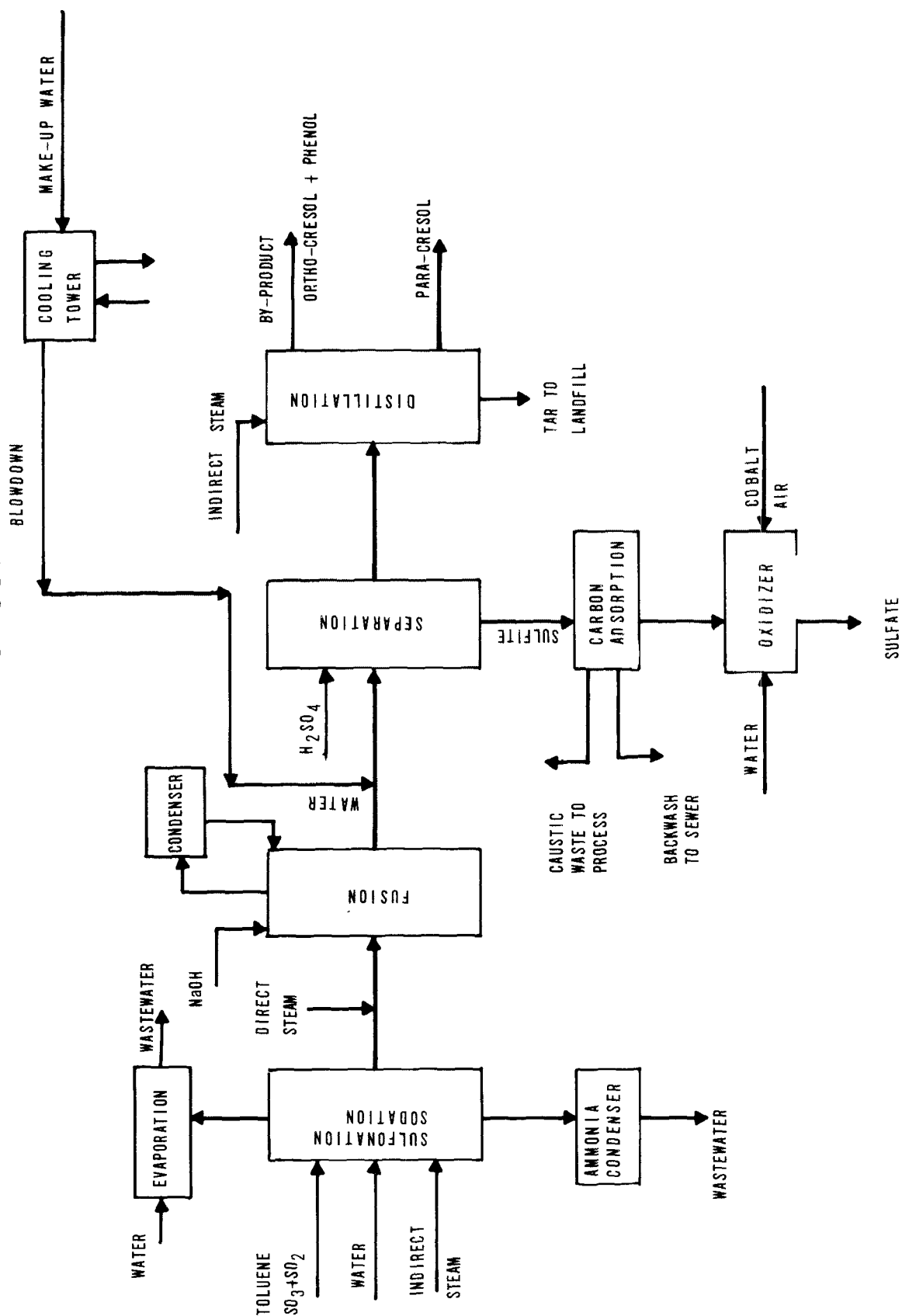
The sulfite and organic contaminants cause the high oxygen demand in the waste water, while the cresol contaminant (10 mg/l) constitutes an odorous nuisance in the atmosphere.

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)

Company	MM lb	Process
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.)	10	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	4,000
	$ 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%)   =   83,310
After Tax Profit   = $ 83,310
After Tax Cash Flow= $83,310 + $14,400= $97,710

$$\text{After Tax RDI} = \frac{\$97,710}{\$144,000} \times 100\% = 67.9\%$$

$$\text{Payout Time} = \frac{\$144,000}{\$97,710} = 1.47 \text{ yrs.}$$

*"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.

Product	Process
Aniline	Nitration and Hydrogenation of Benzene

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

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

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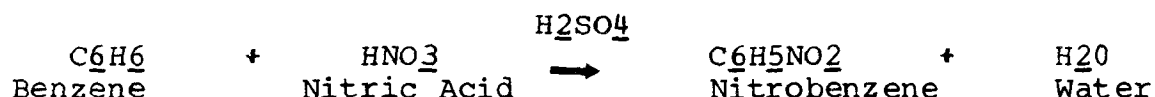
The reactor effluent is decanted into a liquid/liquid separator, where crude nitrobenzene is separated from the acid solution. The acid solution is concentrated by steam stripping and recycled back to the reactor. Crude nitrobenzene is washed, vaporized, and fed to a fluidized-bed reactor containing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

$$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$$

Nitrobenzene   Hydrogen   Aniline   Water
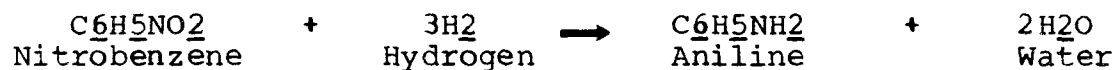
The unreacted hydrogen is recycled to the reactor. Reactor effluent goes to a separator, where two phases are formed. The organic phase contains water, and is fractionated in a two-tower system to remove heavy residue and water from the aniline product. The aqueous layer, formed by the water of reaction, 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
BOD5	15 mg/l 0.02 lb/1,000 lb
TOC	12,150 mg/l 19.2 lb/1,000 lb

FIGURE IV-35
ANILINE
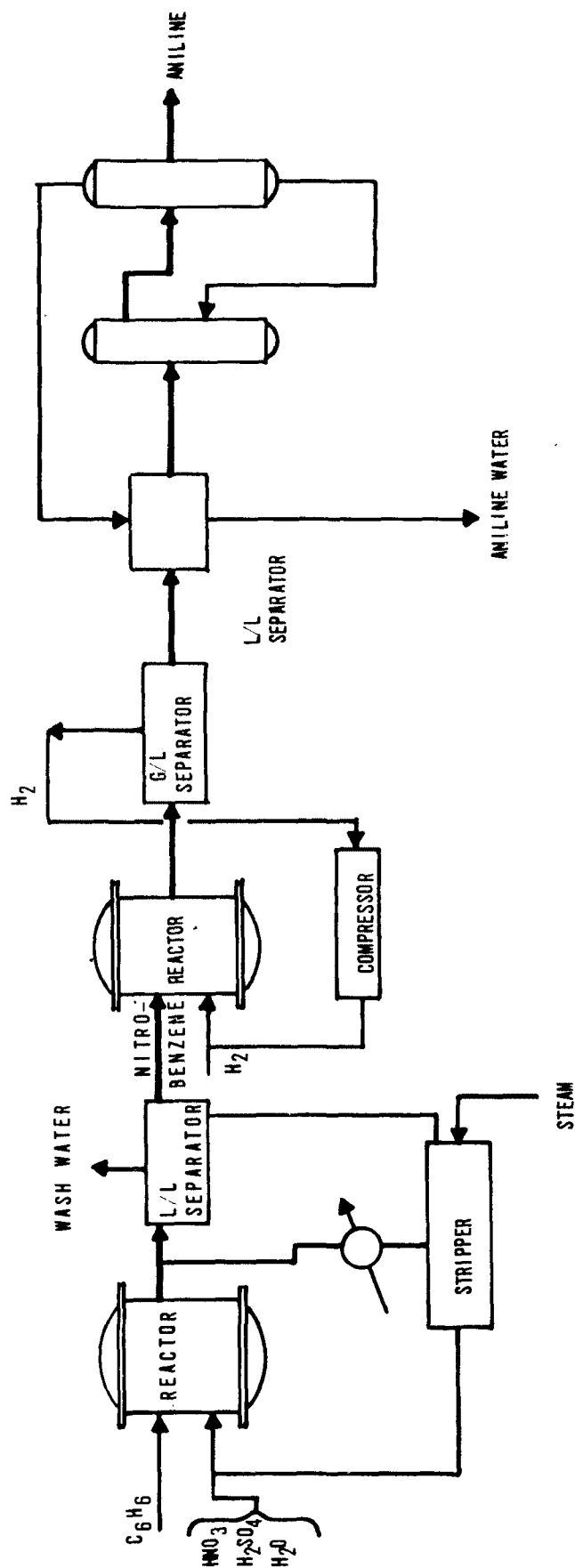
Results of analyses indicate that, in addition to the parameters shown above, sulfate concentrations in waste water streams are at levels inhibitory to biological treatment processes. The high RWL of this process is attributed to the high aniline concentration (3 percent) in aniline water from the final 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 10^8 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/1 2.13 lb/1,000 lb
TOC	1,490 mg/1 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 10^8 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, esti‑ mated 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

248# ANILINE
230# WATER
TO INCINERATOR

100 °F

8236 #/HR.
WATER
264#/HR.
ANILINE

150°F

20 PSIG
150° F

2-1/2' Ø x 40'
18 TRAYS

2500 #/ HR.
40 PSIG
STEAM

180°F

95°F

8006# WATER
16# ANILINE

C.W.
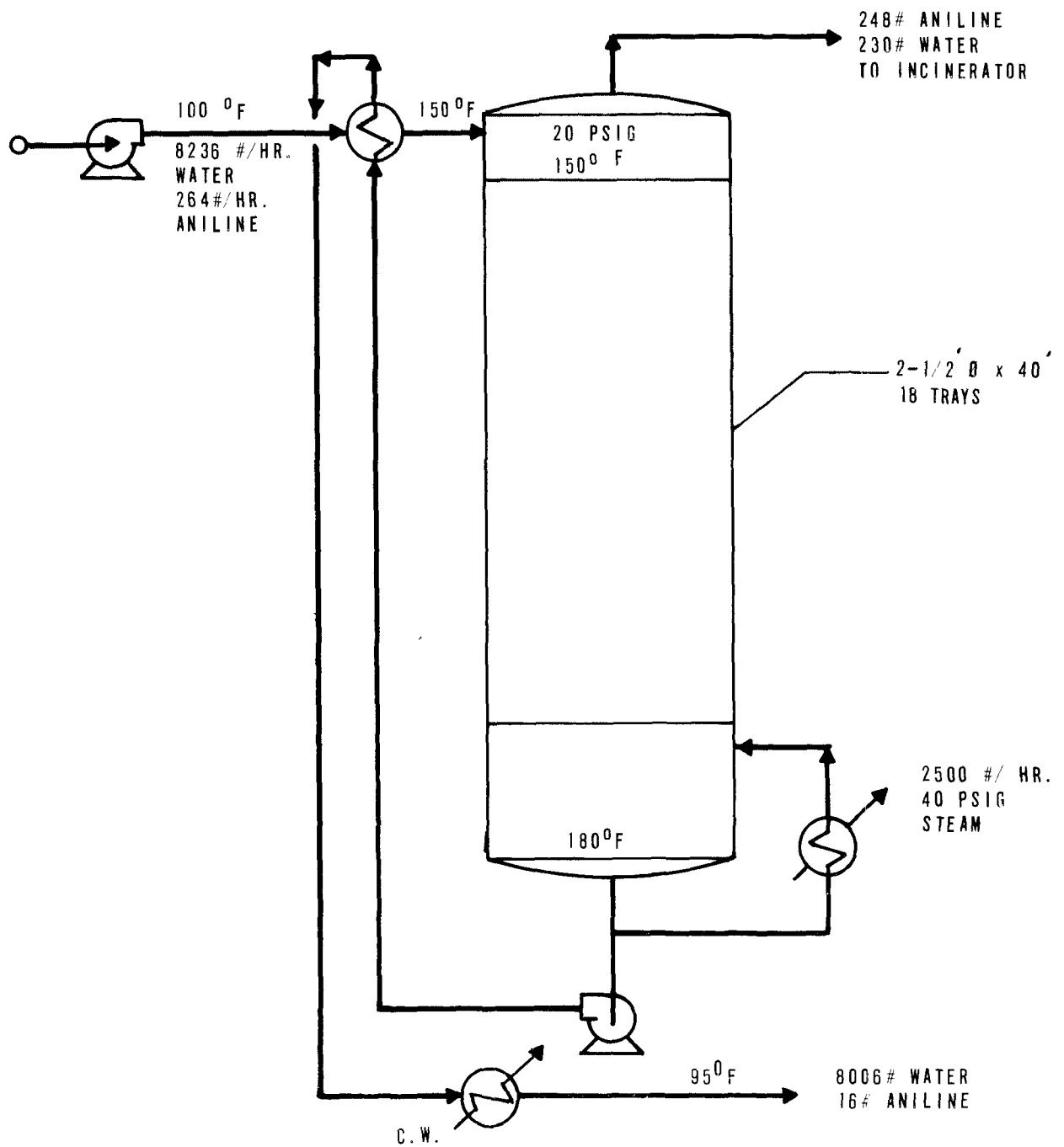
Table IV-54
Aniline Stripper Economics

Investment

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

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)

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

Table IV-56

Estimated Economics for Aniline
(40. MM lb. plant)

Total Fixed Capital=$3.2 MM

Estimated Operation Cost

	Cost ¢/lb. aniline
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
	10.2

Product	Process
Bisphenol-A	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:

$$2C_6H_5OH \quad + \quad CH_3COCH_3 \quad \longrightarrow \quad CH_3C(C_6H_4OH)_2CH_3 \quad + \quad H_2O$$

Phenol   Acetone   Bisphenol-A   Water

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

FIGURE IV-37
BISPHENOL A
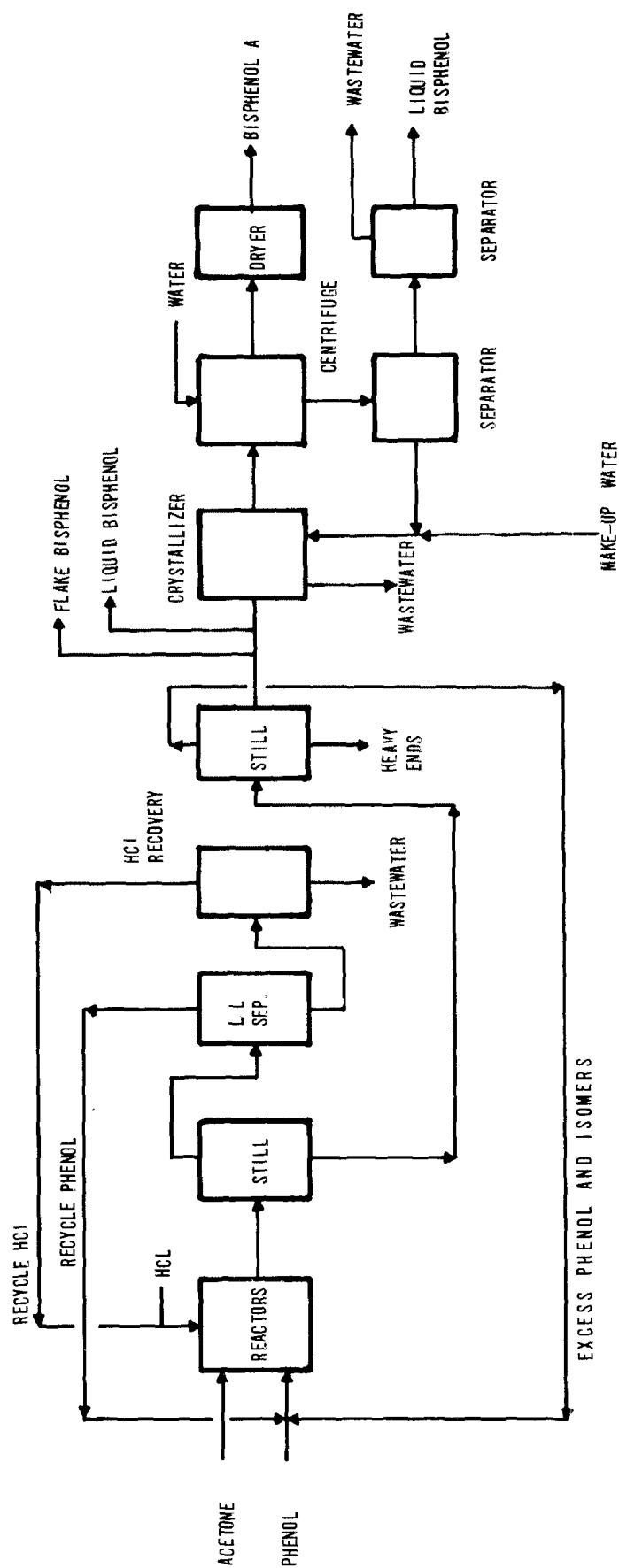
Phenol   12,713 mg/l
          7.1 lb/1,000 lb

The high concentration of phenol produces an inhibitory effect and interferes with the BOD$_5$ 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

Producer	Location	Estimated Capacity* 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	25
	TOTAL	238

*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

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

Product   Process
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:

$$C_6H_{12} + O_2 \xrightarrow{H_3BO_3} C_6H_{11}O \xrightarrow{H_2NOH \cdot HSO_4} C_6H_{11}NOH$$

Cyclohexane   Oxygen   Cyclohexanone   Cyclohexanone Oxime
               or Air

$$\xrightarrow{H_2SO_4} CH(CH_2)_5CONH + (NH_4)_2SO_4$$

               Caprolactam + Ammonium Sulfate
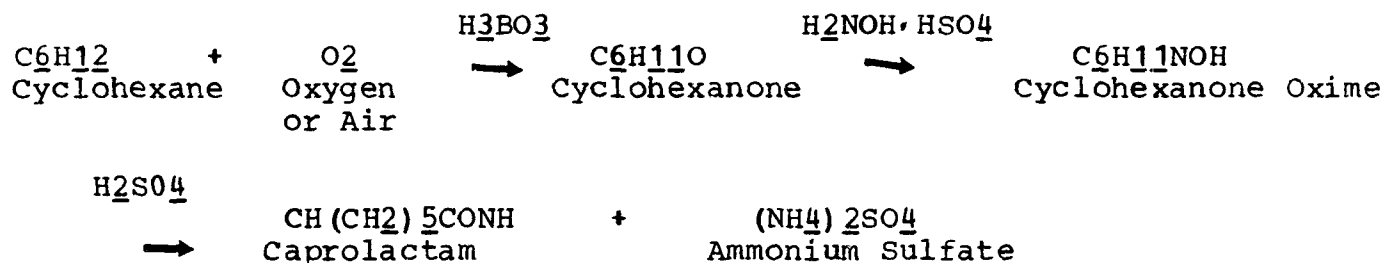
A process flowsheet is shown in Figure IV-38. Feed and recyled cyclohexane are mixed with air in an oxidation reactor in the presence of boric acid, which minimizes adipic acid production. The oxidation is carried out at approximately 150 psig and 160°C. The gaseous effluent is scrubbed to separate unreacted 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 catalytist 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,

FIGURE IV-38
CAPROLACTAM
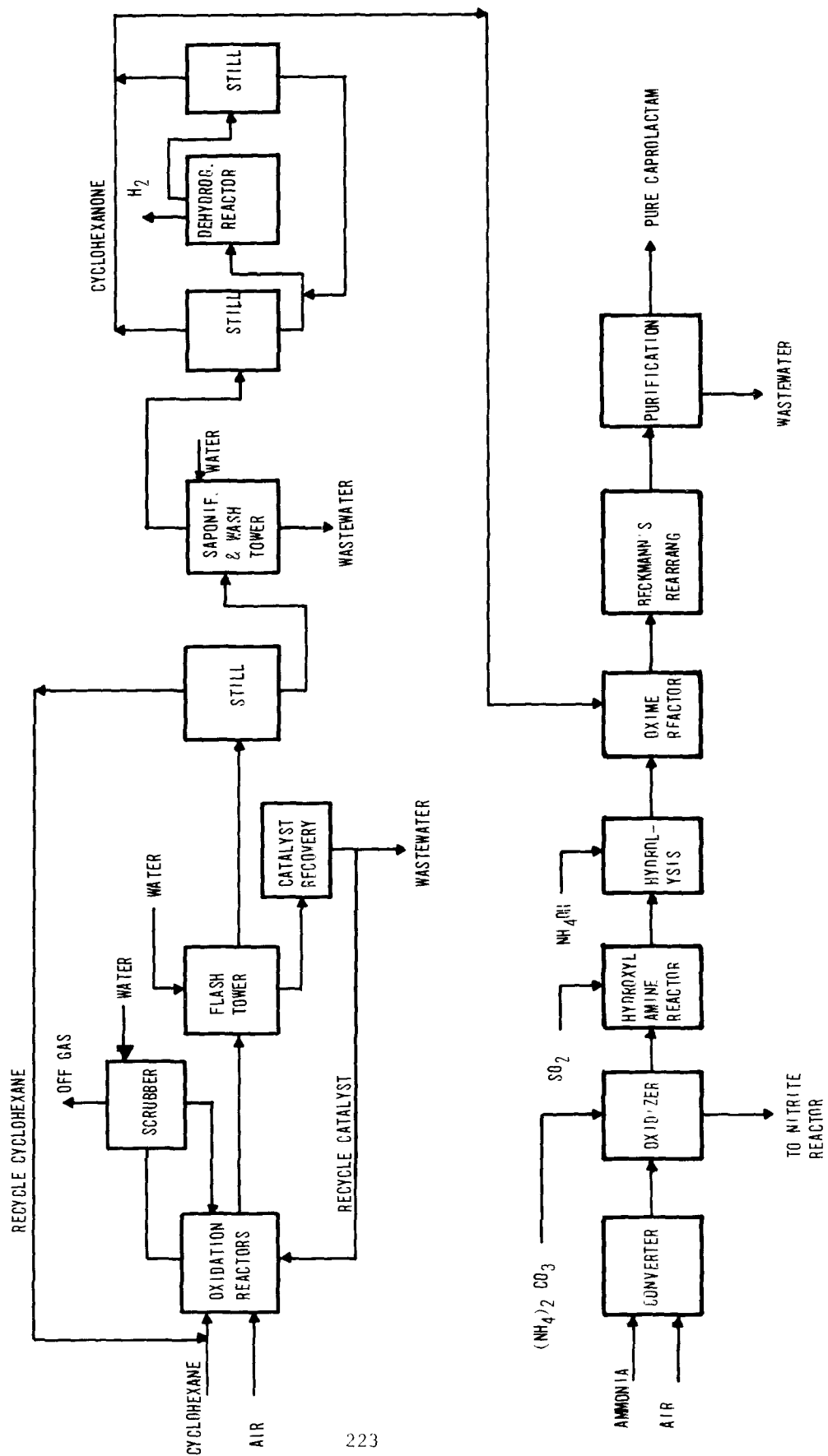
and unrecovered intermediate products. The characteristics of the waste water obtained from the plant survey are summarized in the following tabulation:

	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.
BOD5	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 N_2O_3 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.)

Company	Location	1967	1972	Process
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.	50	shut down	Caprolactone
TOTAL		534	626	

Table IV-60

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

TOTAL FIXED CAPITAL

Process	$ MM
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

	Beckmann	Caprolactone	Toyo Rayon
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.)	2.50	2.66	2.66
TOTAL	18.49	18.13	16.84
By-product credit	4.44	6.22	1.58
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.

Product	Process
Long Chain Alcohols	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 tri-alkoxides. These are hydrolyzed by sulfuric acid to primary alcohols having an even number of carbon atoms. The basic chemical equations are summarized as follows:

$$3C_2H_4 \quad + \quad 1\,1/2H_2 \quad + \quad Al \quad \longrightarrow \quad (C_2H_5)_3Al$$

Ethylene Hydrogen Aluminum Triethyl Aluminum

$$(C_2H_5)_3Al \quad + \quad nC_2H_4 \quad \longrightarrow \quad \begin{matrix} R_1 \\ R_2 \\ R_3 \end{matrix} \Big\rangle Al$$

Triethyl Aluminum Ehtylene Triethyl Aluminum

$$+O_2 \quad \longrightarrow \quad \begin{matrix} R_1-O \\ R_2-O \\ R_3-O \end{matrix} \Big\rangle Al$$

Aluminum Trialkoxides

$$\begin{matrix} H_2SO_4 \\ \longrightarrow \\ H_2O \end{matrix} \quad R_1OH \quad + \quad R_2OH \quad + \quad R_3OH \quad + \quad Al_2(SO_4)_3$$

Long-Chain Alcohols Alum
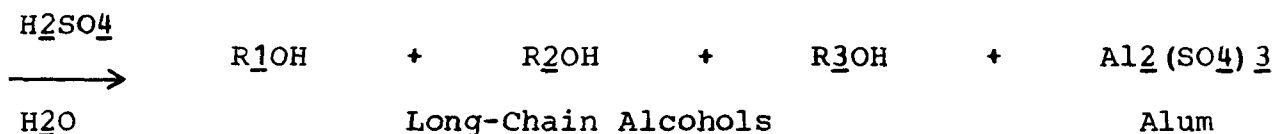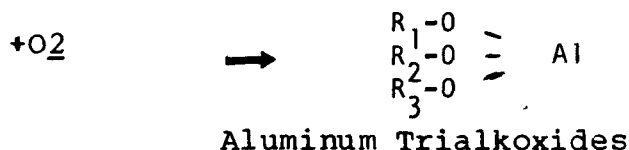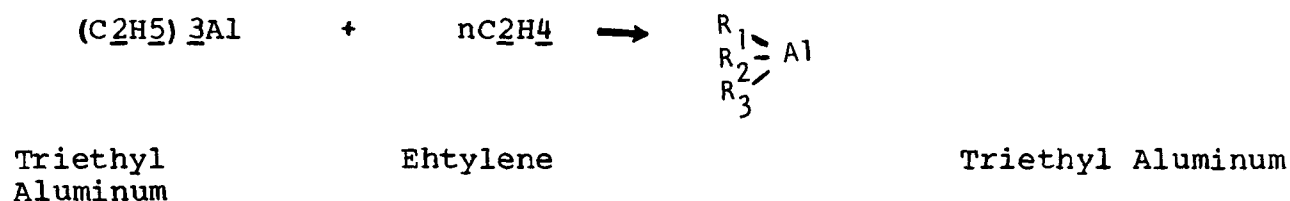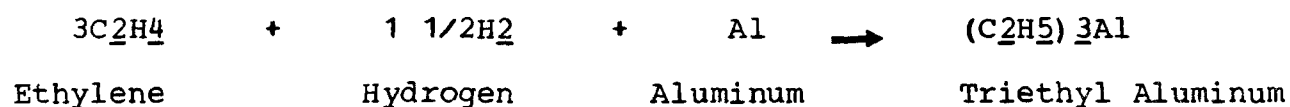
A simplified flow diagram is shown in Figure IV-39. An atomized aluminum powder is first activated in a non-aqueous slurry media and next hydrogenated with dry hydrogen gas under pressure to give diethyl aluminum hydride. The hydride is then contacted with ethylene to produce TEA. Approximately two moles 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 ethlyene under pressure to make trialkyl aluminum, which is then oxidized to produce alkoxides. A non-aqueous solvent such as toluene is circulated and

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FIGURE IV-39
LONG CHAIN ALCOHOL
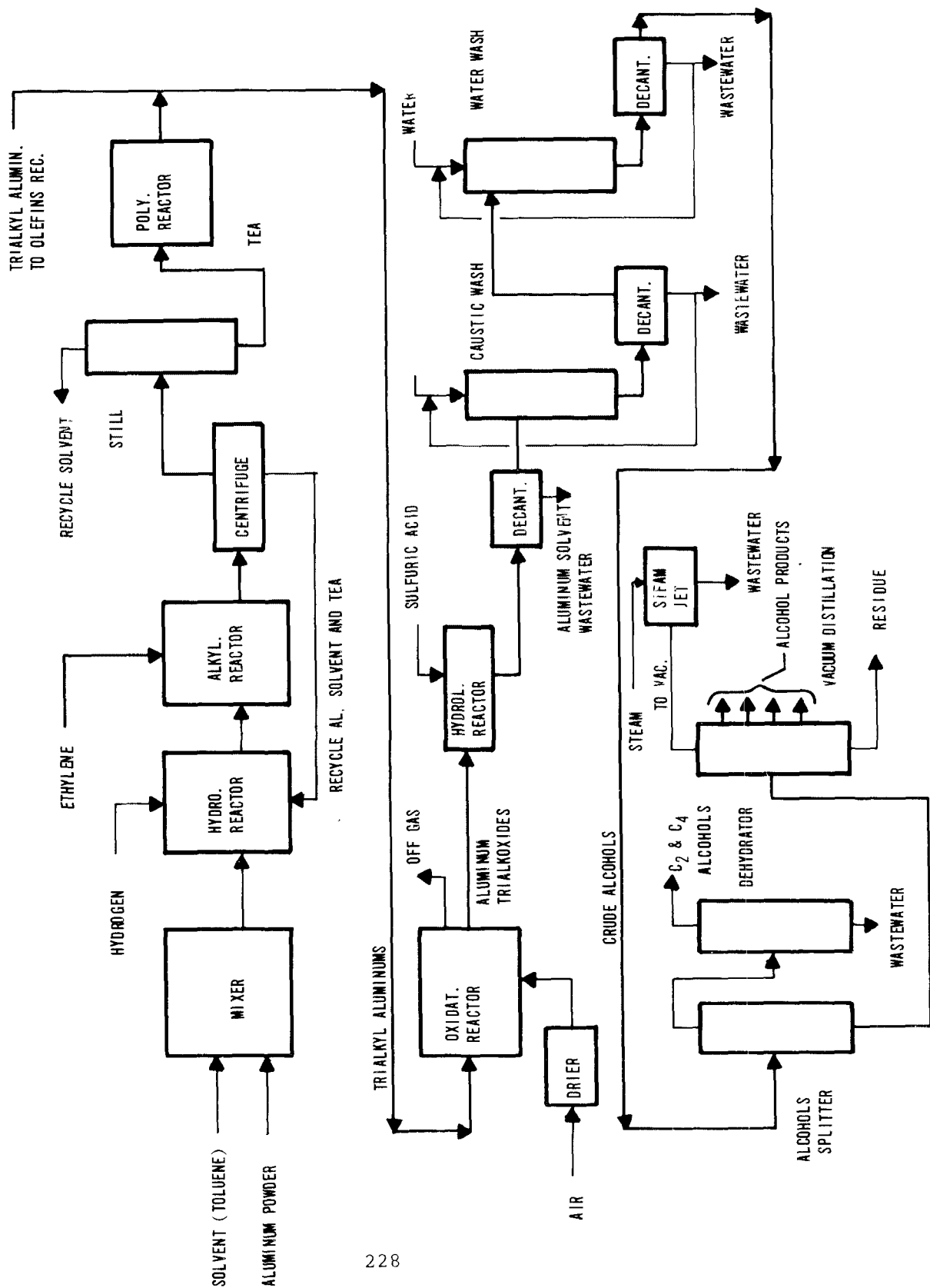
recycled in this section. In the hydrolysis section, the alkoxides are hydrolyzed with sulfuric acid and water to yield alcohols and a solution of alum and water. The alum solution is separated from the alcohols in a decanter. The sulfuric acid residue is first neutralized with dilute caustic solution 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

Producer	Location	1965 Capacity MM lbs/yr.	Type of Alcohol	Process	Raw Material
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.

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, occuring in a horizontal autoclave provided with a reflux condenser to recover any vaporized alkyl halide, yeilds a mixture of TEL, salt, and lead. The reaction, carried out at 60 psig and 70°C, is given below:

$$4PbNa + 4C_2H_5l \rightarrow (C_2H_5)_4Pb + 3Pb$$

4PbNa	4C2H5l	(C2H5)4Pb	3Pb
Sodium Lead Alloy	Ethyl Chloride	TEL	Lead
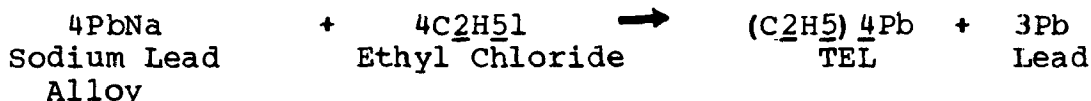
The product mixture is fed batchwise to a still, where the tetraethyl lead is separated from the by-product lead and sodium chloride by direct steam stripping. The tetraethyl lead and stripping steam are condensed and sent to a decanter, where tetraethyl lead is drawn off as a bottoms stream. The upper 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
BOD5	40 mg/l
	4 lb/1,000 lb
TOC	56 mg/l
	5.6 lb/1,000 lb

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FIGURE IV-40
TETRAETHYL LEAD

231
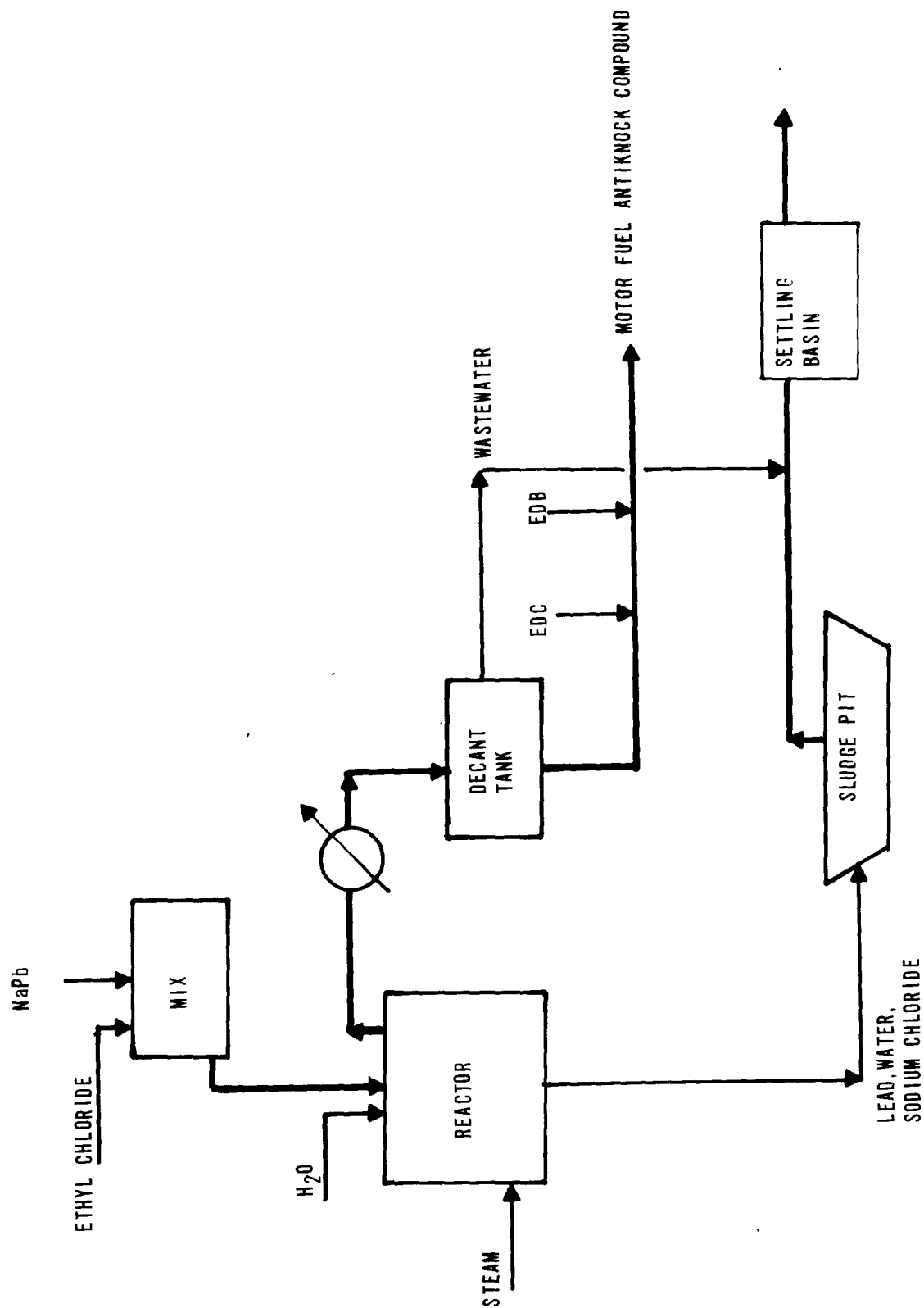
The high amount of waste water is due mainly to the nature of batch processes, which require a large quantity of water in cleaning up the reactor between reaction batches. Another cause of high water use is the vent-gas scrubber at the "lead" recovery unit. The intermittent dosage of "still-aids" such 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 diethylenegylcol 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

	Plant Location	Est. 1970 Capacity (Million Pounds/Year)
DuPont	Antioch, Calif. Deepwater, N.J.	340
Ethyl	Baton Rouge, La. Houston, Texas	390
Houston Chem.	Beaumont, Texas	100
Nalco Chem.	Houston, Texas	65
Total		895

Table IV-63

Estimated Economics for Tetraethyl Lead
(40. MM lb. plant)

Total Fixed Captial=$10.0 MM

Estimated Operation Cost

	Cost, ¢/lb. TEL
Ethyl chloride	4.9
Sodium	3.8
Lead (17¢/lb.)	11.4
Utilities	1.5
Labor and overhead	1.6
Capital charges	8.3
Total	31.5

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Product   Process
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 acqueous 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: segre-
gation of clean water from process waste water, replacement of

FIGURE IV-41
COAL TAR DISTILLATION

235
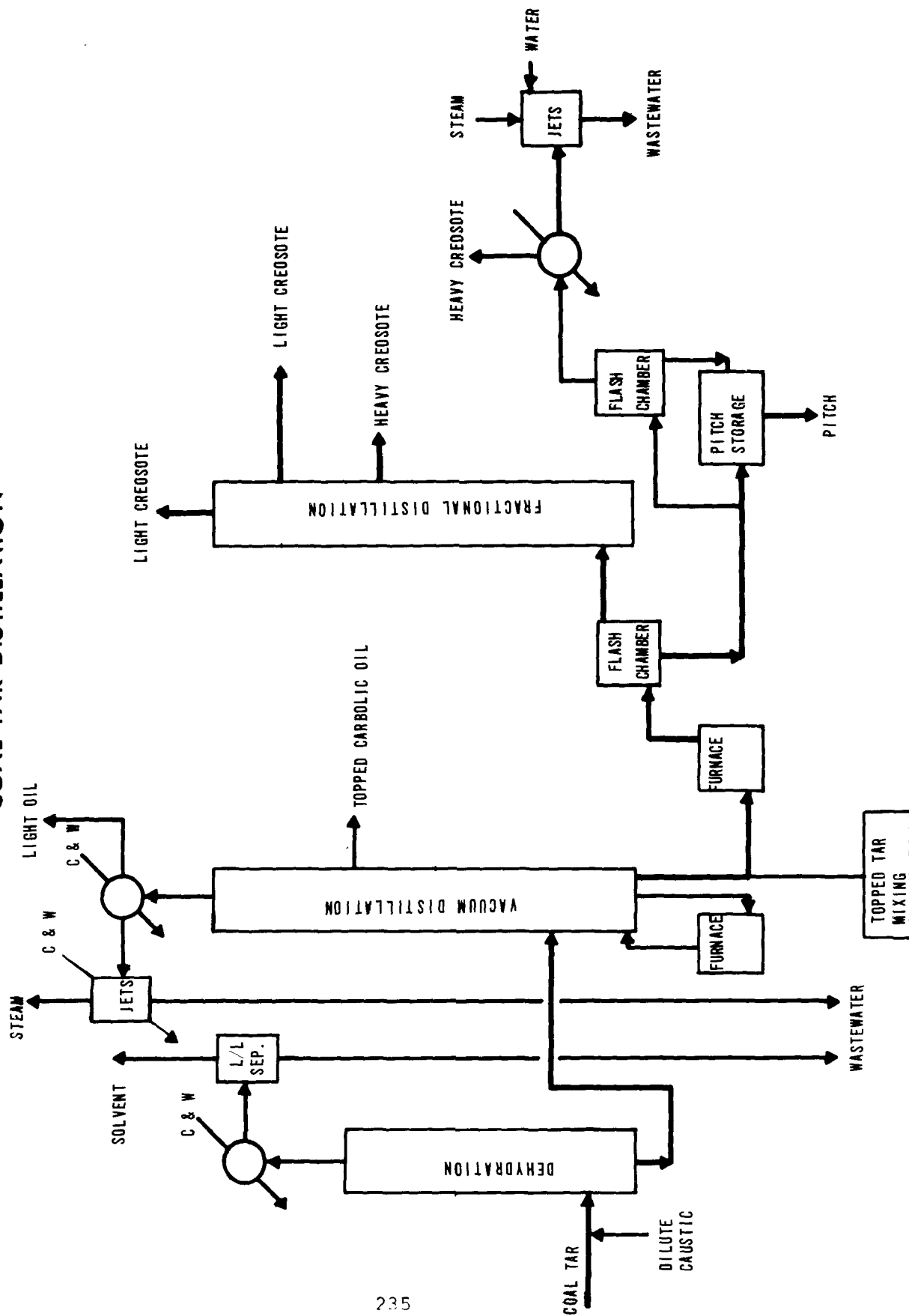
FIGURE IV-42
ANTHRACENE REFINING

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FIGURE IV-43

EXTRACTION AND NAPHTHALENE REFINING

237
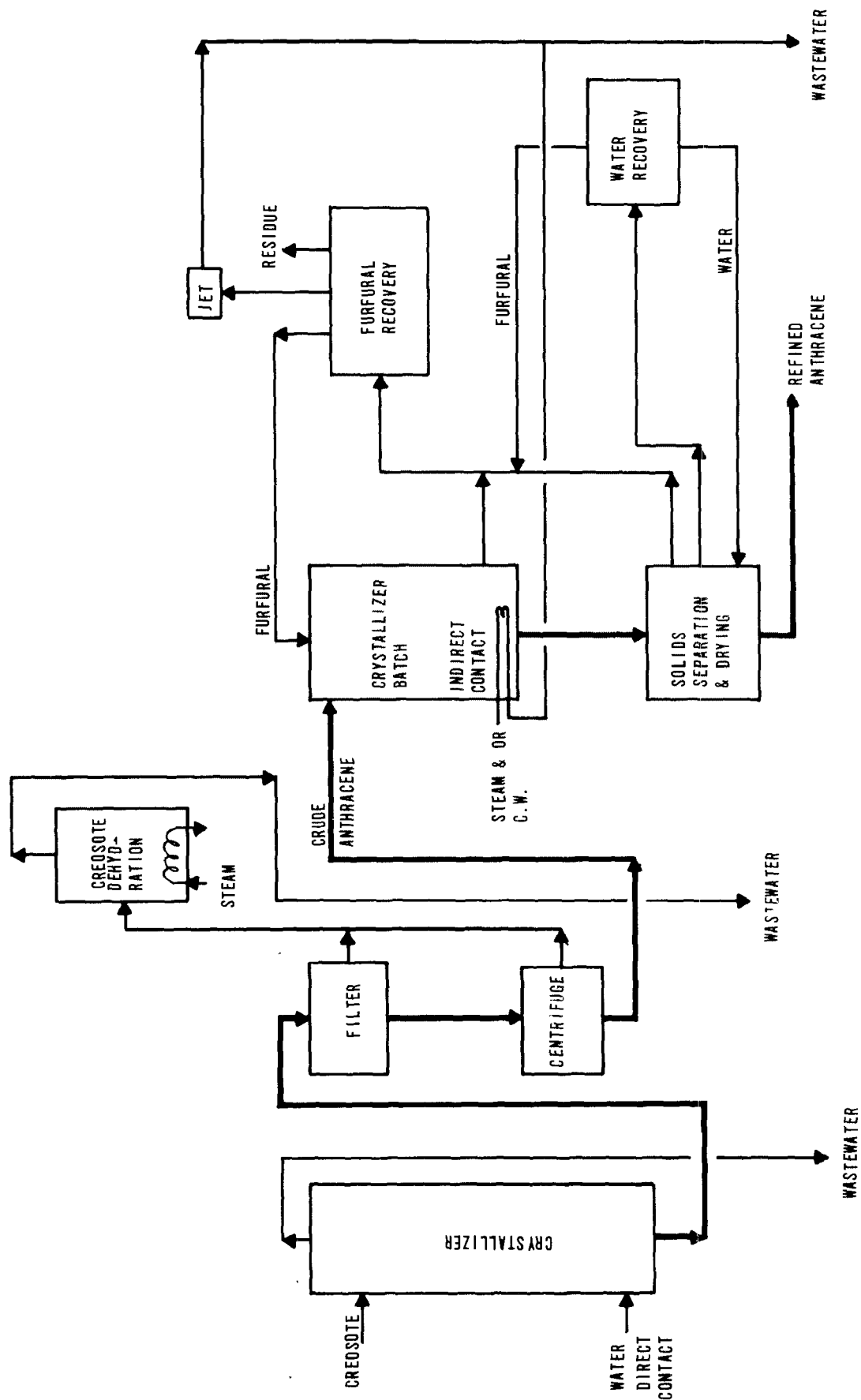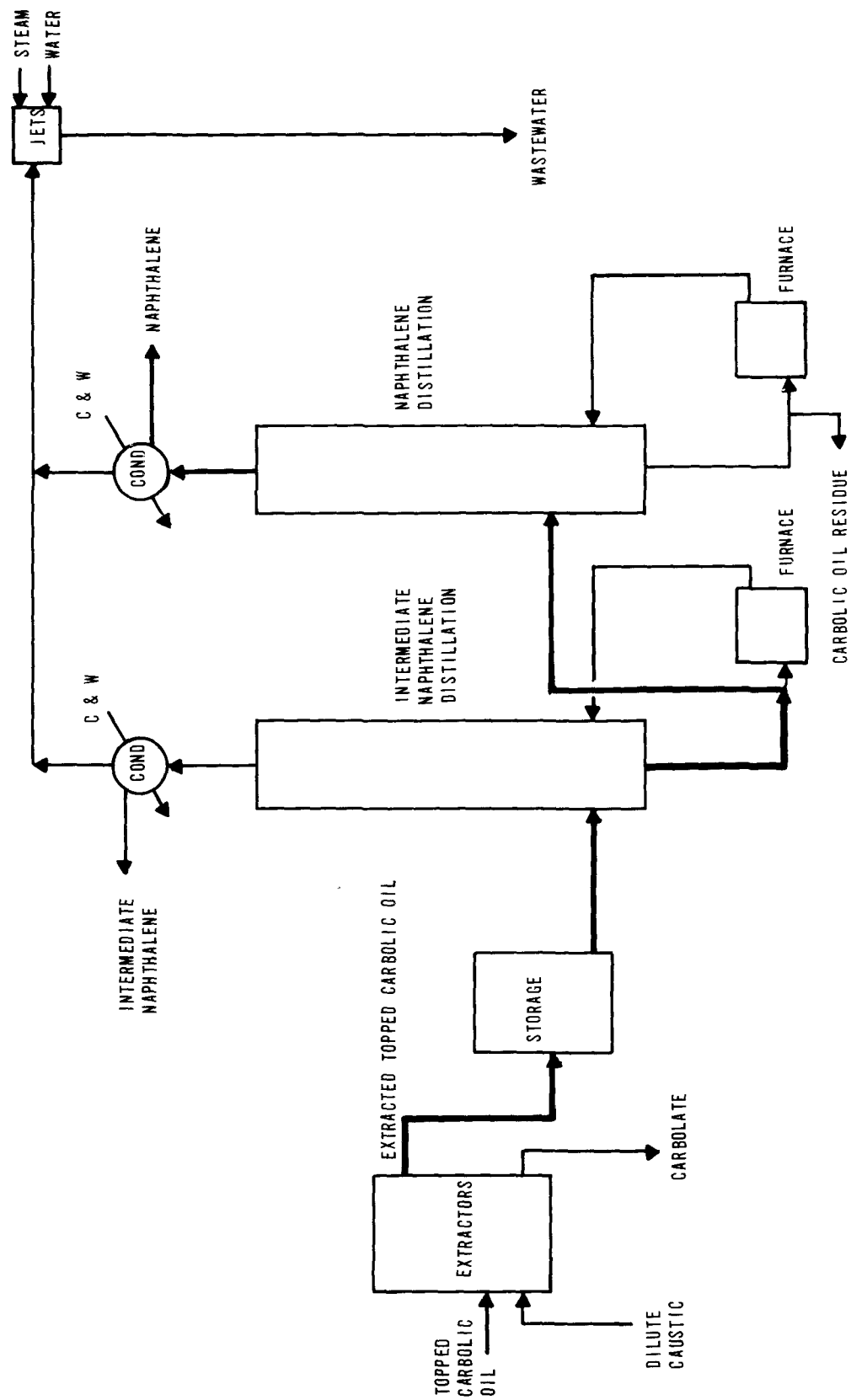
FIGURE IV-44
PITCH FORMING
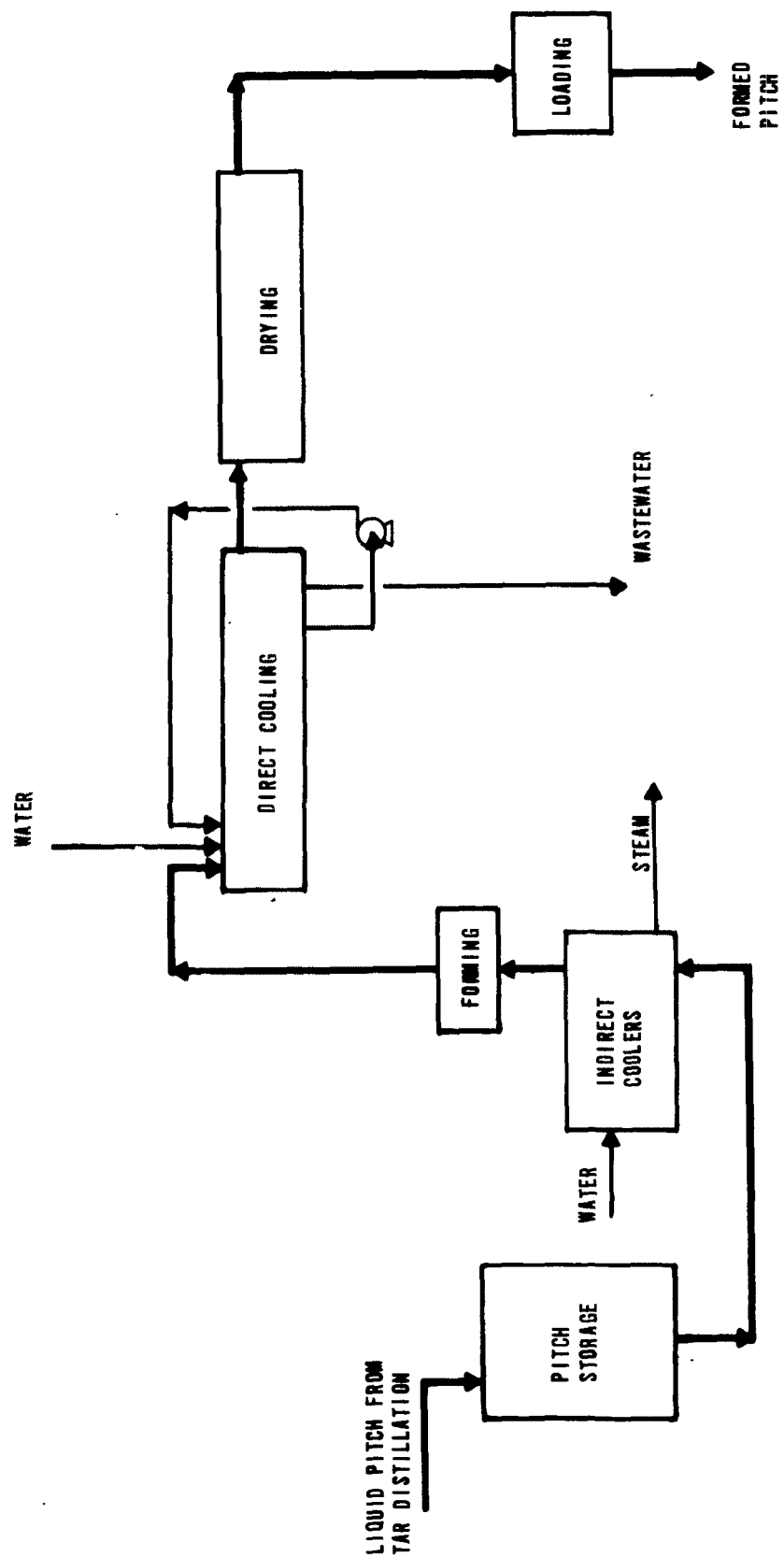
barometric condensers with indirect condensers, installation of phenol recovery units, etc. These modification have resulted in a low RWL.

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
BOD5	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.

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Product   Process
Dyes and Pigments   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 refluctance, 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 additon 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

FIGURE IV-45

DYES
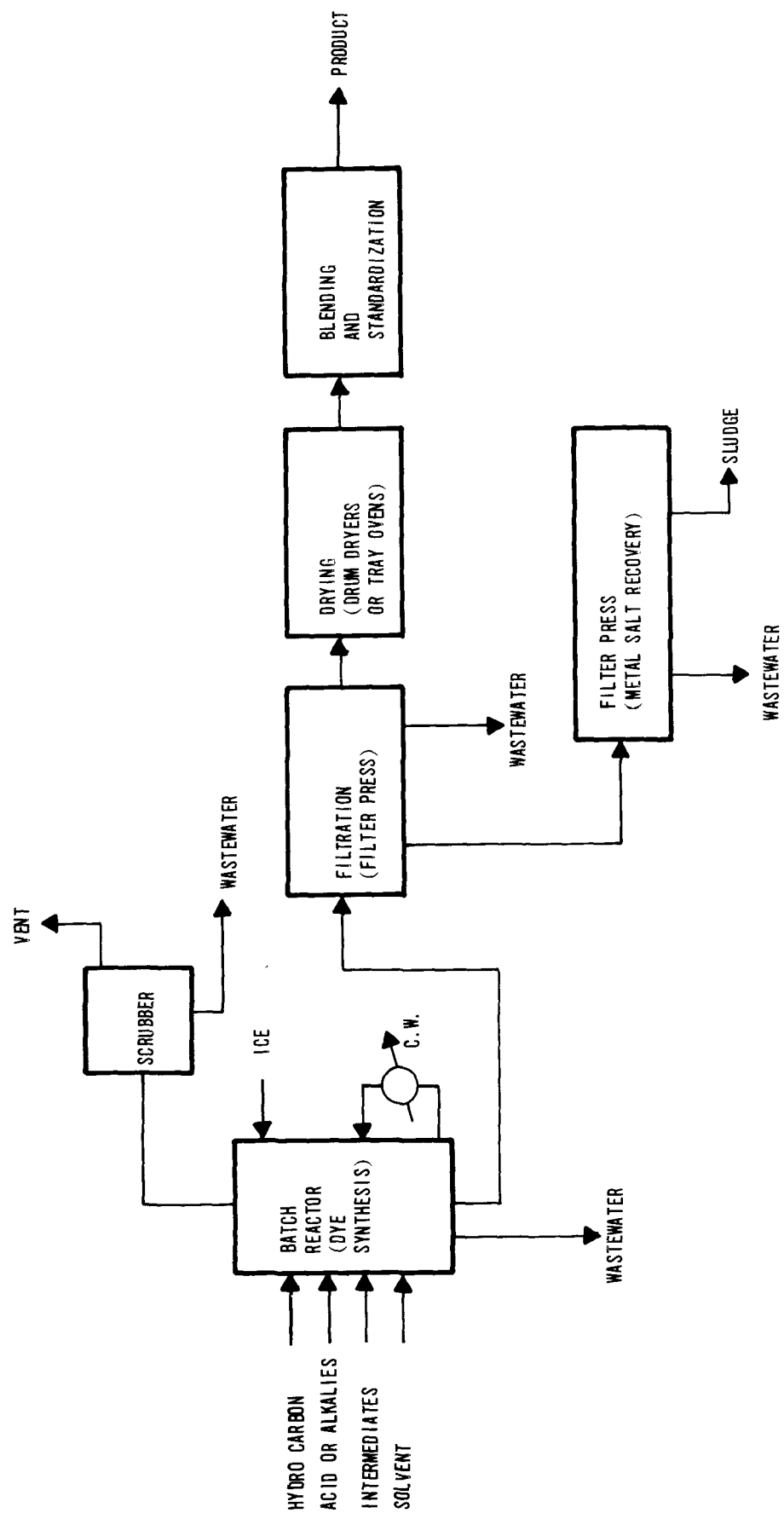
Table IV-64

U. S. Production of Dyes,
by Classes of Application, 1965

Class of application	Production, 1,000 lb.	Sales Quantity, 1,000 lb.	Sales Value, $1,000	Unit value, Per lb.$
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

Chemical class	Production, 1,000 lb.	Sales		
		Quantity, 1,000 lb.	Value, $1,000	Unit value per lb.$
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

Pigments	Short tons	
	1958	1963
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

mother liquor is either directly discharged 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 manufactued 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.

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 calcualtion 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 asscoiated 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/kkg and
    gal/1,000 lbs of product)

2. BOD5 Raw Waste Loading
    (expressed as kg BOD5/kkg and
    lb BO 5/1,000 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
        BOD5 vs. Flow   (Figure V-1)
        COD vs. Flow   (Figure V-2)
        TOC vs. Flow   (Figure V-3)

    Subcategory B
        BOD5 vs. Flow   (Figure V-4)
        COD vs. Flow   (Figure V-5)
        TOC vs. Flow   (Figure V-6)

    Subcategory C
        BOD5 vs. Flow   (Figure V-7)
        COD vs. Flow   (Figure V-8)
        TOC vs. Flow   (Figure V-9)

    Subcategory D
        BOD5 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.   Although

insufficient RWL data were obtained to establish definitive increasing relation between loading and flow the additonal RWL data may provide confirmation of such a relationship.

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.

During Phase II, an additional effort will be made to supplement the date for this category by sampling numerous processes over long periods of time. This will eliminate some of the difficulties associated with sampling and measuring the sporadic flows.

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 purolysis of EDC product contact process waste waters which are not amenable to the BOD5 test. This was caused by

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Table V-1

CATEGORY A - NON AQUEOUS PROCESSES

Best Practicable Control Technology Currently Available

Raw Waste Load Data

Product/Process	Process Description	Flow L/1000 kg(gal/1000#)		BOD kg/1000 kg	COD or lb/1000 lb	TOC
Cyclohexane	Hydrogenation of Benzene	No Discharge		---	---	---
Ethylbenzene	Alkylation of Benzene with Ethylene	315.0	(37.7)	0.132	1.86	0.65
Vinyl Chloride	Addition of HCl to Acetylene	2,004.0	(240)	---	0.12	0.067
BTX Aromatics	Hydrotreating Pyrolysis Gasoline	114.0	(13.6)	0.104	0.31	0.034
BTX Aromatics	Solvent Extraction from Reformate	504.0	(60.4)	---	---	0.144
	AVERAGE	588	(70)	0.12	0.76	0.22
	MEDIAN	504	(60)	0.12	0.31	0.36

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FIGURE V-1

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR CATEGORY A
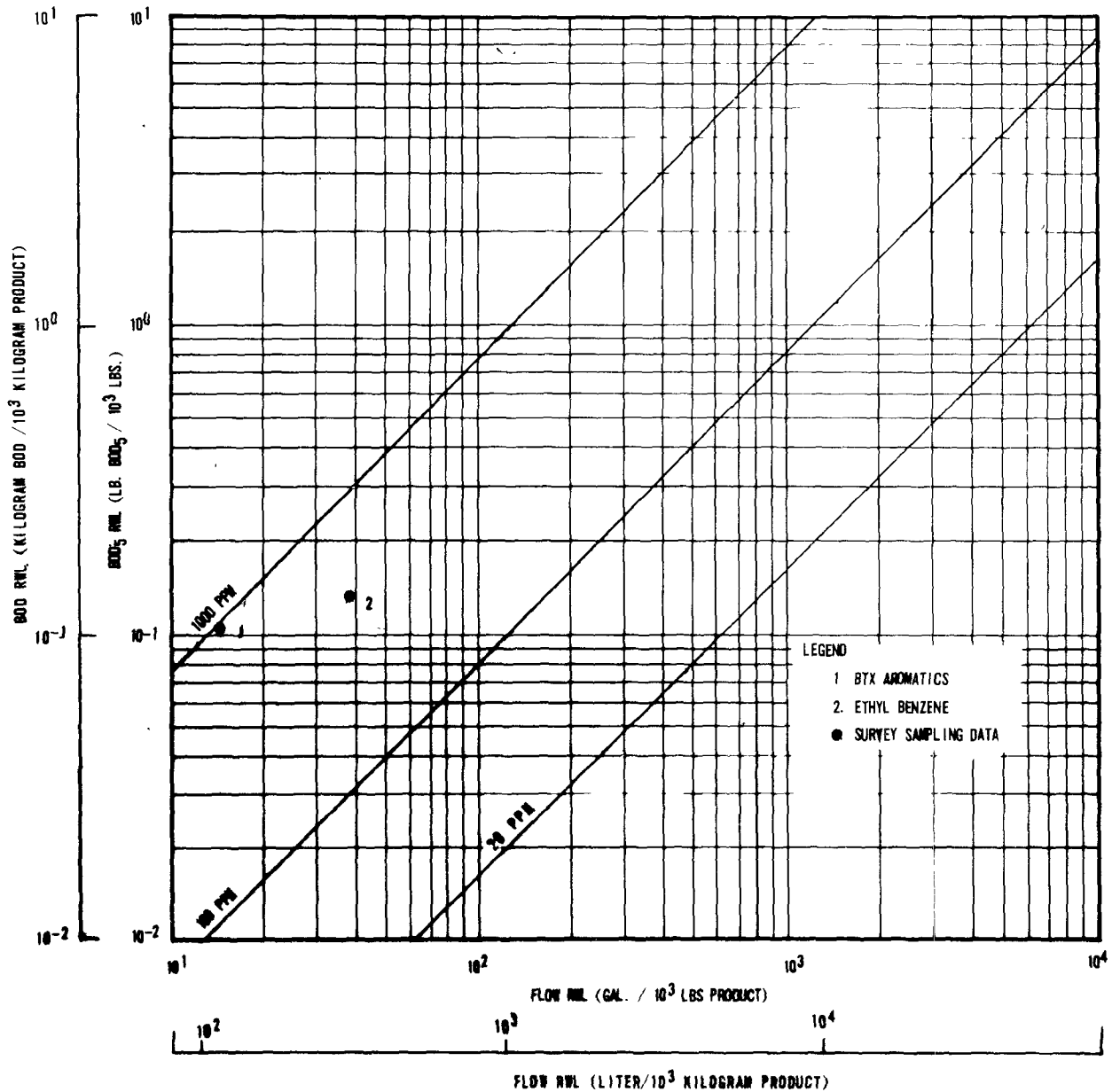
FIGURE V-2

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR CATEGORY A

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FIGURE V-3

RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR CATEGORY A

254
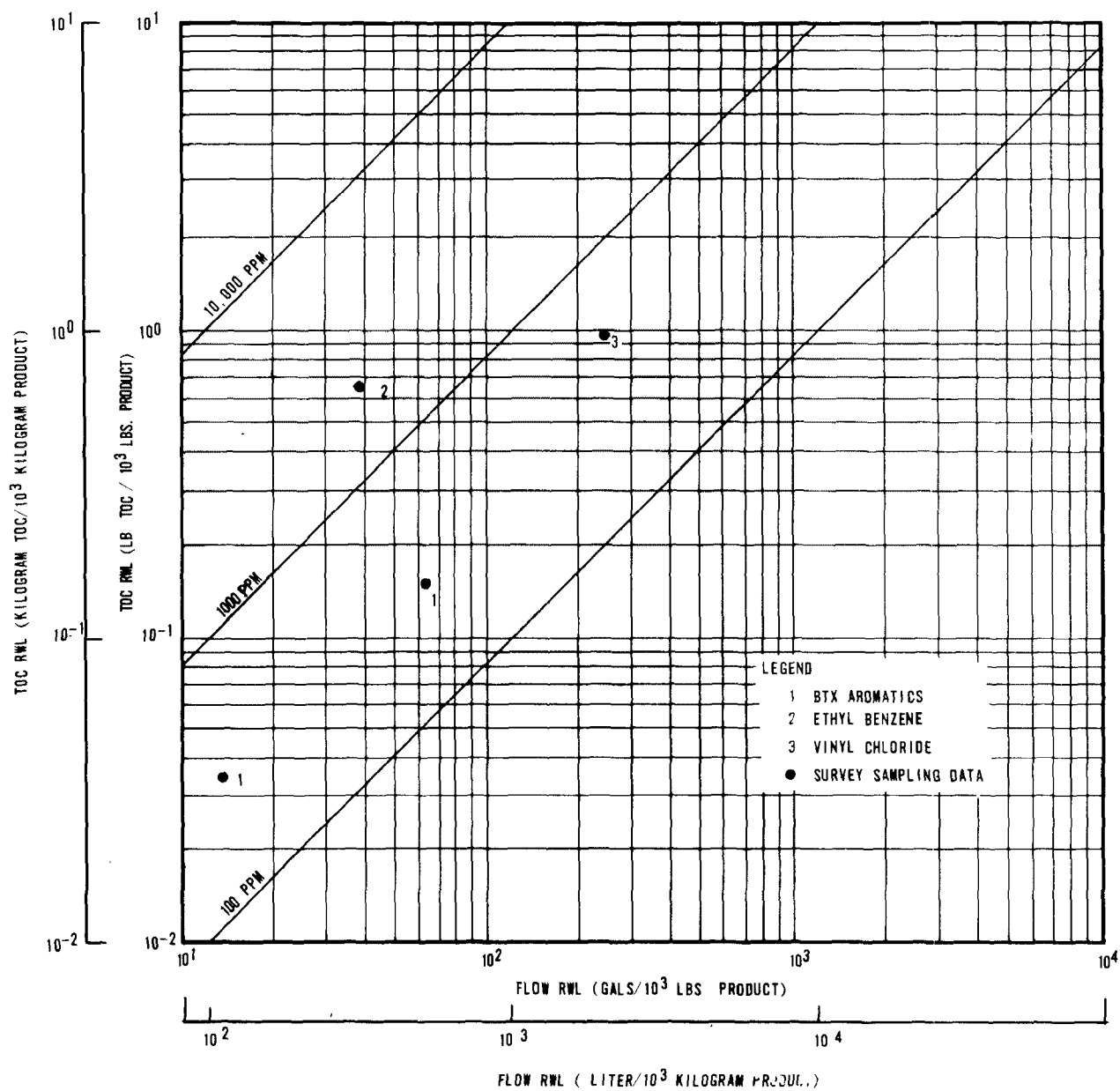
objectionable conditions related to the high concentrations of wastes. In such cases, the wastes may still be degraded biologically, but require dilution with other less concentrated wastes or non-contact cooling water.

The COD RWL concentrations for 16 Subcategory B processes are bewteen 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.

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 establishmnet of two subcategories designated as B1 and B2. The individual products, processes, and associated RWL asllocated 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

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Table V-2

CATEGORY B - PROCESS WATER CONTACT AS STEAM DILUTENT AND FOR ABSORBENT

Best Practicable Control Technology Currently Available

Raw Waste Load Data

| Product/Process	Process Description	Flow L/1000 kg(gal/1000#)	BOD kg/1000 kg or	COD lb/1000	TOC lb
B₁ Product/Processes					
Ethylene	Pyrolysis of Naphtha/LPG	2964 (355)	0.35	2.36	0.89
Butadiene	Co-product of Ethylene	1695 (203)	0.63	2.04	0.81
Methanol	Steam Reforming of Natural Gas	418 (50)	0.49	0.94	0.13
Acetone	Dehydrogenation of Isopropanol	1461 (175)	0.26	1.10	0.36
Acetaldehyde	Dehydrogenation of Ethanol	1169 (140)	----	----	16.7
Vinyl Acetate	Synthesis of Ethylene and Acetic Acid	234 (28)	0.04	0.13	0.05
	AVERAGE	1328 (159)	0.34	1.31	3.15
	MEDIAN	1319 (158)	0.35	1.10	0.58
B₂ Product/Processes					
Butadiene	Dehydrogenation of N-butane	9686 (1160)	2.96	3.23	----
Butadiene	Oxidative-Dehydrogenation of Butane	12,116 (1451)	72	245	231
Acetylene	Oxidation of Methane	4684 (561)	1.92	5.95	1.88
Ethylene Oxide	Oxidation of Ethylene	618 (74)	0.70	6.48	2.93
Formaldehyde	Oxidation of Methanol	1094 (131)	----	----	----
Ethylene Dichloride	Direct Chlorination of Ethylene	802 (96)	Toxic	4.84	0.89
Vinyl Chloride	Cracking of Ethylene Dichloride	2806 (336)	Toxic	7.66	0.33
Styrene	Dehydrogenation of Ethyl Benzene	23,464 (2810)	1.62	5.13	0.52
Methyl Amines	Addition of Ammonia to Methanol	3582 (439)	0.48	12.8	26.3
	AVERAGE	6087 (783)	13.3	36	38
	MEDIAN	3582 (429)	1.77	6.2	1.4

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FIGURE V-4

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR CATEGORY B

FIGURE V-5

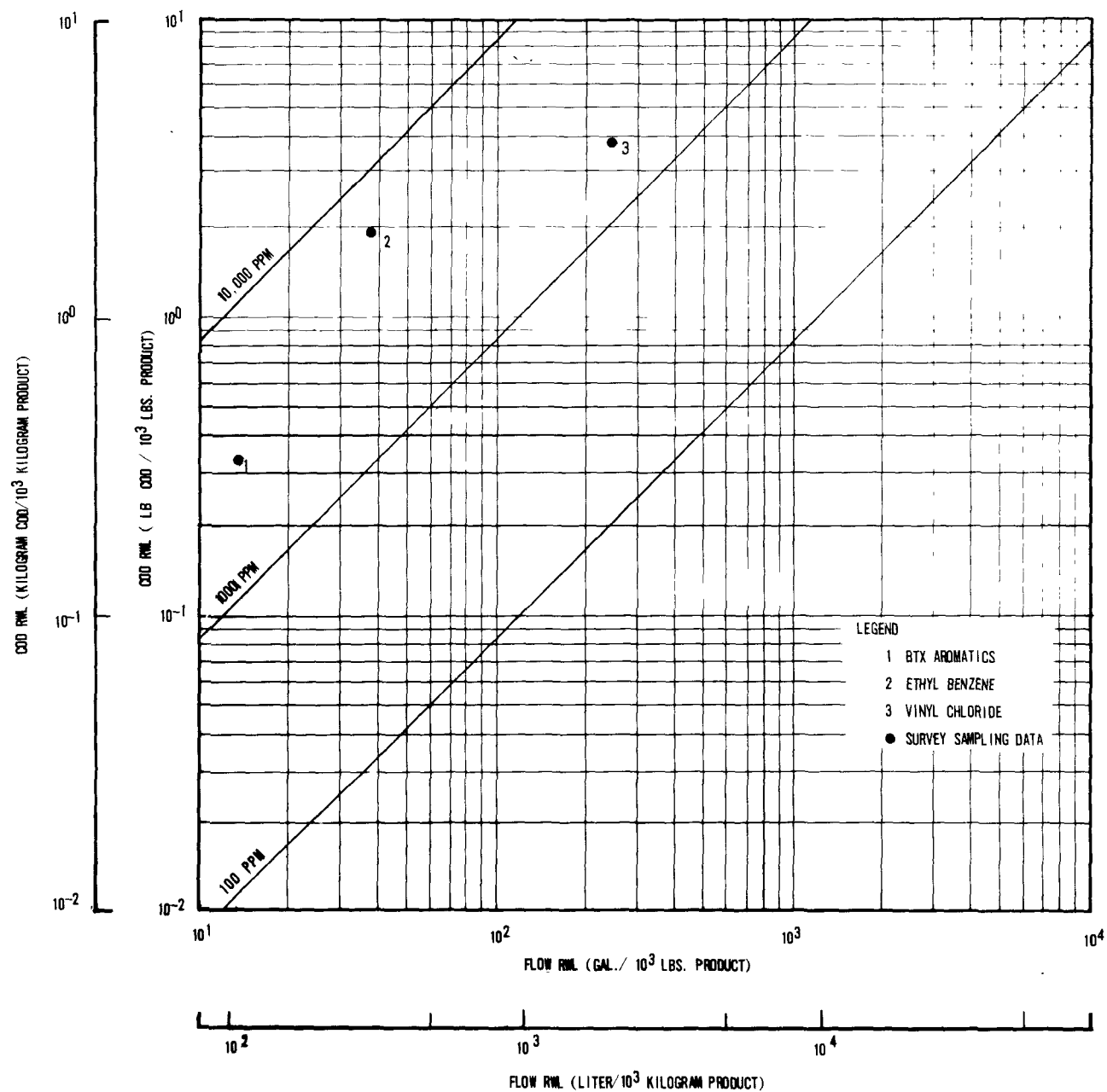## RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR CATEGORY B

LEGEND

1. ACETALDEHYDE FROM ETHANOL OXIDATIVE-DEHYDROGENATION
2. ACETONE FROM IPA DEHYDROGENATION
3. BUTADIENE FROM C_2H_4 EXTRACTIVE DISTILLATION
4. BUTADIENE FROM N-BUTANE DEHYDROGENATION (HOUDRY)
5. STYRENE FROM E.B.
6. ETHYLENE FROM C_2H_5
7. ETHYLENE FROM LPG
8. ETHYLENE FROM NAPHTHA
9. ETHYLENE FROM C_3H_8
10. ETHYLENE OXIDE
11. METHANOL
12. METHYL AMINES
13. ACETYLENE
15. EDC FROM C_2H_4
16. VCM FROM EDC

● SURVEY SAMPLING DATA
  90% OCCURRENCE
  HISTORICAL PLANT DATA
  50% OCCURRENCE
  10% OCCURRENCE

FIGURE V-6
RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR CATEGORY B

Table V-3

Category C - Aqueous Liquid Phase Reaction Systems
Best Practicable Control Technology Currently Available

Product/Process	Process Description	Flow · liters/1000 kg (gal/1000 #)		BOD_5 kg/1000 Kg or lb/1000 lb	COD	TOC
C_1 Product/Process						
Acetaldehyde	Oxidation of Ethylene with Air	752	(90)	26.6	44	2.8
Acetaldehyde	Oxidation of Ethylene with Oxygen	509	(61)	1.9	5.8	5.5
Acetic Acid	Oxidation of Acetaldehyde	4,175	(500)	0.35	0.78	—
Acrylic Acid	Synthesis with Carbon Monoxide and Acetylene	3,966	(475)	0.74	1.64	1.53
Aniline	Nitration and Hydrogenation of Benzene	1,586	(190)	—	21.2	19.2
Bis Phenol A	Condensation of Phenol and Acetone	559	(67)	—	17.1	5.13
Caprolactam	Oxidation of Cyclohexane	10,855	(1,300)	1.64	4.0	—
Coal Tar	Pitch Forming Distillation	1,044 3,340	(125) (400)	— 2.8	0.06 8.7	— 10.2
Dimethyl Terephthalate	Esterification of TPA	2,254	(270)	24.45	38.2	13.8
Ethylene Glycol	Hydrogenation of Ethylene Oxide	4,876	(584)	0.34	8.76	4.52
Oxo Chemicals	Carbonylation and Condensation	3,507	(420)	3.2	4.25	1.92
Phenol	Oxidation of Cumene	2,338	(280)	5.6	11.0	0.45
Terephthalic Acid	Oxidation of P-xylene	1,553	(186)	.82	1.72	0.86
	Average Median	2,973 2,338	(356) · (280)	5.83 1.9	11.3 6.5	6.38 3.6
C_2 Product Processes						
Acrylates	Esterification of Acrylic Acid	15,280	(2,856)	47	118	79
p Cresol	Salfonation of Toluene	10,780	(1,291)	123	256	54
Methyl Methacrylate	Acetone Cyanolrydrin Process	2,171	(200)	45	386	152
Terephthalic Acid	Nitric Acid Process	5,503	(659)	59	104	45
Tetra Ethyl Lead	Addition of Ethyl Chloride to Lead Amalgam	100,000	(12,000)	—	110	5.6
	Average Median	28,499 10,280	(3,413) (1,291)	68 53	195 118	67 54

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FIGURE V-7
RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR CATEGORY C

LEGEND
1   METHYL METHACRYLATE
2   TEREPHTHALIC ACID "POLYMER GRADE"
3   DIMETHYL TEREPHTHALATE
4   TEREPHTHALIC ACID "INDUSTRIAL GRADE"
5   ACRYLATES
6   TETRAETHYL LEAD
7   PHENOL/ACETONE
8   ACETALDEHYDE
9   ACETIC ACID
10 ANILINE
12 ETHYLENE GLYCOL
●   SURVEY SAMPLING DATA

BOD RWL (KILOGRAM BOD /10³ KILOGRAM PRODUCT)

BOD RWL (LB BOD/10³ LBS PRODUCT)

FLOW RWL (GAL/10³ LBS PRODUCT)
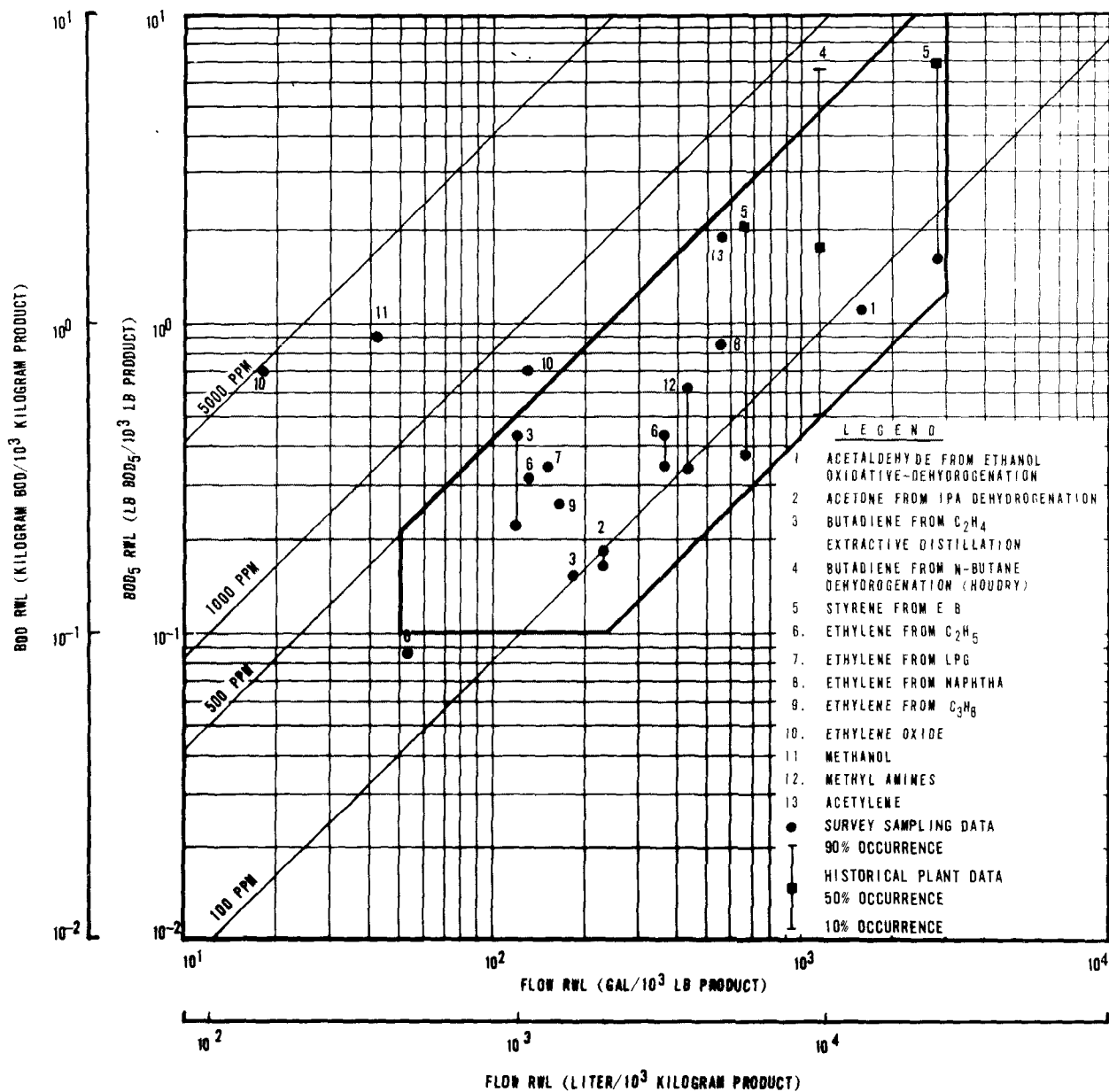
FLOW RWL (LITER 10³ KILOGRAM PRODUCT)

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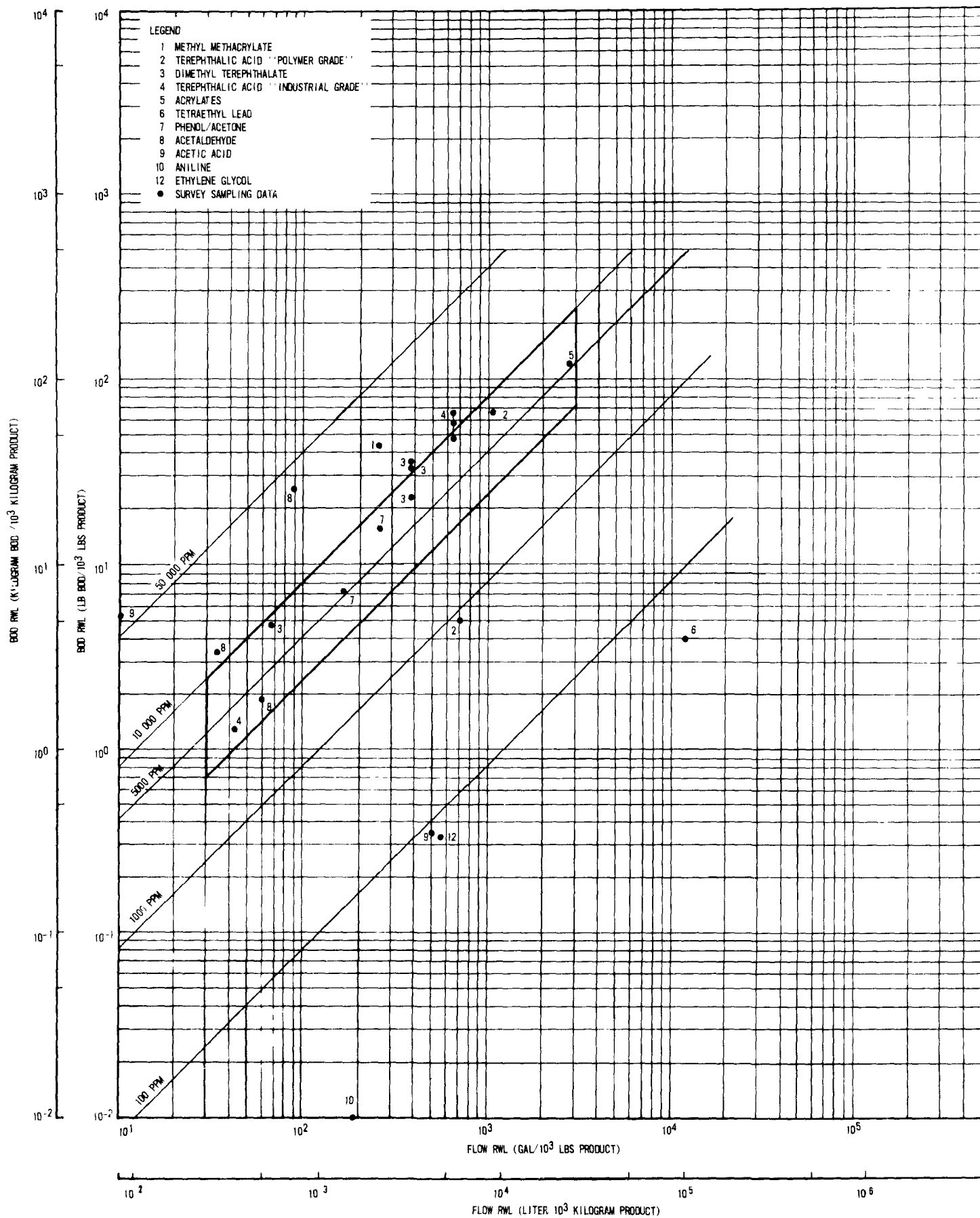
FIGURE V-8

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR CATEGORY C

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FIGURE V-9
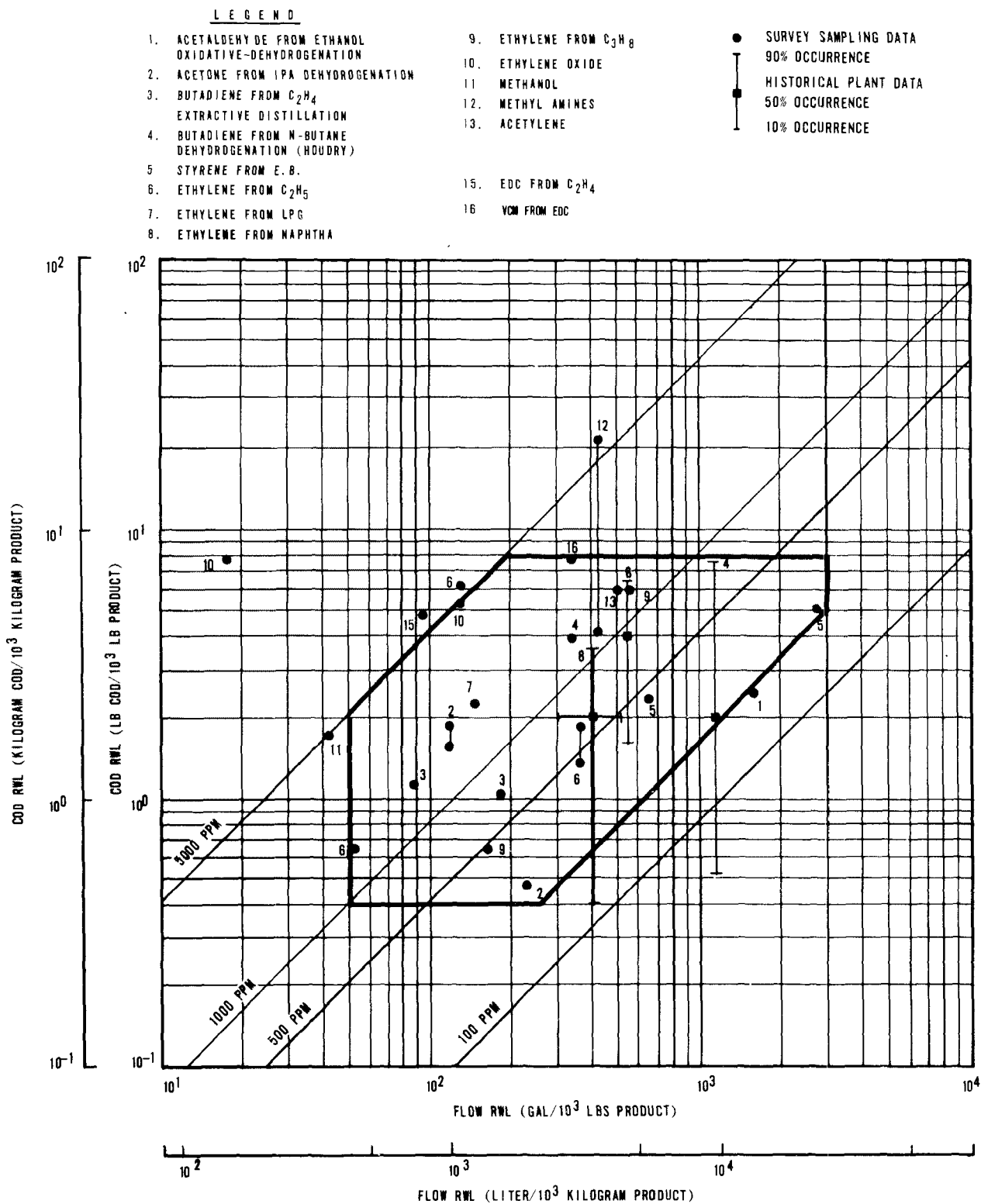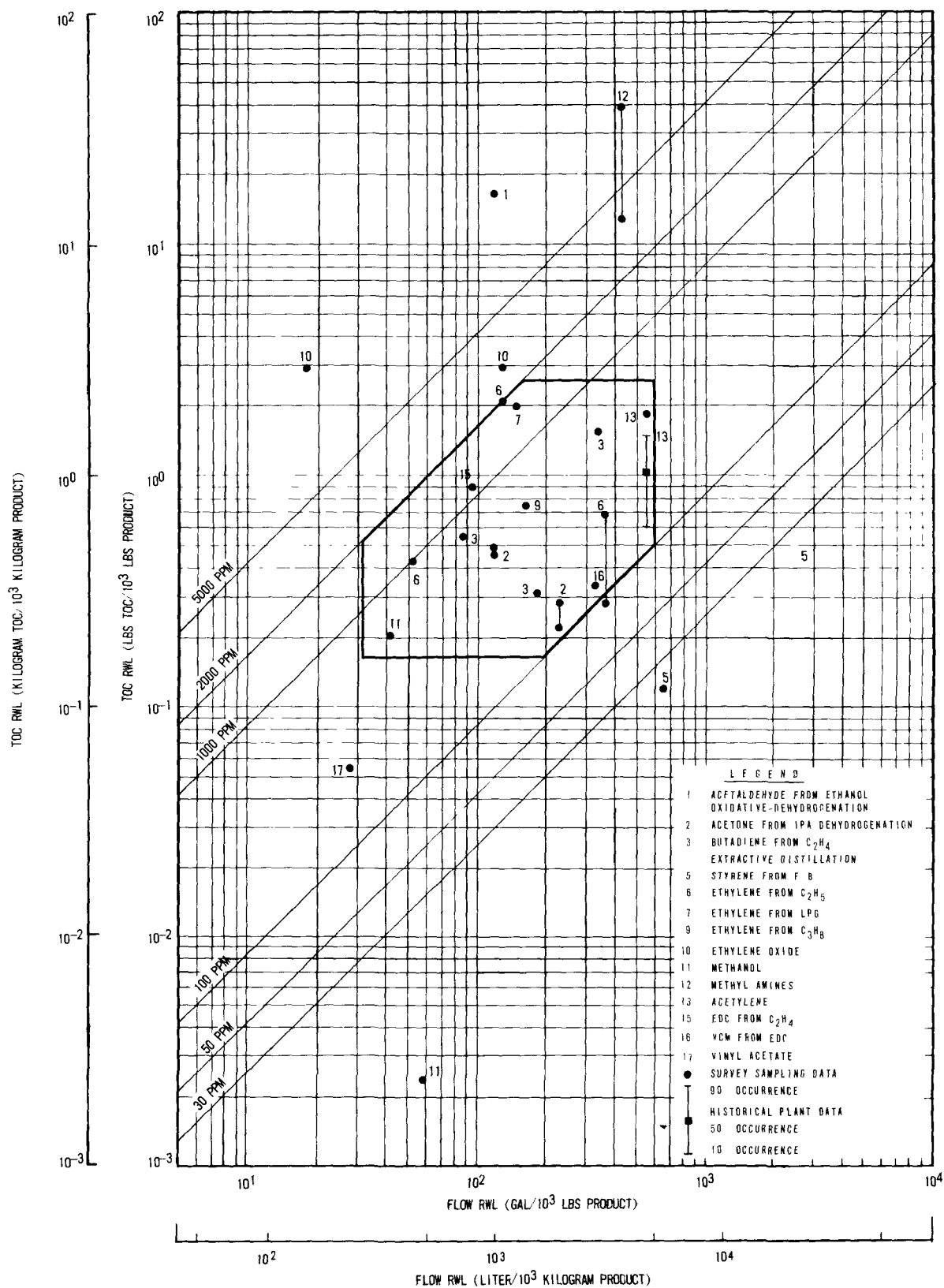## RELATIONSHIP BETWEEN TOC RWL AND FLOW RWL FOR CATEGORY C

LEGEND
1 METHYL METHACRYLATE
2 TEREPHTHALIC ACID "POLYMER GRADE"
3 DIMETHYL TEREPHTHALATE
4 TEREPHTHALIC ACID "INDUSTRIAL GRADE"
5 ACRYLATES
7 PHENOL/ACETONE
8 ACETALDEHYDE
10 ANILINE
11 BIS-PHENOL
12 ETHYLENE GLYCOL
14 OXO-CHEMICALS
15 ACRYLIC ACID
16 CAPROLATAM
17 PARA-CRESOL
● SURVEY SAMPLING DATA
90% OCCURRENCE
HISTORICAL PLANT DATA
50% OCCURRENCE
10% OCCURRENCE

TOC RWL (KILOGRAM TOC/10³ KILOGRAM PRODUCT)
TOC RWL (LB TOC/10³ LBS PRODUCT)
FLOW RWL (GAL/10³ LBS PRODUCT)
FLOW RWL (LITER/10³ KILOGRAM PRODUCT)

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, two subcategories designated as C1 and C2 have been established. The specific products, processes, and associated RWL assigned to each subcategory are indicated in Table V-3. As with Category B, 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 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.

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.

Table V-4

Category D - Batch and Semi Continuous Processes

Best Practicable Control Technology Currently Available

Raw Waste Data

$\underline{D_1}$ - Batch Organic   Azo Dyes

	Flow		BOD	COD	TOC
	liters/1000 kg	(gal/1000 lb)	kg/1000 kg or lb/1000 lb		
@50% occurrence	793,826	(95,069)	79	1,850	790
	114,395	(13,700)	220	1,075	450
	175,768	(21,050)	59	175	60
Average	361,329	(43,273)	119	1,033	433
Median	175,768	(21,050)	79	1,075	450

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FIGURE V-10

RELATIONSHIP BETWEEN BOD RWL AND FLOW RWL FOR CATEGORY D

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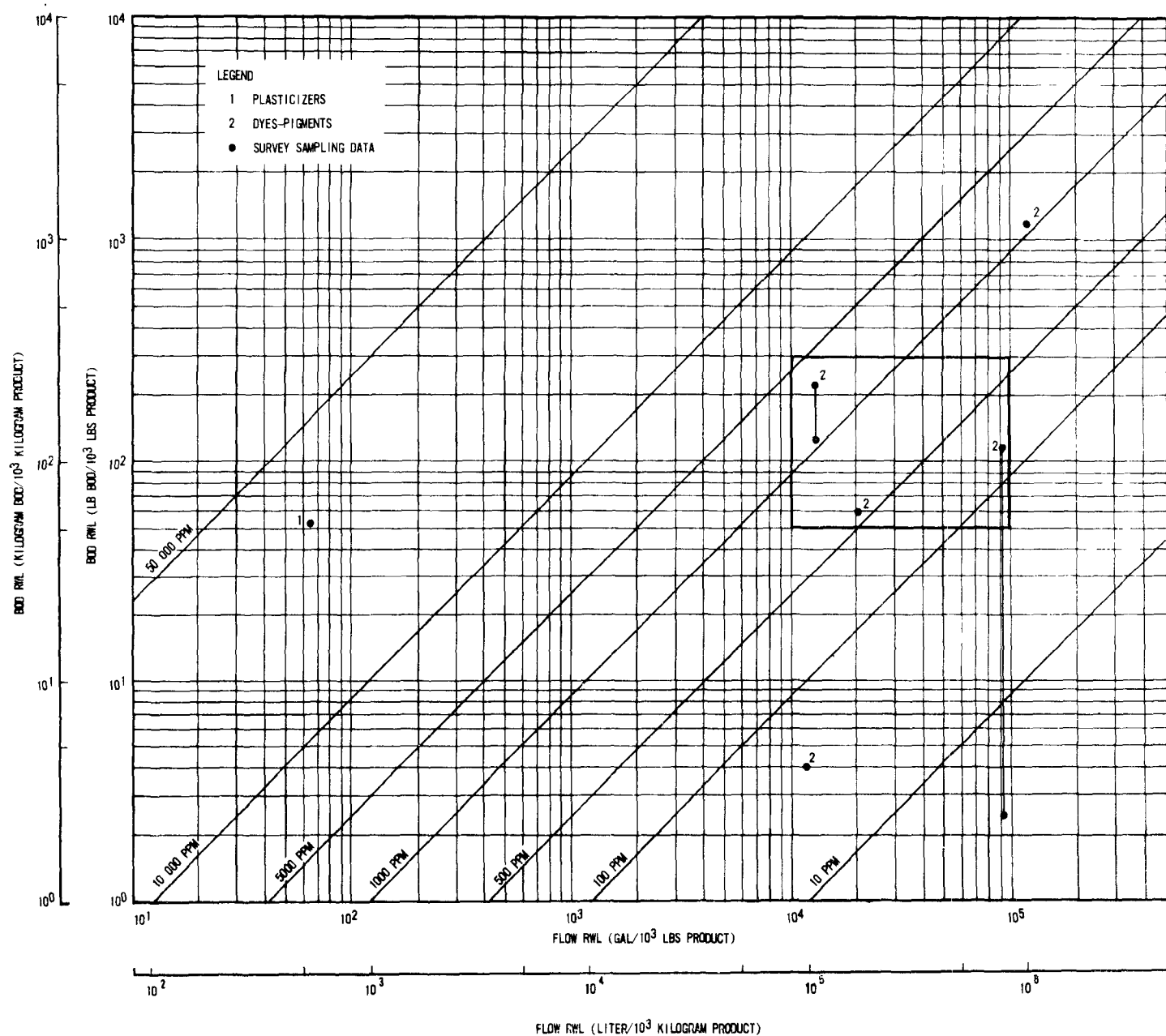
FIGURE V-11

RELATIONSHIP BETWEEN COD RWL AND FLOW RWL FOR CATEGORY D
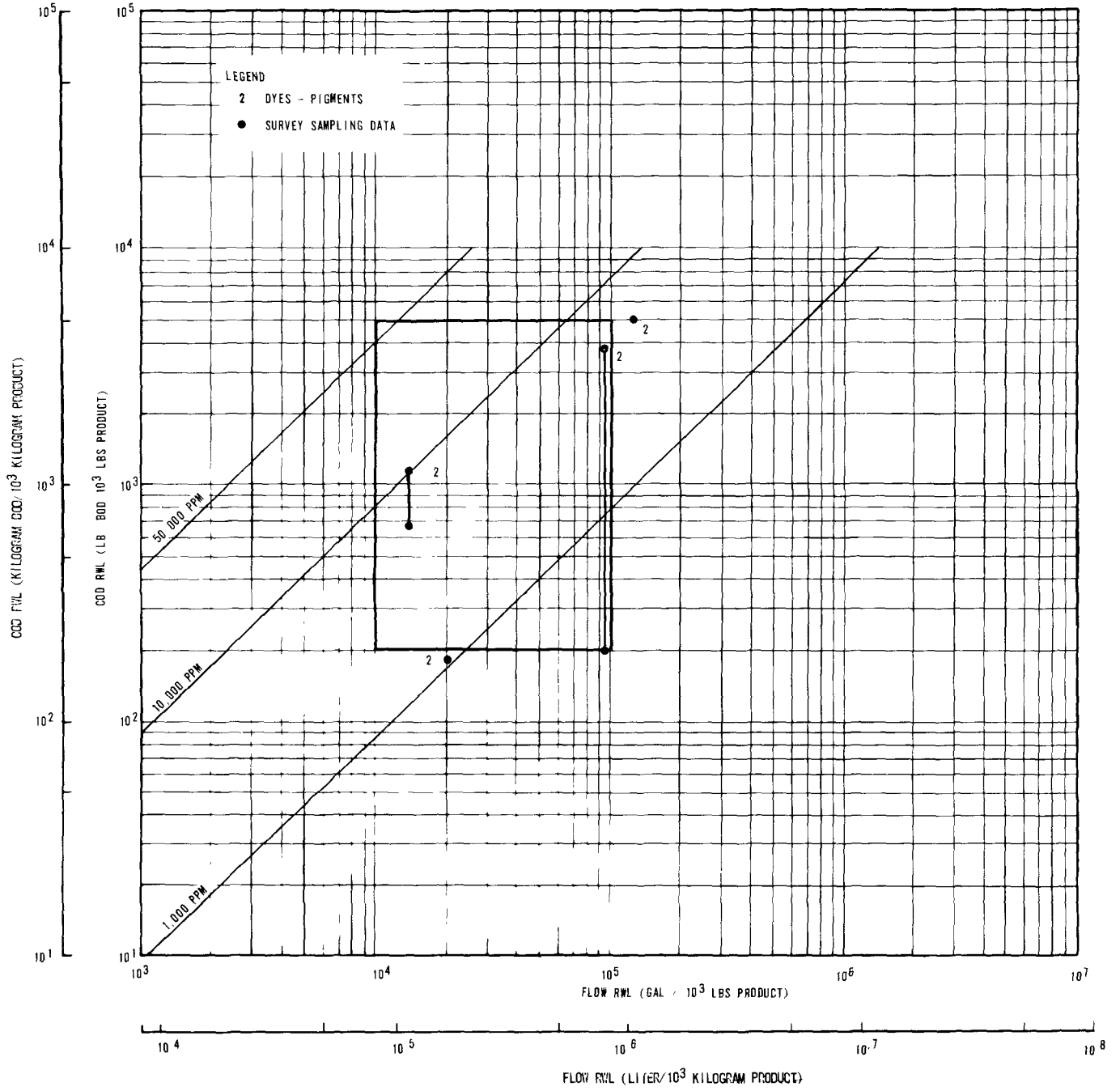
SECTION VI

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.

Based on the degree of impact on the overall environment, the pollutants are divided into subcategories as follows:

> Pollutants of Significance
> Pollutants of Minimal Significance

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 pollutional significance for which effluent limitations were developed in the organic chemicals industry are the major organic parameters of BOD5, COD and TOC.

BOD5

Biochemical oxygen demand (BOD5) refers to the amount of oxygen required to stabilize biodegradable organic matter under aerobic conditions. The BOD5 test has been used to gauge the pollutional strength of a waste water in terms of the oxygen it would demand if discharged into a watercourse. Historically, the BOD test has also been used to evaluate the performance of biological waste water treatment plants and to establish effluent limitation values. However, objections to the use of the BOD5 test have been raised.

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Table VI-1

List of Pollutants Surveyed for the Organic Chemicals Industry

Chemical Oxygen Demand (COD)	Total Dissolved (Filterable) Solids
Biochemical Oxygen Demand (BOD5)	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	

The major objections are as follows:

1. The standard BOD5 test takes five days before the results are available, thereby negating its use as a day-to-day treatment plant operational indicator.

2. At the start of the BOD5 test, seed culture (microorganisms) is added to the BOD5 bottle. If the seed culture was not acclimated, i.e., exposed to a similar waste water in the past, then it may not readily be able to biologically degrade the waste. This results in the reporting of a low BOD5 value. This situation is very likely to occur when dealing with complex industrial wastes, for which acclimation is required in most cases. The necessity of using "acclimated bacteria" makes it very time-consuming for regulatory agencies to duplicate industrial BOD5 values unless great care is taken in seed preparation.

3. The BOD5 test is sensitive to toxic materials, as are all biological processes. Therefore, if toxic materials are present in a particular waste water, the reported BOD5 value may very well be erroneous. This situation can be remedied by running a toxicity test, i.e., subsequently diluting the sample until the BOD value reaches a plateau indicating that the material is at a concentration which no longer inhibits biological oxidation.

There has been much controversy concerning the use of BOD5 a measure of pollution, and there have been recommendations to substitute some other parameter, e.g., COD or TOC. EPA has recently pointed out that some or all of the previously cited reasons make the BOD5 test a non-standard test, and ASTM's Subcommittee D-19 has also recommended withdrawal of the BOD test as a standard test.

However, some of the previously cited weaknesses of the BOD test also make it uniquely applicable. It is the only parameter now available which measures the amount of oxygen used by selected microorganisms in metabolizing a waste water. The use of COD or TOC to monitor the efficiency of BOD5 removal in biological treatment is possible only if there is a good correlation between COD or TOC and BOD5. During the field data analysis, varying ratios within each subcategory and between subcategories were evident. This is particularly true of subcategory D batch chemical production. After consideration of the advantages, disadvantages and constraints, it is felt that BOD5 should continue to be used as a pollutional indicator for the organic chemicals industry.

The BOD5 data acquired during the sampling program for Subcategories, A, B, C, and D are presented in Figures V-1, V-4, V-7, and V-10, which indicate the relationship between BOD RWL and flow RWL for each

previously described subcategory. Typical RWL concentration ranges for each subcategory are presented below:

Subcategory	BOD5 RWL Range mg/l
A	500-1,000
B	100-500
C	3,000-10,000
D	100-3,000

As a matter of reference, typical BOD5 values for minicipal waste waters range between 100 and 300 mg/l.

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.

&%Standards Methods for the Examination of Water and Wastewater, the principal reference for anlaytical work in this field, cautions that aromatic compounds and straight-chain alphatic 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:

Subcategory	COD RWL Range 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.

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 a 150C. 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 vaproize 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:

Subcategory	TOC RWL Range 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 and phenols in all subcategories since these are generally present in all subcategories. Other pollutant parameters which are discussed in this section but no effluent limitations established are

not present in all subcategories, and are generally controled at the source. These may, however, present environmental problems where water quality standards dictate and may ultimately be limited.

TSS

Total Suspended (nonfilterable) Solids in the form of RWL are plotted on Figures VI-1 and VI-2 for Subcategories B and C respectively. In general, most of the data points are below 50 mg/l. There are, however, particular processes and certain plants which ahve very high suspended solids loadings, on the order of 500 mg/l. In some cases (e.g., terephthalic and production), dry housekeeping with minimal use of washdown water would drastically reduce the discharge of Total Suspended (nonfilterable) Solids.

Total Suspended (nonfilterable) Solids concentrations for typical municipal waste waters range from 100 to 300 mg/l.

Oil and Grease

Oil (extractables) is a measure of the insoluble hydrocarbons and the free-floating and emulsified oil in a particular waste water sample. One particular problem of importance is the obtaining of a representative waste water sample when free-floating oil is present. Representative samples may generally be obtained if there is a freefall in a sewer line, e.g., a drop manhole. Sample collection from a sump where there is an oil accumulation attributable to the sump's inherent detention time should be avoided.

Oil and grease RWL's for Subcategories B and C are presented in Figure VI-3, and tabulated in Tables VI-2 and VI-3. Most of the oil extractables are within the range of 5 to 50 mg/l (by carbon tetrachloride solvent). Specific processes involving high oil concentrations are acetaldehyde, acetic acid, phenol via cumene, oxo-chemicals, and ethylene. Only the ethylene production wastes have free-floating and emulsified oils. The oil and grease data for the remaining processes merely reflect the amount of insoluble (in water) hydrocarbons which are soluble in the solvent. Based on the previous qualifications, no effluent limitation values were established for the discharge of oil and grease from the organic chemicals industry.

Nitrogen

Ammonia nitrogen (NH3-N) and total Kjeldahl nitrogen (TKN-N) are two parameters which have received a substantial amount of interest in the last decade. TKN-N is the sum of the NH3-N and organic nitrogen present in the sample. Both NH3 and TKN are expressed in terms of equivalent nitrogen values in mg/l, to facilitate mathematical manipulations of the values.

Organic nitrogen may be converted in the environment to ammonia by saprophytic bacteria under either aerobic or anerobic conditions. The ammonia nitrogen then becomes the nitrogen and energy source for autotrophic organisms (nitrifiers). The oxidation of ammonia to nitrite and then nitrate has a stoichiometric oxygen requirement of approximately 4.6 times the concentration of NH3-N. The nitrification reaction is much slower than the carbonaceous reaction, and, therefore, the dissolved oxygen utilization is generally observed over a much longer period.

Ammonia and TKN RWL data for Subcategories B and C are presented in Figures VI-4 and VI-5 and tabulated in Tables VI-2 and VI-3. Most of the NH3 and TKN data points are below 10 mg/l. This is low compared to the concentrations typical of municipal waste waters, 15 to 30 mg/l. However, Tables VI-2 and VI-3 show that some processes (caprolactam, aniline, butadiene) have extremely high nitrogen values.

Phenols

Phenols in waste water present two major problems; (1) at high concentrations phenols act as bactericides; and (2) at very low concentrations, when disinfected with chlorine, chlorophenols are formed, producing taste and odor. Past experiences has indicated that biological treatment systems may be acclimated to phenol concentrations of 300 mg/l or more. However, protection of the biological treatment system against slug loads of phenol must be given careful consideration in the design. Slug loadings, depending on concentration, could be inhibitary to the biological population.

The phenol RWL data are presented in Figure VI-6 and tabulated in Tables VI-2 and VI-3. The concentrations are generally below 1 mg/l. Specific processes (Bisphenol and phenol via cumene) have concentrations in the 5,000-10,000 mg/l range. In both these processes, phenol is amenable to in-plant recovery and therefore would probably not be discharged in their waste water.

Total Dissolved (Filterable) Solids

Dissolved solids in organic chemicals waste waters consist mainly of carbonates, bicarbonates, chlorides, sulfates, and phosphates. Sulfate RWL data for subcategories B and C are presented in Figure VI-7 and tabulated in Tables VI-2 and VI-3. It is interesting to note that most of the data above 300 mg/l are from Subcategory C, while most of the data below 10 mg/l are from Subcategory B. This is an interesting commentary on the process differences between Subcategories B and C, and is applicable also to dissolved solids concentration. The extensive amount of process water recycle and reuse is primarily responsible for these high concentrations.

The high dissolved solids and sulfate concentrations in Subcategory D (unlike the other subcategories) are the direct result of inorganic chemical additions due to intimate contact with the batch production chemicals. Chemicals compounds introduced in the other subcategories are organic in nature and do not contribute to the overall magnitude of dissolved solids.

Because dissolved solids and sulfate concentrations are intimately tied to process recycle and the quality of the process raw water source, it is recommended that these parameters be dictated by local water quality requirements.

Cyanide, Total

Cyanide was analyzed using the distillation procedure in Standard Methods and the Orion specific ion probe. The cyanide values are reported in terms of CN-ion. The cyanide ion is in equilibrium with hydrogen cyanide as follows:

$$[H^+] \quad + \quad [CN^-] \quad [HCN]$$

At a pH of 8 or less, the HCN is largely undissociated; then as the pH increases, the equilibrium shifts toward CN-.

CN RWL data for Subcategories B and C are presented in Figure VI-8. Much of the data is below 0.1 mg/l, and practically all the data points are below 1.0 mg/l. At these concentrations, the values are such that specific limitations are not required.

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

Table VI-2

Miscellaneous RWL Loads For Category B

Product	Flow gal/1000 lb	Phenol mg/L	Phenol lb/1000 lb	NH$_3$-N mg/L	NH$_3$-N lb/1000 lb	TKN mg/L	TKN lb/1000 lb	CN mg/L	CN lb/1000 lb	Sulfate mg/L	Sulfate lb/1000 lb	Oil mg/L	Oil lb/1000 lb
Acetone via IPA	120	0.1815	1.815×10^{-4}	11.2	1.12×10^{-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	1.63×10^{-3}	149	2.158	20.4	0.2965
Butadiene via C$_2$H$_4$	183	0.01	1.6×10^{-5}	0.97	1.47×10^{-3}	2.6	4.02×10^{-3}	0.19	3.0×10^{-4}	15.8	0.024	8.6	0.013
	88	0.024	1.8×10^{-5}	43.2	0.0317	235	0.172	<0.04	<3.0×10^{-5}	190	0.0142	7.4	0.0053
	339	0.02	6.3×10^{-5}	5907	16.6	12,200	34.4	<0.04	1.2×10^{-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	2.0×10^{-5}	0.5	7.0×10^{-5}	2.9	3.7×10^{-4}	0.046	1.0×10^{-5}	503	0.065	74	9.5×10^{-3}
	336	0.006	1.7×10^{-5}	1.7	4.62×10^{-3}	4.6	0.0127	0.12	3.3×10^{-4}	78	0.218	26	0.0712
Ethylene/Propylene via Pyrolysis	130	6.78	7.33×10^{-3}	6.44	6.96×10^{-3}	65.5	0.071	0.11	1.2×10^{-4}	649	0.7013	483	0.522
	364	0.36	1.08×10^{-3}	19.6	0.058	25.2	0.075	0.12	3.6×10^{-4}	120	0.36	11.7	0.035
	52.5	2.36	1.03×10^{-3}	<0.5	2.2×10^{-4}	<0.5	2.2×10^{-4}	<0.04	2.0×10^{-5}	73.6	0.032	172	0.075
	150	5.59	0.007	3.9	4.9×10^{-3}	9.7	0.012	0.043	5.0×10^{-4}	280	0.353	11	0.014
	554	8.25	0.038	2.2	1.02×10^{-2}	9.0	0.041	0.055	2.6×10^{-4}	0.98	4.5×10^{-3}	188	0.87
	167	7.24	0.01	1.4	1.94×10^{-3}	2.6	3.6×10^{-3}	-	-	1.5	2.13×10^{-3}	10.1	0.014
Ethylene Oxide	131	0.048	5.3×10^{-5}	0.5	5.5×10^{-4}	2.8	3.08×10^{-3}	0.44	4.8×10^{-4}	510	0.56	3.3	3.3×10^{-3}
	17.8	0.154	2.3×10^{-5}	5.6	3.7×10^{-4}	14	2.1×10^{-3}	<0.04	<6.0×10^{-6}	5,400	0.81	1.8	3.2×10^{-4}
Methyl Amines	429	0.031	1.12×10^{-4}	7.9	2.82×10^{-2}	26.3	0.0941	<0.04	<1.42×10^{-4}	<1		4.6	0.0163
Acetylene	560	0.76	3.55×10^{-3}	5.6	0.0262	84	0.3927	0.312	1.46×10^{-3}	280	1.309	1.4	6.55×10^{-3}

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Table VI-2
(continued)

Product	T-P mg/L	T-P lb/1000 lb	Zn mg/L	Zn lb/1000 lb	Cu mg/L	Cu lb/1000 lb	Fe mg/L	Fe lb/1000 lb	Cr mg/L	Cr lb/1000 lb	Cd mg/L	Cd lb/1000 lb
Acetone via IPA	—	—	—	—	—	—	—	—	—	—	—	—
Butadiene via C_4	1.93	0.02795	0.37	5.34×10^{-3}	0.273	3.97×10^{-3}	45.1	0.655	<0.05	$<7.26 \times 10^{-6}$	<0.05	$<7.46 \times 10^{-4}$
Butadiene via C_2H_4	31.5	0.048	0.12	1.8×10^{-4}	0.17	2.6×10^{-4}	5.6	8.5×10^{-3}	<0.05	$<7.6 \times 10^{-5}$	<0.05	$<7.6 \times 10^{-5}$
	0.77	5.6×10^{-4}	—	—	0.17	1.28×10^{-4}	0.65	4.8×10^{-4}	<0.05	$<4.0 \times 10^{-4}$	<0.05	$<4.0 \times 10^{-5}$
	3.50	0.0098	—	—	0.36	0.001	0.5	1.52×10^{-3}	<0.05	$<1.5 \times 10^{-4}$	<0.05	$<1.5 \times 10^{-5}$
Styrene via E.B.	0.66	0.0036	0.14	7.67×10^{-4}	0.21	1.15×10^{-3}	0.5	2.74×10^{-3}	<0.05	$<2.74 \times 10^{-5}$	<0.05	$<2.74 \times 10^{-5}$
EDC via Direct Chlorination	0.544	7.0×10^{-5}	0.62	8.0×10^{-5}	0.24	3.0×10^{-5}	1.06	1.4×10^{-4}	<0.05	$<1.0 \times 10^{-5}$	<0.05	$<1.0 \times 10^{-5}$
	0.09	2.5×10^{-4}	—	—	0.14	3.77×10^{-4}	3.4	9.42×10^{-3}	<0.04	$<1.04 \times 10^{-4}$	<0.05	$<1.49 \times 10^{-4}$
Ethylene/Propylene via Pyrolysis	1.30	1.41×10^{-3}	<0.05	$<5.6 \times 10^{-5}$	0.14	1.48×10^{-4}	1.22	1.32×10^{-3}	0.05	5.44×10^{-5}	<0.05	$<5.56 \times 10^{-5}$
	5.5	0.017	3.2	0.001	0.15	4.5×10^{-5}	3.8	0.011	4.35	0.013	<0.05	$<1.5 \times 10^{-5}$
	1,469	0.64	0.671	2.9×10^{-4}	0.08	3.0×10^{-5}	1.17	5.1×10^{-4}	1.86	8.2×10^{-4}	0.021	1.07×10^{-5}
	0.61	7.6×10^{-4}	0.37	4.6×10^{-4}	0.19	2.4×10^{-4}	0.83	0.001	<0.05	$<6.0 \times 10^{-5}$	0.143	1.8×10^{-4}
	0.196	9.1×10^{-4}	0.153	7.1×10^{-4}	0.1	4.6×10^{-4}	0.64	2.95×10^{-3}	0.197	9.1×10^{-4}	0.051	2.4×10^{-4}
	494	0.686	0.29	4.1×10^{-4}	0.76	1.05×10^{-3}	0.62	8.5×10^{-4}	<0.06	$<7.7 \times 10^{-5}$	<0.06	7.7×10^{-5}
Ethylene Oxide	0.144	1.6×10^{-4}	0.33	3.6×10^{-4}	1.25	1.38×10^{-3}	1.5	1.65×10^{-3}	<0.05	$<6.0 \times 10^{-4}$	<0.05	$<6.0 \times 10^{-4}$
	1.2	1.8×10^{-4}	0.14	2.1×10^{-5}	0.41	6.0×10^{-5}	1.33	2.0×10^{-4}	0.07	1.1×10^{-5}	<0.05	$<8.0 \times 10^{-6}$
Methyl Amines	0.066	2.37×10^{-4}	—	—	0.25	9.0×10^{-4}	3.38	0.0121	—	—	—	—
Acetylene	0.25	1.17×10^{-3}	0.2	9.35×10^{-4}	<0.05	$<2.3 \times 10^{-4}$	0.4	1.87×10^{-3}	<0.05	$<2.34 \times 10^{-4}$	<0.05	$<2.34 \times 10^{-4}$

Table VI-3

Miscellaneous RWL Loads For Category C

Product	Flow gal/1000 lb	Phenol mg/L	Phenol lb/1000 lb	NH3-N mg/L	NH3-N lb/1000 lb	TKN-N mg/L	TKN-N lb/1000 lb	CN mg/L	CN lb/1000 lb	Sulfate mg/L	Sulfate lb/1000 lb	Oil mg/L	Oil 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	0.012	4.2	0.038	0.80	7.4×10^{-3}	260	2.4	29.4	0.011
	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	-	-
	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)

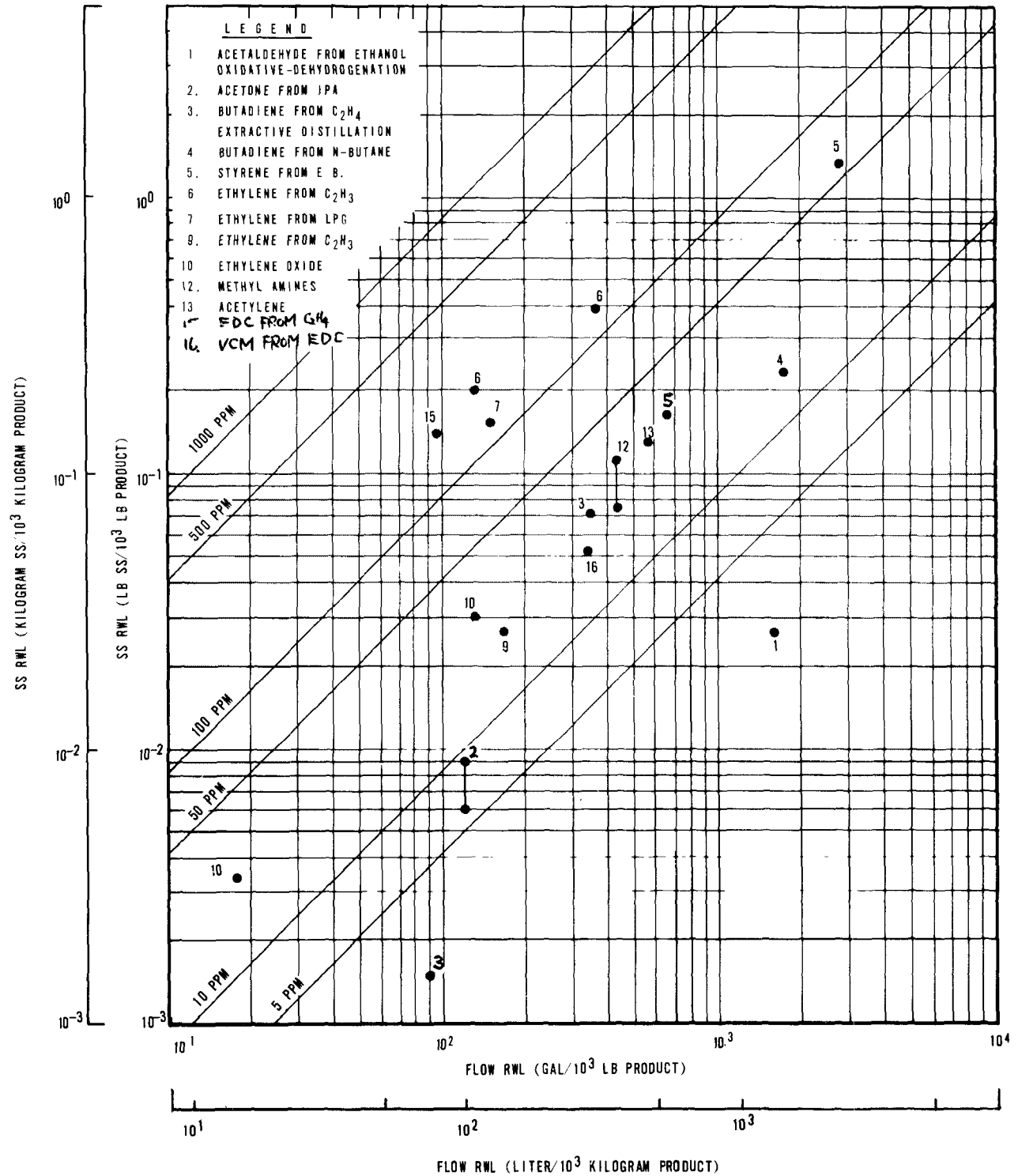| Product	T-P mg/L	T-P lb/1000 lb	Zn mg/L	Zn lb/1000 lb	Cu mg/L	Cu lb/1000 lb	Fe mg/L	Fe lb/1000 lb	Cr mg/L	Cr lb/1000 lb	Cd mg/L	Cd lb/1000 lb
Acetaldehyde	2.58	1.94×10^{-3}	0.36	2.7×10^{-4}	16	0.0124	2.3	1.73×10^{-3}	2.7	1.99×10^{-5}	< 0.05	$< 3.7 \times 10^{-5}$
	17.4	8.9×10^{-3}	0.05	3.0×10^{-5}	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^{-4}	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	-	-	-	-

FIGURE VI-1

RELATIONSHIP BETWEEN SS RWL AND FLOW RWL FOR CATEGORY B

FIGURE VI-2

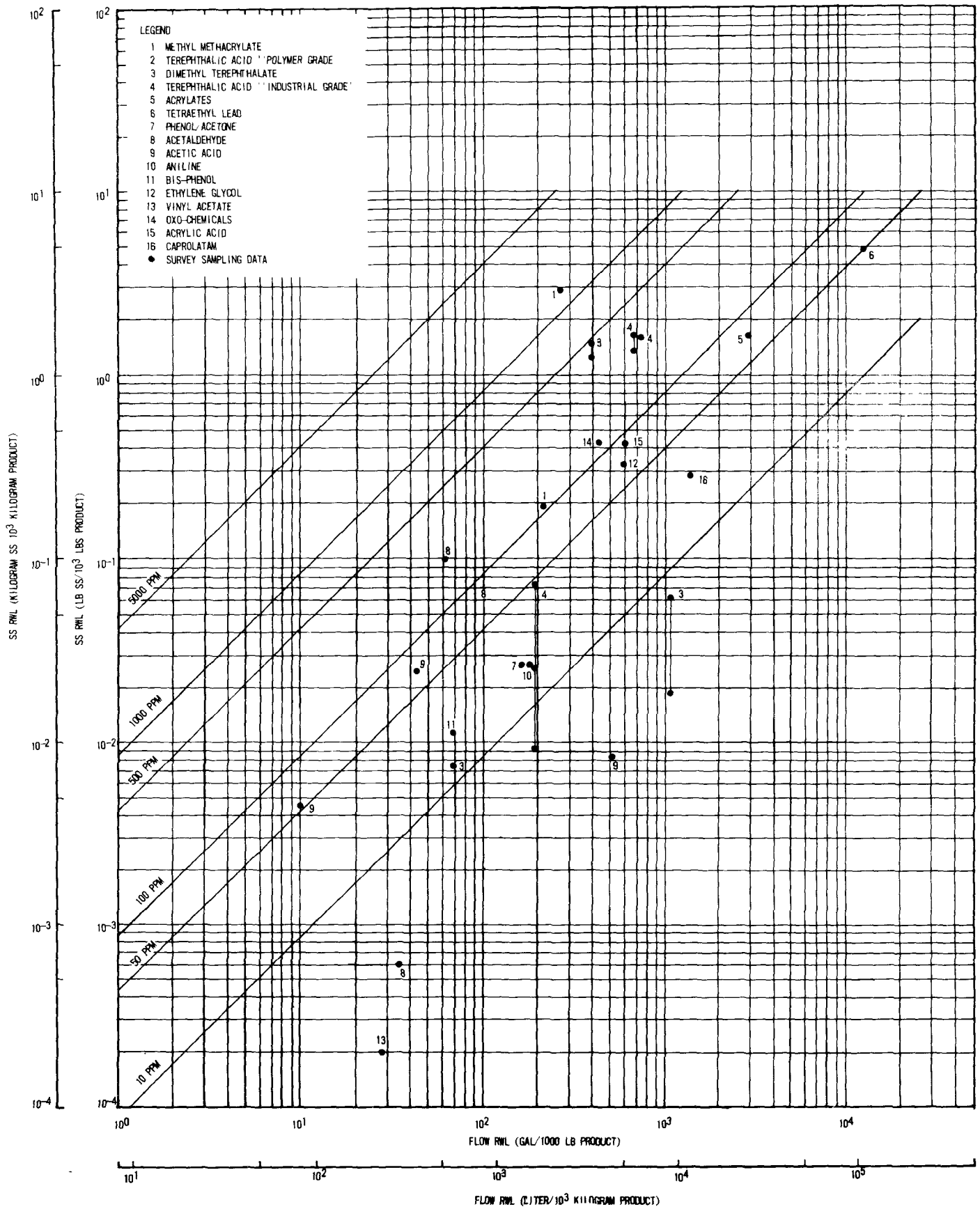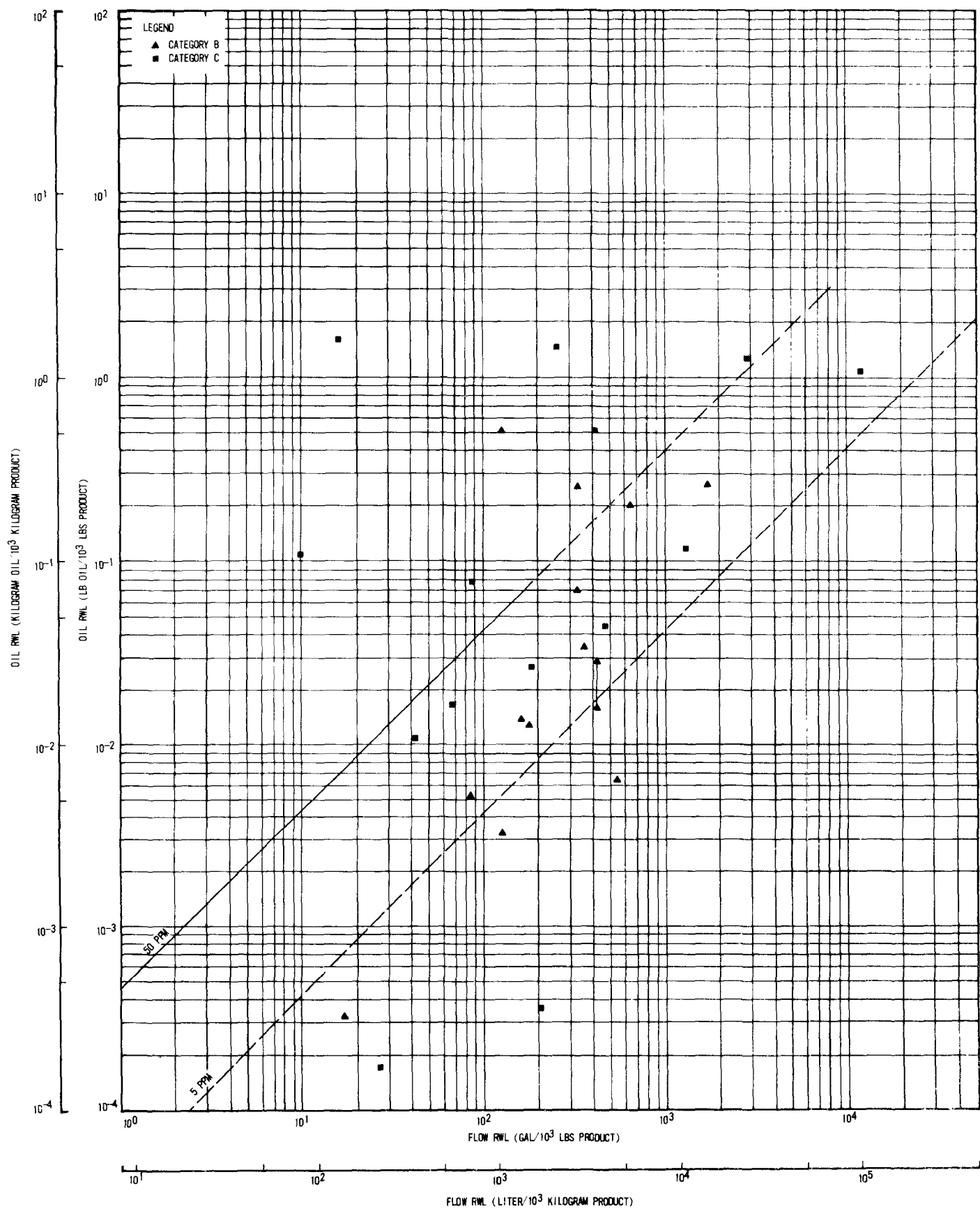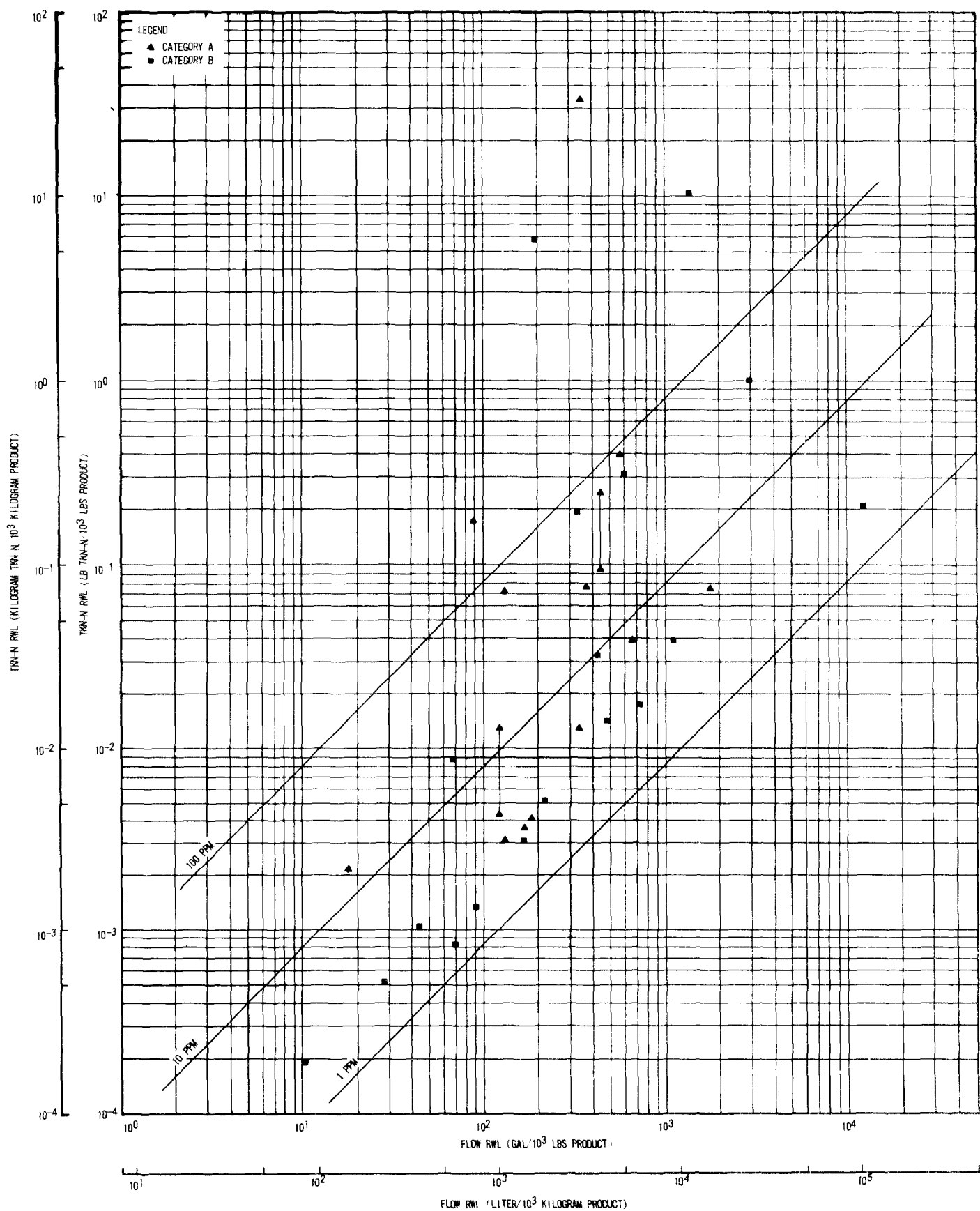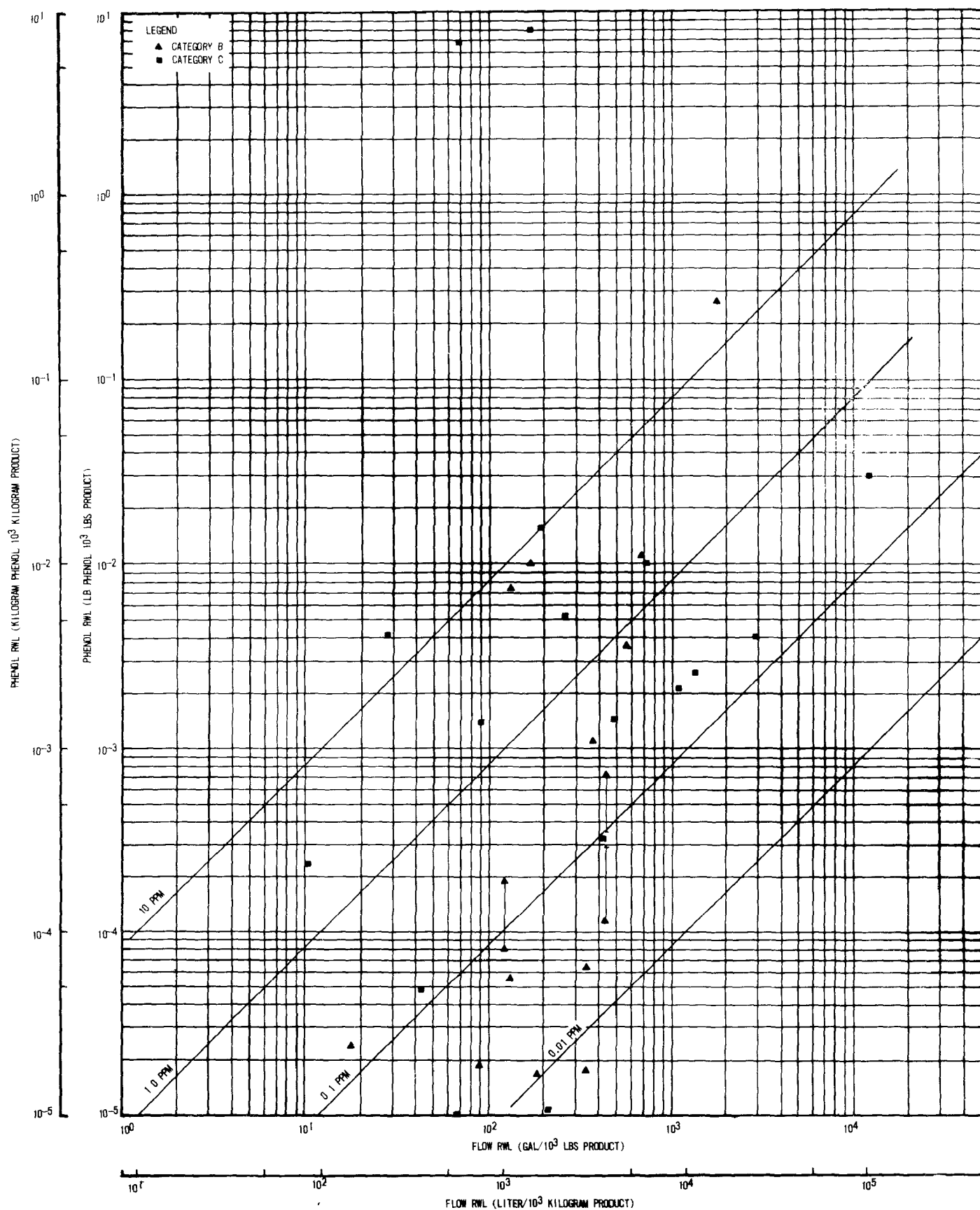RELATIONSHIP BETWEEN SS RWL AND FLOW RWL FOR CATEGORY C

LEGEND

1 METHYL METHACRYLATE
2 TEREPHTHALIC ACID "POLYMER GRADE
3 DIMETHYL TEREPHTHALATE
4 TEREPHTHALIC ACID "INDUSTRIAL GRADE"
5 ACRYLATES
6 TETRAETHYL LEAD
7 PHENOL/ACETONE
8 ACETALDEHYDE
9 ACETIC ACID
10 ANILINE
11 BIS-PHENOL
12 ETHYLENE GLYCOL
13 VINYL ACETATE
14 OXO-CHEMICALS
15 ACRYLIC ACID
16 CAPROLATAM
● SURVEY SAMPLING DATA

SS RWL (KILOGRAM SS 10³ KILOGRAM PRODUCT)

SS RWL (LB SS/10³ LBS PRODUCT)

FLOW RWL (GAL/1000 LB PRODUCT)

FLOW RWL (LITER/10³ KILOGRAM PRODUCT)

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FIGURE VI-3

RELATIONSHIP BETWEEN OIL RWL AND FLOW RWL FOR CATEGORIES B AND C

FIGURE VI-4
RELATIONSHIP BETWEEN NH₃-N RWL AND FLOW RWL FOR CATEGORIES B AND C

283
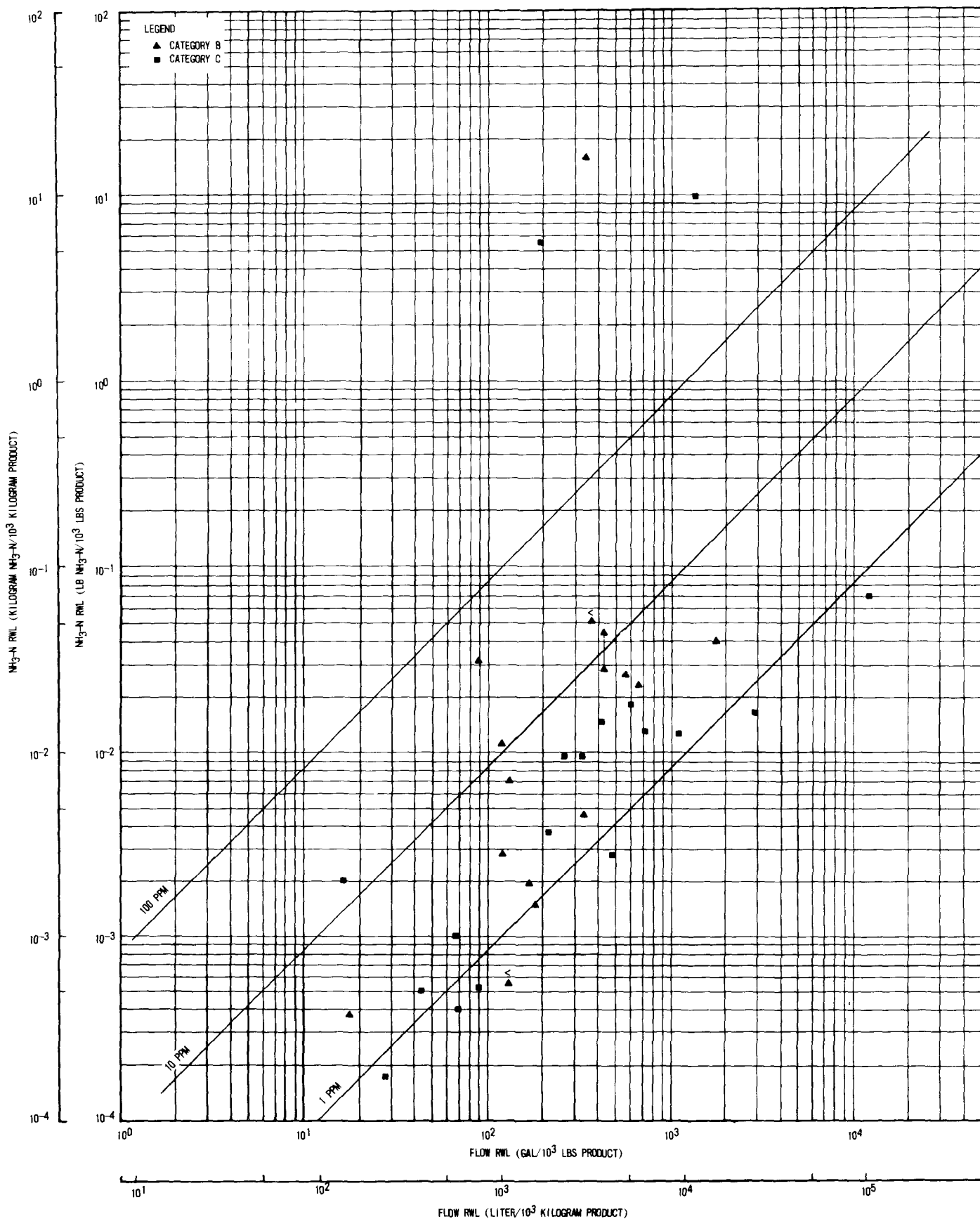
FIGURE VI-5
RELATIONSHIP BETWEEN TKN-N RWL AND FLOW RWL FOR CATEGORIES B AND C

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FIGURE VI-6
RELATIONSHIP BETWEEN PHENOL RWL AND FLOW FOR CATEGORIES B AND C

FIGURE VI-7
RELATIONSHIP BETWEEN SULFATE RWL AND FLOW RWL FOR CATEGORIES B AND C
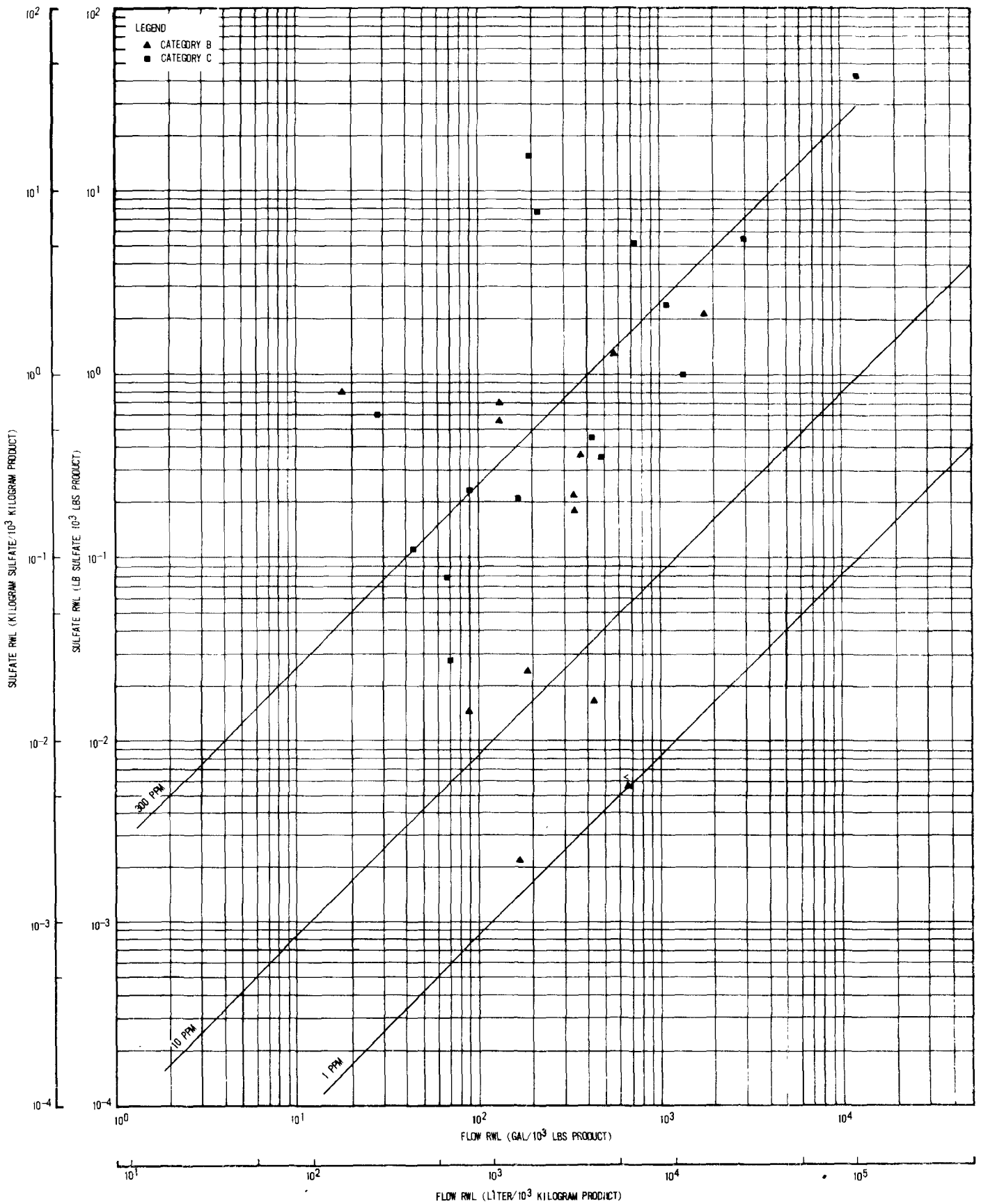
FIGURE VI-8

RELATIONSHIP BETWEEN CN RWL AND FLOW RWL FOR CATEGORIES B AND C
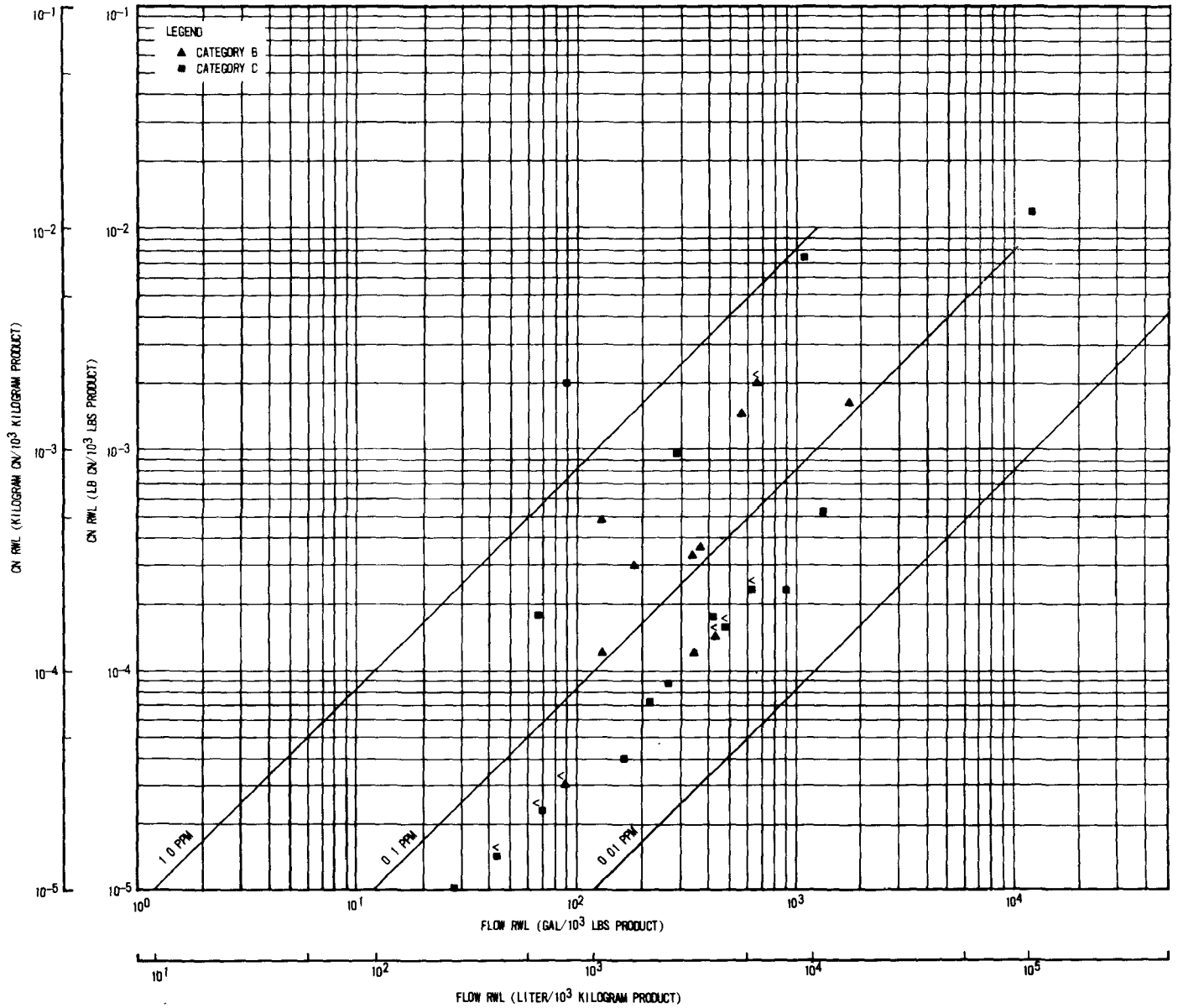
technological questions concerning levels of color removal
for various types of dyes and pigments. This situation can be
be remedied during Phase II of our study by a concentrated
study of the color removal of various waste water unit
processes. However, there is recent evidence that carbon
filters can be a satisfactory treatment agent for many
color problems.

Pollutants of Minimal Significance

The remaining parameters which were examined were calcium, magnesium
total hardness, chlorides, total phosphorus, pH, alkalinity, acidity,
and various heavy metals. These pollutants are generally not considered
significant in comparison to the oxygen demand pollutant parameters.
Effluent limitations for the pH are specified for all discharges within
the range of 6.0 to 9.0. Heavy metals concentrations are not limited
since most processes recover metals catalysts as an in-process control.
This does not preclude the possibility of such limitation being required
for specific processes or situations where such in-process controls are
not applied or properly functioning. Hardness is an indication of the
soap-neutralizing power of water. Any substance which will form an
insolubel curd with soap causes hardness. Waters are commonly
classified in terms of the degree of hardness as follows:

Concentration mg/l as CaCO3	Terminology
0-75	Soft
75-150	Moderately Hard
150-300	Hard
300 and up	Very Hard

The major detrimental effects of hardness include excessive soap
consumption, problems when used for particular process waters (e.g., in
the textile industry), and the formation of scale in boilers and water
heaters.

Many of the specific comments made previously regarding dissolved solids
are directly applicable to these parameters of minimal significance.
Concentrations of calcium, magnesium, chorides and hardness are
generally higher for Subcategory C because of extensive recycling. In
addition, particular processes in Subcategory C product 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 occurs in organic chemical waste waters as orthophosphate
(H_2PO_4, - $HP_4^=$, $PO_4^=$,) or as polyphosphate. All polyphosphates gradually
hydrolyze in an aqueous solution and revert to the ortho from.

Phosphorus concentrations in the organic chemicals industry are relatively low (less than 10 mg/l) and reflect the quality of the intake water and the amount of recycle employed with the process. Phosphates and polyphosphates are used for corrosion control and boiler water conditioning.

Specific processes utilize phosphoric acid as a catalyst (by impregnating silica alumina media) for polymerization, alkylation, and isomerization processes. The spent acid catalyst may be found in process effluents if it is not segregated for separate disposal. In these cases, total phosphorus values over 500 mg/l have been observed.

The acidity of a waste is a measure of the quantity of compounds contained there in which will dissociate in an aqueous solution to produce hydrogen ions. Acidity in organic chemicals wastewaters can be contributed by both organic and inorganic compound dissociation. Most mineral acids found in waste waters (sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid) are typically strong acids. The most common weaker acids found include the organic acids such carboxylic and carbonic.

Compounds which contribute to alkalinity in waste waters are those which dissociate in aqueous solutions to produce hydroxyl ions. Alkalinity is often defined as the acid-consuming ability of the waste water and is measured by titrating a given volume of waste with standard acid until all of the alkaline material has reacted to form salts. In effect, alkalinity is the exact opposite of acidity.

Both inorganic and organic compounds can contribute to alkalinity, but the most important alkaline wastes in the organic chemicals industry are the spent caustics, which contain sodium, calcium, and potassium salts of weak organic acids, and carbonates. These compounds tend to raise the pH to values over 10.

The hydrogen ion concentration in a aqueous solution is represented by the pH of that solution. The pH is defined as the negative logarithm of the hydorgen ion concentration in a solution in gram equivalents per liter. The pH scale ranges from below zero to fourteen, with a pH of seven representing neutral conditions i.e., equal concentrations of hydrogen and hydroxyl ions. Values of pH less than seven indicate increasing hydrogen ion concentration or acidity; pH values greater than seven indicate increasing alkaline conditions. The pH value is an effective parameter for predicting chemical and biological properties of aqueous solutions. It should be emphasized that pH cannot be used to predict the quantities of alkaline or acidic materials in a water sample. However, most effluent and stream standards are based on maximum and mimimum allowable pH values rather than on alkalinity and acidity. Typical pH values recommended for stream standards are 6.5 to 8.5.

Since pH RWL values are not additive, it is not always possible to predict the final pH of a process waste water made up of multiple dischargers. In addition the individual plant's production mix will dictate final pH ranges, which may be kept within the acceptable range merely by equalization, or which may require more sophisticated neutralization facilities.

Minimal concentrations of heavy metals were observed in most of the RWL data. Particular processes in Subcategory C (e.g. terephthalic acid) had higher concentrations of cobalt due to the loss of the catalyst.

Particular waste waters from Subcategory D (e.g. metallic dye production) had very high concentrations of Cu, 10 mg/l. The presence of heavy metals is contingent on batch metallic dye production, which may occur one day per week or five days/week depending on the demand in the market place.

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 avilable, 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 rpocesses 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 infinate 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
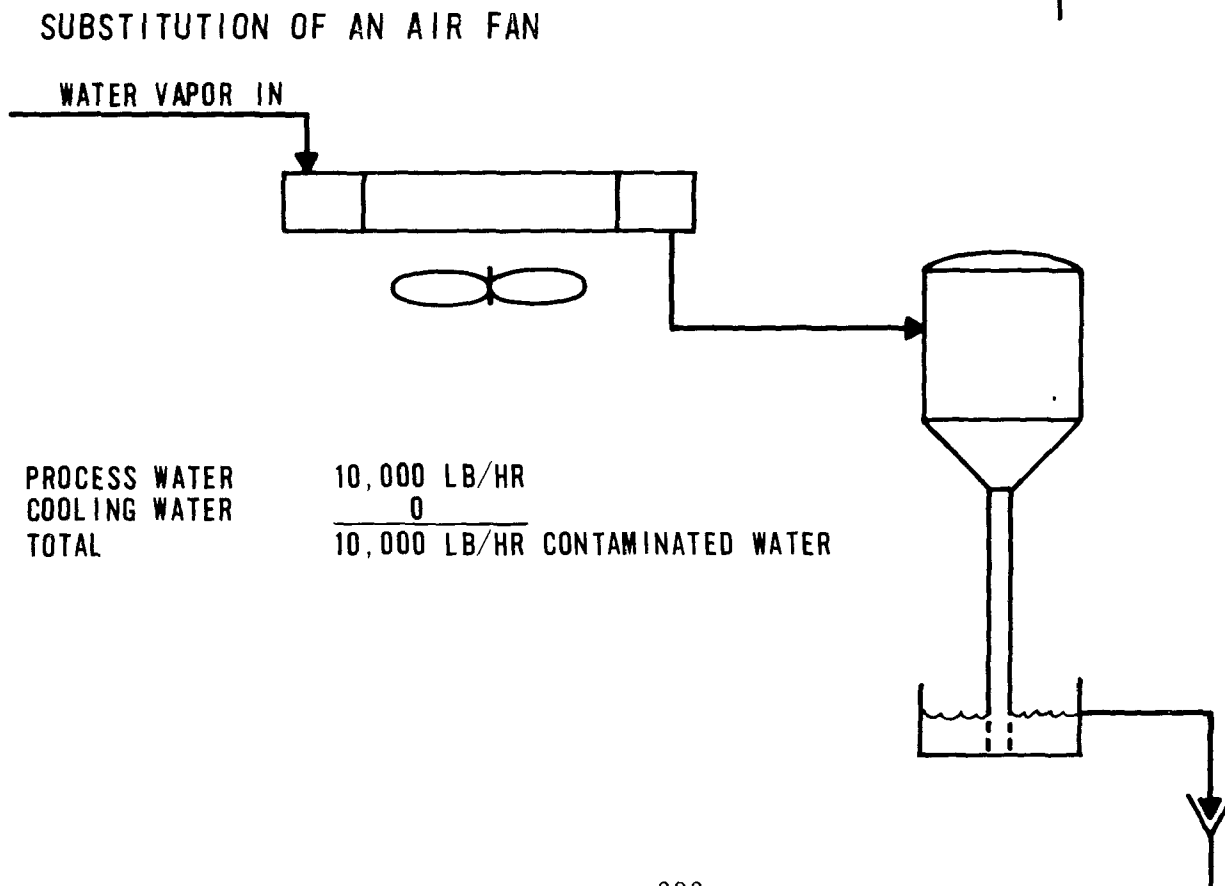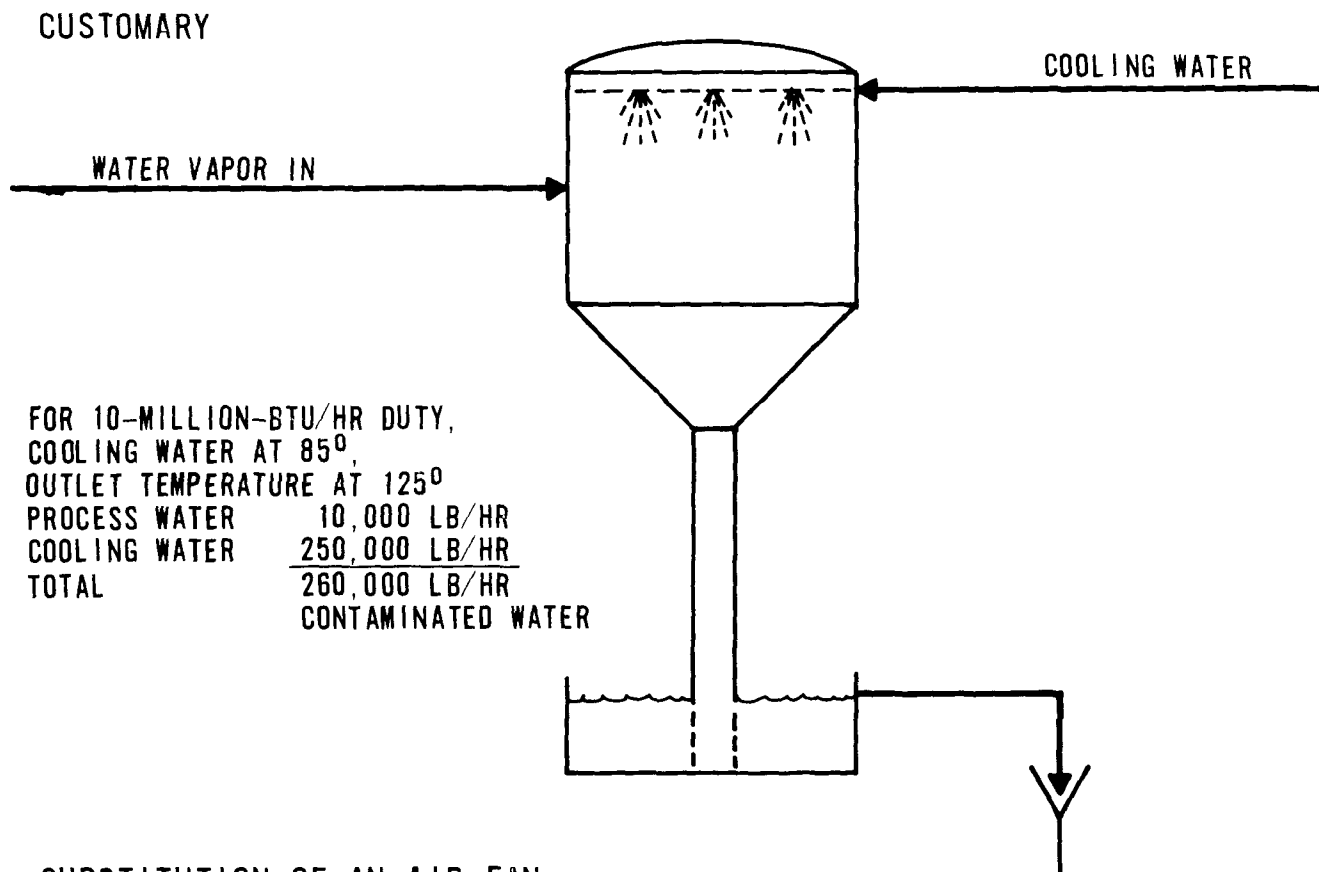
FIGURE VII-1

BAROMETRIC CONDENSER

CUSTOMARY

COOLING WATER

WATER VAPOR IN

FOR 10-MILLION-BTU/HR DUTY,
COOLING WATER AT 85⁰,
OUTLET TEMPERATURE AT 125⁰

PROCESS WATER	10,000 LB/HR
COOLING WATER	250,000 LB/HR
TOTAL	260,000 LB/HR
	CONTAMINATED WATER

SUBSTITUTION OF AN AIR FAN

WATER VAPOR IN

PROCESS WATER	10,000 LB/HR
COOLING WATER	0
TOTAL	10,000 LB/HR CONTAMINATED WATER

FIGURE VII-2

PROCESS STEAM CONDENSATE

CONTAMINATED PROCESS
STEAM CONDENSATE

REGENERATED
PROCESS STEAM

NON-CONTACT STEAM

BLOWDOWN
(CONTACT PROCESS
WASTEWATER)

NON-CONTACT
CONDENSATE

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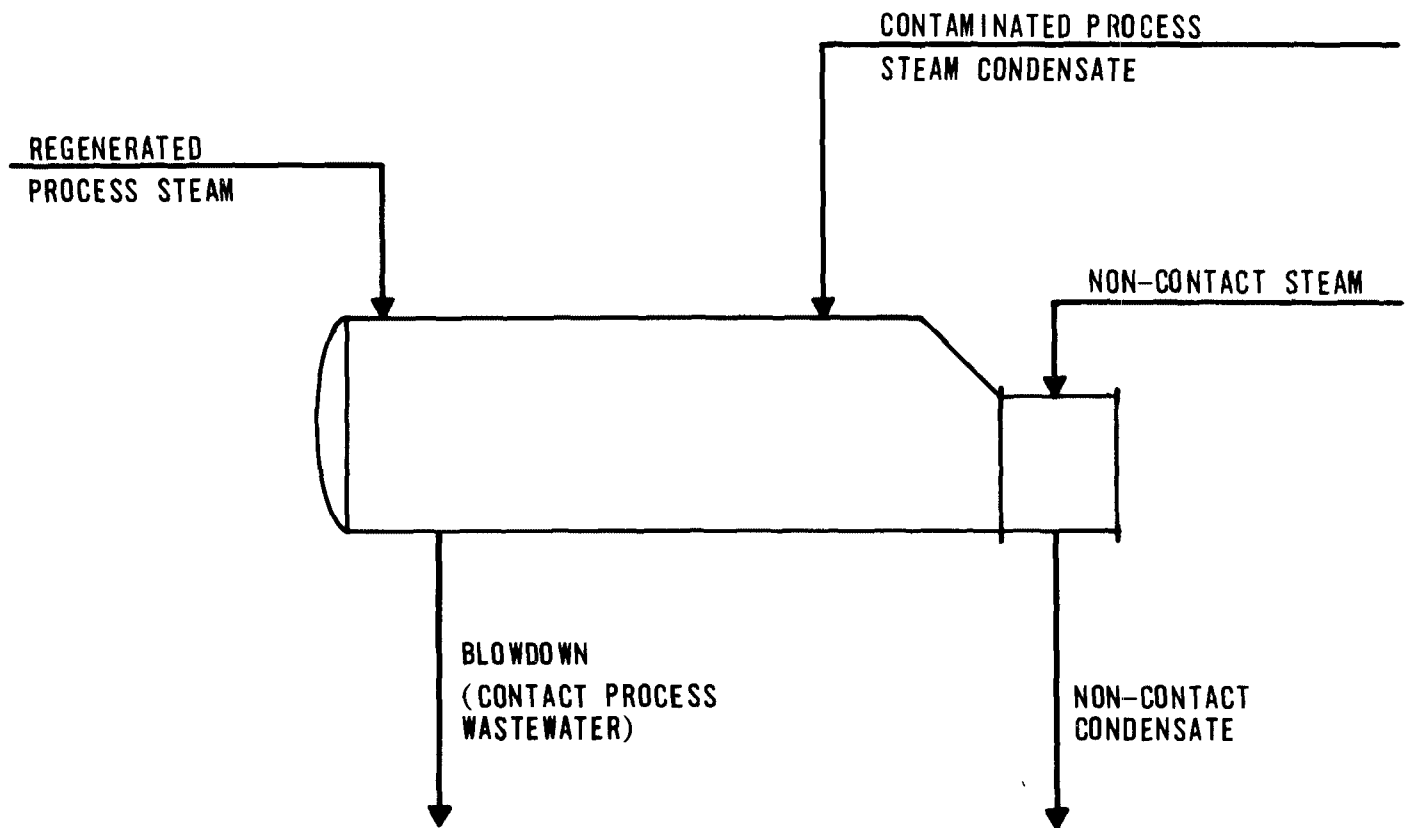
or dilution steam in pyrolysis furnaces. Heat exchange is through a surface shell-and-tube heat exchanger, which can be sized for a wide variety of heat transfer duties. A system similar to this was described in detail for ethylene manufacture in Section IV.

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 bacuum is necessary.

It should be noted that in many cases the steam jet ejector system may be coupled with a barcmetric 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.
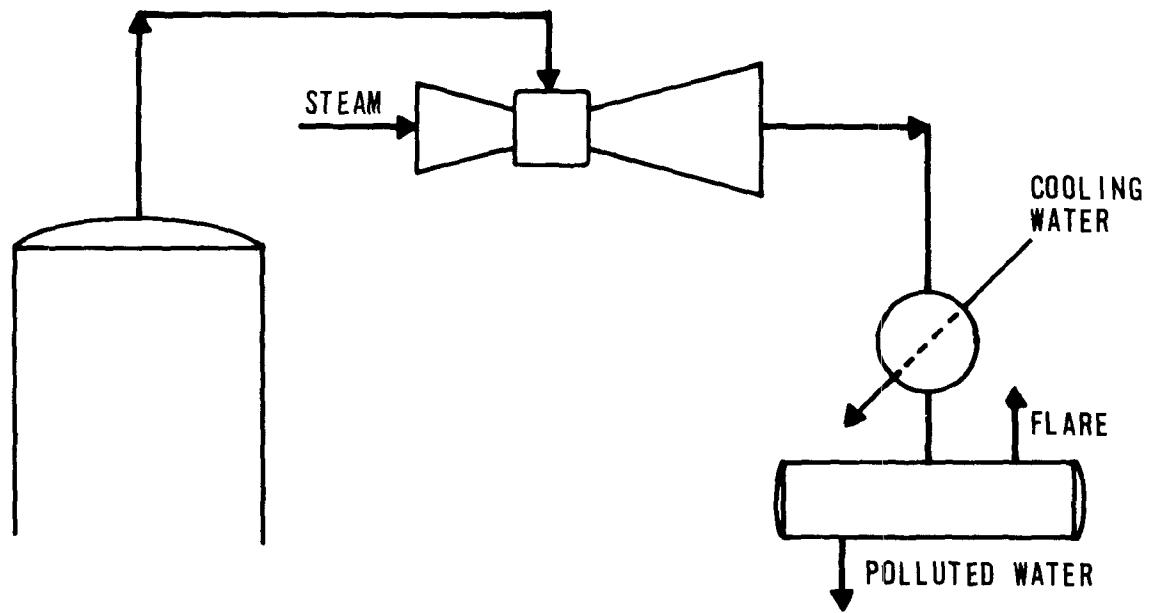
Recovery of Insoluble Hydrocarbons

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

FIGURE VII-3

NON-CONDENSIBLE REMOVAL
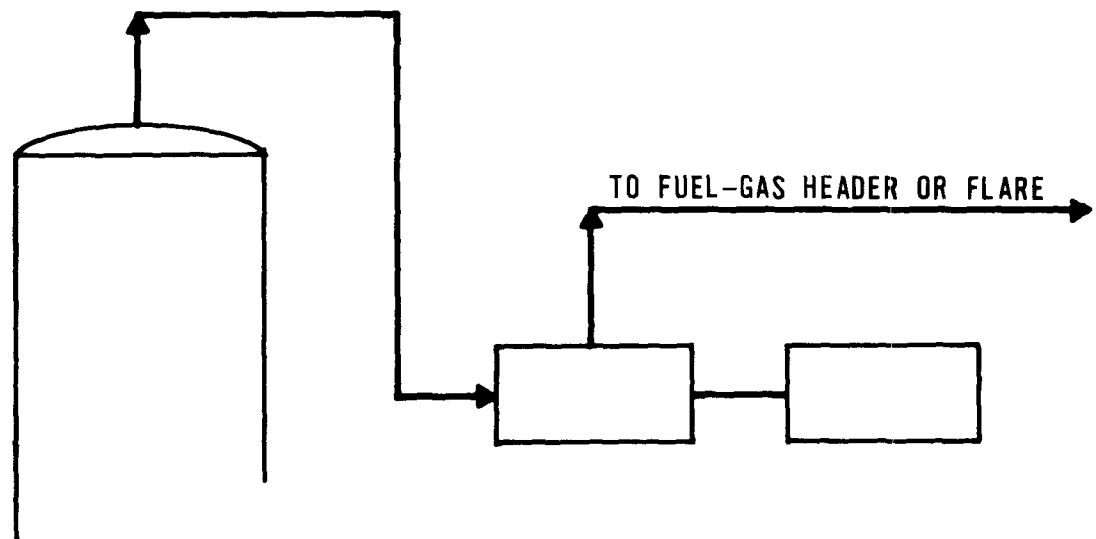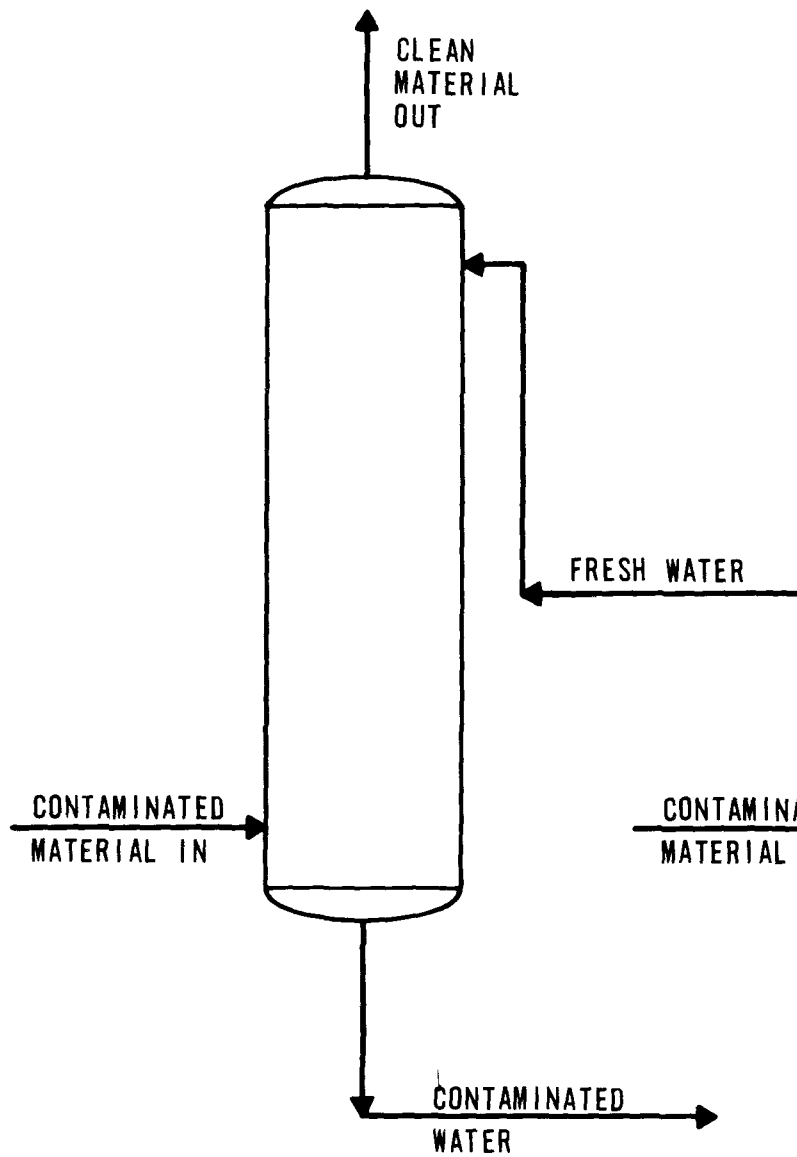
CUSTOMARY — VACUUM JETS

ALTERNATE — VACUUM PUMP
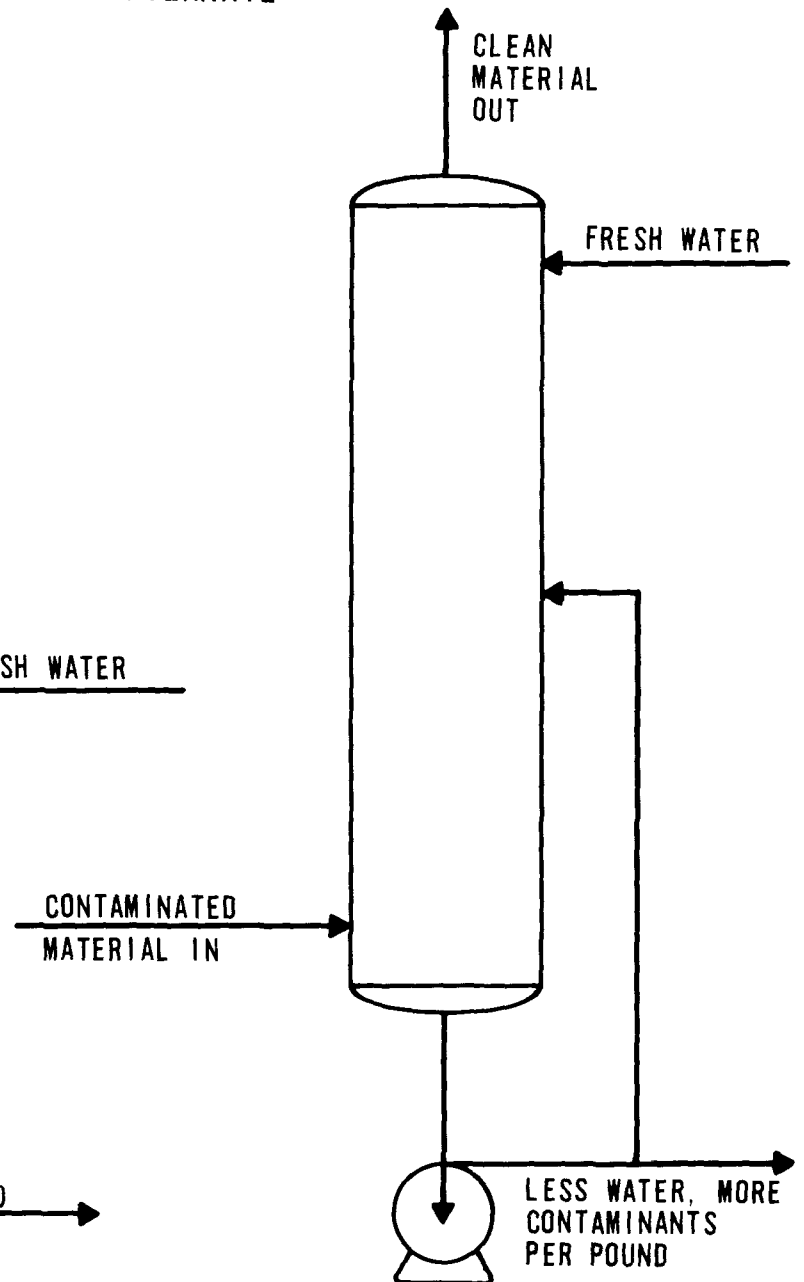
FIGURE VII-4

WATER SCRUBBING

CUSTOMARY

CLEAN
MATERIAL
OUT

FRESH WATER

CONTAMINATED
MATERIAL IN

CONTAMINATED
WATER

ALTERNATE

CLEAN
MATERIAL
OUT

FRESH WATER

CONTAMINATED
MATERIAL IN

LESS WATER, MORE
CONTAMINANTS
PER POUND

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FIGURE VII-5

OIL AND WATER SEPARATION

LIGHT-OIL ADDITION
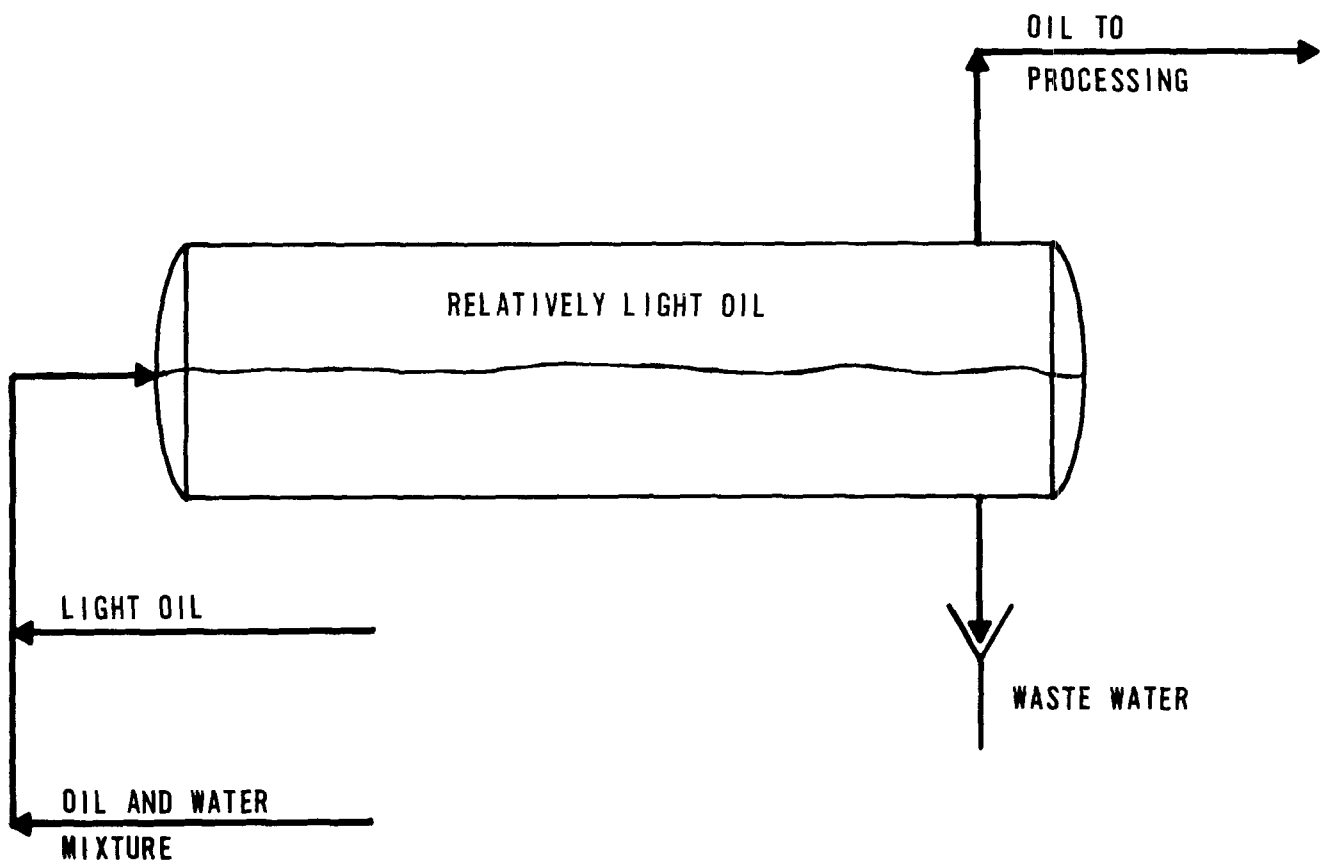
FIGURE VII-6

OIL AND WATER SEPARATION

FUEL-GAS ADDITION

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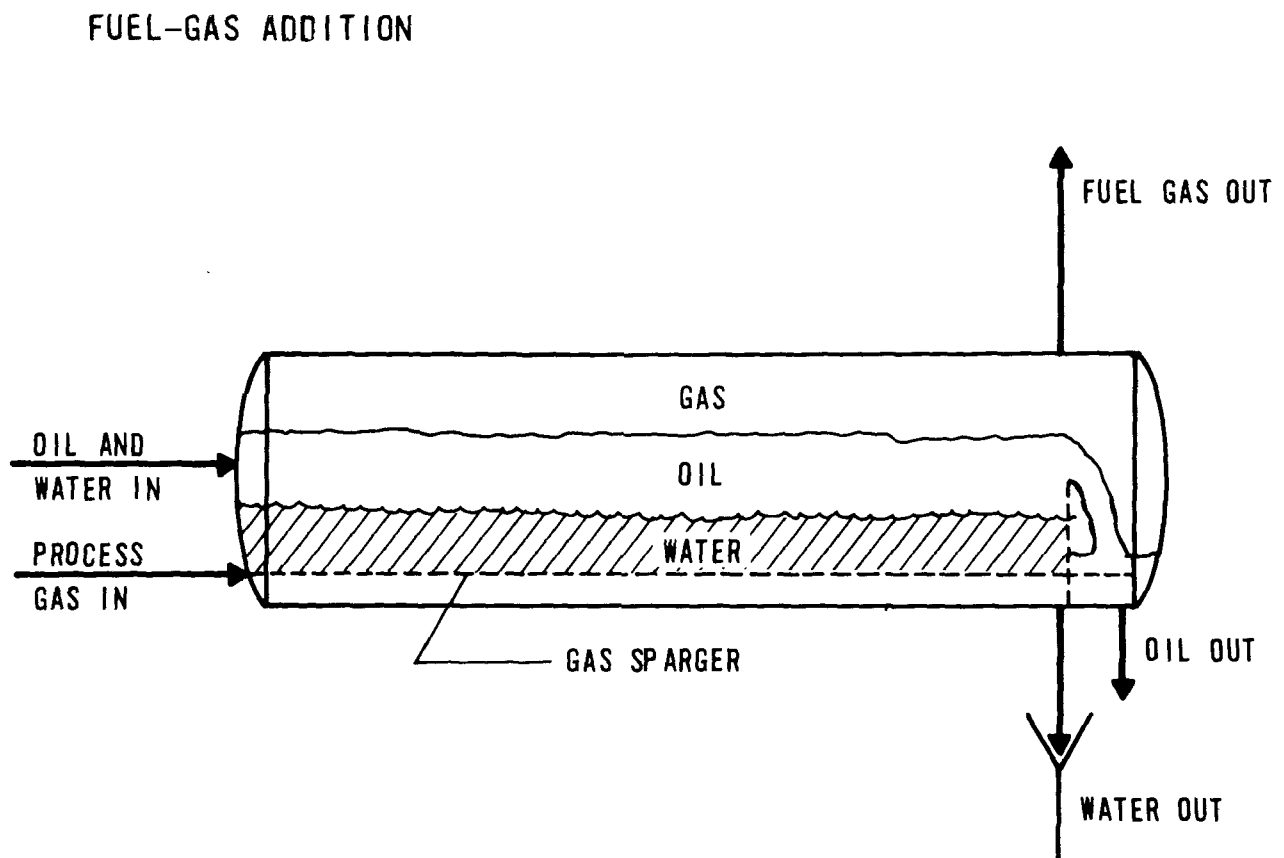
gas quench water. Other systems such as filters and coalescers are also used for this type of separation.

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 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*

Oil Content

Influent (mg/L)	Effluent (mg/L)	Oil Removed %	Type of Separator
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*

Solvent	Phenol Influent, mg/l	Phenol Effluent, mg/l	Phenol Removal (%)
Aromatics, 75% Paraffins, 25%	200	0.2	99.9
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+%

             NH3 removal   95-97%

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.

It must be appreciated that these systems are useful only for specific
processes and may not be recommended on a general basis. This is
definitely true when evaluating the possible use of activated carbon
adsorption as an in-process control measure. Table VII-2 provides
orientation as to its widely varying effectiveness for specific
chemicals. This table illustrates the limited amenability of many

Table VII-2

Relative Amenability To Adsorption Of Typical Petrochemical Wastewater Constitutents*

Compound at 1000 mg/L Initial Concentration	Percentage Removal of Compound at a 5 mg/L powdered carbon dosage
Ethanol	10
Isopropanol	13
Acetaldehyde	12
Butyraldehyde	53
Di-N-propylamine	80
Monoethanolamine	7
Pyridine	47
2-Methyl 5-ethyl pyridine	89
Benzene[1]	95
Phenol	81
Nitrobenzene	96
Ethyl acetate	50
Vinyl acetate	64
Ethyl acrylate	78
Ethylene glycol	7
Propylene glycol	12
Propylene oxide	26
Acetone	22
Methyl ethyl ketone	47
Methyl isobutyl ketone	85
Acetic acid	24
Propionic acid	33
Benzoic acid	91

[1]Benzene test at near saturation level, 420 mg/L

*Conway, P.A. etc., "Treatability of Wastewater from Organic Chemical and Plastics Manufacturing - Experience and Concepts," Research and Development Department, Union Carbide Corporation, South Charleston, West Virginia, Feb. 1973.

common low molecular-weight, oxygenated chemicals to adsorption on activated carbon.

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 incincerator to dispose of polychlorinated biphenyls. Another chemical company has developed an efficient tar-burning unit, and is selling know-how. 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, the system.

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 incincerates chlorinated liquid waste, cools the combustion gases, strips the aqueous product and turns out anhydrous HC1.

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% HC1.

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 HC1 from the gas stream.

Gas from the last absorber enters a final scrubber to reduce HC1 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 HC1 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 HC1 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

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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. Incinceration costs for descruction 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 pruifying 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 indistry, or even one category.

End-of-Pipe Treatment System
General Considerations

One of the initial criteria used to screen organic chemicals plants for the Phase I field survey was the degree of treatment provided by their

waste water treatment facilities. Therefore, the selection of plants was not based on a cross-section of the entire industry, but rather was biased in favor of those segments of the industry that had the more efficient waste water treatment facilities. A summary of the types of treatment technology which were observed during the survey are listed in Table VII-3. Of the plants surveyed in Subcategories A, B, and C over 90 percent provided their own waste treatment facilities while 50 to 60 percent of the Subcategory D plants discharged to municipally owned treatment facilities.

During the survey program, waste water treatment plant performance history was obtained when possible. The sampling data obtained during the survey were then used to verify each plant's analytical procedures. The historical data were analyzed statistically, and the individual plant's performance evaluated in comparison to the origianl design basis. After this evaluation, a group of plants were selected as being exemplary, and these plants were presented in Tables VII-3 and VII-4.

The treatment data in Table VII-4 represent the average historic treatment plant performance (50% probability of occurrence) based on a thirty-day average reporting period, and the data in Table VII-5 represent the sampling data obtained during the plant survey. It is true that the treatment data in Tables VII-4 and VII-5 were obtained from plants producing multi-products from more than one category. However, based on the great majority of the products produced in the plant, most of the plants could be directly associated with a particular category.

In preparing the economic data base, all the waste water treatment plant data were analyzed to develop a basis for subsequent capital and operating costs.

The treatment plant data presented in Tables VII-4 and VII-5 were evaluated on the basis of similar categories and this resulted in the generation of treatment efficiencies for BPCTCA and BATEA affluent levels. These required treatment efficiencies will be presented in the succeeding sections.

A review of the exemplary waste water treatment systems indicated that the biological treatment system is typified by a variety of treatment systems such as physical, chemical or biological waste treatment systems. In order to measure the economic impact of the proposed effluent standards, a series of model treatment systems were developed for each subcategory and were sized to remove 95, 90 and 85 percent of the influent BOD.

The end-of-pipe treatment models were designed to cover the range of actual contact process waste water flows which were encountered within

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Table VII-3

Organic Chemicals Study
Treatment Technology Survey

Number of Plants Observed	
7	Activated Sludge
1	Activated Sludge-aerated lagoon
1	Activated Sludge-polishing pond
1	Trickling Filter-Activated sludge
3	Aerated lagoon-settling pond
2	Aerated lagoon-no solids separation
4	Facultative Anaerobic lagoon
1	Stripping Tower
3	No current treatment - system in planning stage
5	To Municipal Treatment Plant
2	Deep-well disposal
4	Physical Treatment, e.g. API Separator
34 Total	

Table VII-4

Historic Treatment Plant Performance
50% Probability of Occurrence

Treatment System	Category	COD		BOD		TOC		SS	
		% Removal	Effluent mg/L	% Removal	Effluent mg/L	% Removal	Effluent mg/L	% Removal	Effluent mg/L
A.S.	D	75	320	97	10	---	---	---	---
A.S.-P.P.	C	96.4	470	---	---	---	---	---	163
A.S.	D	63	200	93.5	16	---	---	---	55
A.S.	B	64.2	120	---	15	---	---	---	---
T.F.-A.S.	B	73.5	83	---	---	---	---	---	---
A.L.	B	---	75	---	23.5	---	---	---	24.3
A.S.	C	---	---	83	152	60	170	---	130
A.S.	B	74.5	80	90.1	20	---	---	---	---
A.S.-A.L.	C	---	---	99.7	20	97	100	-370	145
A.S.	A-B	---	---	---	---	42	780	---	280

NOTES: A.S. = Activated Sludge   T.F. = Trickling Filter

A.L. = Aerated Lagoon   P.P. = Polishing Pond

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Table VII-5

Treatment Plant Survey Data[1]

Treatment System	Category	COD		BOD		TOC		SS	
		% Removal	Effluent mg/L	% Removal	Effluent mg/L	% Removal	Effluent mg/L	% Removal	Effluent mg/L
A.S.-P.P.	C	64	2,300	90	427	32	2,710	-6,340	4,700
A.S.	D	71	284	73	74	71	132	-18	62
A.S.	B	57	214	82	13	35	80	40	14
T.F.-A.S.	B	59	133	92	12	43	61	97	44
A.L.	B-C	66	980	73	235	11	573	331	362
A.L.	B	69	92	84	6	26	52	99	3
A.S.	C	75	595	92	75	69	242	-34	50
A.S.-A.L.	C	94	337	99	16	27	343	-606	145
A.L.	C	62	600	78	27	66	47	89	30
A.S.	B-C	65	940	90	177	64	470	120	338

NOTES: A.S. = Activated Sludge   T.F. = Trickling Filter

A.L. = Aerated Lagoon   P.P. = Polishing Pond

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[1] Based on a 24 hour composite sample.

each of the process subcategories. The tabulation below summarizes these ranges:

<u>Process Wastewater Flow (gpd)</u>

	<u>Minimum</u>	<u>Average</u>	<u>Maximum</u>
Continuous Process Subcategories A, B, and C	7,200	360,000	2,160,000
Batch Process Subcategory D	72,000	360,000	720,000

There is an approximate correlation between the actual waste water flow and flow RWL as expressed in production units. Generally, the highest actual flow rates are generated by those processes which produce the highest flows per unit of product.

BPCTCA Treatment Systems

The single stage activated sludge system was chosen as a model system for BPCTCA and a general flow diagram for the waste water treatment facilities is shown in Figure VII-7. A summary of the general design basis is presented in Table VII-6.

FIGURE VII-7

BPCTCA WASTE TREATMENT MODEL

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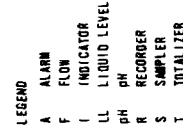
Table VII-6

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 and 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, on in each basin. The lime slurry is added to the neutralization basin from a lime slurry recirculation loop. The lime handling gacilities 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 maninain the ratio of BOD:N: at 100:5:1/

Aeration Basin

Platform-mounted mechnaical 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 O2/lb BOD removed
alpha factor                0.9
beta factor                 0.9
Wastewater Temperature      20 C
Oxygen transfer             3.5 lb O2/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 overfolw rate varies between 100 and 500 gpd/sq ft depending on plant size. Sludge recycle pumps are sized to diliver 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 yields 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 reliablility 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.

The following is a brief discussion of the treatment technology availagle and the rationale for the selection of the previous unit processes to be included in the BPCTCA treatment system. An optional API oil-water separator was sized for an average flow of 720,000 gal/day. This was done in oder to indicate the percentage increase in the total BPCTCA cost which would be involved as a result of excess floating oil.

The pump stations are generally located after the API separator so as to avoid emulsifying the floating oil. Topography of a particular plant site will dicate whether pumping equipment is required. Equalization facilities are provided in order to minimize short-interval (e.g., hourly) fluctuations in the organic loading to the treatment plant, as well as to absorb slug loads from reactor cleanouts, accidental spills, etc. and to minimize the usage of neutralization chemicals, ect. A three-day detention time based on average flow is provided for subcategory D flows, in contrast to one day's retention time for subcategories A, B, and C. This increased retention time is used to reduce the hydraulic as well as the organic variability in the subcategory D chemical production. Also, this system provides for seven-day-per-week operation in the event the manufacturing facilities operate five or six days per week.

After equalization and depending on the individual plant's product mix it may be necessary to neutralize the wastewater, to make it more amenable to biological treatment. Alkaline neutralization is provided in the form of hydrated lime storage and feed facilities. Primary clarification facilities were not included in the facilities for the cost estimate, because the TSS RWL data indicated that it would not be necessary to remove TSS before biological treatment. It should be noted that a plant's particular product mix should be evaluated before a decision is made to omit this process.

An activated sludge process was selected for the biological portion of the system. However, single stage activated sludge is not the only system which may be applicable nor should it be construed as being totally applicable to all process wastewaters which may be generated in the industry. In addition, aerated lagoons are also applicable to meet

the proposed effluent requirements. The following is the rationale for selection of activated sludge and its inclusion in the cost estimates.

Both aerated lagoons and activated sludge processes involve aeration basins, the major difference being that aerated lagoons normally discharge directly without a clarification step. This results in a much lower concentration of microorganisms in the aerated lagoon than in an activated sludge basin because the microorganism mass is not recirculated back to the aeration basin. Therefore, for camparable organic loadings, a much larger aerated lagoon would be required to provide treatment equivalent to that of an activated sludge plant. In actual practice, the aerated lagoon process has found wide application where it is not necessary to provide a mentod of sealing the lagoon or where the soil characteristics are such that they form a natural seal. The activated sludge process was selected for cost estimating purposes in order to provide an estimate of the economic impact of the proposed effluents limits on any treatment facility including the proposed effluent slimis on any treatment facility including those for which it is necessary to make the basin linings impervious.

Beside activated sludge and aerated lagoons, various other combinations of biological treatment processes may be utilized. The combination of available unit processes are numerous and the treatment scheme should be selected only after a thorough engineering as well as economic analysis.

In the biological process, for every pound of BOD removed from a waste water, approximately 0.6 pound of biological solids is produced, and this must be removed from the system. In many areas where aerated lagoons are applicable, settling lagoons are used to separate these biological solids.

These settling lagoons are periodically dewatered and dredged, and the dredgings are pumped to sludge-holding lagoons. (In the activated sludge process sludge wasting is done daily to dewatering facilities). These sludge lagoons may act as solar evaporation ponds or as drying lagoons if the water and precipitation are decanted off. The sludge will generally dewater naturally if applied at depths less than 15 inches. The dewatered sludge may then be landfilled, or the existing lagoon can be covered with earth and a new lagoon constructed. Which alternative is used depends upon individual state' sanitary landfill requirements and the possiblity of ground water pollution through contamination with leachate.

Many plants in the United States are so geographically situated that aerated lagoons provide a viable alernative. However, in order to make the subsequent cost estimates more meaningful and universally applicable, activate sludge was selected. In addition, because the Subcategory C wastes are so concentrated and the TSS mixed liquor levels are so high (as previously discussed), an air flotation unit is included to facilitate solids separation after the secondary clarifier.

Activated sludge facilities pose a distinct sludge disposal problem. Because biological sludge must be wasted on a daily basis from most larger plants, it creates a handling problem which often cannot be solved as expeditiously as with an aerated lagoon.

The relatively small amounts of sludge generated by the BPCTCA plants dictated the selection of the most viable sludge disposal alternative. The quantities of sludge are such that sludge incineration cannot be justified because of the very small equipment sizes that would be involved. Therefore, it was decided, for smaller plants, to aerobically digest the sludge, decant the supernatant, and then vacuum filter the sludge. The sludge cake (which would be at least 20% solids) would then be acceptable at a sanitary landfill.

For the larger plants, sludge thickening is provided to concentrate the waste activated sludge from 0.8% to 2.0% before digestion. Thickening is not applicable for the smaller palnts because the sludge quantities are such that odors could develop because the small equipment would result in long detention times. For these cases, a sludge holding tank is provided in order to add flexibility to the operation. During vacuum filter down time, digested sludge may also be held without upsetting the solid handling facilities.

BATEA Treatment Systems

As previously discussed in in-process recovery systems, activated carbon has possible applications in the organic chemicals industry for in-plant recovery of specific chemicals. In addition, activated carbon has also been demonstrated in many cases that it can be used as an end-of-pipe waste water treatment technology.

During the plant survey program, seven samples of the individual industrial treatment plant effluents from industrial Subcategories B, C, and D were obtained and carbon isotherms were performed using powered activated carbon. The raw carbon isotherm data are presented in Supplement B, and a summary of the analytical results are presented in Table VII-8. The complexity of the organic chemical industry is evidenced by the results of the carbon isotherms. The initial COD varied tenfold, while the variation in carbon exhaustion rate was over one hundred fold.

The carbon adsorption isotherm is widely used to screen various activated carbons and to quantify overall removal efficiencies. However, the exhaustion capacity, generated by a carbon isotherm is not sufficient to be used for design purposes. In pilot scale column operations, the following factors should be recognized: the limitations inherent in extrapolating laboratory data to multi-column systems, and the problems of channeling and wall-effects that limit the utility of data taken in small diameter laboratory columns. Ideally, pilot-plant

continuous column studies should be run to generate reliable design data.

The carbon isotherm data shown in Table VII-8 indicated that, except in the particular case of Plant 6, COD removal efficiencies by carbon adsorption of biological treatment plant effluents are well above 70 percent. In addition, it is known that additional organic substances can be degraded through biological activity which occurs in the carbon bed.

In order to develop BATEA effluent criteria, the activated carbon system in addition to BPCTCA treatment systems was chosen as a model system for BATEA for Subcategories A, B, C, and D.

BATEA effluent criteria may be attained in actual practice via a number of possible routes. In order to quantify the impact of BATEA criteria on the individual categories, two treatment systems were designed and subsequent cost data reported in Section VIII. A general flow diagram for the BPCTCA treatment system for Subcategories A and B is shown in Figure VII-8 and for Subcategories C and D in Figure VII-9. A summary of the general design basis is presented in Table VII-7.

Dual-media gravity filtration is provided since activated carbon typically requires that the concentration of TSS be 50 mg/l or lower in order to maximize carbon adsorption and minimize the filtration function. High TSS would involve shortened filter runs and increased amounts of backwash water usage.

Table VII-7

<u>BATEA End of Pipe Treatment System</u>

Design Summary

<u>Gravity Dual-Media Filtration</u>

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).

<u>Granular Carbon Columns</u>

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.

<u>Filter-Column Decant Sump</u>

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.

<u>Regeneration Furnace</u>

The following exhaustion rates were used for the sizing of the regeneration facilities:

Subcategory	<u>Influent COD</u> mg/l	<u>Exhaustion Capacity</u> 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.

Table VII-8

Carbon Isotherm Data Performed on Individual Biological
Treatment Plant Effluents

Plant ID	Industrial Category	Initial Soluble COD conc mg/L	Final Soluble COD conc mg/L	% Removed	Exhaustion Capacity	
					lbs COD Removed lb. Carbon	lbs Carbon 1000 Gallons
1	B	146	19	87	4.5	0.27
2	D	304	21	93	1.35	1.87
3	C	525	150	71	0.35	12.2
4	C	573	146	75	0.36	13.3
5	B	774	97	87	0.50	18.7
6	B	972	758	22	0.035	232
7	B	1297	397	70	0.34	32.2

The treatment plant effluents were filtered to insure the removal of all insoluble COD.

FIGURE VII-8

BATEA WASTE TREATMENT MODEL
CATEGORIES A AND B
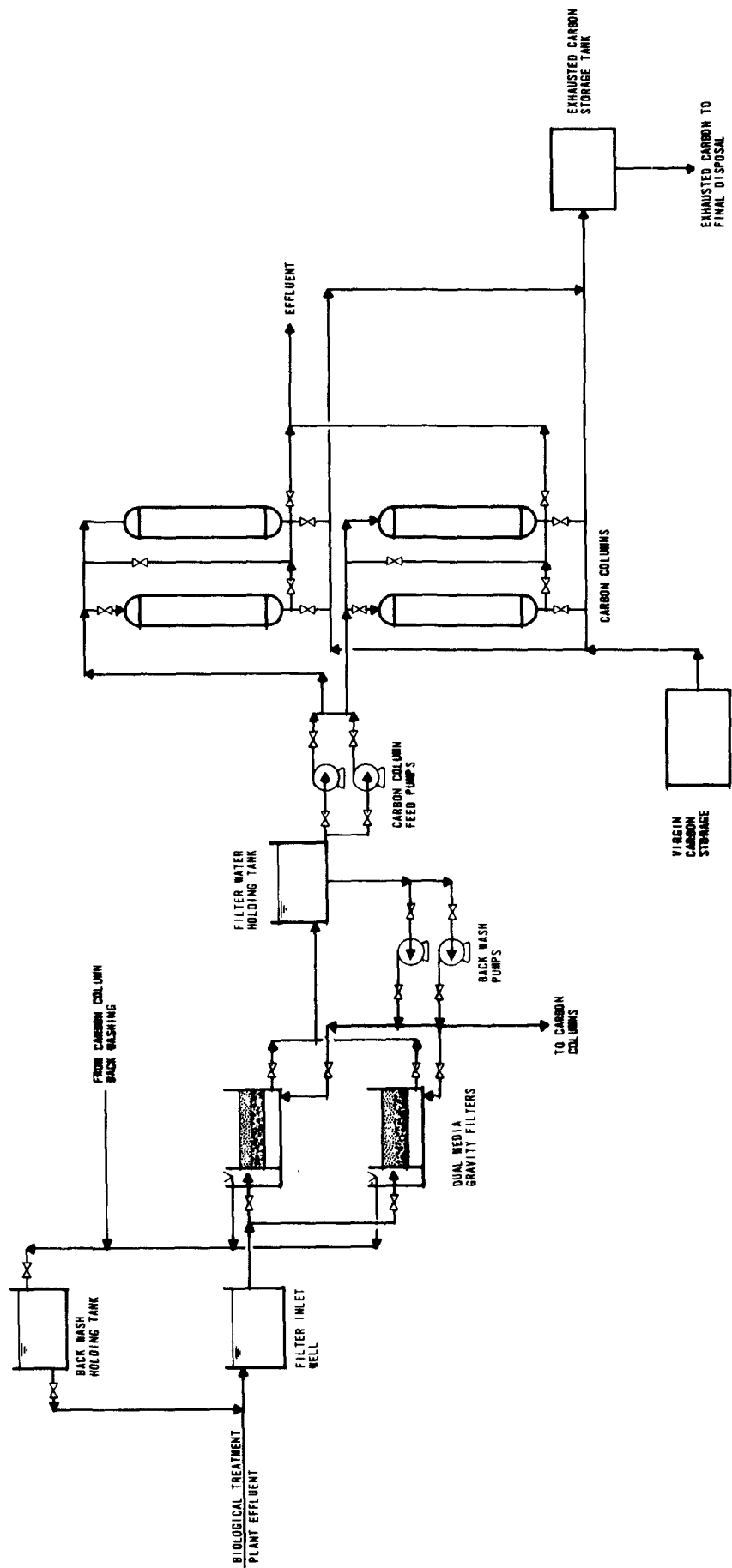
FIGURE VII-9

BATEA WASTE TREATMENT MODEL
CATEGORIES C AND D
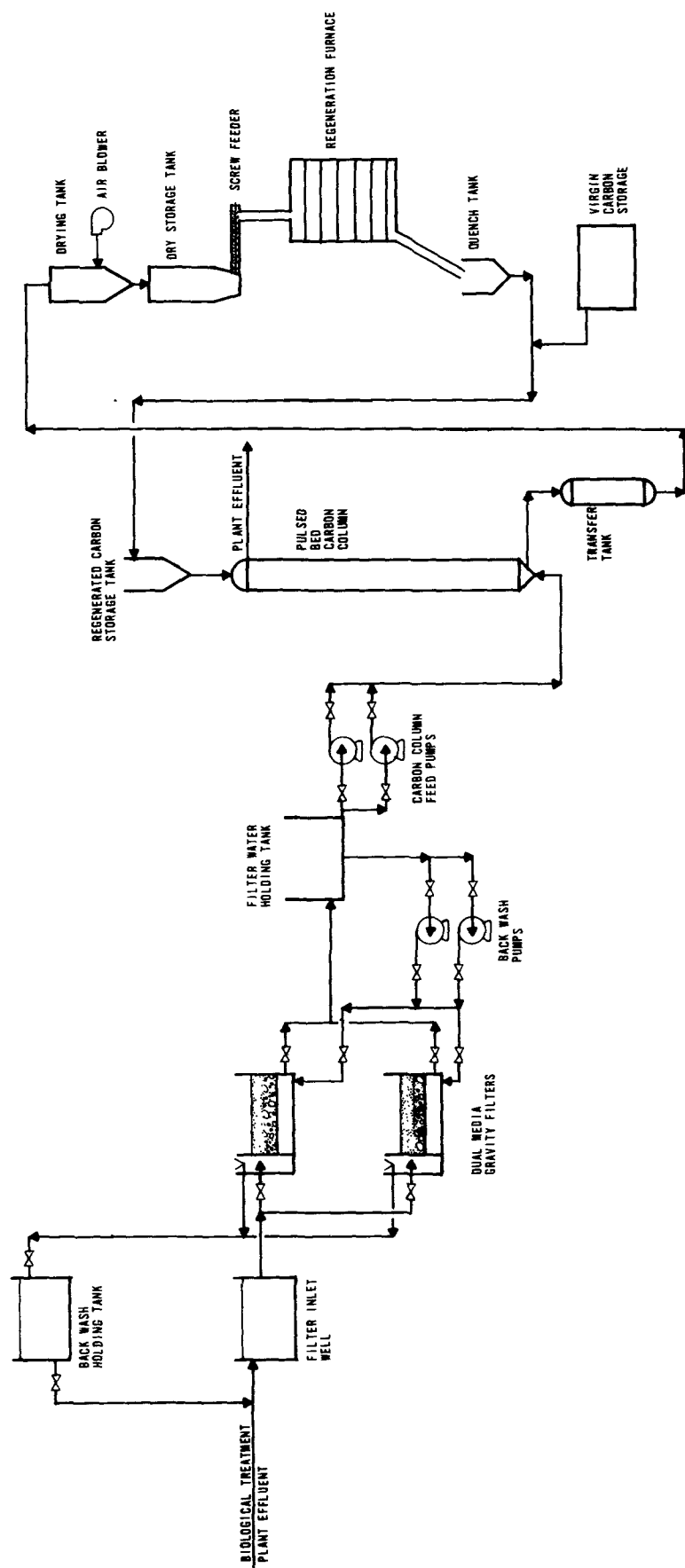
Section VIII

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 an 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, C, and D. 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:

Item	Percent of Unit Process Capital Cost
Electrical	12
Piping	15
Instrumentation	8
Site work	3
Engineering design and Construction supervision fees	15
Construction contiguency	15

Land costs were computed independently and added directly to the total capital costs.

Annual costs were computed using the following cost basis:

Item	Cost Allocation
Amortization	20 years for capital recovery at 8 percent (10.2% of capital costs)
Operations and Maintenence	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:

Technology or Design Criteria	Cost Differential
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 BOD_5. These factors are shown below:

Percent Removal BOD5	Subcategory			
	A	B	C	D
95	1.19	1.0	1.0	1.00
90	1.00	0.84	0.88	0.88
85	0.86	0.72	0.87	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:

Subcategory	Capital Cost $	Annual Costs			
		$/year	$/1000 gal	$/lb BOD5 Removed	Percent BOD5 Removed
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
D	1,878,000	341,900	1.30	0.25	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, Subcategory D-0.05 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

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	Capital $	Annual* $/year	$/1000 gal	% Reduction BOD$_5$	$/lb BOD$_5$ Removed
Subcategory A						
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
Subcategory B						
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
Subcategory C						
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
Subcategory D						
0.05	0.072	823,000	157,100	5.98	95	0.11
0.05	0.360	1,453,000	264,000	2.01	95	0.19
0.05	0.72	1,878,000	341,900	1.30	95	0.25

Costs (1971 Basis)

*Annual Cost Adjustment Factors:

% Reduction BOD$_5$	Subcategory A	Subcategory B	Subcategory C	Subcategory D
95	1.19	1.00	1.00	1.00
90	1.00	0.84	0.88	0.90
85	0.86	0.72	0.87	0.87

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Table VIII-2

TOTAL COSTS** AND EFFECTIVENESS DATA - BPCTCA ORGANIC CHEMICALS MANUFACTURING INDUSTRY

SUBCATEGORY A NON-AQUEOUS PROCESSES

Annual Costs	Percent Removal, BOD5	Effluent Concentration, mg/liter BOD5	Size of Treatment Plant, mgd		
			0.072 mgd	0.72 mgd	2.16 mgd
$/year	95	15	128,000	338,300	No Data
	*90	30	107,600	284,300	Available
	85	45	92,500	244,500	
$/1000 gallons	95	15	4.87	1.28	
	*90	30	4.09	1.08	
	85	45	3.52	0.93	
$/lb BOD5 Removed	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

Annual Costs	Percent Removal, BOD5	Effluent Concentration, mg/liter BOD5	0.072 mgd	0.72 mgd	2.16 mgd
$/year	*95	30	117,700	487,900	745,200
	90	60	98,900	409,800	626,000
	85	90	84,700	351,300	536,500
$/1000 gallons	*95	30	4.48	1.86	0.94
	90	60	3.76	1.56	0.79
	85	90	3.22	1.34	0.68
$/lb BOD5 Removed	*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

Table VIII-2 Cont'd

TOTAL COST** AND EFFECTIVENESS DATA - BPCTCA
ORGANIC CHEMICALS MANUFACTURING INDUSTRY

SUBCATEGORY C AQUEOUS LIQUID PHASE REACTION SYSTEMS

Annual Cost	Effluent Concentration, mg/liter BOD5	Percent % Removal, BOD5	Size of Treatment Plant, mgd			
			0.072 mgd	0.36 mgd	0.72 mgd	2.16 mgd
$/year	45	*95	527,000	No Data Available	1,657,000	2,917,300
	90	90	463,800		1,458,000	2,567,200
	135	85	458,500		1,441,600	2,538,000
$/1000 gallons	45	*95	20.05		6.31	3.70
	90	90	17.64		5.55	3.26
	135	85	17.44		5.48	3.22
$/1b BOD5 Removed	45	*95	0.050		0.17	0.30
	90	90	0.046		0.16	0.28
	135	85	0.048		0.17	0.29

SUBCATEGORY D BATCH AND SEMI-CONTINUOUS PROCESSES

Annual Cost	Effluent Concentration, mg/liter BOD5	Percent % Removal, BOD5	Size of Treatment Plant, mgd			
			0.072 mgd	0.36 mgd	0.72 mgd	2.16 mgd
$/year	30	*95	157,100	264,000	341,900	No Data Available
	60	90	141,400	237,600	307,700	
	90	85	136,700	229,700	297,400	
$/1000 gallons	30	*95	5.98	2.01	1.30	
	60	90	5.38	1.81	1.17	
	90	85	5.20	1.75	1.13	
$/1b BOD5 Removed	30	*95	0.11	0.19	0.25	
	60	90	0.10	0.18	0.24	
	90	85	0.13	0.19	0.25	

*   Basis for Recommended effluent limitations

85 percent removal BOD$_5$. Effluent concentration BOD$_5$ 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:

Subcategory	Percentage Increase In Capital Costs
A	9
B	5
C	2
D	7

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:

Subcategory	Cu yd/year*
A	30 - 200
B	30 - 2,000
C	1,500 - 44,000
D	300

*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 cateogry, 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:

Hydraulically Dependent	Organically Dependent	Hydraulically and Organically Dependent
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 BOD_5 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 requirments 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 sludg followed by dual media filtration. The same annual cost adjustment factors applicable to BPCTCA are also relevant to new sources due to th similarity of these systems. As expected, the end-of-pipe costs are not appreciably higher than those for BPCTCA. The following information wa extracted from Table VII-3

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 BOD5	$/lb BOD5 Removed
Subcategory A						
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
Subcategory B						
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
Subcategory C						
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
Subcategory D						
0.05	0.072	867,000	165,200	6.29	95	0.12
0.05	0.36	1,538,000	278,400	2.12	95	0.20
0.05	0.72	1,992,000	361,000	1.37	95	0.26

*Annual Cost Adjustment Factors:

% Reduction BOD5	Subcategory A	Subcategory B	Subcategory C	Subcategory D
95	1.19	1.00	1.00	1.00
90	1.00	1.84	0.08	0.90
85	0.86	0.72	0.87	0.87

Subcategory	Capital Costs		Annual Costs	
	$	$/year	$/1000 gal	$/lb BOD5 Removal
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
D	1,992,000	361,000	1.37	0.26

The following production capacities were selected for calculation of the $/lb BOD$5$ removed: Subcategory A-10 million lb/day, Subcategory B-5 million lb/day, Subcategory C-1 million lb/day and Subcategory D-0.05 million lb/day.

Capital and annual costs are calculated for the best available technology economically achievable model treatment systems. These systems are discribed 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 and D 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.

Subcategory	Capital Cost		Annual Costs	
	$	$/year	$/1000 gal	$/lb COD Removal
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
D	3,529,700	1,496,100	5.69	0.08

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 and Subcategory D-0.05 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	Capital $	Annual $/year	Costs (1971 Basis) $/1000 gal	Overall % Removed COD*	$/lb COD Removed
Subcategory A						
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
Subcategory B						
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
Subcategory C						
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
Subcategory D						
0.05	0.072	1,238,000	298,000	11.34	90	0.016
0.05	0.360	2,540,300	867,700	6.60	90	0.047
0.05	0.720	3,529,700	1,496,100	5.69	90	0.082

* Chemical oxygen demand pollutant parameter is applicable (rather than BOD5) since activated carbon is the major part of the end-of-process treatment. Anticipated overall BOD5 reductions are as follows:

Subcategories A, B, and D – 99%

Subcategory C – 99.5%

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 PBCTCA 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 aminable 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 extration 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 0.1 to 0.5 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 rpoduces 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 removed 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 should enable all processes within each category to attain the following standard raw waste loads. These values are listed in Table IX-1.

End-of-pipe treatment technologies commensurate with BPCTCA are based on the ulitization of biological systems including the activated sludge process, extended aeration, aerated lagoons, trickling filters, and anaerobic and faculative 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 filteration are considered as commensurate with BPCTCA. Effluent suspenced solids are expected to be maintained below 30 mg/liter average concentration.

The following waste reductions are considered consistant with BPCTCA:

	Percent Reduction of BPCTCA Raw Waste Load Median Values	
Subcategory	BOD5	COD*
A	90%	75%
B1	90%	75%
B2	98%	75%
C1	95%	75%
C2	99%	75%
D	95%	75%

* COD effluent limitations are not specified for BPCTCA

These reductions have been applied to the standard raw waste loads for each subcategory to give a set of effluent limitations for each subcategory. The effluent limitations for BPCTCA are listed in Table IX-2.

It should be noted that because biological systems have been proposed as the mode of treatment consistant 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 de 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 consective days. The rationale and basis for determining the daily amd monthly maximum variations are presented in Section XIII.

Table IX-1
Summary of Median Raw Waste Load Data as the
Basis for Calculating Effluent Limitations

Subcategory	Process Wastewater Flow liter/kkg	(gal/1000lb)	BOD5 kg/kkg	COD or lb/1000 lb
A	500	(60)	0.12	0.31
B1	1320	(158)	0.35	1.1
B2	3580	(429)	1.77	6.2
C1	2340	(280)	1.90	6.5
C2	10,800	(1300)	53.0	118.0
D	175,800	(21,050)	79.0	1075.0

Table IX-2
BPCTCA Effluent Limitations

Effluent Characteristic	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days kg/kkg Production*	Maximum for Any One Day kg/kkg Production
Subcategory A		
BOD5	0.025	0.045
TSS	0.023	0.038
Phenols	0.00025	0.0005
Subcategory B		
B1 Product-Processes		
BOD5	0.06	0.10
TSS	0.06	0.10
Phenols	0.00066	0.0013
B2 Product-Processes		
BOD5	0.17	0.30
TSS	0.16	0.27
Phenol	0.0017	0.0034
Subcategory C		
C1 Product-Processes		
BOD5	0.17	0.30
TSS	0.16	0.27
Phenols	0.0017	0.0034
C2 Product-Processes		
BOD5	0.9	1.5
TSS	0.49	0.8
Phenols	0.005	0.011
Subcategory D		
BOD5	9.0	15.0
TSS	7.88	13.0
Phenols	0.088	0.17

*kg/kkg production is equivalent to 1b/1000 1b production.

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.

End-of-process treatment 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 filtation 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 Subcategories C and D).

These systems or equivalent combinations can provide the reduction in BOD5 and COD pollutant parameters as listed below:

Subcategory	BOD5	Percent Removal Basis COD	
	Percent BPCTCA RWL	Percent BPCTCA RWL	Percent BADCT Effluent
A	99	90	70
B1	99	94	70
B2	99.5	94	70
C1	99.5	94	70
C2	99.7	94	70
D	99	90	70

The applicable reductions were used as a basis for determining effluent limitations. Low concentrations for TSS and phenols are also attainable via BATEA treatment and control technologies. The maximum average for any 30 consecutive day period, and daily maximum effluent

concentrations for TSS are 15 mg/l and 25 mg/l respectively. For phenols these values are 0.1 mg/l and 0.2 mg/l for the 30-day and daily values respectively.

BATEA treatment and control technologies are expected to provide maximum control of effluent variability by process controls and end-of-process investment.

Effleunt limitations for BATEA are presented in Table X-1.

Table X-1
BATEA Effluent Limitations

Effluent Characteristics	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days kg/kkg Production*	Maximum for Any One Day kg/kkg Production*
Subcategory A		
COD	0.02	0.04
BOD5	0.002	0.004
TSS	0.004	0.006
Phenols	0.000025	0.00005
Subcategory B		
B1 Product Processes		
COD	0.065	0.13
BOD5	0.004	0.008
TSS	0.01	0.017
Phenols	0.000065	0.00013
B2 Product Processes		
COD	0.37	0.74
BOD5	0.01	0.02
TSS	0.0025	0.0042
Phenols	0.00017	0.00034
Subcategory C		
C1 Product Processes		
COD	0.39	0.78
BOD5	0.01	0.02
TSS	0.005	0.0083
Phenols	0.00034	0.00068
C2 Product Processes		
COD	7.2	14.4
BOD5	0.2	0.4
TSS	0.16	0.27
Phenols	0.0011	0.0022
Subcategory D		
COD	65.0	130.0
BOD5	0.4	0.8
TSS	1.30	2.19
Phenols	0.0085	0.017

* kg/kkg production is equivalent to lb/100 lb production

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 desicribed 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 of 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 medai 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.

The reduction in major pollutant parameters as defined by BADCT is listed by Category in the following tabulation:

| | Percent Reduction of BPCTCA Raw Waste Load Median Values | |
Subcategory	BOD5	COD
A	95	80
B1	95	80
B2	97	80
C1	97	80
C2	99.5	80
D	97	80

Total suspended solids and phenol effluent concentration with BADCT technology are equivalent to those for the BATEA. Daily and any 30 consecutive day period maximum concentrations for suspended solids are 25 mg/liter and 15 mg/liter respectively. Phenol concentration on a daily and any 30 consecutive day period maximum are at 0.2 mg/l and 0.1 mg/liter respectively.

Effluent limitations are presented in Table XI-1 for new sources for major organic sources.

Table XI-1
New Sources Performance Standards
(BADCT)

Effluent Characteristics	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days kg/kkg Production*	Maximum for Any One Day kg/kkg Production*
Subcategory A		
BOD5	0.012	0.020
COD	0.10	0.15
TSS	0.0075	0.012
Phenols	0.00005	0.00010
Subcategory B		
B1 Product Processes		
BOD5	0.035	0.06
COD	0.40	0.55
TSS	0.02	0.033
Phenols	0.00013	0.00026
B1 Product Processes		
BOD5	0.085	0.15
COD	2.2	3.0
TSS	0.05	0.083
Phenols	0.00034	0.00068
Subcategory C		
C1 Product Processes		
BOD5	0.085	0.15
COD	2.3	3.3
TSS	0.05	0.083
Phenols	0.00034	0.00068
C2 Product Processes		
BOD5	0.40	0.75
COD	40.0	60.0
TSS	0.16	0.27
Phenols	0.0011	0.0022
Subcategory D		
BOD5	0.85	1.5
COD	390.0	540.0
TSS	2.60	4.38
Phenols	0.017	0.034

*kg/kkg production is equivalent to lb/1000 lb production

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	_Subgroup 2_
Subcategory A	Subcategory C
Subcategory B	Subcategory D

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, and waste waters associated with dye/pigment production (Subcategory D) also may have high metal concentrations due to the presence of metallic dyes.

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 degradeable 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 BOD_5 concentration of 20 mg/l, will also produce an effluent with 90 mg/l of BOD_5 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 BOD_5 in the plant effluent.

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Table XIII-I

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
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

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.

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:

Ratio of Probability	Daily	BOD5 Weekly	Thirty Consecutive Day Period
99/50	8.0	3.5	2.7
95/50	4.5	2.5	2.0
90/50	3.0	2.0	1.7
		COD	
99/50	5.3	3.6	2.8
95/50	3.4	2.5	2.0
90/50	2.5	2.0	1.8
		TOC	
99/50	3.0	2.2	1.9
95/50	2.2	1.7	1.6
90/50	1.8	1.5	1.4

The daily 90/50 BOD ratio is 3.0, while the corresponding monthly ratio is 1.7. This indicates that a substantial day-to-day variation witnessed in plant performance is tempered when the variation is based on monthly data. For this reason, it is recommended that a 30 consecutive day period average be used as the time basis for the effluent guidelines. In addition, a 90% confidence limit should be used, in that the 90/50 values should be within a range typically observed in the past as being reasonable when treatment plant data were anlyzed statistically.

The following effluent variability factors are proposed for the following pollutant parameters and time intervals:

Parameter	Average Thirty Consecutive Day Effluent Adjustment Factor[1]	Weekly Effluent Adjustment Factor[1]	Daily Effluent Adjustment Factor[1]
BOD5	1.7	2.0	3.0
COD	1.8	2.0	2.5

[1] 90/50 ratio of confidence limits

Both of these treatment plants utilize activated sludge and were designed based on the criteria presented in Table XIII-2. 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.

TABLE XIII-2

Summary of Plant Design Criteria

Description	Plant A	Plant B
Flow - mgd	1.0	0.55
Primary Settling		
Detention Time - days	2.5	9.1
Aeration Basin		
Sludge Recycle - percent forward flow	50	100
Detention Time - hours including recycle	20	36
Aeration Equipment - Hp/M.G.	450	540
Final Clarifier		
OFR - gpd/sq.ft.	425	150
SWD - ft.	10	10
Diameter - ft.	40	40
Flotation Unit		
Solids - lbs/sq.ft./day	-	7.5
Detention Time - hours	-	2.5
Polymer Dosage - mg/l	-	100
Polishing Pond		
Detention Time - days	0.6	118
.Aeration Equipment - Hp/M.G.	10	1.5

SECTION XIV

ACKNOWLEDGEMENTS

SECTION XV

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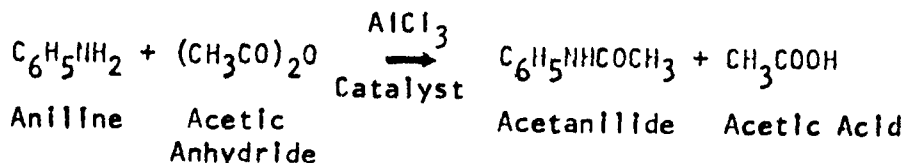
The terms defined here relate to common chemical conversions utilized extensively in the organic chemicals industry.

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, ROCOCl, or anhydrides, $(RCO)_2O$. The catlyst 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:

$$C_6H_5NH_2 + (CH_3CO)_2O \xrightarrow[\text{Catalyst}]{AlCl_3} C_6H_5NHCOCH_3 + CH_3COOH$$

Aniline   Acetic   Acetanilide   Acetic Acid
   Anhydride

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.

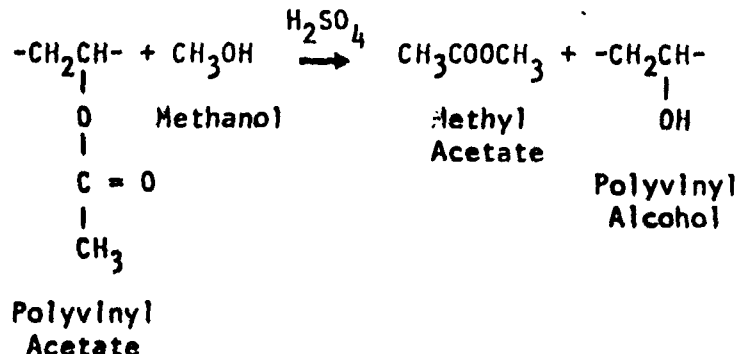## Alcoholysis (Transesterification)   Subcategory C

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:

$$RCOOR' + R''OH \underset{\longleftarrow}{\overset{H_2SO_4}{\rightleftharpoons}} RCOOR'' + R'OH$$
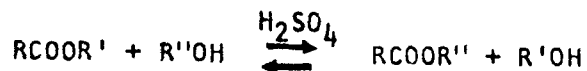
Transesterification is an equilibrium reaction. To shift the equilibrium to the right it is necessary to use a large excess of the alcohol whose ester is desired, or else remove one of the products from the reaction mixture. The second approach is used in most industrial applications, since in this way 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.

$$-CH_2CH- + CH_3OH \xrightarrow{H_2SO_4} CH_3COOCH_3 + -CH_2CH-$$

```
      |                                              |
      O      Methanol           Methyl              OH
      |                         Acetate
      C = O                                    Polyvinyl
      |                                         Alcohol
      CH_3

Polyvinyl
Acetate
```

Although there are hundreds of acetate groups in every modecule 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
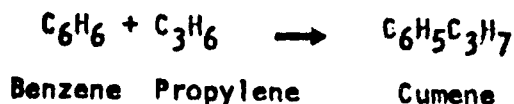
The reaction is classified within Subcategory C as it is conducted with an aqueous catalyst system.

Alkylation   Subcategories A and B
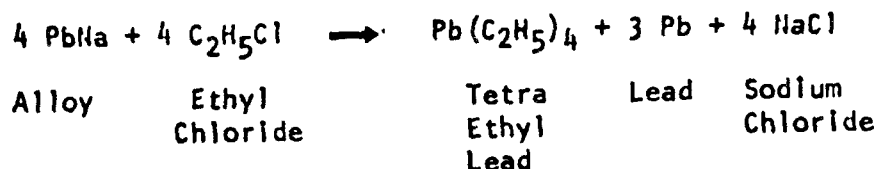
Alkylation refers to the addition of an aliphatic group to another molecule. The media in which this reaction is accomplished can be vapor or liquid phase, as well as aqueous or non-aqueous.

Benzene is alkylated in the vapor phase over a solid catalyst (silica-alumina impregnated with phosphoric acid) with propylene to produce cumene.

$$C_6H_6 + C_3H_6 \longrightarrow C_6H_5C_3H_7$$

Benzene Propylene   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.

$$4\ PbNa + 4\ C_2H_5Cl \longrightarrow Pb(C_2H_5)_4 + 3\ Pb + 4\ NaCl$$

Alloy   Ethyl   Tetra   Lead   Sodium
           Chloride   Ethyl   Chloride
                            Lead

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:

$$C_6H_5NH_2 + 2\ CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2\ H_2O$$

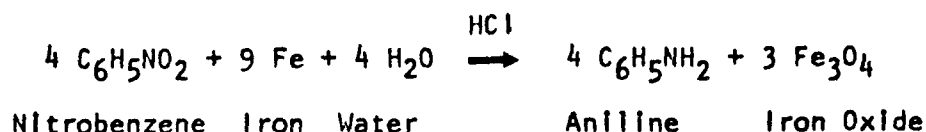| Aniline | Methanol | Dimethylaniline | Water |
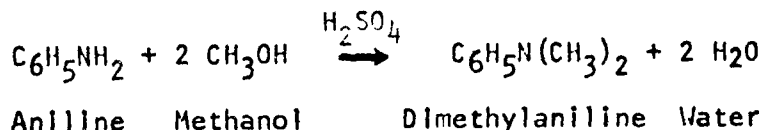
Aniline, with an excess of methanol and aqueous sulfuric acid, is heated in an autoclave. The dealkylated product is discharged through a cooling coil, neutralized, and vacuum distilled. This is again typical of the chemical conversions with Subcategory D.

Amination by Reduction   Subcategories B and D

Amination by reduction involves the formation of an amino group (-NH$_2$) through the reduction of a nitro group (-NO$_2$). 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:

$$4\ C_6H_5NO_2 + 9\ Fe + 4\ H_2O \xrightarrow{HCl} 4\ C_6H_5NH_2 + 3\ Fe_3O_4$$

| Nitrobenzene | Iron | Water | Aniline | Iron Oxide |

This batch reaction for reducing nitrobenzene with iron to aniline is being replaced by the continuous vapor phase reduction shown below:

$$C_6H_5NO_2 + 3\ H_2 \longrightarrow C_6H_5NH_2 + 2\ H_2O$$

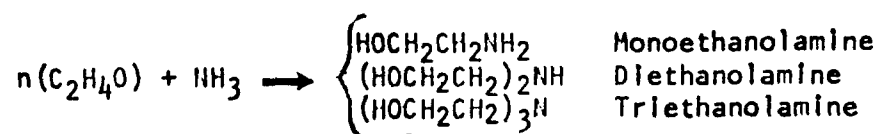| Nitrobenzene | Hydrogen | Aniline | Water |
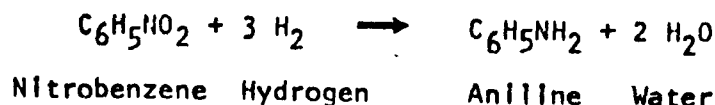
The reaction is conducted with a very short contact time in a tube packed with copper on SiO_2 as the catalyst. The hydrogen is adsorbed to the catalyst surface. Molecules of nitrobenzene are next adsorbed on the hydrogenated surface. The reaction products, aniline and water vapor, then desorb from the 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:
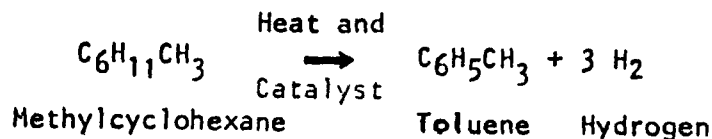
$$n(C_2H_4O) + NH_3 \longrightarrow \begin{cases} HOCH_2CH_2NH_2 & \text{Monoethanolamine} \\ (HOCH_2CH_2)_2NH & \text{Diethanolamine} \\ (HOCH_2CH_2)_3N & \text{Triethanolamine} \end{cases}$$

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:

$$C_6H_{11}CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat and}} C_6H_5CH_3 + 3 H_2$$

Methylcyclohexane   Toluene   Hydrogen

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:

$$2 \ C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

Ethanol   Ethyl Ether   Water
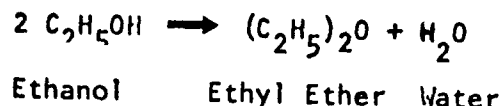
Esterification   Subcategory C

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:

$$CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Ethanol   Acetic Acid   Ethyl Acetate   Water
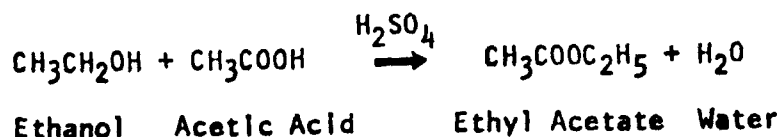
Continuous esterification reactions are considered within Subcategory C.
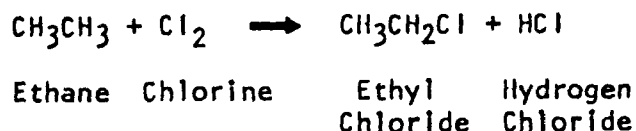
Friedel-Crafts Reactions   Subcategory A

Friedel-Crafts reactions involve the alkylation or acylation of an aromatic ring in the presence of such catalysts as $AICI_3$, BF_3, $SnCI_4$, 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 (CI_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.

$$CH_3CH_3 + CI_2 \longrightarrow CH_3CH_2CI + HCI$$

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:

$$C_2H_4 + Cl_2 \xrightarrow{C_2H_2Br_2} C_2H_2Cl_2$$

Ethylene   Chlorine   Ethylene Dichloride
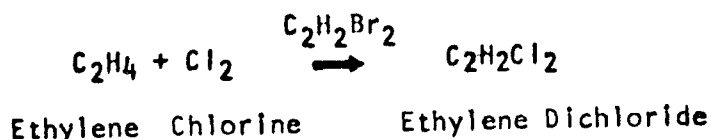
The chlorine gas is bubbled through a tank of liquid ethylene dibromide (catalyst), and the mixed vapors are sent to a chlorinating tower where they meet a stream of ethylene. The products from the tower pass through a partial condenser, followed by a separator, with the crude ethylene dichloride passing 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 (OXO 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:

$$C_3H_6 + CO + H_2 \xrightarrow{HCo(CO)_4} C_4H_8O$$

Propylene Carbon   Hydrogen   n-Butyraldehyde
           Monoxide
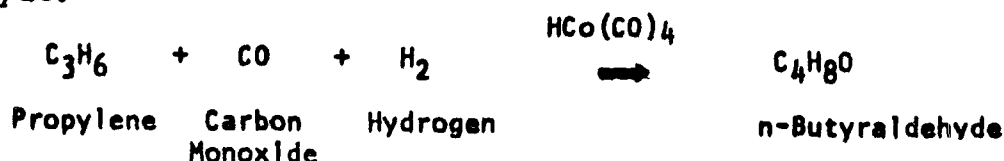
The reaction itself is nonaqueous. However, the regeneration of the cobalt carbonyl catalyst complex requires extensive usage of aqueous solutions of sodium carbonate and sulfuric acid. This aqueous catalyst regeneration causes the hydroformylation reaction to be classified in Subcategory C.

## 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.
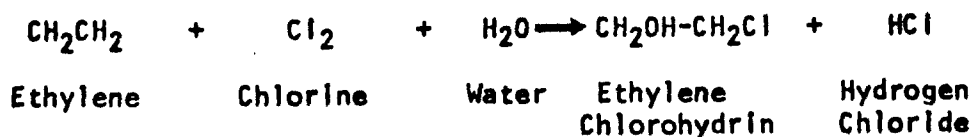
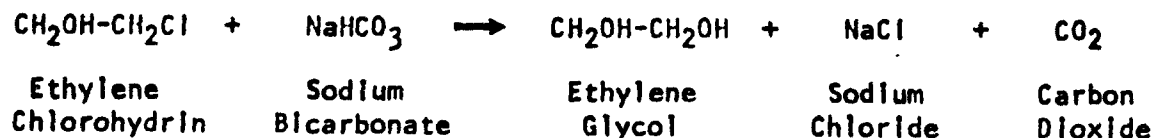## Hydration (Hydroylsis)   Subcategories B and C

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 corresponsing vapor phase routes are carried out over solid H_3PO_4 catalysts. The equation shown for ethanol can be done either way:

$$C_2H_4 \;+\; H_2O \longrightarrow C_2H_5OH$$
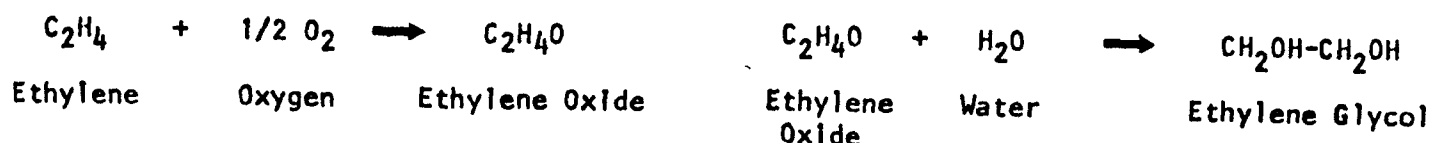
Ethylene   Water   Ethanol
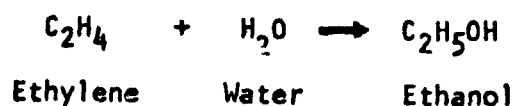
Ethylene glycol and ethylene oxide can also be produced by either a liquid or vapor phase route. The liquid reaction involves the formation of ethylene chlorohydrin, which is produced by the reaction of aqueous chlorine with ethylene.

$$CH_2CH_2 \;+\; Cl_2 \;+\; H_2O \longrightarrow CH_2OH\text{-}CH_2Cl \;+\; HCl$$

Ethylene   Chlorine   Water   Ethylene   Hydrogen
                                            Chlorohydrin   Chloride

The ethylene chlorohydrin is treated with aqueous sodium bicarbonate solution to produce ehtylene glycol.

$$CH_2OH\text{-}CH_2Cl \;+\; NaHCO_3 \longrightarrow CH_2OH\text{-}CH_2OH \;+\; NaCl \;+\; CO_2$$

Ethylene   Sodium   Ethylene   Sodium   Carbon
Chlorohydrin   Bicarbonate   Glycol   Chloride   Dioxide

More recently the chlorohydrin route to ethylene oxide and glycol has been replaced by the reaction of ethylene with oxygen and water:

$$C_2H_4 \;+\; 1/2\,O_2 \longrightarrow C_2H_4O \qquad\qquad C_2H_4O \;+\; H_2O \longrightarrow CH_2OH\text{-}CH_2OH$$

Ethylene   Oxygen   Ethylene Oxide   Ethylene   Water   Ethylene Glycol
                                                 Oxide

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.
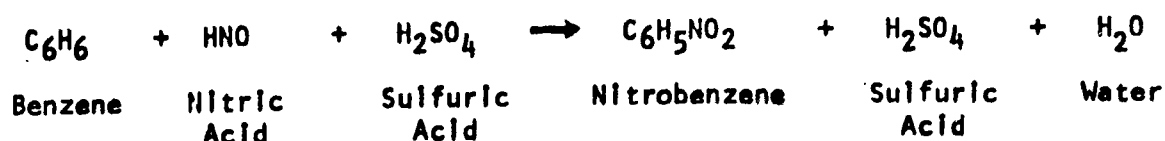

Neutralization   Subcategory C

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 liquidliquid 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:

$$C_6H_6 \;+\; HNO \;+\; H_2SO_4 \;\longrightarrow\; C_6H_5NO_2 \;+\; H_2SO_4 \;+\; H_2O$$

Benzene   Nitric Acid   Sulfuric Acid   Nitrobenzene   Sulfuric Acid   Water

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.

$$CH_3CHO \;+\; 1/2\;O_2 \;\longrightarrow\; CH_3COOH$$

Acetaldehyde   Oxygen   Acetic Acid
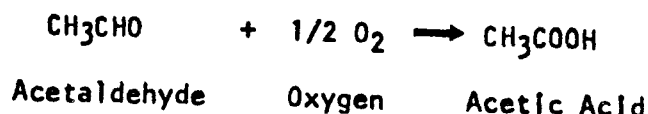
Alternatively, acetadehyde can be produced by the vapor phase oxidation of ethanol over a silver gauze catalyst.

$$C_2H_5OH \ + \ 1/2 \ O_2 \ \longrightarrow \ H_3CHO \ + \ H_2O$$

Ethanol   Oxygen   Acetaldehyde   Water
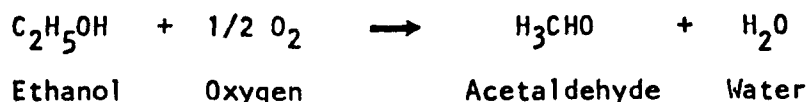
Depending on whether the reaction is vapor or liquid phase it may be considered within Subcategory B or C.

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:

$$CH_3CH_2CH_3 \ \longrightarrow \ CH_2CH_2 \ + \ CH_4$$

Propylene   Ethylene   Methane
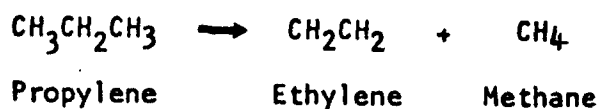
The reactions are all carried out in the vapor phase at very high temperature. Steam is usually added as a diluent to prevent the formation of coke. For this reason, the reactions are considered within Subcategory B.