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DEVELOPMENT DOCUMENT FOR
EFFLUENT LIMITATIONS GUIDELINES
AND STANDARDS OF PERFORMANCE

ORGANIC CHEMICALS INDUSTRY
PHASE II

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FOR UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
UNDER CONTRACT NUMBER 68-01-1509

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NOTICE

The attached document is a DRAFT CONTRACTOR'S REPORT. It includes technical information and recommendations submitted by the Contractor to the United States Environmental Protection Agency ("EPA") regarding the subject industry. It is being distributed for review and comment only. The report is not an official EPA publication and it has not been reviewed by the Agency.

The report, including the recommendations, will be undergoing extensive review by EPA, Federal and State agencies, public interest organizations and other interested groups and persons during the coming weeks. The report and in particular the contractor's recommended effluent limitations guidelines and standards of performance are subject to change in any and all respects.

The regulations to be published by EPA under Sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended, will be based to a large extent on the report and the comments received on it. However, pursuant to Sections 304(b) and 306 of the Act, EPA will also consider additional pertinent technical and economic information which is developed in the course of review of this report by the public and within EPA. EPA is currently performing an economic impact analysis regarding the subject industry, which will be taken into account as part of the review of the report. Upon completion of the review process, and prior to final promulgation of regulations, an EPA report will be issued setting forth EPA's conclusions concerning the subject industry, effluent limitations guidelines and standards of performance applicable to such industry. Judgments necessary to promulgation of regulations under Sections 304(b) and 306 of the Act, of course, remain the responsibility of EPA. Subject to these limitations, EPA is making this draft contractor's report available in order to encourage the widest possible participation of interested persons in the decision making process at the earliest possible time.

The report shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the Contractor who studied the subject industry and prepared the information and recommendations. It cannot be cited, referenced, or represented in any respect in any such proceedings as a statement of EPA's views regarding the subject industry.

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U.S. Environmental Protection Agency   ii

ABSTRACT

A study of the secondary products segment of the organic chemicals manu-
facturing industry was conducted by Roy F. Weston, Inc. for the United
States 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 its proposed regulations were undertaken
in fulfillment of Sections 304, 306, and 307 of the Federal Pollution
Control Act Amendments of 1972.

For the purposes of this study, 54 product/process segments of the in-
dustry were investigated. Sufficient data on process raw waste load
were obtained for 44 of these so that effluent limitations guidelines
could subsequently be developed. This study was the second part of a
two phase effort. In the first phase, process raw waste loads and ef-
fluent limitations guidelines were established for 40 product/process
groups. Total coverage of the industry has now been extended to include
84 groups.

In both studies, the product/process groups were put into four major
subcategories, based on process technology as related to contact wastes
usage. These industry segments were further subcategorized on the
basis of the quantities of pollutants, measured as the process raw waste
load. The first phase of this study focused on major organic products
and used six subcategories. This second phase focused on secondary
products and used thirteen subcategories.

Separate effluent limitations guidelines have been developed for each
subcategory on the basis of treatment and control technologies. Sup-
portive data and the rationale for development of the proposed effluent
limitations guidelines and standards of performance are contained in
this report.

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SECTION 1

CONCLUSIONS

The complex task of establishing effluent guidelines limitations for the Organic Chemicals Industry required that the industry be divided into a two-phase study. A draft of the Phase 1 development document was issued in June 1973. The document recommended the use of process-oriented sub-categories which were developed as follows:

Subcategory A: Nonaqueous Processes

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

Subcategory B: Processes with Process Water Contact only 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 reactants 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 non-continuous production equipment constitutes a major source of wastewater.

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The recommended effluent limitations were computed on a sliding scale employing a flow/pollutant relationship. During the EPA review procedure, it was decided that the flow parameter was too cumbersome for use in large chemical complexes. The Contractor's approach was replaced with a procedure utilizing 6 subcategories, namely A, B1, B2, C1, C2 and D. The BPCTCA-RWL data for each subcategory was based on median RWL calculations. The previously recommended effluent guidelines were recomputed on the basis of the new subcategories, and the new limitations were published recently in the Federal Register. The supporting development document was published by EPA in December 1973.

The Contractor has been directed by EPA Effluent Guidelines Division to handle the Phase 2 data independently of the Phase 1 data; data handling should complement the previous EPA development document of December, 1973.

With this background, the data from 44 product/processes were grouped into 13 subcategories, e.g. B3, B4, B5, etc. The product mix within each major subcategory is based on order-of-magnitude differences between each subcategory's mean RWL.

Individual effluent limitations were recommended for all 13 subcategories for BOD and COD. TSS effluent concentrations were recommended for each technology level, i.e. BPCTCA, BADCT, and BATEA. In order that excessively stringent effluent limitations are not implemented, minimal pollutant concentrations are recommended as being indicative of a technology level as follows:

BPCTCA	20 mg/l	BOD
BATEA	10 mg/l	BOD
	50 mg/l	COD

Other RWL parameters were considered during the study, and specific products/pollutants which might be inhibitory or incompatible with BPCTCA treatment technology were cited in Section VI.

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 may require pH control and equalization in order to control variable waste loads, and also may require clarification with the addition of chemicals to aid in removing suspended solids. 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 may be inhibitory to the biological waste treatment system.

Best available technology economically achievable, BATEA, (1983 Standard) is based upon the addition of activated carbon after biological treatment. This technology is based upon substantial reductions of dissolved or-ganics 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.

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

In conclusion, effluent limitations were derived on the basis of the maximum for 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 consider the normal variations of exemplary designed and operated waste treatment systems.

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SECTION II

RECOMMENDATIONS

Effluent limitations commensurate with the best practicable control technology currently available are presented for each industrial sub-category of the organic chemicals manufacturing industry. Major product/process segments of the industry which are applicable to these limitations are listed in Table 2-1, and effluent limitations for the 1977 standard (BPCTCA) are presented in Table 2-2. It should be noted that process wastewaters subject to these limitations include all contact process water but do not include non-contact sources such as boiler and cooling water blowdown, laboratories, and other similar sources.

Implicit in BPCTCA RWL data is the segregation of non-contact wastewaters from process wastewaters and the maximum utilization of applicable in-plant pollution abatement technology in order to minimize capital expenditures for end-of-pipe wastewater treatment facilities.

End-of-process technology for BPCTCA involves the application of biological treatment as typified by activated sludge, trickling filters, aerated lagoons, or anaerobic lagoons. Equalization with pH control and oil separation may be required in order to provide optimal as well as a uniform level of treatment. Chemical flocculation aids, when necessary, should be added to the clarification system in order to control suspended solids levels.

Effluent limitations to be attained by the application of the best available technology economically achievable are presented in Table 2-3 for the major product/process segments listed in Table 2-1. End-of-process treatment for BATEA includes the addition of activated carbon systems to biological waste treatment processes. Exemplary in-process controls, as discussed in the later sections 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 2-4.

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Table 2-1

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

Subcategory A	Process Description
Cumene	Alkylation of Benzene by Propylene
p-Xylene	Isomerization, Crystallization, and Filtration of Mixed Xylenes

Subcategory B
B-3 Products

Chloromethanes	Chlorination of methyl chloride and Methane mixture
Chlorotoluene	Chlorination of Toluene
Diphenylamine	Deamination of aniline
Perchloroethylene	Chlorination of chlorinated hydrocarbons
Phthalic Anhydride	Oxidation of naphthalene
Tricresyl Phosphate	Condensation of Cresol and Phosphorus Oxychloride

B-4 Products

Adiponitrile	Chlorination of Butadine
Benzoic acid and Benzaldehyde	Catalytic oxidation of Toluene with Air
HMDA	Hydrogenation of Adiponitrile
Methyl Chloride	Esterification of Methanol with Hydrochloric Acid

B-5 Products

HMDA	Ammonolysis of 1,6-Hexanediol
Maleic anhydride	Oxidation of Benzene
Methyl Ethyl Ketone	Dehydrogenation of Sec. Butyl Alcohol

Subcategory C
C-3 Products

Cyclohexane Oxime	Hydroxylamine Process
Isopropanol	Hydrolysis of propylene

C-4 Products

Formic acid	Hydrolysis of Formamide
Oxalic acid	Nitric acid oxidation of carbohydrates

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C-5 Products

Calcium Stearate	Neutralization of Stearic acid
Caprolactam	DSM Caprolactam Process
Hydrazine Solutions	Raschig Process and Formaldehyde
Isobutylene	Extraction from a mixture of C_4 Hydrocarbons
Propylene Oxide	Chlorohydrin Process
Sec. Butyl Alcohol	Sulfonation and Hydrolysis of Mixed Butylenes

C-6 Products

Acrylonitrile	Ammoxidation of Propylene
Hexamethylene Tetramine	Synthesis with Ammonia

C-7 Products

p-Aminophenol	Catalytic reduction of Nitrobenzene
Cresol, Synthetic	Methylation of Phenol
Pentaerythritol	Aldehyde Condensation
Saccharin	Synthesis from Phthalic Anhydride Derivatives

Subcategory D
D-1 Products

o-Nitroaniline	Ammonolysis of o-Nitrochlorobenzene
p-Nitroaniline	Ammonolysis of p-Nitrochlorobenzene

D-2 Products

Citronellol and Geraniol	Citronella Oil Distillation
Fatty acids	Hydrolysis of Natural Fats
Fatty acid derivatives	Esterification, Amination, etc.
Ionone and Methyl Ionone	Condensation and Cyclization of Citral

D-3 Products

Plasticizers	Condensation of Phthalic Anhydride

D-4 Products

Citric acid	Fermentation of Molasses
Dyes and Intermediates	Batch Manufacture
Naphthenic acid	Extraction and acidification of Caustic sludge from Petroleum refinery
Pigments	Diazotization and coupling of amine, sulfuric, etc.
Monosodium Glutamate	Fermentation of Beet Sugar and Molasses
Tannic acid	Extraction of Natural Vegetable Matter

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Table 2-2

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[1]		
	Average Daily	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum Value For Any One Day
Subcategory A2			
BOD[2]	0.000892	0.00178	0.00401
COD	0.00388	0.00776	0.0132
Subcategory B			
B3 Products			
BOD[2]	0.0457	0.0934	0.210
COD	0.927	1.94	3.15
B4 Products			
BOD[2]	1.33	2.66	5.99
COD	20.2	40.4	68.7
B5 Products			
BOD[2]	9.6	19.2	43.2
COD	97.9	135.8	231.
Subcategory C			
C3 Products			
BOD[2]	0.0796	0.159	0.358
COD	1.44	2.88	4.90
C4 Products			
BOD[2]	1.18	2.36	5.31
COD	4.43	8.86	15.1
C5 Products			
BOD[2]	1.79	3.58	8.06
COD	29.7	50.4	101.
C6 Products			
BOD[2]	5.74	11.5	25.8
COD	63.2	126.	215.
C7 Products			
BOD[2]	36.6	73.2	165.
COD	365.	730.	1,240.
Subcategory D			
D1 Products			
BOD[2]	3.08	6.16	13.9
COD	28.5	57.0	96.9
D2 Products			
BOD[2]	2.30	4.60	10.4
COD	21.0	42.0	71.4
D3 Products			
BOD[2]	4.30	8.60	19.4
COD	25.6	51.2	87.0
D4 Products			
BOD[2]	19.8	39.6	89.1
COD	403.	806.	1,370.

Average Monthly Effluent Limitations Guidelines for TSS = 65 mg/l

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[1] kg/kkg production is equivalent to lb/1000 lb production.
[2] Controlling design Parameter.

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Table 2-3

Effluent Limitations for the Best Available
Technology Economically Achievable (BATEA)

Organic Chemical Manufacturing Industry
Major Product-Processes By Subcategory

Effluent Characteristics	Effluent Limitations - kg/kkg Production[1]		
	Average Daily	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days	Maximum Value For Any One Day
Subcategory A2			
BOD	0.000443	0.000886	0.00199
COD	0.0012	0.0024	0.00408
Subcategory B			
B3 Products			
BOD	0.0234	0.0468	0.105
COD	0.287	0.574	0.976
B4 Products			
BOD	0.133	0.266	0.599
COD	6.26	12.5	21.3
B5 Products			
BOD	0.960	1.92	4.32
COD	21.1	42.2	71.7
Subcategory C			
C3 Products			
BOD	0.00796	0.0159	0.0358
COD	0.446	0.892	1.52
C4 Products			
BOD	1.18	2.36	5.31
COD	4.43	8.86	15.1
C5 Products			
BOD	0.179	0.358	0.806
COD	9.21	18.4	31.3
C6 Products			
BOD	0.574	1.15	2.58
COD	19.6	39.2	66.6
C7 Products			
BOD	3.66	7.32	16.5
COD	113.	226.	384.
Subcategory D			
D1 Products			
BOD	1.54	3.08	6.93
COD	8.84	17.7	30.1
D2 Products			
BOD	0.230	0.460	1.04
COD	6.51	13.0	22.1
D3 Products			
BOD	0.430	0.860	1.94
COD	7.94	15.9	27.0
D4 Products			
BOD	1.98	3.96	5.91
COD	125.	250.	425.

Average Monthly Effluent Limitations Guidelines for TSS = 15 mg/l

[1]kg/kkg production is equivalent to lb/1000 lb production.

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Table 2-4

Standards of Performance for New Organic Chemicals Manufacturing Sources
Major Product-Processes By Subcategory

Effluent Characteristics	Effluent Limitations - kg/kkg Production[1]		
		Maximum Average of Daily Values for Any Period of	Maximum Value For Any One
Subcategory A2	Average Daily	Thirty Consecutive Days	Day
BOD	0.000443	0.000886	0.00199
COD	0.00310	0.0062	0.014
Subcategory B			
B3 Products			
BOD	0.0234	0.0468	0.105
COD	0.742	1.48	2.52
B4 Products			
BOD	1.11	2.22	5.0
COD	16.2	32.4	55.1
B5 Products			
BOD	7.97	15.9	35.9
COD	54.3	108.	185.
Subcategory C			
C3 Products			
BOD	0.066	0.132	0.297
COD	1.15	2.30	3.91
C4 Products			
BOD	1.18	2.36	5.31
COD	4.43	8.86	15.1
C5 Products			
BOD	1.49	2.98	6.71
COD	23.8	47.6	80.9
C6 Products			
BOD	4.76	9.52	21.4
COD	50.6	101.	172.
C7 Products			
BOD	30.4	60.8	137.
COD	292.	584.	993.
Subcategory D			
D1 Products			
BOD	1.54	3.08	6.93
COD	22.8	45.6	77.5
D2 Products			
BOD	1.91	3.82	8.60
COD	16.8	33.6	57.1
D3 Products			
BOD	3.57	7.14	16.1
COD	20.5	41.	69.7
D4 Products			
BOD	16.4	32.8	73.8
COD	322.	644.	1,095.

Average Monthly Effluent Limitations Guidelines for TSS = 15 mg/l

[1] kg/kkg production is equivalent to lb/1000 lb production.

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SECTION III

INTRODUCTION

The Organic Chemicals Industry was originally defined to include only those commodities listed under SIC 2815 (Cyclic Crudes and Intermediates) and SIC 2818 (Industrial Organic Chemicals Not Elsewhere Classified), and those manufacturers included in industry group 281. Although these boundaries may seem practical for purposes of dividing U.S. private industry into manageable point-source categories for the development of effluent limitations guidelines, serious problems arise when one attempts to "force fit" an industry as diverse as this one into such constraints based on SIC code.

Tables 3-1 and 3-2 show 260 materials listed under SIC 2815 and 2818. The lists are somewhat ambiguous in that many specific commodities (e.g. ethylene, adiponitrile, hydrazine, synthetic vanillin, sodium sulfoxalate formaldehyde, etc.) are in the same list with references to very large families of products (e.g. synthetic organic dyes, coal tar distillates, organic pigments, alcohols, flavors, enzymes, etc.).

It must be understood that these lists are developed by the United States Department of Commerce and are oriented toward the collection of economic data related to gross production, sales, and unit costs. They are not related to the true nature of this industry in terms of actual plant operations, production, or considerations associated with water pollution control. As such, they do not provide a realistic or definitive set of boundaries for this study. It should also be noted that all the major producers of organic chemicals are not included in the 281 group. Major companies not in group 281 are covered in such diverse classifications as petroleum refining, meat and dairy products, and photographic and optical equipment.

Some appreciation of the number of distinct commodities which are manufactured and subsequently offered for sale can be gained by examining the OPD CHEMICAL BUYERS DIRECTORY, which lists over 5,000 organic chemicals.

It must also be understood that the exact nature of the manufacturing operations at any specific facility is unique and characteristic only of that facility. There are very few, if any, organic chemicals plants which manufacture one product by a single process. Instead, almost all plants are multi-product/process facilities where the final mix of products shipped from each plant is unique. In some cases, the actual number of commodities produced can be in the thousands (such as a batch chemicals complex), while other facilities manufacture only two or three high-volume products.

Table 3-1
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
    distillation
Benzoic acid
Benzol, product of coal tar
    distillation
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: ex-
    cept 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
    distillation
Creosote oil, product of coal tar
    distillation
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

Table 3-1
(continued)

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
    distillation
Pulp colors, organic
Quinoline dyes
Resorcinol
Scarlet 2 R lake
Stilbene dyes
Styrene
Styrene monomer
Tar, product of coal tar dis-
    tillation
Toluene, product of coal tar
    distillation
Toluol, product of coal tar
    distillation
Toluidines
Toners (reduced or full strength
    organic colors)
Vat dyes, synthetic
Xylene, product of coal tar
    distillation
Xylol, product of coal tar
    distillation

Table 3-2
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: de-
  natured (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
  propionate
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
Cream of tartar
Cyclopropane
DDT, technical
Decahydronaphthalene
Dichlorodifluoromethane
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 3-2
(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 alco-
   hol)
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, or-
   ganic: accelerators and anti-
   oxidants--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 salts
Tartrates
Tear gas
Terpineol
Tert-butylated bis (p-phenoxy-
   phenyl) ether fluid

Table 3-2
(continued)

Tetrachloroethylene
Tetraethyl lead
Thioglycolic acid, for permanent
    wave lotions
Trichloroethylene
Trichloroethylene stabilized,
    degreasing
Trichlorophenoxyacetic acid
Trichlorotrifluoroethane tetrachloro-
    difluoroethane isopropyl alcohol
Tricresyl phosphate
Tridecyl alcohol
Trimethyltrithiophosphite (rocket
    propellants)
Triphenyl phosphate
Urea
Vanillin, Synthetic
Vinyl acetate

Furthermore, the production quantities associated with the product mix shipped from a plant are not necessarily a true indication of the extent or type of manufacturing activities carried out within that plant. In many cases, several products are produced captively within the plant and subsequently utilized as feedstocks in the production of those products ultimately shipped from the plant.

These factors are worthy of consideration in that the water usage and subsequent water pollution caused by the Organic Chemicals industry are directly related to the specific nature of its diverse manufacturing processes. Analysis of these manufacturing processes is, therefore, the logical starting point for any study whose objective is the development of production-based effluent limitations guidelines.

In order to develop such production-based effluent limitations guidelines, it was necessary to utilize some "common denominator" which would relate diverse production activities (waste generating activities) with water pollution control technologies (waste treatment activities). The process raw waste load (RWL) was considered as the best tool for accomplishing this objective.

For purposes of this study, the process RWL is defined as the quantity of waste and pollutants generated by a manufacturing process, divided by the quantity of chemical product derived from the process. In this context, the process represents a unique set of chemical conversions and unit operations by which a specific feedstock is transformed into a specific set of products, co-products, and by-products. The quantities of water and pollutants are measured prior to any treatment for removal of pollutants. These quantities include all water which contacts chemicals within the process battery limits and excludes non-contact water associated with heating and cooling surface heat exchangers. This differentiation was drawn on the basis that oxygen-demanding hydrocarbon parameters (for which effluent limitations guidelines are subsequently developed) are associated primarily with such contact wastes. It is appreciated that surface run-off, tank drainage, and other sources outside the battery limits may also contribute to this type of pollution, but very little data are available to indicate the significance of these sources compared to actual process wastes.

A much more detailed discussion of the process RWL, contact and non-contact water usage, and the interactions of feedstocks, products, and associated chemical conversions and unit operations within the manufacturing plant context is given in the Development Document for Phase 1 of this study (EPA440/1-73/009).

During Phase 1, process RWL's were established for 40 product/process groupings considered to be the Major Organic Products in terms of the magnitude of their gross production. It was anticipated that data on many more product/process groups could be obtained by utilizing historic

monitoring data provided by manufacturers. However, industry could not provide useful data of this type because most previous sampling efforts considered only the unique combination of total plant wastes for each facility and could not be allocated on an individual product basis. Subsequently, the Phase 1 RWL data were obtained by field sampling in-dividual process facilities for periods of 3 to 5 days. The sampling periods were so limited because of the necessity to collect data on as wide a variety of product/processes as possible.

During Phase 2, 54 additional product/process groupings were sampled, with the data from 44 considered as adequate for establishment of mean-ingful process RWL's. This second group was defined as Secondary Organic Products in that they were commodities generally manufactured in smaller volumes than those surveyed in the Phase 1 study.

In order to complement the EPA development document, 13 additional sub-categories were established for the 44 groups for which data were ob-tained during the Phase 2 study. Effluent limitations were then calcu-lated for each of these sub-categories.

The development of these waste reduction factors is another item requiring preliminary comment. It was originally anticipated that these factors (relating to demonstrated treatment technologies commensurate with BPCTCA, BATEA, and BADCT) could be obtained from performance data on many operat-ing treatment plants in the Organic Chemicals Industry.

It was known that this industry did not have numerous wastewater treat-ment facilities; however, the original assumptions proved to be overly optimistic. Relatively few organic chemicals manufacturers provide substantial treatment of their wastewaters.

Information from the plant survey visits in both phases of this study, from previous industry surveys, and from Refuse Act permit applications was used to define the extent of treatment facilities in the organic chemicals industry. Approximately 80 percent of the industry's 600 pro-duction facilities provide no on-site treatment other than neutralization of their wastewaters. (It should be understood that many of these pres-ently discharge to municipal treatment systems.) Of the remainder, ap-proximately 10 percent provide miscellaneous physical treatment such as sedimentation, while approximately 10 percent provide biological treat-ment of some type.

Although not widely practiced, biological treatment as defined by the activated sludge process was considered as BPCTCA. The addition of ac-tivated carbon or a second biological stage with suspended solids removal by filtration was considered as BATEA, while the addition of a filtration step to the BPCTCA activated sludge process was considered as BADCT. These choices appear to be the most reasonable considering the lack of available data and diversity of wastes involved.

Reduction factors based upon the performance of existing biological systems and information available in the literature were the basis used to develop each technology level. These factors were uniformly applied to each of the mean RWL's for each of the 13 subcategories subsequently presented.

SECTION IV

INDUSTRY CATEGORIZATION

Discussion of the Rationale of Categorization

The goal of this study is to broaden the RWL data base and to further substantiate the Phase 1 subcategorization. The following is a synopsis of the subcategorization rationale which was thoroughly discussed in the Phase 1 study.

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

Manufacturing processes have been examined for the type of contact process water usage associated with each. Contact 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 mechanical devices such as steam-jet ejectors for drawing a vacuum on the process.

5. Water used as a quench or direct-contact coolant such as in a barometric condenser.

Non-contact flows not included in the RWL data include the following:

1. Sanitary wastewaters.

2. Boiler and cooling tower blowdowns or once-through cooling water.

3. Chemical regenerants from boiler feed water preparation.

4. Storm water runoff from nonprocess plant areas, e.g., tank farms.

The type and quantity of contact 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 and are discussed in the following text. Subcategories A, B, and C relate to continuous processes, while Subcategory D relates to batch processes.

Subcategory A: Continuous Non-Aqueous Processes

This group involves 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 variations caused only by spills or process upsets.

Subcategory B: Continuous Vapor-Phase Processes Where Process Water is Used as 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 decoking of catalyst. It appears feasible to reduce some process raw waste loads almost to zero through increased recycle and/or reuse of contact water in this subcategory.

Subcategory C: Continuous Liquid-Phase Reaction Systems

Liquid-phase reactions involve a catalyst in an aqueous medium such as dissolved or emulsified mineral salt, or acid/caustic solution. Continuous regeneration of the 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 for final purification or neutralization of products. Requirements for purging waste materials from the system may prevent process raw waste load from approaching zero.

Subcategory D: Batch Processes

Processes are carried out in reaction kettles equipped with agitators,
scrappers, 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 centri-
fuges are commonly used to separate solid products from liquid.
Where drying is required, air or vacuum ovens are used.   Cleaning
of non-continuous production equipment constitutes a major source of
wastewater.

Basis for Assignment to Subcategories

The categorization 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 subcate-
gory since 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 chemicals and manufacturing processes which
have been assigned to each of the four subcategories is provided in the
Phase 1 study.

It should be pointed out that the field sampling in Subcategory D for
fatty acids, dyes, pigments and plasticizers were based on end-of-pipe
sampling.   Therefore, the associated RWL flow data contains minimal
amounts of non-contact waters.   This is in contrast to other products
where non-contact waters were able to be excluded.

Product: Cumeme

Process: Alkylation of Benzene by Propylene

Process RWL Category: A

Chemical Reactions:

$$C_6H_5 + CH_3CH = CH_2 \xrightarrow[90\%]{H_3PO_4} C_6H_5CH\,(CH_3)_2$$

Benzene Propylene   Cumene
                                           (Isopropyl Benzene)

Typical Material Requirements:

	1000 Kg Cumene
Benzene	722 Kg
Propylene	389 Kg
Phosphoric Acid (SPA)	666 Kg

Cumene is an intermediate in the production of phenol. (Acetone and Acetophenone are co-products.) Cumene is also an excellent blending fuel in high-octane gasoline.

Although cumene is a naturally-occurring chemical, present in many crude oils, the commercial product is synthesized by the catalytic alkylation of benzene by propylene. The principal side reactions, depending on the catalyst system employed, include polyalkylation to form di- and tri-isopropyl-benzene, polymerization of a portion of the propylene, and the production of n-propylbenzene by isomerization.

Catalyst systems that have been used to produce cumene include such materials as sulfuric acid, hydrofluoric acid, boron trifluoride, silica, zinc chloride on alumina, and others. However, the two catalyst systems most commonly used for commercial production are aluminum chloride and solid phosphoric acid (SPA). The catalyst system used at the process plant visited during the field data collection program employed the SPA catalyst.

A typical flow diagram for the solid phosphoric acid process of producing cumene is illustrated in Figure 4-1. As shown, this process requires a reactor and three distillation columns - one for rejection of propane, one for the recycle of unreacted benzene, and the third to rerun the cumene product so as to reject a minor quantity of polyalkylated materials (mainly diisopropylbenzene). Yields obtained by this process are over 90% of stoichiometric values on both benzene and olefin.

The aluminum chloride process is similar to that illustrated for solid phosphoric acid but requires additional equipment for the drying of recycle streams and neutralization of the reactor products.

A mixture of propylene and propane is blended with both fresh and recycled benzene in a raw materials feed tank. Water (as steam condensate) at 100-150 ppm is injected into the reaction mixture, and the reaction mixture is feed to the top of a fixed-bed reactor, where the liquid trickles down through the catalyst bed. Steam (non-contact) is used to preheat the reaction mixture. The process is carried out in a continuous manner.

The reaction product (effluent from the reactor) is filtered; the water phase (<1.0 liter/day) is removed to a water drain. A depropanizer still receives the organic phase, and propane is separated out; the propane can be recycled to the reactor. Wastewater from the propane accumulator amounts to about 0.3 kg/1000 kg of product.

Unreacted benzene is removed in a benzene distillation column. The benzene is recycled with fresh benzene to the raw materials mix or feed tank. Bottoms from the "benzene column" contain cumene and higher alkyl-aromatics.

Cumene is removed as a product in the finishing still. Diisopropylbenzene is the major by-product removed as still bottoms.

The only continuous wastewater streams are from the benzene storage area, the wastewater following the propane accumulator (~0.3 liter/1,000 cumene produced), and the water phase from the filter following the reactor. This latter stream is an intermittent flow (<1.0 liter/day).

In newer processing plants, a combination air/water cooling system can greatly reduce the non-contact water requirement. This is illustrated as follows:

Cooling Water Circulation Requirement

With air cooling	24,200 liters/kkg product
Without air cooling	82,600 liters/kkg product

Contributions from storm water runoff, housekeeping, maintenance, water leaks, and small non-process streams in the cumene area amount to about 65,000 liters/day. Steam required to heat the distillation towers is 7,590 kg per 1000 kg of product.

Process RWL based on contact wastewater flows are indicated in the tabulation below:

PROCESS FLOW	
liters/kkg	0.334
gal/M lbs	0.04
BOD$_5$ RWL	
mg/liter[1]	180
kg/kkg[2]	0.0001
COD RWL	
mg/liter[1]	490
kg/kkg[2]	0.0001
TOC RWL	
mg/liter[1]	180
kg/kkg[2]	0.0001

[1] Raw waste concentrations are based on unit weight of pollutants per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutants per 1000 unit weights of product.

The raw waste load from cumene is minimal when expressed on a production basis. The very small contact process wastewater flows make it impractical to assign any specific effluent limitation to this process. However, it is recommended that an allowance be made for runoff from the process area. This should be done on an individual plant basis. Wastes of this type should be treated such that the BOD concentration is 20 mg/L or less. It should be noted that this plant (like all cumene plants) is only part of a large multi-process facility. As such, it would be more practical to calculate an allowance for runoff based on the entire plant.

FIGURE 4-1

CUMENE—ALKYLATION OF BENZENE BY PROPYLENE
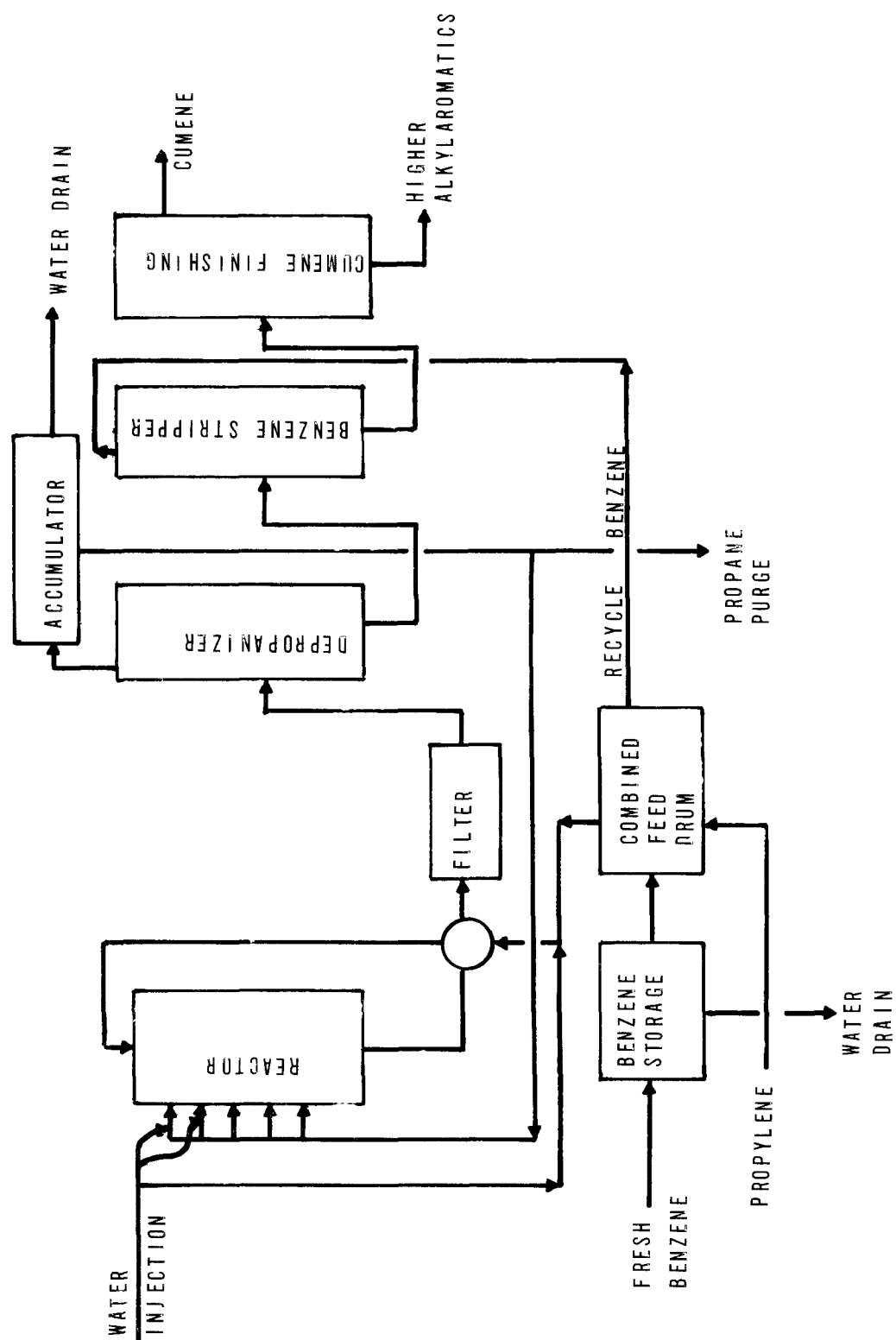
Product: p-Xylene

Process: Isomerization, Crystallization, and Filtration of
mixed Xylenes.

Process RWL Category: A

Because of the rapidly increasing demand for aromatic di-functional acids,
interest in pure xylene isomers have been growing. The C_8 aromatics found
in catalytic reformate consist roughly of 45 percent m-xylene, 20 percent
each o- and p-xylene, and 15 percent ethylbenzene. It so happens that
there is much less demand for m-xylene than for either of the other two
xylene isomers. Therefore, an isomerization unit, which is used to shift
methyl groups, converting m- and o-xylene to additional p-xylene, is
frequently built onto existing xylene-isomer separation facilities.

All p-xylene processes currently in operation use a combination of crystal-
lization and centrifugation to separate and purify p-xylene. The crystal-
lization step is usually in concert with o-xylene and/or ethylbenzene
removal and isomerization.

Figure 4-2 illustrates a typical two-stage crystallization process with
an isomerization unit.

Crystallization processes generally have the following steps in common,
although the techniques may vary:

- Feedstock drying
- First-stage crystallization (to about -80°F to -90°F)
- Recovery and melting of crystals from first stage
- Second-stage crystallization (to about 0°F to -25°F)
- Recovery and melting of crystals from the second stage

It is necessary to lower the water content in the feedstock to about 10
ppm, because water introduced into the process will freeze and cause
plugging of the centrifuges and rotary filters. All processes utilize
similar drying techniques, which usually consist of passing the feed
through alumina or silica-gel beds. One bed is on-stream while the
other bed is being regenerated either by electric heaters or with
jacketed steam.

The major differences in the processes are the mechanics of the crystal-
lization and separation facilities. Most processes use direct refrigera-
tion. The feed is precooled to about -40°F using propane and ethylene,
and the chilled feed is then sent to the first-stage crystallizer at an
operating temperature of -80°F to -90°F. The first-stage crystallizers
are usually scraped-surface tubular exchangers or tank crystallizers.
In each of these devices, an agitator with spring-loaded blades is used
to scrape the p-xylene crystals from the walls.

The crystals formed in the first stage are relatively small. Therefore, strict control of their size is necessary to insure that the centrifuges or filters used in their recovery will be of adequate size. Increasing the residence time in the first stage at a relatively low chilling rate enhances crystal growth.

Considerable advances have been made in the last several years in development of more efficient solid-liquid separation devices. Most modern domestic plants utilize continuous solid-bowl centrifuges in the first stage. Two bowls rotating horizontally at different speeds cause a helical screw motion on the outer surface of the inner bowl. The helical motion moves the solids from the settling slurry pool through a draining section and then emits a near-dry cake. The centrifuges can be regulated for bowl revolution speeds, bowl differential, and slurry pool depth. This can achieve p-xylene first-stage purity of 85%. The centrifuges can be fitted for backwash, but its benefit to p-xylene is doubtful. Crystals grown in the first stage tend to be long and thin monoclinic needles that drain with difficulty. As a result, a sizable portion of mother liquor tends to remain occluded in the interstices between the p-xylene crystals.

Crystals from the first stage are melted (or partially melted) and re-crystallized at about -25°F. The second-stage crystallizers are similar to the first-stage units. The second-stage crystals tend to be cylindrical in shape, approximately 200 X 360 microns, and drain more easily. Furthermore, the viscosity of the mother liquor in the second stage is about 1 cp (compared to 5 cp in the first stage); this difference in viscosity enhances the drainage rate. Also, a pusher-plate mechanism is available, and this tends to increase the drainage rate in the exit section of the crystallizer. About 99.5% pure p-xylene is obtained from this type of operation.

The filtrates from the first- and the second-stage liquid-solid separation are sent to the isomerization reactor after mixing with hydrogen gas. In the reactor, m-xylene is isomerized over a platinum catalyst into a equilibrium mixture of the three isomers, which is then recycled through the p-xylene crystallization steps. The isomerization reaction is run to extinction, that is, only the para isomer of xylene is withdrawn from the manufacturing operation. The hydrogen gas is required to provide the hydrogen atmosphere necessary for conducting the xylene isomerization process and is generally produced on the site. Consequently, the isomerization and the hydrogen facilities are an integral part of the p-xylene process.

Other than spills and pump leakages, the major sources of wastewater are the regeneration water used during decoking of catalyst beds and the steam drum washdown from the hydrogen plant. These streams are inter-mittent, and the amounts are insignificant. In addition, the monoethanol-amine (MEA) contaminated wastewater from the hydrogen plant is difficult to treat biologically, and is usually hauled off-site for deep-well dis-posal.

During the sampling visits, only one (out of three) plant was accessible for sampling, and the averages of four sets of composite samples are presented in the tabulation below:

PROCESS FLOW		
liters/kkg		44.3
gals/M lb		5.3
BOD_5 RWL		
mg/liter[1]		238
kg/kkg[2]		0.01
COD RWL		
mg/liter[1]		580
kg/kkg[2]		0.025
TOC RWL		
mg/liter[1]		159
kg/kkg[2]		0.007

[1]Raw waste concentrations are based on unit weight of pollutants per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutants per 1000 unit weights of product.

As with the cumene processes, it is not considered practical to establish a single-value effluent limitation for the production of p-xylene as previously described. Instead, it is recommended that waste allocation assigned to this process be related to runoff or drainage from the process area. Such an allocation should be based on treating these wastewaters to a BOD concentration of 20 mg/L. It should also be noted that p-xylene plants do not exist as separate entities but rather are part of a facility manufacturing other aromatic chemicals or oxidized product acids, such as terephthalic acid.

FIGURE 4-2

PARA-XYLENE, ISOMERIZATION; CRYSTALLIZATION, AND FILTRATION OF MIXED-XYLENE
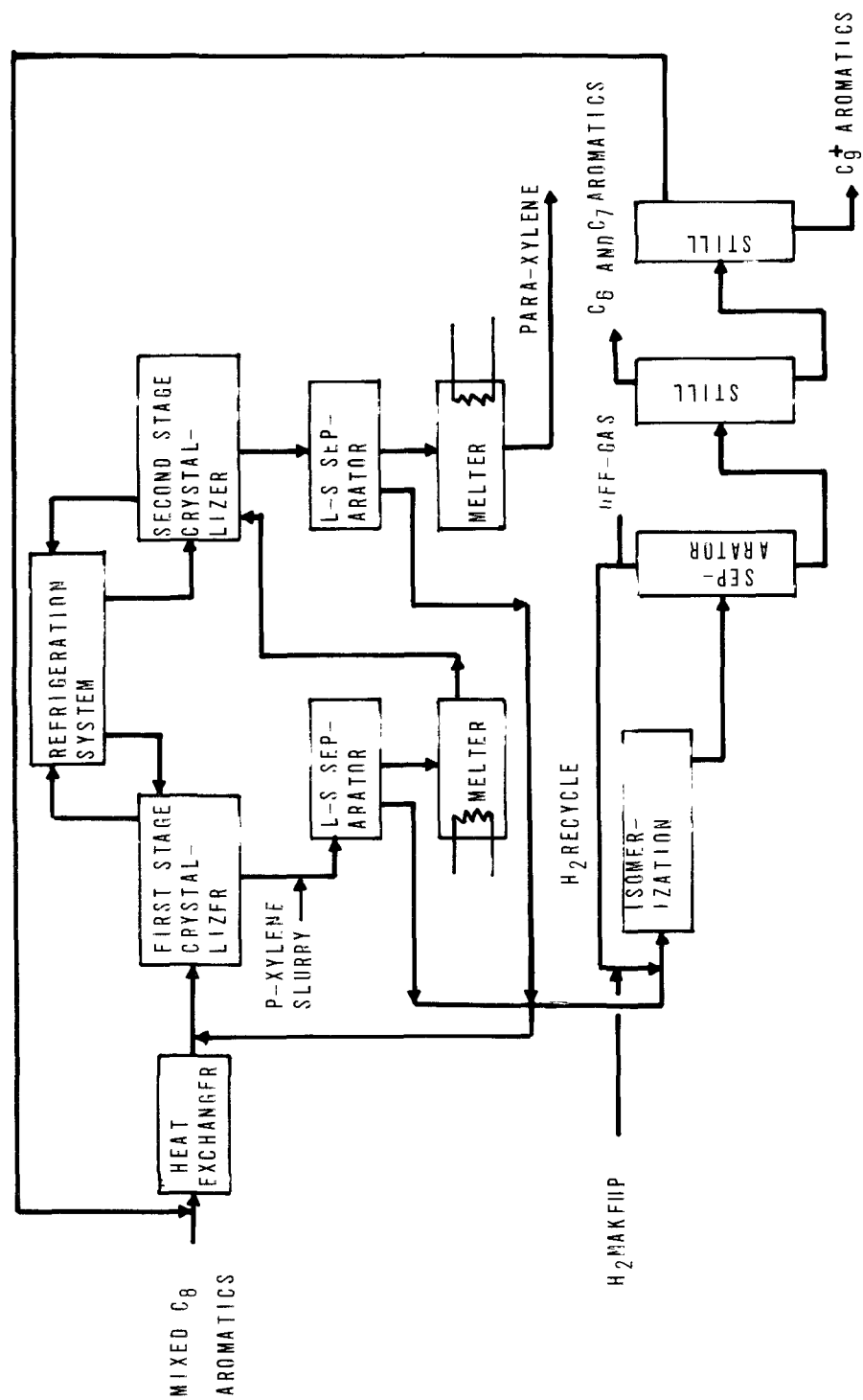
Product: BTX (Benzene, Toluene and Xylene)

Process: Extraction with Diethylene Glycol (Licensed UOP Process)

Process RWL Category: A

Chemical Reactions: None (Liquid - Liquid Extraction)

This process is a licensed (UOP) extraction process that handles both
reformate charges as well as pyrolysis gasoline. The reformate charge
(naphtha feed) is first fractionated, and only the intermediate fraction
is charged to the extraction unit. The heavy and light ends from the
fractionator are sent to motor gasoline production. The two sources of
feed (reformate and pyrolysis gasoline) are charged into the extraction
column, along with the extraction solvent (diethylene glycol). The raf-
finate is stripped of any carryover solvent and sent back to the refinery.
The extract is treated to remove the solvent and then fractionated to
obtain (primarily) benzene and toluene. No attempt is made to recover
any xylenes, much less separate them in this unit. The main sources of
water pollution are the final wash waters of the sulfiner unit, the glycol
recovery unit, and pump cooling water.

The product/process has been investigated in Phase I of this study, and
the detailed process description and process flow diagram can be found
on Pages 86-88 of EPA's document, EPA 440/1-73/009 (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) published December, 1973.

The process RWL calculated from flow measurements and analyses of waste-
water samples obtained in the Phase II survey period are shown in the
tabulation below:

| | Plant 1 | | | Plant 2 |
	Sample Period #1	Sample Period #2	Sample Period #3	Sample Period #1
PROCESS FLOW				
liters/kkg	933	933	933	312
gals/M lbs	112	112	112	37.4
BOD_5 RWL				
mg/liter[1]	34	26	34	2990
kg/kkg[2]	0.032	0.025	0.032	0.92
COD RWL				
mg/liter[1]	121	135	120	37500
kg/kkg[2]	0.113	0.126	0.112	11.6
TOC RWL				
mg/liter[1]	37	34	29	64430
kg/kkg[2]	0.035	0.032	0.027	19.9

[1]Raw waste concentrations are based on unit weight of pollutant per unit
volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit
weight of product.

These data are reported to supplement the information on RWL for this type of process obtained in Phase I. However, since effluent limitations for the process have already been established, they are not included in the subsequent development of Phase II limitations.

Product: BTX Aromatics

Process: Fractional Distillation

Process RWL Category: A

Chemical Reactions: None

The product obtained here is a mixed one consisting of benzene, toluene, and xylenes which are separated from parafinic, olifinics, and mixed high-boiling aromatic organics (over 150°C). Some ethyl benzene is also recovered. The process involves a series of fractionating columns. There is no direct contact water; consequently raw waste loads are very low.

$$
\begin{array}{ll}
\text{PROCESS FLOW} & \\
\quad \text{liters/kkg} & 46.7 \\
\quad \text{gals/M lbs} & 5.6 \\
\\
BOD_5 \text{ RWL} & \\
\quad \text{mg/liter}[1] & 320 \\
\quad \text{kg/kkg}[2] & 0.015 \\
\\
\text{COD RWL} & \\
\quad \text{mg/liter}[1] & 1150 \\
\quad \text{kg/kkg}[2] & 0.053 \\
\\
\text{TOC RWL} & \\
\quad \text{mg/liter}[1] & 328 \\
\quad \text{kg/kkg}[2] & 0.015 \\
\end{array}
$$

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

These data are reported to supplement the process RWL data obtained in Phase I. Since effluent limitations for this type of process have already been established, these data are not included in the subsequent development of Phase II limitations.

Product: Ethyl Benzene

Process: Alkylation of Benzene with Ethylene

Process RWL Category: A

Chemical Reactions:

$$C_6H_6 + C_2H_4 \xrightarrow[\text{Al Cl}_3]{} C_6H_5C_2H_5$$

Benzene Ethylene   Ethyl Benzene
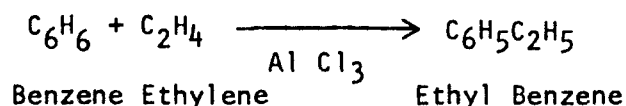
This particular product process and reaction were covered in Phase I of this study and can be found on Pages 76 and 77 of EPA's document, EPA 440/1-73/009 (Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category) published December 1973.

However, this product/process has also been surveyed in Phase II of this study, and process RWL calculated from the flow measurements and analyses of wastewater samples are shown in the tabulation below:

	Plant 1		Plant 2
	Sample Period #1	Sample Period #2	Sample Period #1
PROCESS FLOW			
liters/kkg	339	315	717
gals/M lbs	40.6	38.7	86
BOD$_5$ RWL			
mg/liter[1]	6	34	302
kg/kkg[2]	0.002	0.011	0.217
COD RWL			
mg/liter[1]	1,700	1,270	1,400
kg/kkg[2]	0.576	0.411	1.01
TOC RWL			
mg/liter[1]	139	120	443
kg/kkg[2]	0.047	0.039	0.318

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

These data are reported to supplement the process RWL data obtained in Phase I. Since effluent limitations for this type of process have already been established, these data are not included in the subsequent development of Phase II limitations.

Product: Adiponitrile

Process: Chlorination of Butadiene

Process RWL Category: B

Chemical Reactions:

$$CH_2CH\ CH\ CH_2 + Cl_2 \longrightarrow \text{Mixture of isomeric dichlorobutenes} \xrightarrow{NaCN}$$
Butadiene + Chlorine

$$NCCH_2CH = CH\ CH_2CN \xrightarrow{\ \ H_2\ \ } NC\ (CH_2)_4CN$$
Dicyanobutene   Adiponitrile

Adiponitrile (ADN) is commonly used during the manufacture of hexamethylene diamine (HMDA). Hexamethylene diamine is in turn used as a raw material during the production of Nylon 6/6.

A schematic flow diagram of the process is given in Figure 4-3, and the general process information is described in the following paragraphs:

The first step in the manufacture of ADN via butadiene is the vapor-phase chlorination of butadiene. The reaction is carried out at 250°C and at pressures slightly above atmospheric. The inlet section of the reactor is designed to insure complete and rapid mixing of the reactants, and the rest of the vessel should be constructed to guarantee plug-flow conditions, which favor the high degree of chlorine conversion desired. By-product formation is minimized if the molar ratio of butadiene to chlorine is kept around 6.5 to 1 and if the vapor phase is diluted with nitrogen gas to keep a 10% (volume) of inerts in the reactor feed stream. The ratio of fresh to recycle butadiene is approximately 0.2 to 1. When the chlorine conversion is close to 100%, the molar yield of chlorine to chlorinated butenes is 95%. The ratio of the 1,4 and 3,4 dichlorobutene isomers is of no importance since in subsequent reaction steps both isomers are converted to the same final product. The composition of the chlorinated butenes is as follows: 93.4 wt % dichlorobutenes, 1.6 wt % low boilers and 4.9 wt % high boilers. The vapor-phase reaction is carried out in an empty reactor. The reactants enter at 120°C and are heated up to the reaction temperature (250°) by the heat evolved from the reaction, which is 39 kilocalories per mole.

The effluent stream from the reactor is cooled down to room temperature, and condensed. The unreacted butadiene is separated from the liquid phase, which contains the chlorinated products, and recycled back to the reactor. The liquid phase is sent to the cyanization section of the plant. This liquid is composed of a mixture of dichlorobutenes, chlorobutenes, chlorinated butanes, and heavy materials such as tar and polymeric compounds.

The cyanization reaction is carried out in the liquid phase at 100°C and under atmospheric pressure in the presence of an inert gas such as nitrogen. The reaction is catalyzed by an aqueous mixture of cuprous chloride, copper powder, and cuprous cyanide. The molar ratio of hydrogen cyanide to dichlorobutenes is close to 2.3 to 1. The composition of the liquid feed to the reactor is given below on a weight percent basis.

cuprous cyanide	0.93
calcium carbonate	15.6
water	54.6
hydrogen cyanide	9.6
dichlorobutenes	19.5

The reaction time to achieve a 92.5 mole % conversion to 1,4-dicyanobutenes is approximately 40 minutes.

The next step in the production of ADN is the isomerization and purification of cyanobutenes. The purpose of the isomerization is the conversion of some of the 1,4-dicyanobutene-2 to its isomer, 1,4-dicyanobutene-1. The purpose of the purification is to render the crude dicyanobutene mixture non-corrosive.

The liquid reaction product stream leaving the cyanization reactor is cooled to 25°C. The cyanobutenes and organic by-products are extracted with benzene and diluted until the benzene concentration is approximately 66% by weight. This organic mixture is sent to an agitated tank, where the temperature is raised to 60°C and the pH is adjusted, with 10% sodium hydroxide, to 11.5. The two liquid phases that result are separated in a liquid-liquid separator; the aqueous phase is sent to the waste treatment plant, while the organic phase, after being heated to 70°C, is sent to another agitated tank where dilute (10%) sodium hydroxide is added until its weight percent in the aqueous phase is around 15. The two liquid phases are agitated vigorously in the tank, which has an average residence time of 25 minutes. The two-phase effluent stream is sent to a decanter where the organic and aqueous phases are separated; the aqueous phase is sent to the waste treatment plant, and the organic phase (containing the isomeric mixture of 1,4-cyanobutenes) is sent to the adiponitrile plant.

The benzene-cyanobutene mixture is diluted with benzene until the cyanobutene concentration is 20% by weight, and then is fed to the hydrogenation reactor. This reaction vessel contains a packed bed of activated charcoal promoted with 2% (by weight) palladium. The hydrogenation reaction is carried out under a hydrogen pressure of 400 psig and at a temperature between 100 and 120°C. The hydrogen is bubbled cocurrently with the liquid at a ratio of 35 moles of hydrogen per mole of dicyanobutene. The liquid space velocity in the reactor is approximately 0.4

volumes of liquid per hour per volume of catalyst. The molar conversion to adiponitrile is 95%, with a selectivity of 99%. Since the reaction is quite exothermic, the reactor must be equipped with an efficient heat-removal system. For example, the reaction should be carried out inside of tubes packed with the catalyst while cooling water runs through the shell side of the reactor. The catalyst has an active life of about 500 hours, and it can be easily regenerated by passing hydrogen at $500^{\circ}C$ over the catalyst until no more sulfur is evolved from the reactor tubes.

The reactor effluent stream is cooled down to room temperature, and the hydrogen is separated from the liquid phase and recycled back to the reactor. The crude adiponitrile organic phase is sent to the adiponitrile purification plant.

The first step in the purification consists of flashing the liquid in order to vaporize the hydrogen dissolved in the liquid. The flashed vapors contain some benzene; after cooling to $50^{\circ}C$ this benzene is condensed and returned to the benzene tank, while the non-condensable gas is flared. The liquid stream leaving the flash drum (containing most of the benzene, adiponitrile, unreacted byanobutenes, and organic impurities) is sent to the benzene evaporator. The benzene recovered in the evaporation step is condensed and sent to the benzene storage units.

The bottoms from the evaporator are sent to a distillation column, where the unreacted cyanobutenes and the benzene remaining in the system are distilled off and recycled back to the hydrogenation reactor. The crude adiponitrile leaving at the bottom of this column is usually further purified prior to hydrogenation to HMDA. The purification begins by removing water with a dehydration agent such as HMDA. This is achieved by sending the crude adiponitrile to a dehydration column where a water-HMDA azeotropic mixture is collected as distillate. The water phase is discharged, and the HMDA-rich phase is used as the column recycle. The bottoms from this column are sent to a second distillation unit, where low boilers are distilled off. In a subsequent distillation step, refined adiponitrile is collected as the distillate.

The wastewater pollution sources of this process include various scrubber effluents and stream jet condensates from each reaction step as indicated in the process flow diagram. Although it is apparent from the previous process description that the sections of the process associated with the manufacture of dicyanobutene and adiponitrile involve aqueous liquid-phase reaction mixtures, the wastewaters discharged to the sewer are primarily spent scrubber water and vacuum jet condensates. These wastes are typical of a Category B vapor-phase manufacturing operation. Process raw waste loads calculated from flow measurements and analyses of these streams are shown in the following tabulation:

Adiponitrile

PROCESS FLOW	Sample Period #1	Sample Period #2	Sample Period #3	Average
Liter/kkg	9766	9766	9766	9766
(gal/M lb)	1170	1170	1170	1170
BOD_5 RWL				
mg/liter[1]	1250	2850	1800	1970
kg/kkg[2]	12.2	27.8	17.6	19.2
COD RWL				
mg/liter[1]	15,000	14,400	12,000	13,800
kg/kkg[2]	146	141	118	135
TOC RWL				
mg/liter[1]	4600	4500	4450	4500
kg/kkg[2]	44.9	43.8	43.4	44.0

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.
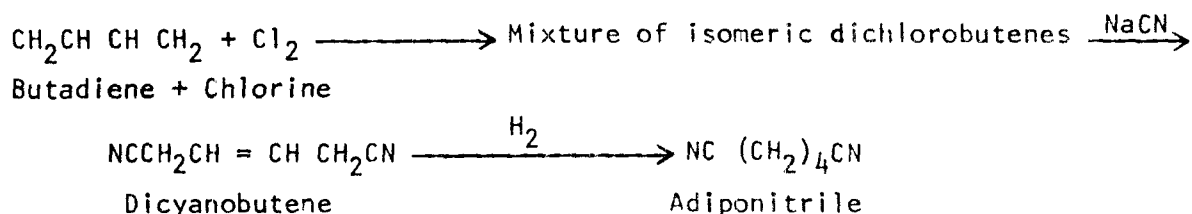
The analytical results indicate that the pollutants in the wastewaters (such as ammonia nitrogen, sulfate, cyanide, chloride, and copper) are at levels hazardous to biological treatment processes. The low BOD_5 values shown in the tabulation are due to the interference of the biological-inhibiting pollutants.

It should be noted and clearly understood that although biological treatment was chosen as the model treatment system most generally applicable for BPCTCA, several of the process plants surveyed utilize other means of disposal, such as deep-well injection. This is the case with this adiponitrile plant. The raw waste loads shown previously are all treated by filtration prior to disposal by deep-well injection. The effluent limitations developed subsequently for adiponitrile would be applicable only if deep-well injection were no longer feasible. In this regard, it should be noted that this adiponitrile plant uses non-contact cooling water on a once-through basis. The volume of cooling water amounts to 424,000 liters/kkg of adiponitrile. If it becomes necessary to treat the wastes from this adiponitrile plant in a biological system, dilution with some of the once-through cooling water might lessen the inhibitory characteristics of the waste in its present concentrated state.

FIGURE 4-3

ADIPONITRILE-CHLORINATION OF BUTADIENE

Product: Benzoic Acid and Benzaldehyde

Process: Catalytic Oxidation of Toluene with Air

Process RWL Category: B

Chemical Reactions:

$$2C_6H_5CH_3 + 3O_2 \longrightarrow 2C_6H_5COOH + 2H_2O$$

Toluene   Benzoic acid

$$C_6H_5CH_3 + O_2 \longrightarrow C_6H_5CHO + H_2O$$

Toluene   Benzaldehyde

A simplified flow diagram for this oxidation process is shown in Figure 4-4.
Toluene and air, with a mixture of recycle gas and toluene, are combined
in the reactor. Reaction temperatures may range from $150^\circ C$ to $500^\circ C$., with
a corresponding pressure range of 10 to 1 atmospheres. Specific manufac-
turers operate at different conditions. Depending upon the operating
conditions, the material in the reactor may be in the liquid or vapor
phase, and reaction conditions may be varied to give different selectiv-
ities to benzoic acid or benzaldehyde. The plant surveyed produces 6-7
kg of product benzoic acid for every kg of benzaldehyde co-product. The
process RWL's have been calculated on the basis of the total production
of benzoic acid and benzaldehyde during the sampling period. Waste
streams associated with either the benzoic acid or the benzaldehyde recovery
sections can be allocated by using the product/co-product ratio mentioned
above.

The catalysts most frequently used consist of oxides of metals belonging to the
fifth or sixth groups of the periodic system. A mixture of uranium oxide
(93 percent) and molybdenum oxide (7 percent), impregnated on a pumice or
asbestos carrier, is claimed to give relatively high yields of benzaldehyde,
with low percentages of toluene going to complete combustion. The addi-
tion of small amounts of copper oxide to the catalyst mixture reduces by-
product maleic anhydride formation. A cobalt acetate catalyst in aqueous
solution has also been successfully used; in this case, the metal catalyst
concentration is kept below 100 mg/l in the reactor.

As shown in Figure 4-4, the reactor effluent is sent to a decant tank.
A three-phase mixture of gas, organic liquid, and aqueous liquid usually
exists in this vessel. The gas (mainly inert nitrogen) is vented under
pressure control, with a portion recycled to the reactor to maintain
proper dilution. The aqueous liquid phase (containing water of reaction)
is decanted off using an interfacial level controller.

The organic layer is sent to the main stripper, where toluene is taken overhead and recycled to the reactor, which normally operates at 30-35% toluene conversion per pass. The bottoms from the main stripper are crude benzoic acid and by-products such as maleic anhydride, anthraquinone, and complex high-boiling aromatics of unknown composition. The crude acid is sent to the product (benzoic acid) purification section of the process.

A side stream containing crude benzaldehyde co-product is also taken off the main stripper as shown in Figure 4-4. The crude benzaldehyde is sent to the benzaldehyde stripper, where benzaldehyde is taken overhead and the bottoms recycled to the main stripper.

The benzaldehyde is washed with an aqueous solution of sodium carbonate in the wash tank. This step is necessary to neutralize organic acid by-products (and some benzoic acid) present with the benzaldehyde. The aqeous layer from the wash tank is drained and discharged. The organic layer from the wash tank is sent to the benzaldehyde still, where purified benzaldehyde is taken overhead. The benzaldehyde still operates under vacuum drawn by a vacuum pump. Seal water from the pump is continuously discharged. An organic residue, which must be removed periodically by water washing, forms in the bottom of the benzaldehyde still. This material is discharged.

The benzoic acid purification section consists of two rectifying columns and a batch tar stripper. Each of these distillation columns operates under vacuum drawn by steam jet ejectors. The steam is not condensed, but rather is discharged directly into the atmosphere; consequently, this steam was not considered in the process RWL calculations. It should be noted that the gases drawn into the jets have been scrubbed; consequently, little carryover of organic material is anticipated.

The crude benzoic acid from the main stripper is sent to the middles column, where partially rectified benzoic acid is drawn off as bottoms. The overhead gases are drawn by vacuum through the middles column scrubber, where they are scrubbed with an aqueous caustic solution prior to discharge through the steam jets. The caustic solution is recycled by means of the scrubber recycle tank; fresh caustic is added periodically to the circulating solution, with a portion drawn off to maintain a high pH.

The bottoms from the middles column are sent to the product column, where product benzoic acid is drawn off. The overhead vapors from the product column are scrubbed with caustic in a recirculating system similar to that used with the middles column (see Figure 4-4). Bottoms from the product column are sent to the tar stripper, where additional benzoic acid is stripped batchwise from by-product tar.

The major RWS's for this process are summarized in the following tabulation:

Waste Stream	Flow 1/kkg	BOD$_5$ kg/kkg	COD kg/kkg	TOC kg/kkg
Water of Reaction	247	8.74	15.0	6.52
Aqueous Drain from Benzaldehyde Wash Tank	52.2	11.9	16.1	8.34
Benzaldehyde Still Residue	5.0	--	--	--
Vacuum Pump Seal Water	2,200	0.91	1.61	0.73
Middles Column Scrubber Blowdown	209	1.31	1.71	1.04
Product Column Scrubber Blowdown	122	2.74	5.36	2.97
TOTAL	2,840	25.6	50.8	19.6

The major source of waste loadings in the process is the aqueous drain from the benzaldehyde wash tank, where organic concentrations are greater than 100,000 mg/l. Materials present include sodium benzoate and other aromatics such as biphenyls. It is questionable whether this stream could be incinerated, because of its high alkalinity. However, some removal of organics may be possible by acidification of the wastewater followed by gravity separation. The organics removed could then be burned.

The raw waste load as presented in the foregoing tabulation was considered as BPCTCA. It is discharged, without pretreatment, to the municipal sewer system.

FIGURE 4-4
BENZOIC ACID AND BENZALDEHYDE
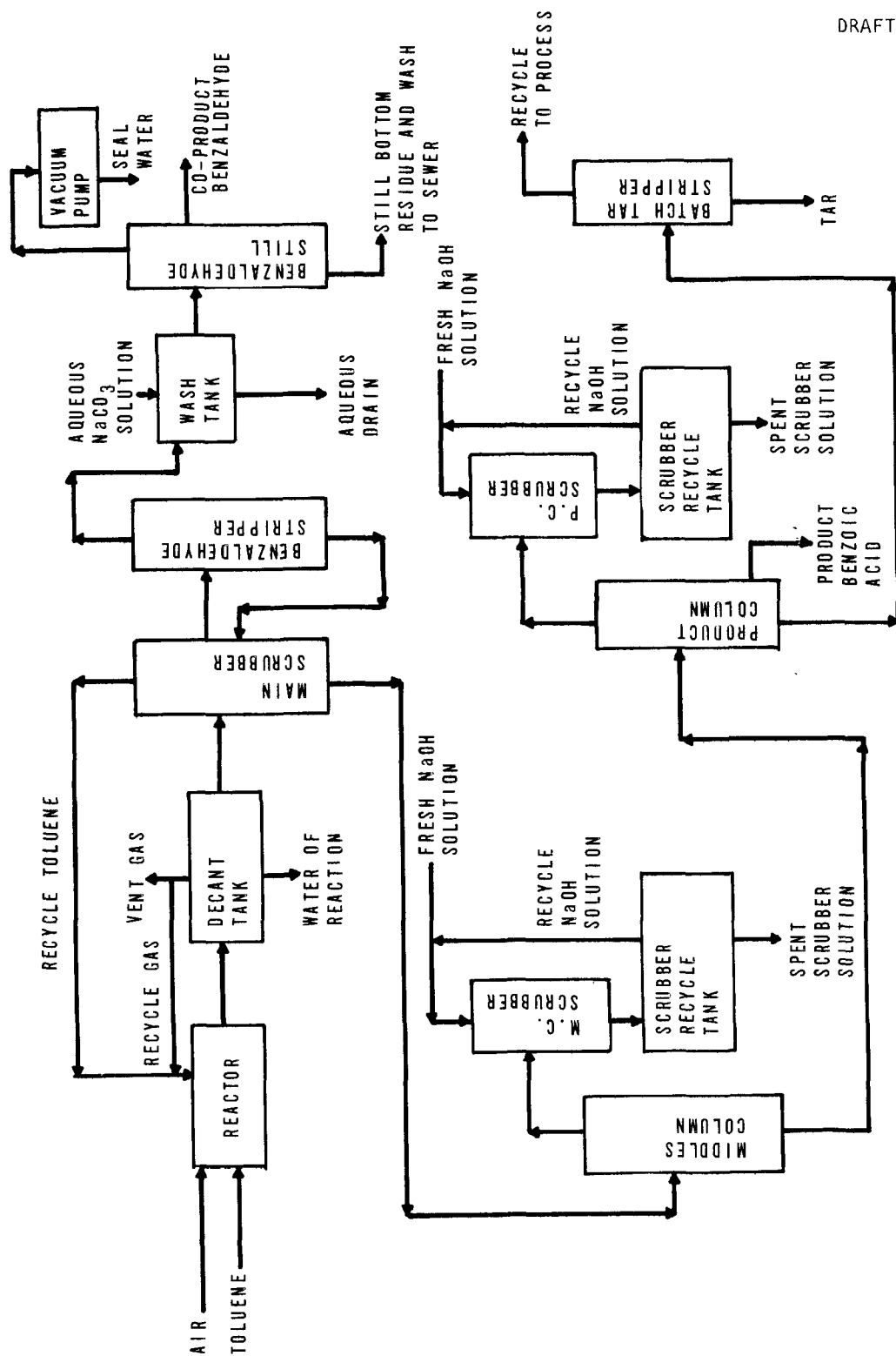
Product: Chlorinated Methanes (Methylene Dichloride, Chloroform, and
Carbon Tetrachloride)

Process: Chlorination of Methyl Chloride and Methane Mixture

Process RWL Category: B

Chemical Reactions:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Methane   Methyl   Hydrogen
        Chloride   Chloride

$$CH_3Cl + 2Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

Methyl Chloride   Methylene
         Dichloride

$$CH_3Cl + 2Cl_2 \longrightarrow CHCl_3 + 2HCl$$

Methyl Chloride   Chloroform

$$CH_3Cl + 3Cl_2 \longrightarrow CCl_4 + 3HCl$$

Methyl Chloride   Carbon
         Tetrachloride

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

Methylene Dichloride   Chloroform

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Chloroform   Carbon
       Tetrachloride
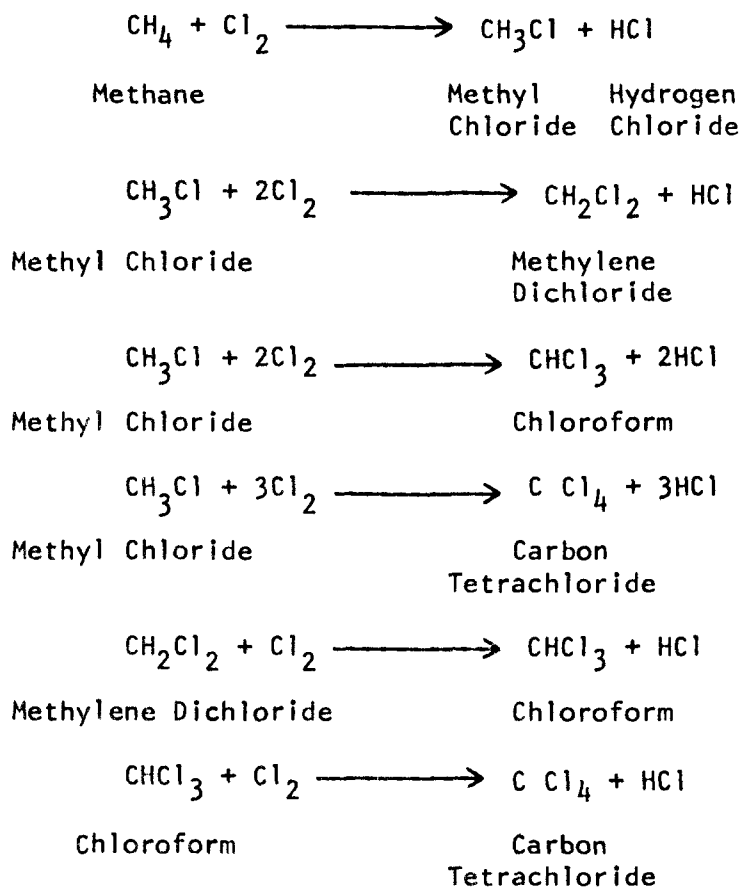
Typical Material Requirements:

The material requirements depend upon which of the chlorinated products is
desired. In general, the chlorine consumption is 7% beyond theoretical
needs, but it may be lowered depending on the chloromethanes products mix.
The methyl chloride requirement also is approximately 7% beyond theoretical
needs.

Chloromethanes find their widest application as solvents. Methylene di-
chloride 's used in the plastics field as a solvent for polycarbonates,
isocyar?tes, and cellulouse diacetate, a urethane-foam blowing agent; in

Europe, it is important as the spinning solvent for cellulose acetate. Chloroform is used as a solvent for textile degreasing and an extractant for food flavors, steroids, and antibiotics. Carbon tetrachloride is used as a solvent in non-flammable cleaning agents.

In addition to their wide use as solvents, there are numerous other applications of chloromethanes. Methylene dichloride is used as a non-flammable paint remover, and also in purification of steroids as a reaction medium, e.g., in the manufacture of phosphates, insecticides, and vegetable oil extracts. Two developments of great potential importance are the use of methylene dichloride as a polyurethane-foam blowing agent and in aerosal hair sprays.

Chloroform finds wide use as an intermediate in the production of other materials. In addition, chloroform is used in certain pharmaceutical formulations such as cough medicines, rubbing liniments, and anesthetics.

Carbon tetrachloride is used primarily in the manufacture of methylene chloride and chloroform. However, it is also used as a fluid in certain fire extinguishers.

Chlorinated methanes can be produced from methane, from methyl chloride, or from a mixture of both materials. The reactions may be carried out by either thermal or photo activation. The former, which requires a temperature of approximately 700°F, is preferred commercially, because it requires lower investment and maintenance, and allows more complete conversion of chlorine.

A typical process flow diagram for producing chloromethanes starting with a mixture of methane and methyl chloride is shown in Figure 4-5.

The feed methane is first purified and dried in a purification unit, and then is fed to the chlorination reactor along with fresh and recycled methyl chloride and chlorine gas. Following the reaction step, the chlorinated products are quenched and absorbed in a refrigerated mixture of recycle carbon tetrachloride and chloroform. Methane and HCl are taken overhead from the quench column and are absorbed in weak hydrochloric acid, which removes the HCl. The remaining methane is then passed through a caustic scrubber before being returned to the chlorination reactor.

The bottoms stream from the quench tower is stripped of its light constituents. These are absorbed in water to remove the remaining HCl, and are then neutralized with caustic solution. This light-product stream is then passed through a series of distillation towers from which methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride are in turn obtained as final products for sale or recycled back to the process as raw material or as absorbent.

The major water pollution sources of the process are the waste streams discharged from the HCl absorber and the caustic scrubber. Process RWL calculated from the flow measurements and analyses of water samples obtained in the survey period are presented in the following tabulation. The analytical results also indicate that, in addition to the parameters shown in the tabulation, parameters such as pH and chloride are at levels hazardous to biological treatment processes.

	Plant 1		Plant 2
	Sample Period #1	Sample Period #2	Sample Period #1
PROCESS FLOW			
liter/kkg	598	598	2800
gal/M lb	72	72	335
BOD$_5$ RWL			
mg/liter[1]	7	18	77
kg/kkg[2]	0.004	0.011	0.22
COD RWL			
mg/liter[1]	113	385	335
kg/kkg[2]	0.07	0.23	0.94
TOC RWL			
mg/liter[1]	420	42	132
kg/kkg[2]	0.25	0.25	0.37

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewater.

[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

The RWL shown for Plant 2 was considered commensurate with BPCTCA. These wastewaters are neutralized and discharged to surface waters. The wastes shown for Plant 1 are not considered as representative of the process, in that the chloromethanes process was integrated as part of a chemical complex so that both of the waste streams could be utilized elsewhere in plant. The values shown for Plant 1 represent only surface runoff.

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FIGURE 4-5

CHLORINATED METHANES- CHLORINATION
OF METHYLCHLORIDE AND METHANE MIXTURE

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Product: Chlorobenzene

Process: Chlorination of Benzene

Process RWL Category: B

Chemical Reaction:

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

Benzene   Chlorobenzene
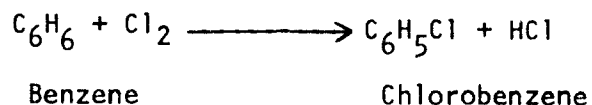
Chlorobenzene, an important intermediate in the manufacture of dyes and insecticides, is manufactured by the chlorination of benzene. Two faciil- ities were visited during the field-data collection program, one which manufactured chlorobenzene exclusively, and one which also produced di- chlorobenzene. Figures 4-6 and 4-7 are process flow diagrams of these two facilities, respectively.

At the first facility (chlorobenzene only), benzene and chlorine are fed to the reactor, and the hydrochloric acid produced by the reaction is absorbed in water to make aqueous hydrochloric acid; the chlorobenzene formed by the reaction is neutralized by sodium hydroxide and then puri- fied by distillation. The brine formed during the neutralization step goes to the sewer, and a tar-like residue from the chlorobenzene distil- lation is incinerated.

The second facility (chlorobenzene-dichlorobenzene) uses a very similar processing strategy, with a few additions. The hydrochloric acid coming from the absorption step is purified by carbon adsorption, and the tail gas which passes through the absorber is scrubbed with water prior to exhaust to the atmosphere. Another difference in the processing strategy at this facility is in the purification of the chlorobenzene reaction products. The products proceed to a distillation column, where any un- reacted benzene is taken overhead and recycled to the chlorinator. The monochlorobenzene proceeds from the bottom of this distillation column to a second distillation column, where chlorobenzene product is taken over- head while the bottoms from the distillation column proceed to dichloro- benzene refining.

In the survey period, wastewater samples from each facility were collected for analysis. Unfortunately, the flow rates (in terms of gal/1000 lbs of product) were not provided by the manufacturers, and no RWL can be calcu- lated.

FIGURE 4-6
CHLOROBENZENE — CHLORINATION OF BENZENE

FIGURE 4-7

DICHLOROBENZENE—CHLORINATION OF BENZENE
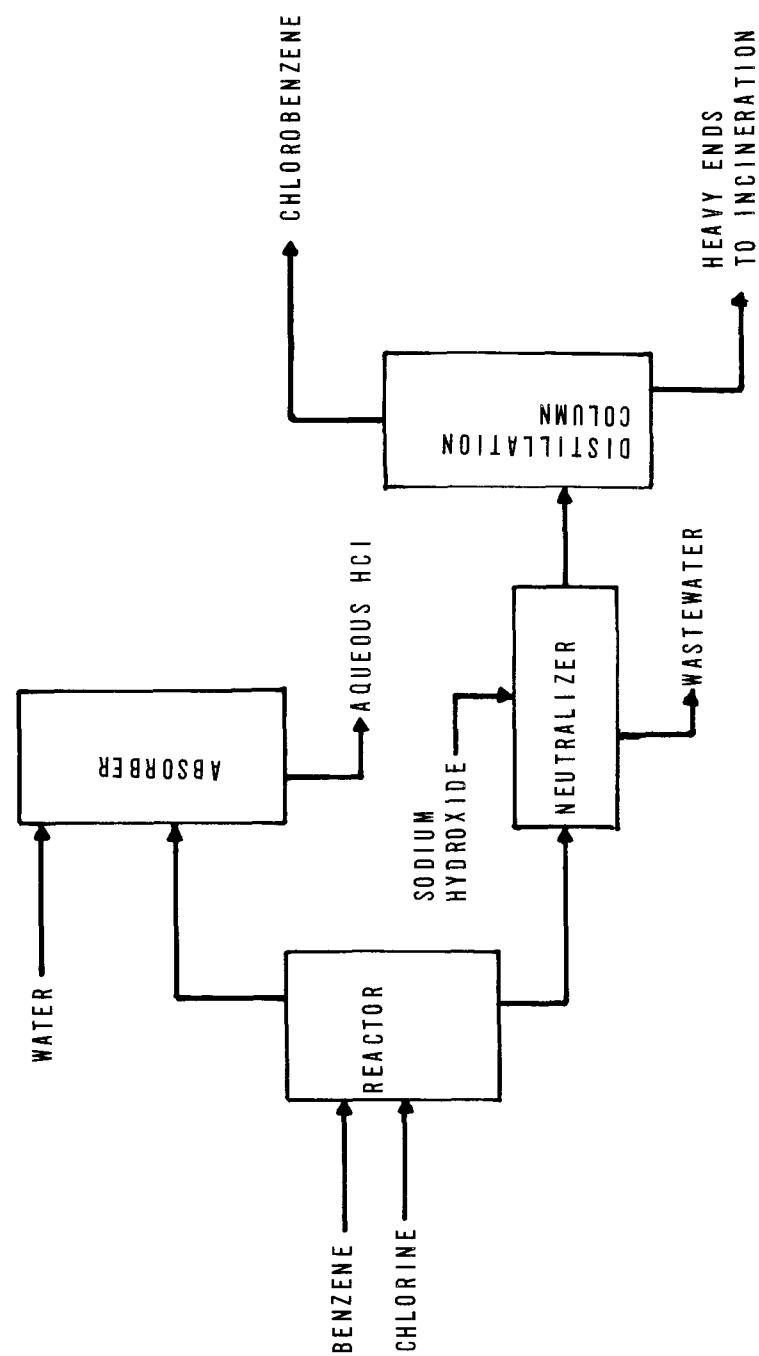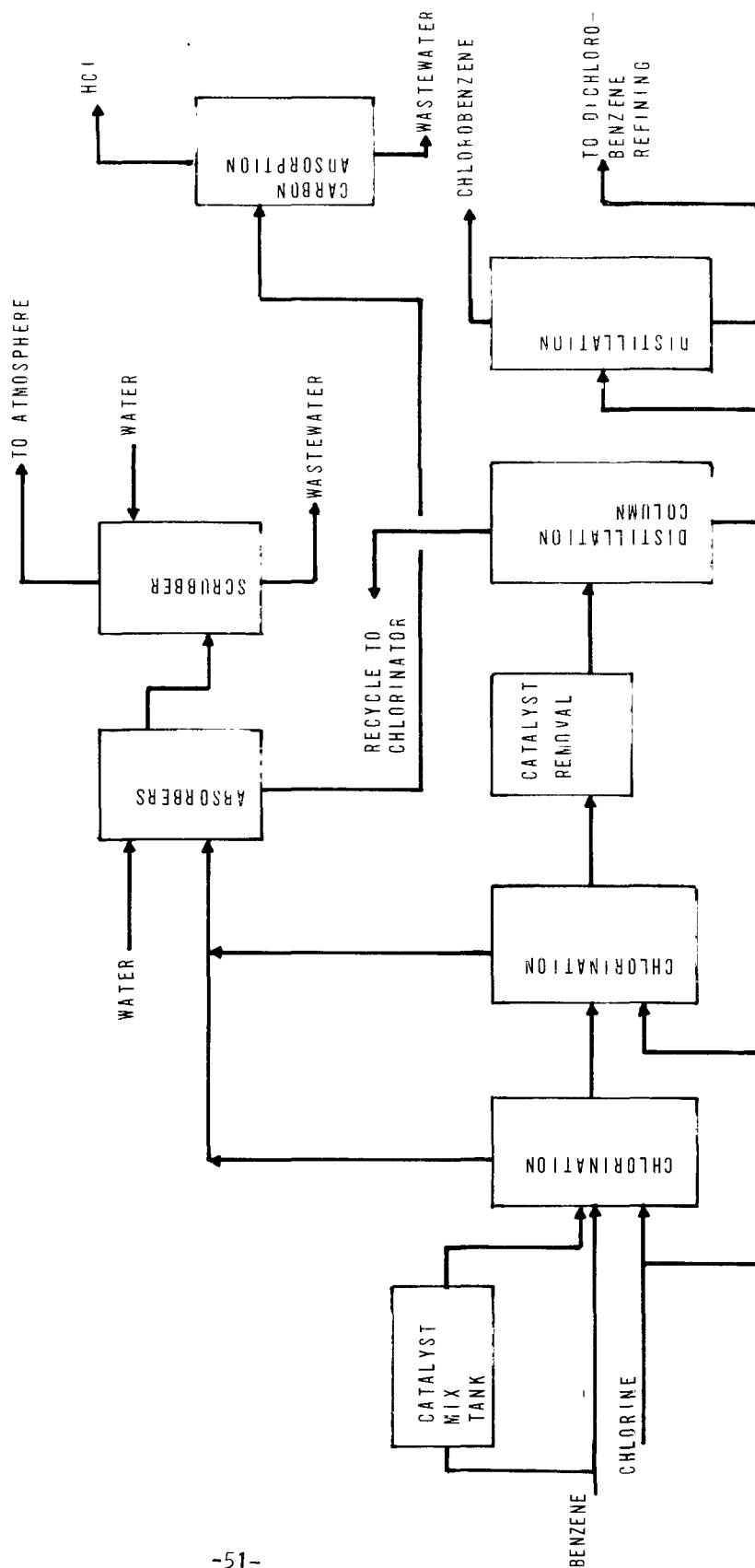
Product: Chlorotoluene

Process: Chlorination of Toluene

Process RWL Category: B

Chemical Reaction:

$$C_6H_5CH_3 + Cl_2 \longrightarrow C_6H_4 (CH_3) Cl + HCl$$

Toluene Chlorine   Chlorotoluene Hydrogen Chloride
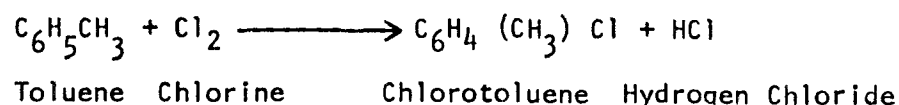
A simplified process flow diagram for the manufacture of chlorotoluene is shown in Figure 4-8. The chlorine gas is reacted with liquid toluene in the presence of a catalyst in the reactor. The unreacted chlorine gas is absorbed by water in an absorption tower, and the resulting aqueous hydrochloride is sent to the muriatic acid plant for reprocessing. The crude product mixture is purified by passing through a series of distil- lation stills. The light ends and residues are disposed of by incineration, while the unreacted toluene is recycled back to the reactor.

Vacuum distillation is employed in purifying the crude product. The steam jets (with barometric condensers) used to pull the vacuum consti- tute the only wastewater pollution source of the process. The process RWL calculated from flow determinations and the analyses of the waste stream are indicated in the tabulation below:

PROCESS FLOW	
liter/kkg	121,000
gal/M lb	14,500
BOD$_5$ RWL	
mg/liter[1]	2
kg/kkg[2]	0.24
COD RWL	
mg/liter[1]	15
kg/kkg[2]	1.82
TOC RWL	
mg/liter[1]	2
kg/kkg[2]	0.24

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per one thousand unit weights of product.

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The only wastewater from this process is the large quantity of steam jet condensate from the vacuum still. The contaminant concentrations in these streams are, however, quite low. In the near future, the process will be modified from vacuum distillation to atmospheric distillation. Plant personnel anticipate that this modification will reduce the waste-water volume and pollutants by 25%. At the present time, all process wastewater is discharged to the local municipal wastewater treatment plant.

All cooling water is non-contact. Steam which is used in the process is also non-contact, and the condensate is returned to the boiler plant.

FIGURE 4-8

CHLOROTOLUENE - CHLORINATION OF TOLUENE

WATER

ABSORBER

TOLUENE

CHLORINE

REACTOR

AQUEOUS HCL TO
MURIATIC ACID
PLANT

STEAM JET

DISTILL-
ATION
COLUMNS

CHLORO-
TOLUENE

STEAM JET
CONDENSATE

RESIDUE TO
INCINERATION
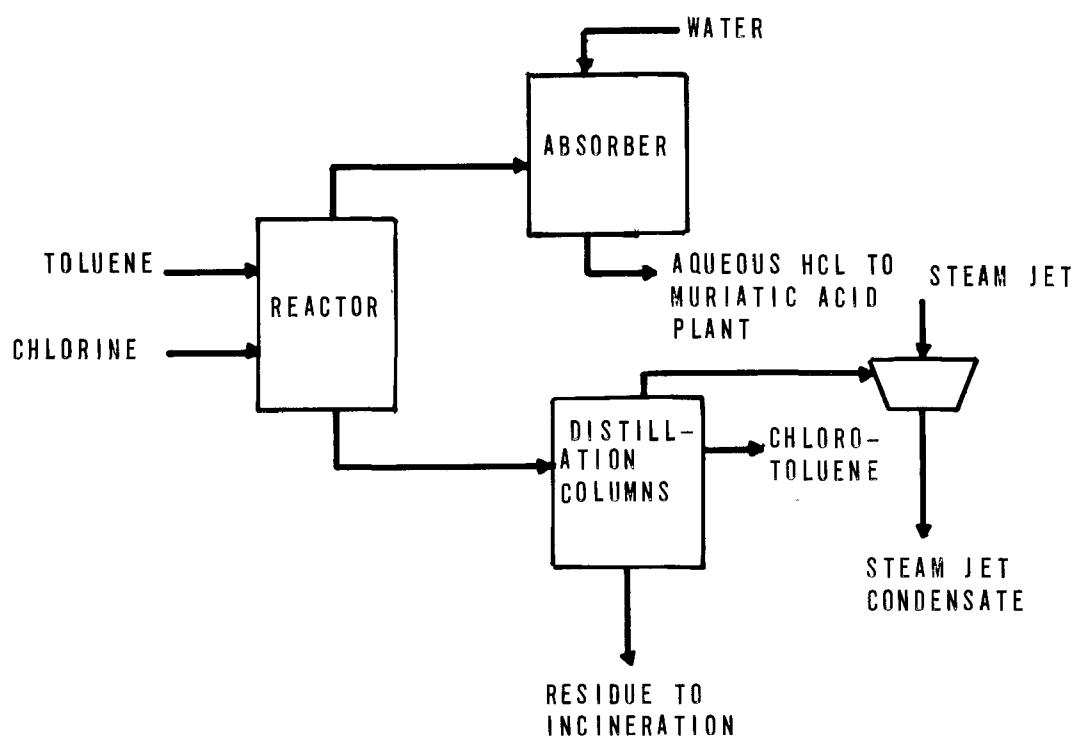
Product: Diphenylamine

Process: Deamination of aniline

Process RWL Category: B

Chemical Reaction:

$$2\ C_6H_5NH_2 \longrightarrow C_6H_5NHC_6H_5 + NH_3$$

Aniline   Diphenylamine   Ammonia
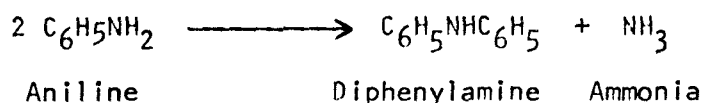
Typical Material Requirements:

	1000 kg Diphenylamine
Aniline	800 kg
By-Products:	
Ammonia	80 kg
Tars	120 kg

Diphenylamine (DPA) is used extensively in the rubber chemicals field, generally as a retarder, and its derivatives are employed as antioxidants.

Production of diphenylamine may proceed by various routes; however, the plant visited during the field survey utilized a vapor-phase catalytic reaction involving the deamination of aniline. A simplified process flow diagram is shown in Figure 4-9.

As shown in the diagram, liquid aniline is pumped at a uniform rate from storage tanks into the externally-heated vessel which serves as preheater and vaporizer. In this vessel, aniline is vaporized, and the vapors are heated to a temperature of approximately 400°C to 500°C. Hot aniline vapors pass through the catalyst chamber, which is maintained at approximately 400°C to 550°C. The exit gases of the DPA converter then pass into an aniline stripper, in which aniline and other volatile constituents (such as ammonia, small amounts of water, and other volatile by-products) remain in the vapor state, while DPA condenses with some aniline and is drawn off as crude DPA. The crude product is then purified in a series of distillation columns.

The gases leaving the aniline stripper are cooled in an aniline condenser. A portion of the liquid aniline is refluxed, and the remainder is recycled to the aniline feed line. The vapors (containing mostly ammonia, small amounts of water, and other volatiles) pass to an ammonia scrubber.

DPA convertors will not operate indefinitely, because the reaction causes a certain amount of decomposition of aniline, which deposits carbonaceous residues in the catalyst. These residues reduce the efficiency of the catalyst, and it is necessary to regenerate. As a result, in a normal plant there is more than one DPA convertor. Some convertors are on a regeneration cycle while the remaining ones are on a production cycle. On the average, each production cycle lasts 50 hours.

Regeneration is effected by the following procedures:

1. Steam is introduced to vaporize the aniline and DPA.

2. Steam and air are introduced to burn the carbonaceous impurities deposited on the catalyst surface.

3. Steam is then introduced to purge the reactor.

4. An aniline purge is used to remove water vapor.

The off-gases resulting from the burning of tars are exhausted, and aniline and DPA are recycled.

The major wastewater source in this process is the effluent from the ammonia scrubbing tower. The wastewaters from the catalyst regeneration process are usually disposed of by incineration and are not included in the raw waste load calculations. The total process RWL from flow measurements and the analyses of the contact wastestreams during the sampling survey are presented in the following tabulation:

PROCESS FLOW	Sample Period #1	Sample Period #2
liter/kkg	526	526
gal/M lb	63.0	63.0
BOD RWL		
mg/liter[1]	220	108
kg/kkg[2]	0.116	0.057
COD RWL		
mg/liter[1]	550	650
kg/kkg[2]	0.287	0.339
TOC RWL		
mg/liter[1]	450	420
kg/kkg[2]	0.237	0.218

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The arithmetic average of the values presented in the foregoing tabulation for BPCTCA. Process wastes are discharged to surface waters.

All cooling water used during the production of diphenylamine is indirect; tube and shell exchangers are employed. Steam usage is 1.15 lbs per lb product (including the steam employed during catalyst regeneration), and approximately 75% of the condensates are collected. Steam used in the regeneration cycle is live steam, and the rest is reboiler steam.

Diphenylamine can also be produced by catalytic liquid-phase process, in which a mixture of primary arylamine and catalyst is mixed with re-actant aniline in a stainless steel reaction chamber. The temperature of the reaction mixture is raised to 175°C to 450°C, and the pressure is per-mitted to build up to keep the reaction mixture in a liquid state. During the course of the reaction, ammonia is split and vaporized. The ammonia vapor pressure can be utilized to maintain the reaction mixture in a liquid state. After holding the reaction mixture for the requisite time at the desired temperature and pressure, the hot mixture is permitted to flow into the receiver. On cooling the mixture to about 275°C, the catalyst is substantially crustallized from the mixture. The crude reaction mixture can be filtered and then purified to the final product.

FIGURE 4.9

DIPHENYLAMINE-DEAMINATION OF ANILINE
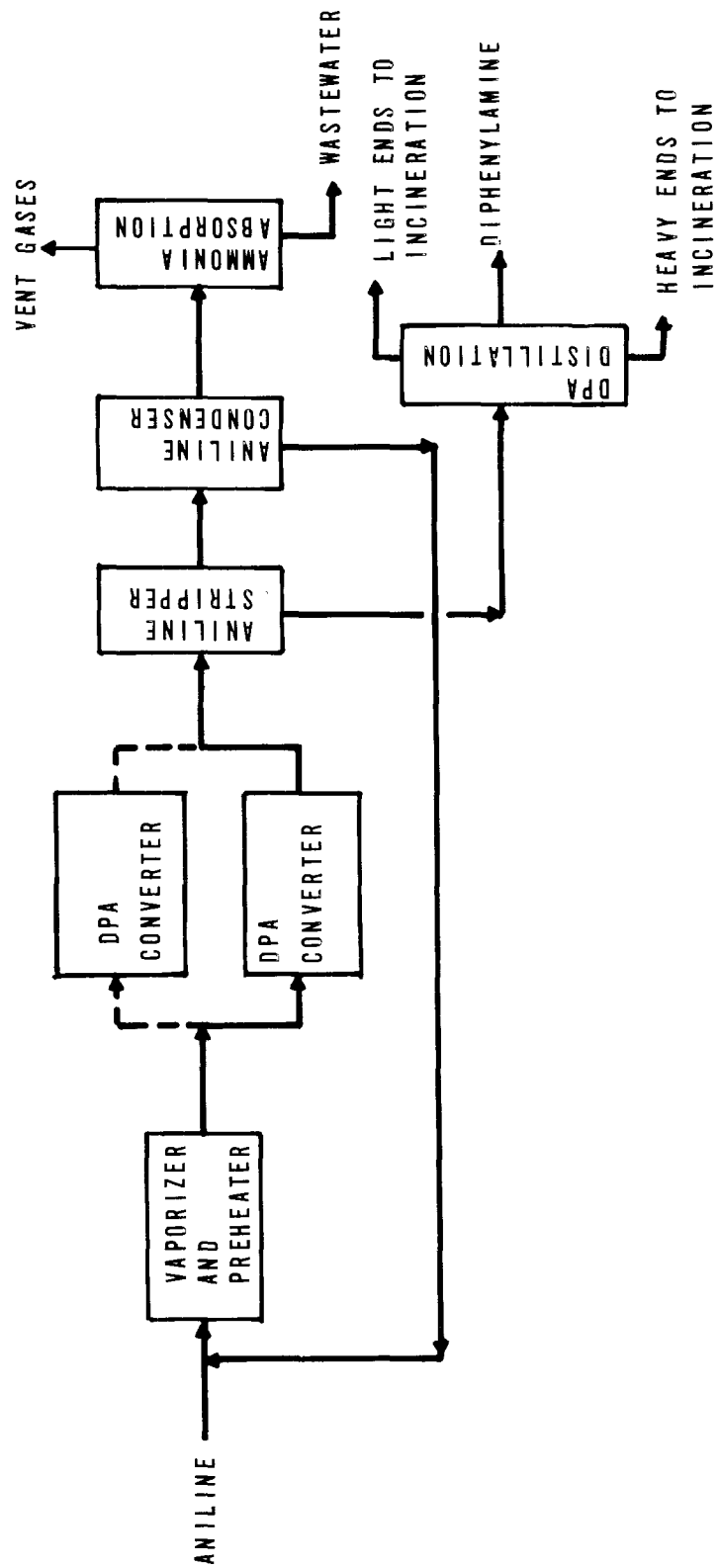
Product: Hexamethylenediamine (HMDA)

Process: Hydrogenation of Adiponitrile (ADN)

Process RWL Category: B

Chemical Reactions:

$$NC(CH_2)_4CN + 4H_2 \xrightarrow{\quad NH_3 \quad} H_2N(CH_2)_6NH_2$$
$$\text{Adiponitrile} \qquad\qquad\qquad \text{Hexamethylenediamine}$$
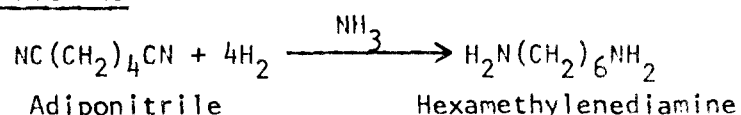
Hexamethylenediamine (HMDA) is used in the production of nylon, where it is combined with adipic acid to form polyhexamethylene adipamide, commonly known as nylon. The demand for HMDA is estimated to be 900 million pounds by 1975, and 1,250 million pounds by 1980.

Figure 4-10 presents a process flow diagram of hexamethylenediamine production via the hydrogenation of adiponitrile.

The hydrogenation of adiponitrile is carried out by contacting hydrogen with an ammonia-solvent-ADN liquid mixture in a fixed-bed reactor contain-ing 8-14 mesh cobalt-oxide catalyst at 100-250°C and 200-700 atmospheres. This transformation is characterized by its high selectivity to HMDA at almost complete conversion of ADN.

Fresh adiponitrile and the recycle solvent (toluene) are mixed at 90°F before being pumped to about 4,400 psia pressure and heated to 190°F. This stream is then mixed with fresh and recycled hydrogen and ammonia. The gaseous effluent is recycled, while the liquid effluent is depressur-ized to 3,000 psia and heated to 400°F. This stream goes to a separator followed by a flasher for ammonia removal. A portion of the ammonia is compressed and recycled to the reactor, and the remainder proceeds to an absorber; water is used to absorb the ammonia, which then proceeds to an ammonia stripper. The stripped ammonia is recycled to the reactor, while the bottoms from the column go to the sewer.

The liquid product stream from the flasher is sent to a toluene stripper. Overhead toluene is recycled to the reactor, and the bottoms are recovered for further purification.

The first step in refining consists of removal of HMDA (water azeotrope) as bottoms from the first column operated at 18 psia. The overhead water-imine mixture is discarded for fuel, and the bottoms are sent to the medium boiler stills (concentrators) to recover HMDA. The bottoms stream from the medium boiler column is then discharged to the HMDA refining column. Refined HMDA is taken overhead under vacuum.

The major water pollution sources of this process are the bottoms from the ammonia recovery column, water withdrawn as overhead from the medium boiler stills, and the steam jet condensate from the HMDA refining column. Process RWL calculated from flow rate data and the analyses of wastewater samples collected in the survey period are presented in the following tabulation.

	Plant 1 Sampling Period		Plant 2 Sampling Period		
	#1	#2	#1	#2	#3
PROCESS FLOW					
Liter/kkg	1,695	1,695	1,010	1,010	1,010
gal/M lbs	203	203	121	121	121
BOD$_5$ RWL					
mg/liter[1]	58,850	12,800	5,500	4,500	1,800
kg/kkg[2]	99.8	21.7	5.55	4.54	1.82
COD RWL					
mg/liter[1]	71,850	62,400	20,200	22,200	20,300
kg/kkg[2]	122	106	204	22.4	20.5
TOC RWL					
mg/liter[1]	17,800	31,400	4,600	5,700	5,000
kg/kkg[2]	30.2	53.2	4.65	5.76	5.05

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The data shown in the above tabulation reveal that there are significant differences in RWL from the plants surveyed. There are three major reasons for these differences. Plant 2 partially recycles the bottoms from the ammonia recovery column to the HMDA refining section and incinerates all the light-end organics from the refining portion of the operation, while Plant 1 totally discharges such streams into the sewer line. Another reason is the effective separation by the ammonia absorber in Plant 2. Plant 1 is equipped with a stack which uses water to quench the unabsorbed vapors, and discharges the quench water into the sewer. If the above-mentioned reasons are taken into account, the data from both plants become comparable.

An average RWL value calculated from the data obtained at Plant 1 is considered commensurate with BPCTCA. Again, it should be noted that the process wastes from both Plant 1 and Plant 2 are actually disposed of by deep-well injection. Therefore, the effluent limitations presented would only be applicable if deep-well injection were no longer feasible.

The following paragraphs describe the pretreatment system used at Plant 2. It should be noted that this system also handles wastes from adiponitrile manufacture.

Aqueous waste from the hexamethylene diamine (HMDA) process is fed along with by-product brine from other plant operations into a settling tank; HMDA-waste comprises less than 10% of the total flow. Sludge which settles out is pumped to a pit for further settling, while the main stream goes through primary filtration in precoated, horizontal, leaf filters. After a second filtration, the waste stream is pumped into injection wells for disposal. Backwash from both filtration steps is pumped to the sludge pits.

The primary purpose of the waste treatment area is to remove all solids which might cause plugging of the injection wells.

Geological conditions in this area are favorable for deep-well injection, and experience has been good for the past 20 years. These wastes are being injected into a porous sandstone stratum at 3,700 - 4,200 feet capped both top and bottom by practically impervious shale formations.

Non-contact cooling water usage for both plants is tabulated below:

        Plant 1   -   453,000 liters/kkg of product
        Plant 2   -   31,500 liters/kkg of product

HMDA can also be produced by the ammonolysis of 1,6 hexanediol, a process which will be described in the following sub-section.

FIGURE 4-10

HEXAMETHYLENEDIAMENE-HYDROGENATION OF ADIPONITRILE

Product: Hexamethylenediamine (HMDA)

Process: Ammonolysis of 1,6 - Hexanediol

Process RWL Category: B

Chemical Reaction:

$$HO(CH_2)_6OH + 2 NH_3 \xrightarrow{H_2} H_2N(CH_2)_6NH_2 + 2 H_2O$$

Hexanediol   Hexamethylenediamine

A typical process flow diagram of hexamethylenediamine production via the ammonolysis of 1,6 - Hexanediol is shown in Figure 4-11.

The ammonolysis reactor is a flooded, fixed-bed, catalytic reactor. The fresh and recycled hydrogen and liquid ammonia are pumped to the reactor at a pressure of 3,000 psig. The liquid ammonia is preheated to a temperature of 180 - 220°C and fed to the reactor bottom. At this temperature, the ammonia is above its critical temperature (T_c = 132.6°C). The organic feed stream, consisting of recycle hexamethyleneimine (HMI) (30 wt %) plus fresh and recycle hexanediol is also pumped as a liquid into the reactor. By means of two heat exchangers (one a product-feed exchange, and the second a preheater), the organic liquid phase is raised to the reaction temperature of 180 - 220°C (356-428°F). Positive displacement pumps are necessary to transfer both liquid NH_3 and the liquid organic feed at the 3,000-psig pressure level.

Within the reactor, the liquid organic phase floods the fixed-bed catalyst, and the liquid product stream overflows through a discharge line at the top of the bed. Both H_2 and NH_3 enter the bottom of the fixed bed as gases, but because of the high pressure and the solvent action of the HMI, the NH_3 gas is absorbed in the HMI and subsequently reacts in the liquid phase with the 1,6-hexanediol to produce HMDA. Since the concentration of HMI in the liquid phase is already at its equilibrium value, further conversion of the diol and NH_3 to the imine is negligible. A reflux condenser is situated at the top of the reactor to condense DIOL-HMI-HMDA carryover. The liquid condensate is returned to the top of the fixed bed. The vapor stream leaving this condenser is used to pre-cool the hydrogen gas prior to recycle to the compressor, and to condense NH_3 vapor carryover from the reactor. This ammonia condensate is returned to the reactor ammonia feed.

The ammonolysis reactor operates at a pressure of 2,800 to 3,300 psig and at a temperature of 180 to 220°C. Catalysts suitable for the ammonolysis step include Raney cobalt, Raney nickel, reduced copper, Raney copper, and nickel on kieselguhr. The preferred catalyst is pelletized Raney nickel. At reaction conditions, an ammonia feed stream of 19 moles

NH_3 per mole of diol (2.73 kg NH_3/kg diol) and a hydrogen supply of 0.125 moles H_2 per mole of NH_3 (0.0147 kg H_2/kg NH_3) have been found to give high yields. A yield of 93 mole % HMDA on a diol-reacted basis is practical, and conversions of 70 mole % per reactor pass are used for design. A residence time of 1 hour is employed. The reactor material of construction is normally 316 Stainless Steel and is fabricated in multi-layer construction to meet the high-pressure rating. Catalyst life amounts to about 100 kg HMDA produced per kg of catalyst.

The liquid reactor product consisting of HMDA, HMI, dissolved NH_3 and H_2, unreacted diol, by-product H_2O, and high boilers is heat exchanged with the incoming HMI-diol feed stream and then fed to a series of three flash drums. The flashing operation provides a stagewise reduction in pressure and recovers the dissolved hydrogen as a vapor for refeeding to the compressor. A small portion of the dissolved NH_3 is also vaporized, and this is recovered in the knockout drums of the compressor facility. The major part of the dissolved ammonia is recovered in the ammonia stripper column. Ammonia is liquefied overhead by a water-cooled condenser, from which it is pumped back to the NH_3 feed tank.

The ammonia stripper column operates at about 200 psig, to condense the ammonia overhead at 100°F. The bottoms temperature averages about 390°F. The bottoms product (containing HMDA, HMI, diol, H_2O and high boilers) is fed to a drying column and then to the Water Stripper column. The stripper column operates as an azeotropic column using cyclohexane as the entraining agent to promote separation of the water. The use of cyclohexane counteracts the formation of the H_2O/HMI azeotrope. (This azeotrope has been reported as a means of separating the HMI from the HMDA.) The overhead stream from this tower consists of the heterogeneous cyclohexane-water azeotrope, which condenses as a two-phase liquid in the overhead decanter. The cyclohexane upper layer is returned to the column as a reflux, and the lower layer, mostly water, is sent to waste. This column normally operates at atmospheric pressure, with an overhead temperature of about 165°F and a bottoms temperature of 212°-225°F.

The bottoms from this tower, essentially anhydrous, are fed to the HMI stripper Column to remove HMI for recycling. This stripper column is operated under vacuum of about 200 mm Hg. such that reboiler temperatures in the range of 310-330°F are not exceeded. Temperatures of 390°F and higher tend to promote reactions between the HMDA and the unreacted diol to produce high boilers. The HMI Stripper bottoms are then fed to the HMDA product column, where the HMDA is taken overhead at 99.94% purity. The bottoms, consisting of a small percentage of HMDA and the unreacted diol plus high boilers, are recycled to the diol feed tank. Periodic buildup of the high-boiler concentration will necessitate an intermittent purge of the bottoms. Alternatively, a 1,6-hexanediol polishing still may be added to provide for continuous separation of the diol from the high boilers. In actual operation, the reactor conditions may possibly be adjusted so that the high-boiler content is minimized to some equilibrium value.

The major wastewater pollution sources for this process are wastewaters from the drying column, the decanter associated with the azeotropic column, and the steam jet condensate. The analytical results obtained from the sampling survey are shown in the following tabulation.

PROCESS FLOW
    liter/kkg   1,100
    gal/M lb   132

BOD_5 RWL
    mg/liter[1]   3,630
    kg/kkg[2]   4.0

COD RWL
    mg/liter[1]   10,600
    kg/kkg[2]   11.7

TOC RWL
    mg/liter[1]   2,260
    kg/kkg[2]   2.5

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

It should be noted that most of the wastewater upon which the previous RWL calculations are based is disposed of via deep-well injection. Only wastes such as slab washdown water and storm runoff are treated in an aerated lagoon.

FIGURE 4-11

HEXAMETHYLENEDIAMINE- AMMONOLYSIS OF 1,6-HEXANEDIOL
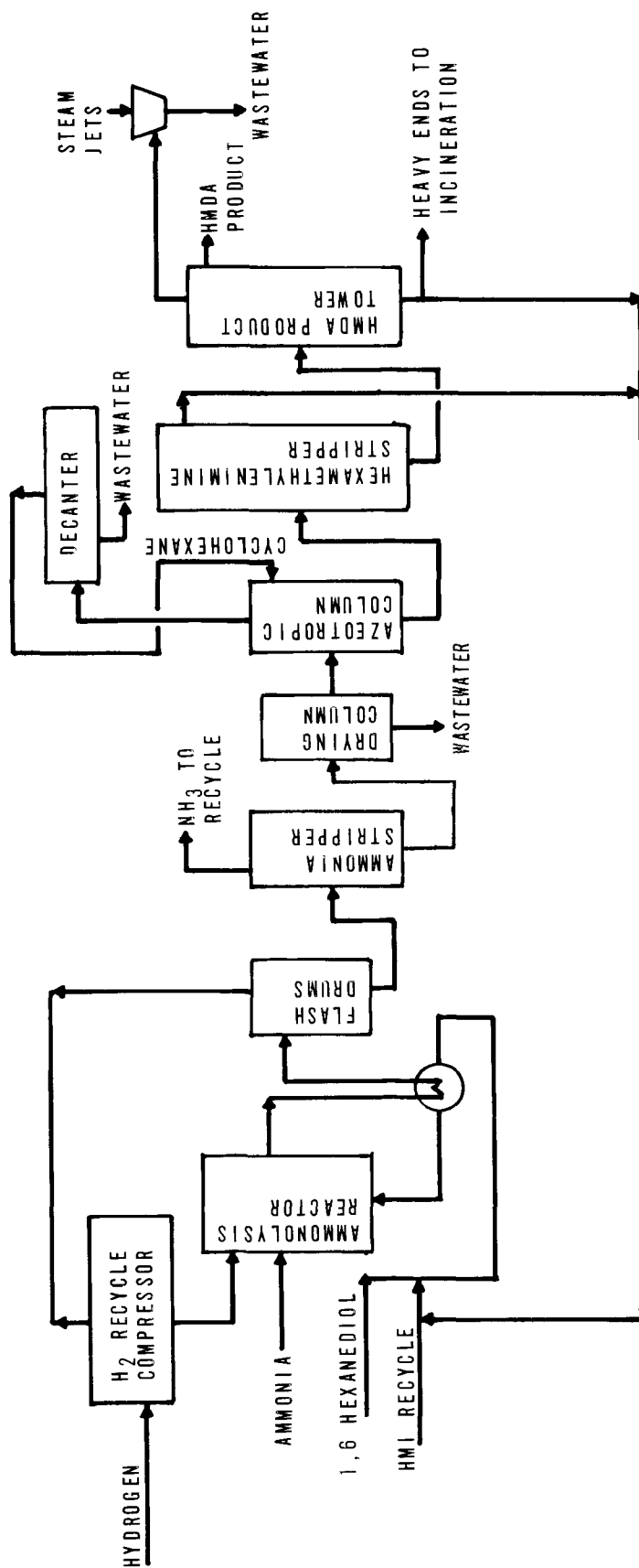
Product: Maleic Anhydride

Process: Oxidation of Benzene

Process RWL Category: B

Chemical Reactions:

$$C_6H_6 + 4\tfrac{1}{2}\,O_2 \xrightarrow{V_2O_5} (CH)_2\text{-}(CO)_2\text{-}O + 2\,CO_2 + H_2O$$

Benzene   Maleic Anhydride
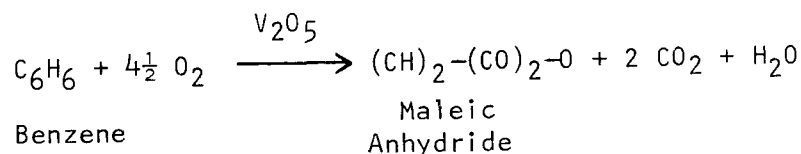
15 percent per year after having remained static for several years; the growing use of polyester resins is the main reason for this rapid increase in demand. Additional uses of maleic anhydride include pesticides, surface coatings, plasticizers, and lubricants. Also, maleic anhydride is used as a raw material for the production of fumeric and maleic acid. Fumeric acid finds wide use as a food acidulant; additional applications of fumeric acid resemble those of maleic anhydride. Maleic acid is used solely as a food acidulant.

Essentially all maleic anhydride in the U.S. is based on the oxidation of benzene. A process flow diagram of this oxidation process is shown in Figure 4-12. As shown in the process flow diagram, the production of maleic anhydride is achieved by a process consisting of:

1. A reaction section, where benzene is oxidized with air to form maleic anhydride.

2. A recovery section, in which maleic anhydride is separated from noncondensibles.

3. A dehydration section, in which maleic acid is dehydrated to maleic anhydride.

4. A fractionation section, in which pure maleic anhydride is produced.

Benzene is vaporized and fed to a fixed-bed reactor, to which compressed air is also fed. Typical operating conditions are 25 psig and 750°F. Conversion of benzene is essentially complete on a once-through basis. Temperature control is achieved by circulation of a heat-transfer salt through the shell side of the reactor, with indirect steam generation. Vanadium pentoxide is used as the catalyst.

Reactor off-gas is cooled at a precondenser to condense as much of the maleic anhydride as possible from the vapor. Condensed maleic anhydride is piped to crude storage tanks prior to fractionation. The remainder of maleic anhydride is recovered by scrubbing with water, forming maleic acid. The acid is then dehydrated, thus forming maleic anhydride. Xylene is added to the dehydrator to form an azeotropic mixture, thus facilitating dehydration. The xylene is recovered from the excess water by decantation.

The recovered maleic anhydride in the separator and dehydrator is fed to a fractionator, where pure maleic anhydride is produced. The light and heavy ends are withdrawn from the dehydration and fractionation columns respectively, and are disposed of by incineration.

The major water pollution sources of this process are the excess water withdrawn from the decanter and the periodic washings from the dehydrator, fractionator, and storage tanks. Process RWL calculated from the flow measurements and analyses of wastewater samples obtained in the survey periods are presented in the following tabulation:

	Plant 1	Plant 2
PROCESS FLOW		
liter/kkg	6,600	2,300
(gal/M lb)	788	274
BOD$_5$ RWL		
mg/liter[1]	63,500	47,000
kg/kkg[2]	418	108
COD RWL		
mg/liter[1]	90,000	126,000
kg/kkg[2]	592	287
TOC RWL		
mg/liter[1]	23,500	52,500
kg/kkg[2]	155	120

[1] Raw waste concentration are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weight of product.

Based on the previous process description, the flow and raw waste loadings for Plant 1 appear extremely high. This may be partially explained by the fact that wastewaters from the dehydrator are presently discharged rather than recycled to the scrubber. This flow is approximately 2/3 of

the total flow. These wastewaters contain high concentrations of fumeric acid, thus contributing to a high BOD, COD, and TOC. It is anticipated that this stream will be recycled in the near future. At the Plant 2 facility, the dehydrator water is recycled, and both the flow and pollutant level are lower than that of Plant 1. An arithmetic average of the RWL from Plant 1 and 2 was used for BPCTCA.

Wastewater from Plant 1 is combined with other process wastes from the facility and is treated by the activated sludge process. The wastewater is fed to the biological system at a slow, controlled rate because of its high concentrations. The wastewater from Plant 2 is hauled away by a contract disposal service.

FIGURE 4-12
MALEIC ANHYDRIDE-OXIDATION OF BENZENE
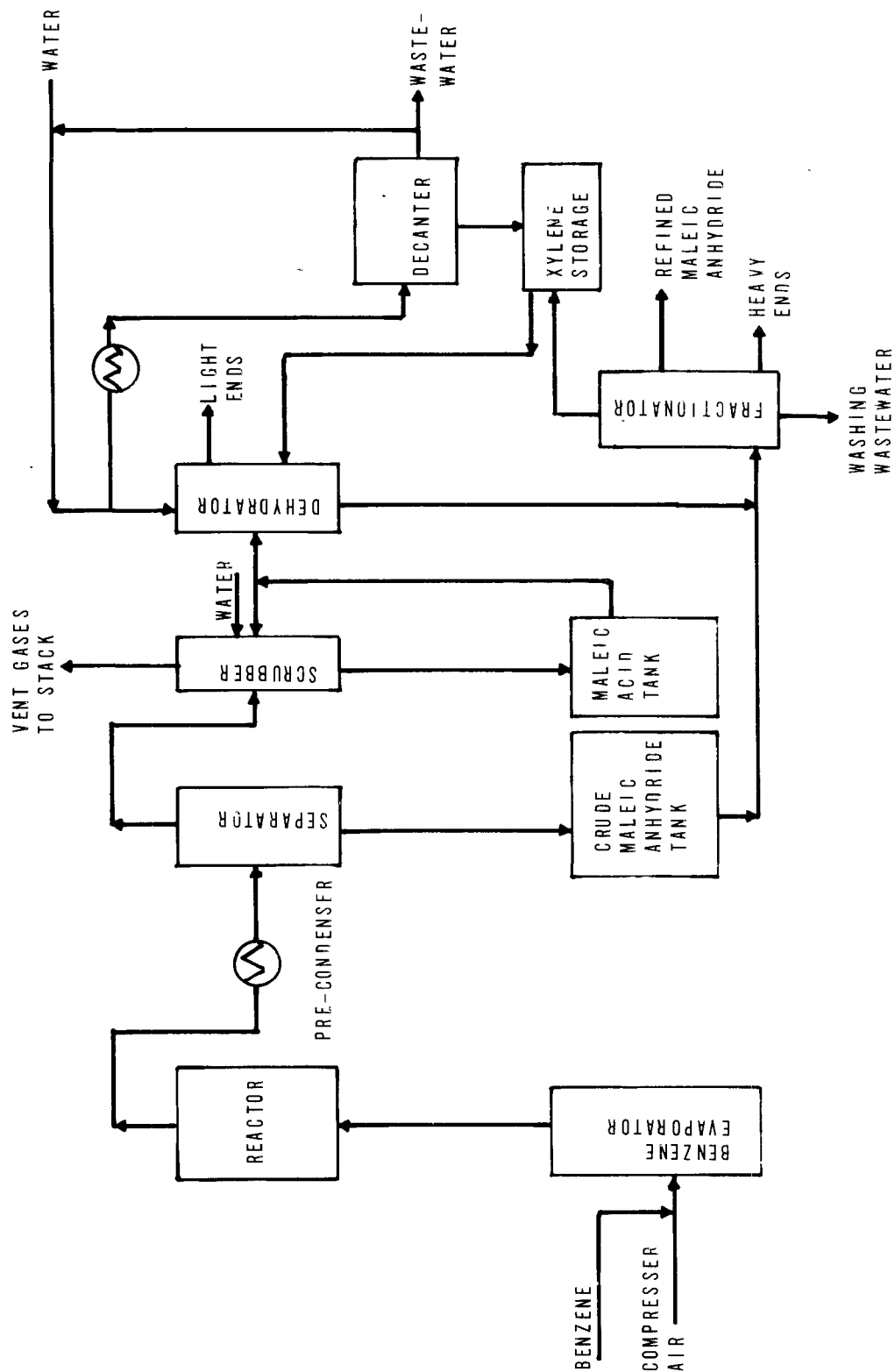
Product: Methyl Chloride

Process: Esterification of Methanol with Hydrochloric Acid

Process RWL Category: B

Chemical Reactions:

$$CH_3OH \quad + \quad HCl \quad \xrightarrow{\text{Metal Catalyst}} \quad CH_3Cl \quad + \quad H_2O$$

Methanol Hydrochloric Acid   Methyl Chloride
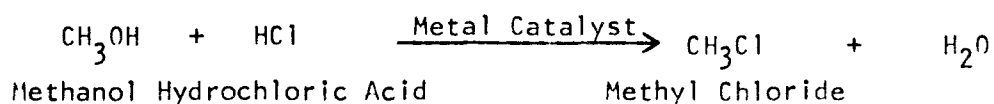
Methyl Chloride is used primarily as an intermediate during the production of other chemicals. Primary end-products include silicones, tetra methyl lead, and cellulose ethers. Chlorinated solvents such as carbon tetrachloride can also be manufactured, using methyl chloride as a raw feedstock. Methyl chloride is also used as a catalyst solvent during the production of butyl rubber.

A process flow diagram for the production of methyl chloride by esterification of methanol with hydrochloric acid is shown in Figure 4-13.

Methanol and hydrochloric acid are heated and then combined in the presence of $ZnCl_2$ in the reactor. The crude product is discharged into a fractionator from which the catalyst stream is recycled back to the reactor. The vapor phase from the fractionator is then passed through a series of scrubbing units. Water and caustic solution are used to scrub the product vapor, which is then sent to a condenser. Finally, the product is treated with highly concentrated sulfuric acid to remove the water from the product stream.

The major pollution sources of this process are the waters discharged from various scrubbing units and the concentrated sulfuric acid stream from the drying unit. Process RWL calculated from the flow measurements and the analyses of wastewater samples obtained in the survey periods are presented in the following tabulation:

	Plant 1		Plant 2*	Plant 3
	Sample Period #1	Sample Period #2	Sample Period #1	Sample Period #1
PROCESS FLOW				
liter/kkg	583	583	12,000	842
(gal/M lb)	69.9	69.9	1,430	101
BOD_5 RWL				
mg/liter[1]	1,210	1,940	1,480	371
kg/kkg[2]	0.703	1.13	17.7	0.314
COD RWL				
mg/liter[1]	119,700	112,800	5,240	4,090
kg/kkg[2]	69.8	65.8	62.7	3.45
TOC RWL				
mg/liter[1]	29,000	31,600	1,070	1,080
kg/kkg[2]	16.9	18.4	12.8	0.908

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewater.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

*BPCTCA

In the foregoing examples, a considerable difference in flow is evident. This may be explained partially by the fact that Plants 1 and 2 utilize scrubbers for removal of hydrochloric acid while Plant 3 employs a freezing step. Wastewaters common to both installations include pump leakages and washdowns.

The analytical results also indicate that, in addition to the parameters shown in the tabulation, water pollution parameters such as pH, sulfate, chloride, and zinc are at levels hazardous to biological treatment processes; the low BOD_5 values shown in the tabulation for Plant 1 are the results of these biological inhibiting factors. The differences in pollutant loadings among three facilities visited in the survey period are attributed to differences in operating efficiencies in the scrubbing and drying units. The values represented by Plant 3 can be considered as BATEA control technology. The RWL in Plant 2 is considered BPCTCA.

The final disposition of process wastewaters for the three plants surveyed is indicated below:

Plant 1 - deep-well injection
Plant 2 - municipal treatment
Plant 3 - neutralization and discharge to surface waters.

An alternative method for producing methyl chloride is by direct chlorina-
tion of methane. Despite the ample availability of cheaper methane,
approximately 65% of all methyl chloride is produced in the U.S. from
methanol. Part of the reason lies in the economics of chlorine utiliza-
tion.

FIGURE 4-13

METHYL CHLORIDE— ESTERIFICATION OF METHANOL WITH HYDROCHLORIC ACID
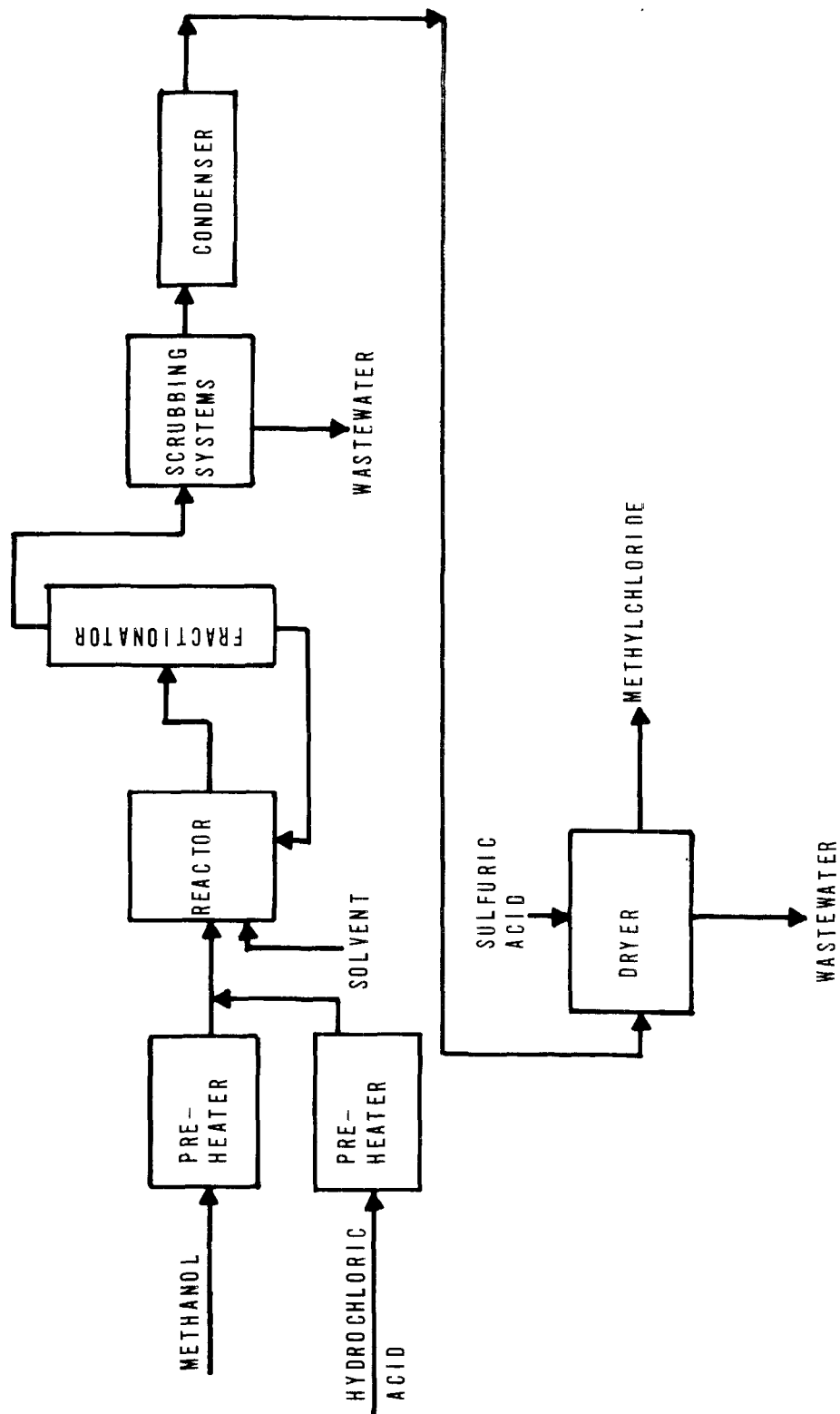
Product: Methyl Ethyl Ketone (MEK)

Process: Dehydrogenation of Secondary Butyl Alcohol (SBOH)

Process RWL Category: B

Chemical Reactions:

$$CH_3CH(OH)CH_2CH_3 \longrightarrow CH_3COCH_2CH_3 + H_2$$
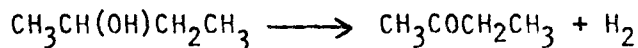
Sec-butyl Alcohol   methyl ethyl ketone

A flow diagram for this process is shown in Figure 4-14. Secondary butyl alcohol is passed through a reactor containing a catalyst bed of zinc oxide or brass (zinc-copper alloy), maintained at 400 to 550°C. The vapor-phase dehydrogenation reaction takes place at near atmospheric pressure, with MEK, by-product hydrogen, and unreacted secondary butyl alcohol subsequently separated. This process is analogous to the production of acetone via the dehydrogenation of isopropyl alcohol. Both are considered typical of Category B vapor-phase processes.

The MEK process, however, is complicated by the fact that the secondary butyl alcohol feed is a minimum boiling point azeotropic binary mixture containing approximately 70 wt. % alcohol and 30 wt. % water. The presence of this water in the feed complicates the process because of the azeotropes it forms with both the feed alcohol and product MEK.

As shown in Figure 4-14, the crude secondary butyl alcohol is fed to the azeotrope column, where light hydrocarbons are taken overhead and heavy organics are discharged as bottoms. These heavy hydrocarbons are usable by-product material and are used in other processing. Relatively concentrated streams of secondary butyl alcohol and water are taken off as side streams in this distillation.

The alcohol stream is used first to scrub the hydrogen gas produced in the reactor to remove unreacted alcohol, and then is sent from the alcohol scrubber to the conversion furnaces and reactors for dehydrogenation.

A condensed product stream containing MEK and unreacted alcohol is taken from the reactor and sent to two distillation columns. The first dehydrates the product mix by taking water and light hydrocarbons overhead. Product MEK is separated from recycle alcohol in the second column (MEK column in Figure 4-14).

Figure 14-4 illustrates the extensive reuse of water observed at one of the two process plants surveyed. Fresh water (in addition to that present in the SBOH feed) is added in the azeotrope column to facilitate separation, and is also added to the hydrogen scrubber. The hydrogen scrubber recovers

additional SBOH from the gas leaving the alcohol scrubber. The hydrogen gas leaving the hydrogen gas scrubber is burned as fuel.

The aqueous bottoms from the hydrogen scrubber are combined with water cuts taken from the azeotrope and dehydration columns, and the combined aqueous stream is sent to the butyl water column. Light hydrocarbons are taken overhead in this column, and part of the aqueous bottoms is discharged as wastewater while the remainder is reused in the light-ends scrubber which recovers additional SBOH from the light material distilled in the azeotrope column. The aqueous bottoms from the light-ends scrubber are sent to the dehydration column for recovery of SBOH.

The following tabulation summarizes the raw waste load data obtained from the two plants sampled. The RWL shown for Plant 2 is much higher because some of the light hydrocarbons purged (used elsewhere or burned) in Plant 1 are discharged in the wastewater from Plant 2.

	Plant 1	Plant 2
PROCESS FLOW		
liters/kkg	1,310	795
gal/M lb	157	95
BOD$_5$ RWL		
mg/liter[1]	3,000	91,000
kg/kkg[2]	3.92	72.1
COD RWL		
mg/liter[1]	1,627	260,000
kg/kkg[2]	2.13	206
TOC RWL		
mg/liter[1]	521	102,000
kg/kkg[2]	0.68	80.9

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact processed wastewaters.

[2]Raw waste loadings are based on unit weight of pollutants per 1000 unit weights of product.

An average of the RWL values presented above was considered as BPCTCA. In both plants, the MEK process is part of a large chemical complex. Process wastes from MEK are combined with large volumes of other wastes prior to treatment and discharge to surface waters.

FIGURE 4-14

METHYL ETHYL KETONE (MEK)-DEHYDROGENATION OF SEC-BUTYL ALCOHOL (SBOH)
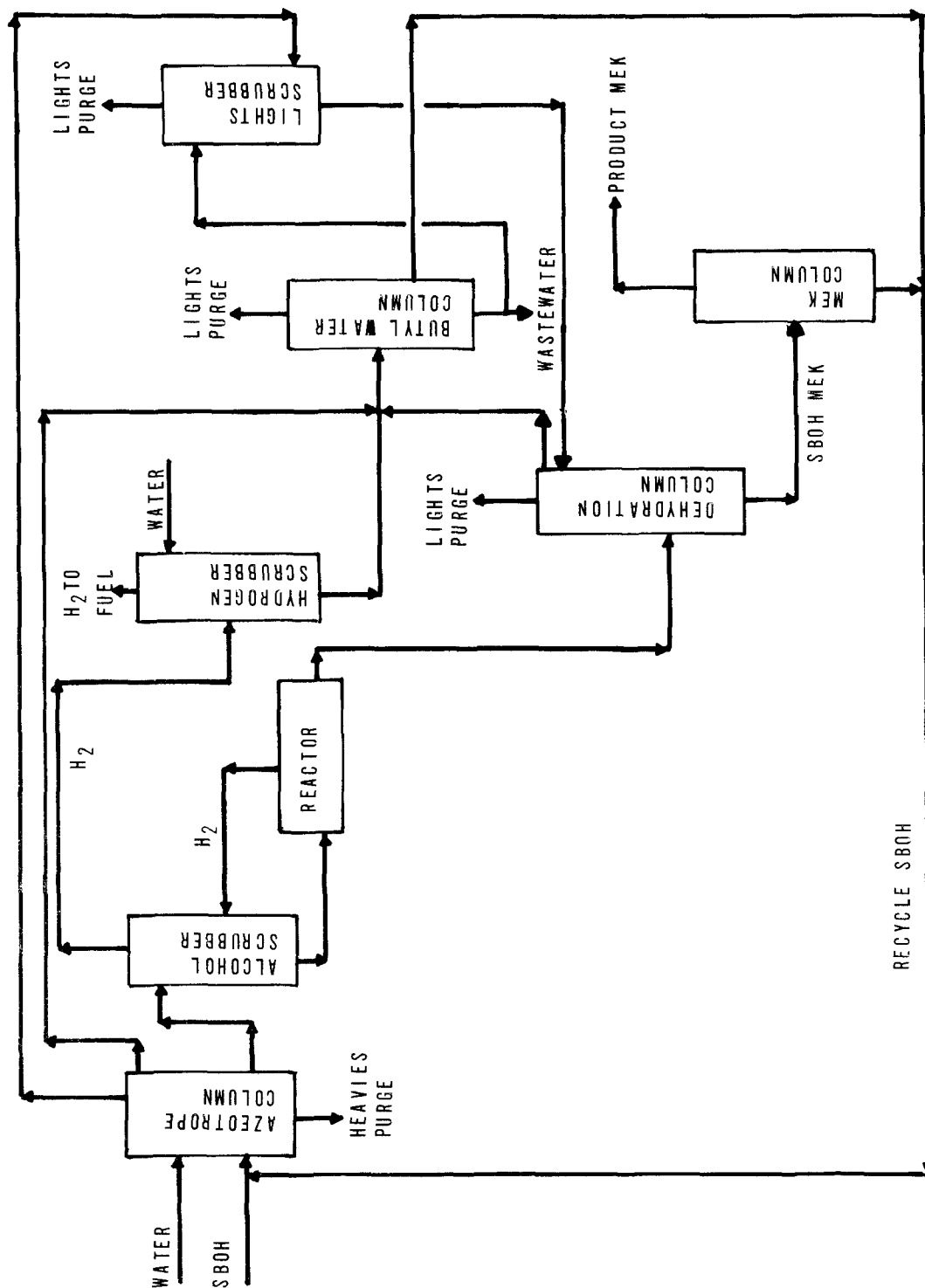
Product: Perchloroethylene

Process: Chlorination of chlorinated hydrocarbons

Process RWL Category: B

Chemical Reactions:

$$\text{Chlorinated Hydrocarbons} \;+\; Cl_2 \longrightarrow Cl_2C = C\,Cl_2$$

Chlorine   Perchloroethylene

Perchloroethylene is used largely in dry-cleaning and vapor degreasing. Dry-cleaning consumes approximately 85 percent of the total; the rest going into general solvent services and as an intermediate for fluorocarbons.

A process flow diagram for the manufacture of perchloroethylene is shown in Figure 4-15.

The chlorinated hydrocarbons and chlorine gas are reacted thermally (rather than catalytically) at temperatures in the range of 500-700°C. The reactions are highly exothermic, and control of heat transfer is a key to smooth and efficient reactor performance.

The reaction mechanism may be visualized in terms of an initial, very rapid, thermally activated, free-radical chlorination to transient compounds having high chlorine/carbon ratios. These transient compounds decay quickly, primarily to the low free-energy forms. The perchloroethylene/carbon tetrachloride mixture then shifts toward equilibrium in the rate-controlling step.

The reactor effluent is quenched, and the gas stream leaving the quench vessel is absorbed with recycled HCl solution in an absorption tower. The remaining unabsorbed chlorine gas is then dehydrated and recycled back to the reactor.

The liquid reaction product stream goes from the quench vessel to the separator, where the aqueous stream is removed as HCl solution. The product mixture (carbon tetrachloride and perchloroethylene) is separated by distillation. The perchloroethylene/carbon tetrachloride mixture is controlled by suitable recycle and by provision of appropriate residence time in the reactor.

The wastewater pollution sources of this process are pump-seal leakages and miscellaneous reactor washdowns. Process RWL calculated from flow measurements and analyses of the wastewater streams are shown in the following tabulation.

	Sample Period #1	Sample Period #2
PROCESS FLOW		
liter/kkg	5,400	5,400
gal/M lb	643	643
BOD$_5$ RWL		
mg/liter[1]	83	79
kg/kkg[2]	0.449	0.427
COD RWL		
mg/liter[1]	357	695
kg/kkg[2]	1.92	3.73
TOC RWL		
mg/liter[1]	30	31
kg/kkg[2]	0.164	0.169

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact processed wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

An average of the foregoing values was considered as BPCTCA. The wastes from this process are disposed of by deep-well injection.

An alternative method for the manufacture of perchloroethylene is by the Detrex-SD process, in which the feedstocks (ethylene and chlorine) enter a liquid-phase chlorination reactor. Temperature and pressure are moderate, and concentrations are carefully controlled by recycle quantity and composition to give the desired product distribution at optimum economics.

In the classical route, perchloroethylene is prepared from acetylene, via trichloroethylene. The chemical reaction is shown as follows:

$$C_2H_2 + 2Cl_2 \longrightarrow Cl_2CHCHCl_2 \xrightarrow{-HCl} ClCH = CCl_2$$

Acetylene   Tetrachloroethane   Trichloroethylene

$$\xrightarrow{Cl_2} Cl_2HC - CCl_3 \xrightarrow{-HCl} Cl_2C = CCl_2$$

Pentachloroethane   Perchloroethylene

The chlorine and acetylene are brought into contact with each other in a reactor at a temperature of 250-300°C in the presence of barium chloride deposited on carbon as catalyst. The product, tetrachloroethane, is then

dehydrochlorinated in a catalytic reactor to produce trichloroethylene, which is chlorinated at 80-90°C over a catalyst containing 0.2-0.3% FeCl$_3$ to yield pentachloroethene. The perchloroethylene is then obtained by the dehydrochlorination of pentachloroethane by milk of lime at 110°C and 200 mm Hg.

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FIGURE 4-15

PERCHLOROETHYLENE-CHLORINATION OF CHLORINATED HYDROCARBONS

-81-
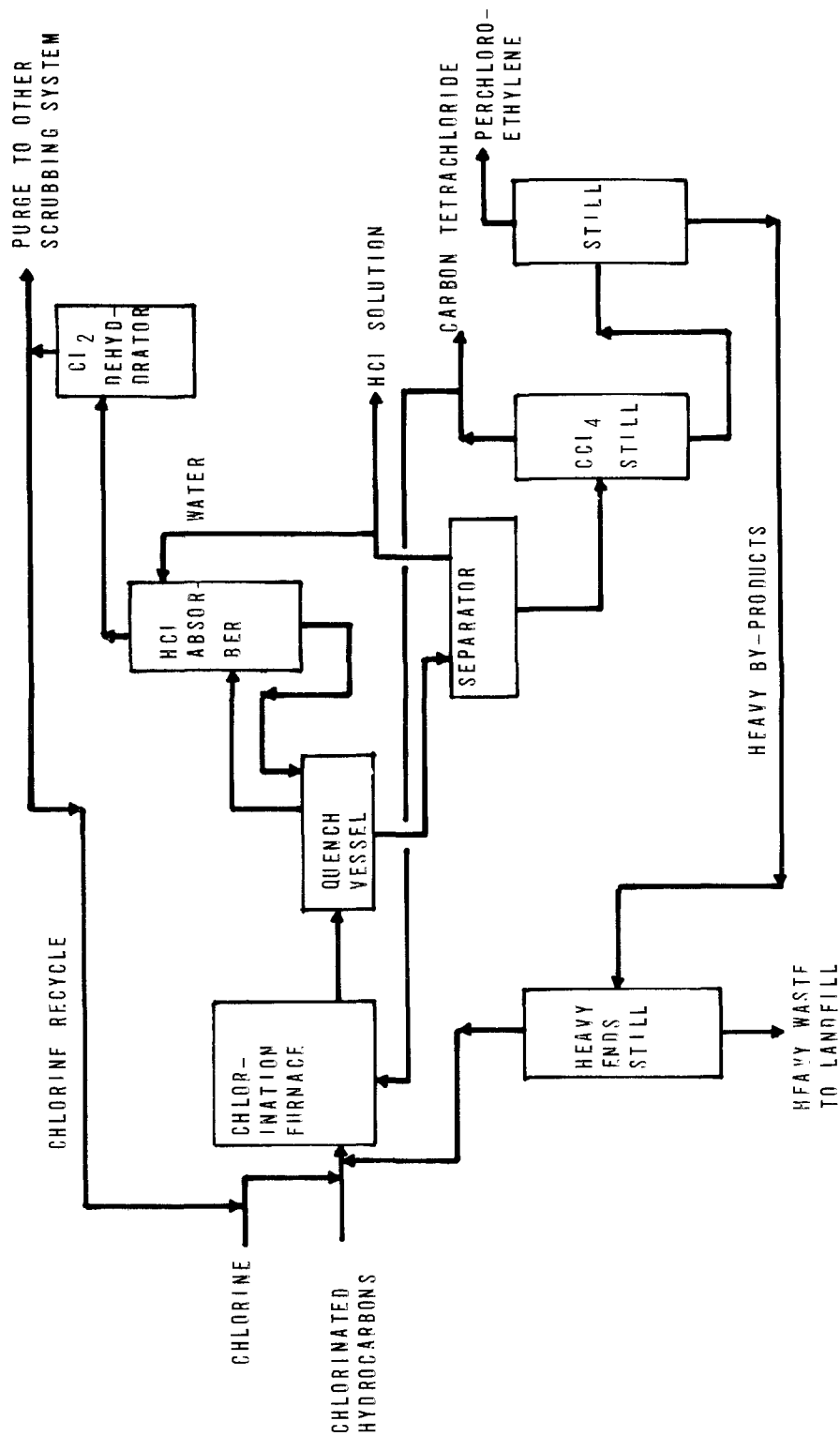
Product: Phthalic Anhydride

Process: Oxidation of o-Xylene

Process RWL Category: B

Chemical Reactions:

$$C_6H_4 (CH_3)_2 + 3O_2 \longrightarrow C_6H_4 (CO)_2O + 3H_2O$$

o-xylene   phthalic
anhydride
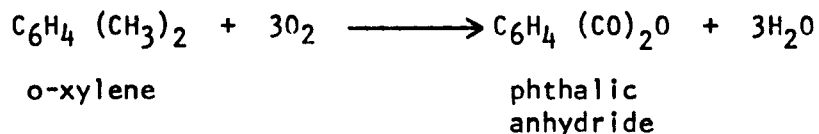
Phthalic anhydride is commonly produced by either of two methods: oxidation of o-xylene, or oxidation of naphthalene. In the U.S., about 80% of the capacity is still based on napthalene, although there is a definite trend in favor of the vapor-phase oxidation of o-xylene. This trend is based primarily on economics (o-xylene feedstock is cheaper than naphthalene). A description of the production of phthalic anhydride using a naphthalene feedstock is found in the following section.

Phthalic anhydride has become one of our most important intermediates. It is commonly used during the production of plasticizers. The less volatile phthalates are used principally in wire- and cable-coatings which are subject to higher temperatures. Phthalic anhydride derivatives are also used in the production of alkyl resins. These resins are in turn used in coatings, such as latex paints, thermosetting acrylic finishes, and epoxy coatings. Phthalic anhydride is used directly in making a number of dyes such as eosin, quinoline yellow, phenolphthalein, and copper phthalocyanine. It is also used during the production of anthraquinone and anthraquinone derivatives by condensation (Friedel Crafts) procedures

Production of phthalic anhydride by oxidation of o-xylene is based on vapor-phase, fixed-bed technology. Typical operating conditions are 5 psig and 700°F. The process uses a carrier-supported vanadium pentoxide catalyst, which normally lasts from 3 to 5 years. The crude product obtained is 99-99.5% phthalic anhydride, with some maleic, benzoic, and other acids.

An ortho-xylene oxidation process flow diagram is shown in Figure 4-16. Filtered air is first compressed and preheated in a heat exchanger. The o-xylene feedstock is also preheated and vaporized by injection into the hot-air stream; unevaporated o-xylene is trapped before the stream enters the reactor.

During the reaction step, a considerable quantity of heat is generated. The heat is removed by molten salt circulating on the shell side of the reactor. The molten-salt solution is passed from the top of the reactor to a heat-exchange system, where process steam is produced. Gases leaving the reactor at 375°C are passed through a waste-heat boiler for additional steam generation. Cooled gases enter a bank of automatically controlled switch condensers.

When a condenser is on the crystallization cycle, cold mineral oil is circulated through the coils to cool and crystallize phthalic anhydride from the gaseous phase. When the condenser is switched to phthalic anhydride recovery, hot oil is circulated through the coils to remelt the crude product. The crude product is then drawn off to an intermediate storage tank. Residual gases from the condensers are scrubbed to reduce the volatile organic content. The scrubbed gas passes through a demister and is vented to the atmosphere.

Crude product from the storage tank is then passed through a heater and into the continuous pretreatment section. Dissolved phthalic acid is dehydrated under a slight vacuum to the anhydride. Additives may be introduced at this point to remove impurities produced by polycondensation of heat-sensitive compounds. The crude phthalic anhydride is then pumped through a pre-cooler to a continuous distillation section. Two columns are employed, both operating under vacuums created by two-stage steam ejectors; wastewaters from these ejectors are sent to an incinerator. In the first-stage stripper column, maleic anhydride and benzoic acid are separated as overheads. Bottoms from the first-stage column are passed to a second-stage rectifier column. Final product (99.99% phthalic anhydride) is withdrawn as distillate overhead.

Since waters from stream ejectors are disposed of by incineration, the only water pollution source of the process is the waste stream withdrawn from the vent gas scrubber. Process RWL calculated from the flow measurements and analyses of water samples obtained during the survey period are shown in the following tabulation:

PROCESS FLOW
liter/kkg   593
(gal/M lb)   71.2

BOD_5 RWL
mg/liter[1]   215
kg/kkg[2]   0.128

COD RWL
mg/liter[1]   1,080
kg/kkg[2]   0.642
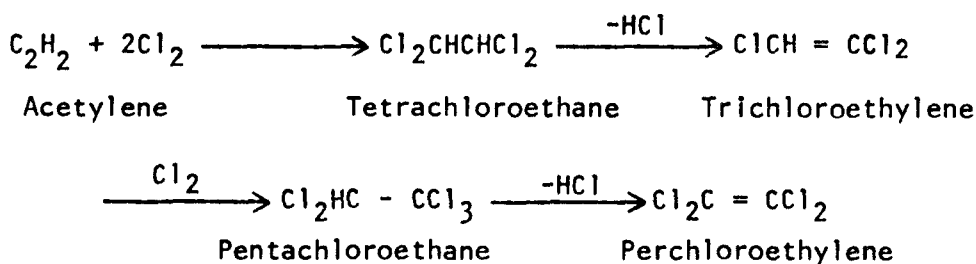
TOC RWL
mg/liter[1]   34
kg/kkg[2]   0.02

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact processed wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

These waste loads are considered as BPCTCA. They are combined with other wastes in this plant and treated in a biological system prior to discharge.

FIGURE 4-16

PHTHALIC ANHYDRIDE—OXIDATION OF O-XYLENE
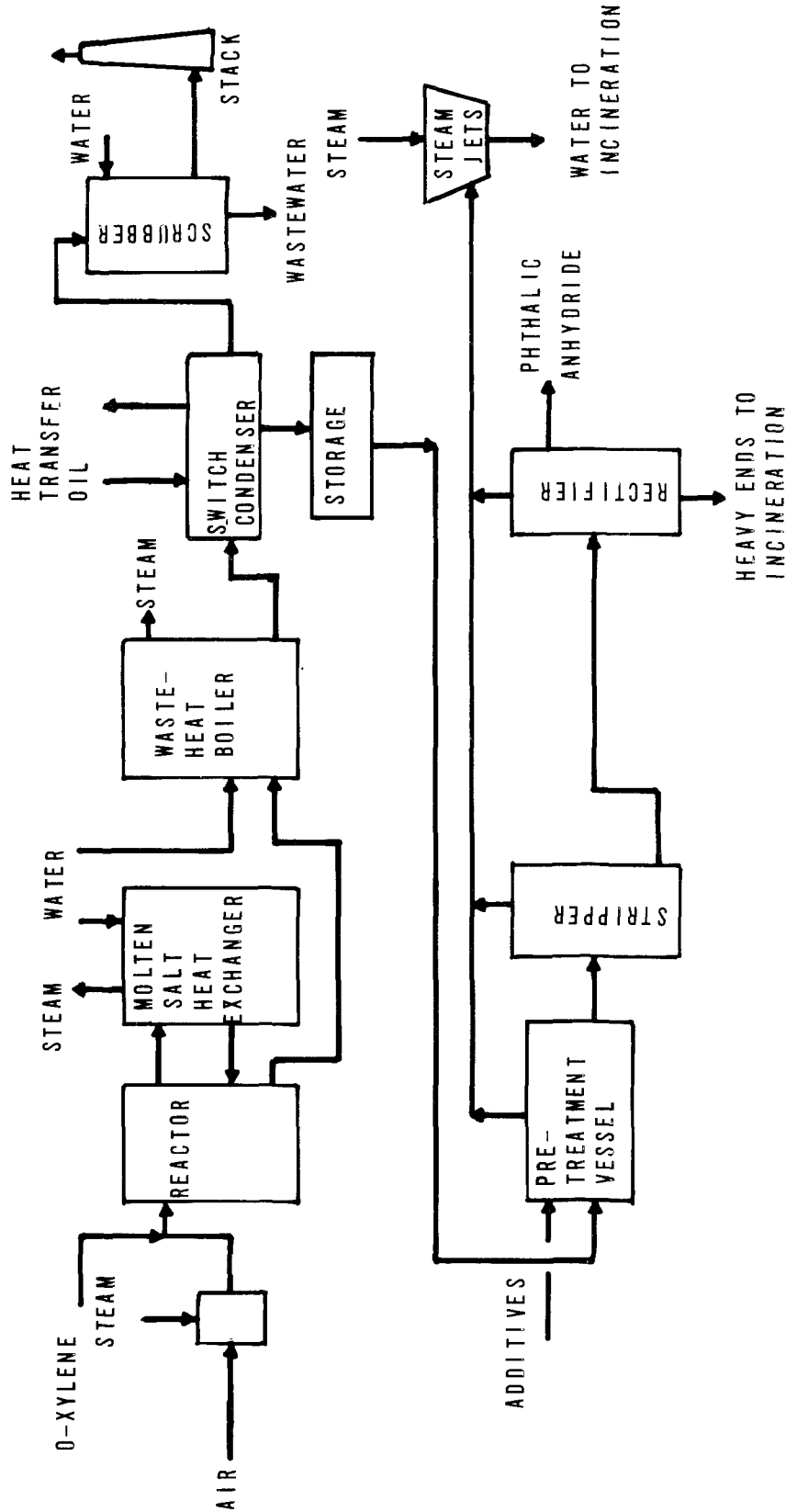
Product: Phthalic Anhydride

Process: Oxidation of Naphthalene

Process RWL Category: B

Chemical Reactions:

$$C_{10}H_8 + 4\tfrac{1}{2}O_2 \xrightarrow{V_2O_5} C_6H_4(CO)_2O + 2CO_2 + 2H_2O$$

Naphthalene   Phthalic Anhydride
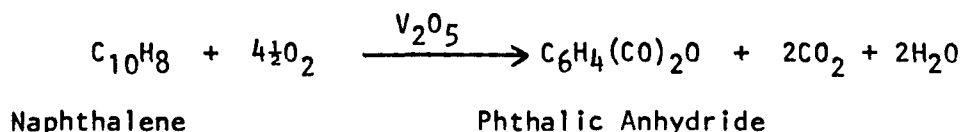
In the United States, approximately 80% of the present phthalic anhydride capacity is based upon the oxidation of naphthalene. However, there is a trend toward the vapor-phase oxidation of o-xylene, which has been discussed in the previous section. Phthalic anhydride may be produced from naphthalene using either a fixed or fluid catalyst bed. In addition to process variations, the purity of the final product is a function of the reactor type, in that maleic anhydride is formed as a by-product in the fixed-bed reactor but it is not formed in the fluidized-bed reactor.

During the sampling period, an installation employing a fluidized-bed reactor was visited; the fluid catalyst consisted of a finely powdered vanadium catalyst.

A process flow diagram for the naphthalene oxidation process is shown in Figure 4-17. The reactor containing the catalyst is heated to an operating temperature of approximately 900°F. Molten naphthalene is then introduced into the reactor and vaporized by direct contact with the catalyst charge. The vapors become admixed immediately because of the agitated nature of the catalyst bed. The air-naphthalene vapor mixture passes upward through the bed, and the naphthalene is converted to phthalic anhydride, carbon dioxide, carbon monoxide, and water vapor. The product gases, after leaving the dense catalyst phase, pass through a settling zone and into a cyclone system for removal of the catalyst. Recovery of the catalyst is reported to be 100%; thus, make-up catalyst is not required. Following removal of the catalyst, the product gases pass through a condensing system. Aqueous products are then purified, using a series of distillation columns.

There are two major discharges from the phthalic anhydride process area. The most significant of these discharges is a gaseous waste stream vented during the reaction step. The gas contains a high concentration of organics and is discharged to an incinerator.

The second discharge is primarily steam vapor from a vacuum jet in the distillation section. The stream is contaminated with a low concentration of phthalic anhydride. This stream is also discharged to the incinerator.

Since the only source of wastewater is periodic process washings, the raw waste load approaches zero. Although it is recognized that pollutant loadings from the washings contribute to the raw waste load, it is not possible to obtain representative samples of the wastewaters. Thus, equipment washings have not been included in the raw waste evaluations.

Non-contact wastewaters associated with phthalic anhydride include an involuntary blowdown from the internal tempered water system in the crude-product condensing step. In the condensing step, there is a swing between the use of steam and tempered water. During the swing, the tempered water condenses the trapped steam and is discharged. The only pollutants are corrosion inhibitors which are in the initial water.

FIGURE 4-17

PHTHALIC ANHYDRIDE- OXIDATION OF NAPHTHALENE
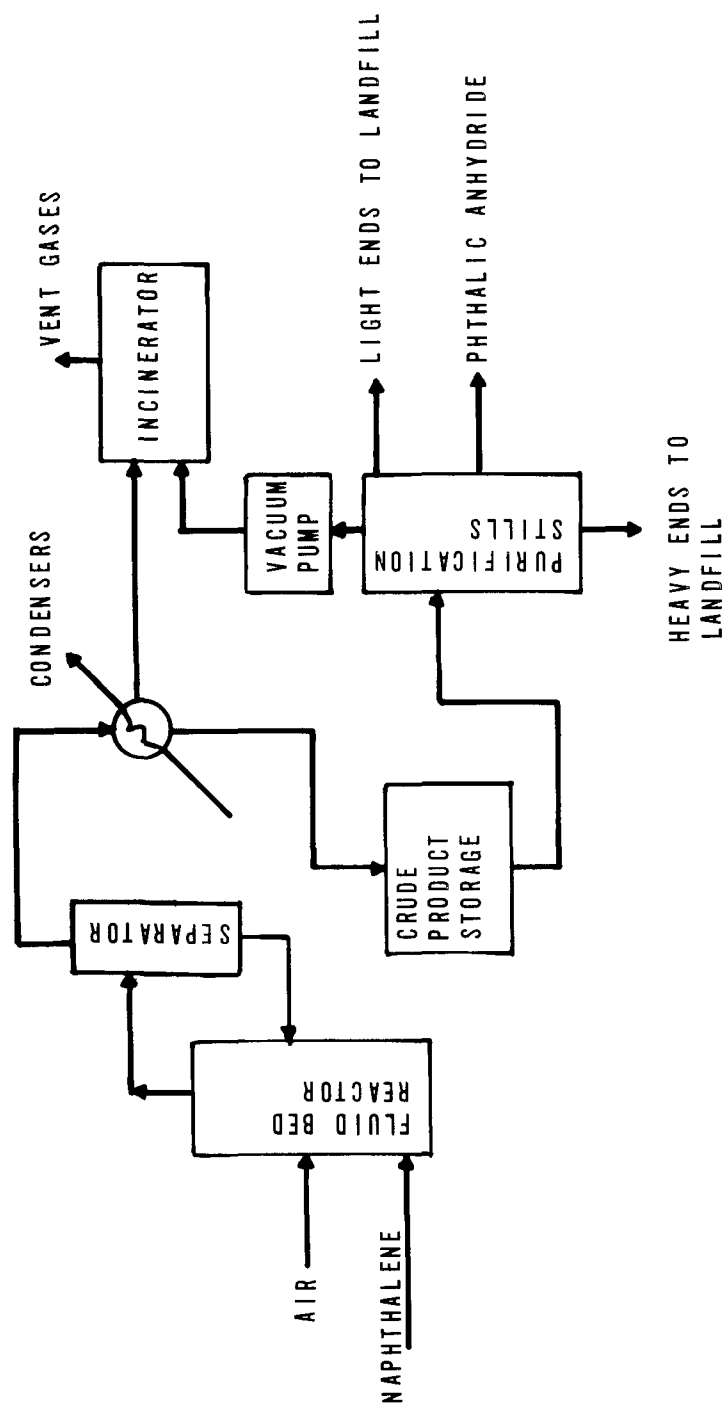
Product: Tricresyl Phosphate (TCP)

Process: Condensation of Cresol and Phosphorus Oxychloride

Process RWL Category: B

Chemical Reaction:

$$3\ C_6H_4(CH_3)OH\ +\ POCl_3\ \longrightarrow\ (C_6H_4(CH_3)O)_3PO\ +\ 3HCl$$

cresol (mixture of o-,   phosphorus   tricresyl
m-, and p-isomers)   oxychloride   phosphate
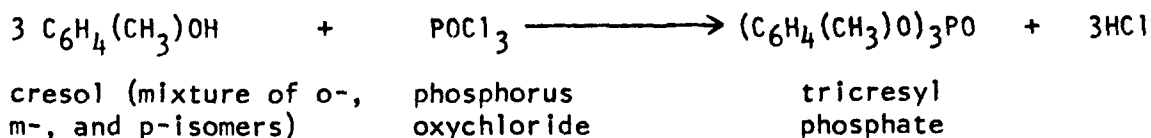
TCP has the property of reducing the flammability of films. This property has led to its use as a plasticizer for nitrocelluous and vinyl chloride plastics. This flammability-reducing property qualifies it for use as an additive in hydraulic fluids and lubricants. TCP is also used as a gasoline additive.

Figure 4-18 presents a simplified process flow diagram of tricresyl phosphate production. Basically, the processing involves purification and then condensation of the raw materials, preliminary purification, and final purification of the product.

Cresol supply has been a problem to manufacturers of tricresyl phosphate for a number of years, both as to availability and quality. Until the post-war period almost all cresol for tricresyl phosphate manufacture was derived from coal tar acids. Most recently, improved processing of carbolate liquids from petroleum sources has resulted in cresols essentially equivalent to those produced from coal tar acids. Furthermore, the shortage of cresols which has long plagued tricresyl phosphate producers and which, probably more than any other factor, had led to commercialization of cresyl diphenyl phosphate in the post-war period, appears to have been eliminated. Since the ortho form of tri-cresyl phosphate is considerably more toxic than those derived from m- and p-cresols, the cresol used for the production of plasticizer-grade tricresyl phosphate is primarily a mixture of m- and p-cresol. Although the xylenol content may be allowed to reach as high as 30 or 40%, the o-cresol content is held below 3%. Because of the random distribution of the three isomers in the resulting phosphate ester, the tri o-cresyl phosphate content of the product is quite low. The cresols used for production of tricresyl phosphate for addition to gasoline may contain a slightly higher o-cresol content and a higher percentage of xylenols.

Cresols react rather readily with phosphorus oxychloride at a temperature of approximately 100°C. to form a mixture of aryl and diaryl phosphoryl chlorides, with only small amounts of triaryl phosphate. The diaryl phosphoryl chloride being the least reactive, more drastic conditions are

required to obtain complete reaction. The presence of significant quantities of aryl phosphoryl chlorides not only reduces yield but leads to difficulty in subsequent refining operations. Therefore, the condensation of cresol and the oxychloride is carried out at elevated temperatures (150° to 300°C.) depending upon catalyst, and the purification scheme employed. A slight excess of cresol favors complete esterification. The time required for the condensation will vary with the catalyst and temperature of reaction. Loss of oxychloride in the hydrogen chloride off-gas is minimized by operating under moderate pressure and/or venting through a condenser. Many catalysts have been reported, but the metal halides appear to be preferred, becuase they permit condensation times of 6-9 hours at temperatures of approximately 200°C. Because the reaction mixture is highly corrosive, glass-lined or alloy kettles are used. The condensation may be operated continuously, by permitting the reaction mixture to pass through a series of reactors at successively higher temperatures.

The purification techniques employed appear to have become rather well standardized. Variation lies rather in the sequence of application, the use of classical batch washing in lieu of the use of columns, and the extent of purification required for product end-use. Preliminary purification may involve direct flash distillation of the crude reaction mixture, or the crude reaction product may first be washed with dilute caustic to neutralize any hydrogen chloride and to hydrolyze and extract traces of partial esterification products and unreacted cresylic compounds. The addition of lime to the reaction mixture prior to distillation, to minimize corrosion, has been reported. Final purification of plasticizer-grade products employs washing with dilute caustic and water (to remove traces of organic acidity), treatment with dilute permanganate solution (to improve color and oxidation stability of the product, a widely accepted quality factor), dehydration by heating under reduced pressure, bleaching with activated carbon and/or earth, and finally filtration. The use of an amphoteric metal in conjunction with an alkaline wash has also been claimed as a color-improvement refining step. In production of tricresyl phosphate as a gasoline additive, some or all of the final purification steps may be omitted; low acidity is required, but color and oxidation stability are not critical.

As indicated in the process flow diagram, each step of the process is performed under vacuum conditions, and each step is equipped with steam jets and barometric condensers. The major pollution sources are the waste streams from those barometric condensers. The analytical results from the sampling program are presented in the following tabulation.

```
PROCESS FLOW
    liter/kkg              28,000
    gal/M lbs               3,355

BOD
    mg/liter[1]                40
    kg/kkg[2]                1.12

COD
    mg/liter[1]               408
    kg/kkg[2]                11.4

TOC
    mg/liter[1]                70
    kg/kkg[2]                1.96
```

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per one thousand unit weights of product.

By using surface condensers it is possible to reduce the process flow requirements, although the process RWL will remain at the same level. Non-contact wastewaters include cooling water flows and steam condensate; the cooling water usage is approximately 740 kg per kg of product, while condensate flow to the sewer is at the rate of 0.96 kg per kg of product.

The process RWL shown above are considered as BPCTCA. All wastes from the plant are discharged to the municipal sewer system.

FIGURE 4-18

TRICRESYL PHOSPHATE- CONDENSATION OF
CRESOL AND PHOSPHOROUS OXYCHLORIDE
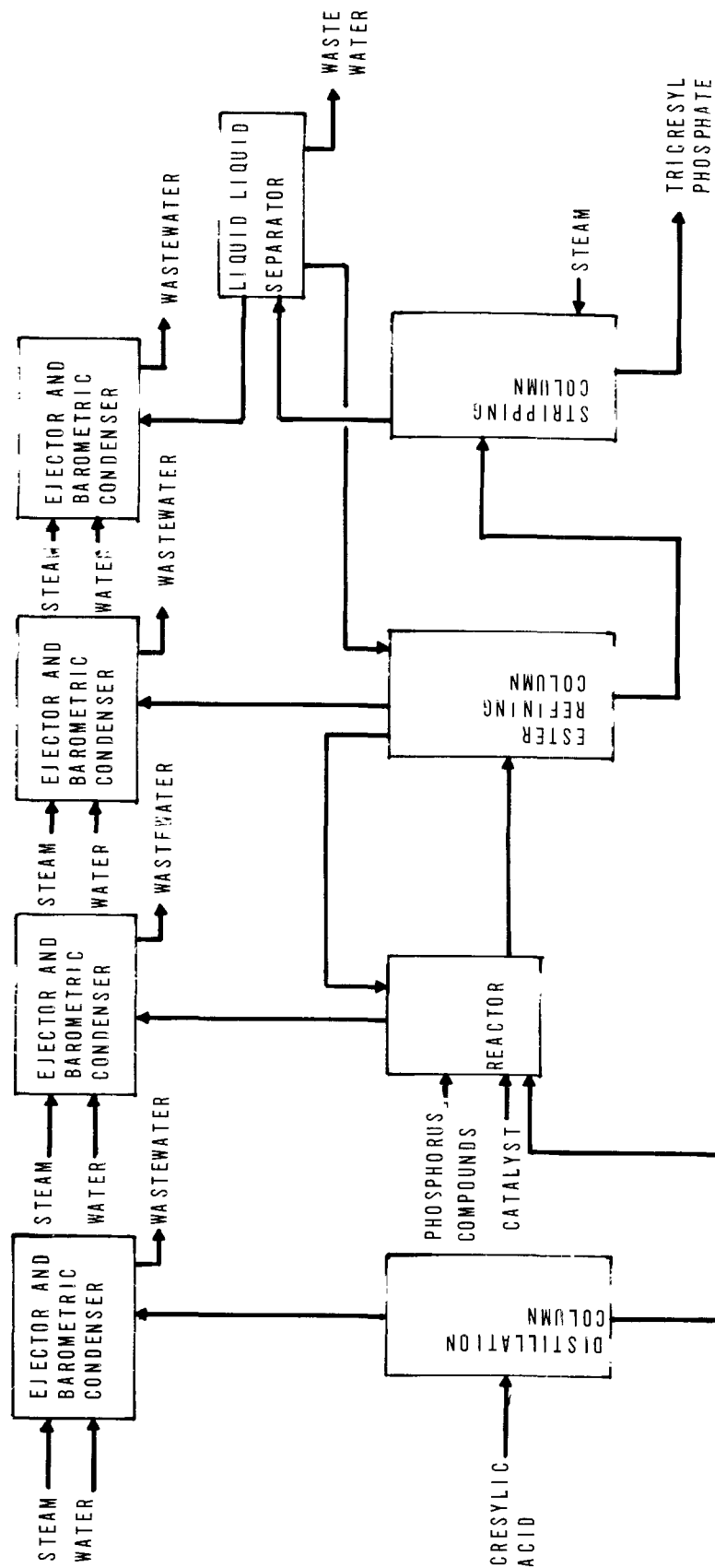
Product: Acetone

Process: Dehydrogenation of Isopropyl Alcohol

Process RWL Category: B

Chemical Reaction:

$$CH_3CHOHCH_3 \longrightarrow CH_3COCH_3 + H_2$$

Isopropanol   Acetone   Hydrogen

This product/process was investigated in Phase 1 of this study, and the detailed process description and process flow diagram can be found in EPA's document, EPA 440/1-73/009 (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) published December, 1973.

Process RWL calculated from flow measurements and analyses of wastewater samples obtained in Phase 2 survey period are shown in the tabulation below:

	Plant 1	Plant 2
PROCESS FLOW		
liter/kkg	2,300	
gal/M lb	276	540
BOD$_5$ RWL		
mg/liter[1]	500	2,530
kg/kkg[2]	1.15	11.4
COD RWL		
mg/liter[1]	8,820	5,150
kg/kkg[2]	20.3	23.2
TOC RWL		
mg/liter[1]	2,400	3,150
kg/kkg[2]	5.53	14.2

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Product: Ethylene Dichloride

Process: Combination of Oxychlorination and Direct Chlorination of Ethylene

Process RWL Category: B

Chemical Reactions:

Direct chlorination: $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$

Ethylene   Ethylene Dichloride

Oxychlorination: $C_2H_4 + 2HCl + \frac{1}{2}O_2 \longrightarrow C_2H_4Cl_2 + H_2O$

Ethylene   Ethylene
                                   dichloride

This product/process was investigated in Phase 1 of this study, and the detailed process description and process flow diagram can be found in EPA's document, EPA 440/1-73/009 (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) published December, 1973.

Process RWL calculated from flow measurements and analyses of wastewater samples obtained in Phase 2 survey period are shown in the tabulation below:

	Sample Period #1	Sample Period #2
PROCESS FLOW liter/kkg gal/M lb	28.2	28.2
BOD$_5$ RWL mg/liter[1] kg/kkg[2]	4,200 0.988	6,200 1.46
COD RWL mg/liter[1] kg/kkg[2]	14,100 3.32	12,900 3.05
TOC RWL mg/liter[1] kg/kkg[2]	6,300 1.48	6,200 1.46

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[1] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Product: Styrene

Process: Dehydrogenation of Ethyl Benzene

Process RWL Category: B

Chemical Reactions:

$$C_6H_5C_2H_5 \longrightarrow C_6H_5C_2H_3 + H_2$$

ethyl benzene   Styrene

This product/process was investigated in Phase I of this, study and the detailed process description and process flow diagram can be found in EPA's document, EPA 440/1-73/009 (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) published December, 1973.

Process RWL calculated from flow measurements and analyses of wastewater samples obtained in Phase 2 survey period are shown in the following tabulation:

	Plant 1	Plant 2		
	Sample Period #1	Sample Period #1	Sample Period #2	Sample Period #3
PROCESS FLOW				
liter/kkg	4,100	5,970	5,970	5,970
gal/M lb	490	715	715	715
BOD$_5$ RWL				
mg/liter[1]	85	49	42	220
kg/kkg[2]	0.35	0.29	0.25	1.31
COD RWL				
mg/liter[1]	380	325	370	525
kg/kkg[2]	1.56	1.93	2.19	3.14
TOC RWL				
mg/liter[1]	80	56	20	100
kg/kkg[2]	0.31	0.33	0.12	0.60

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Both of the production facilities visited during the sampling period have
initiated various pollution abatement programs aimed at achieving BATEA
technology. Process modifications include:

1. Condensing the steam used to pull the vacuums in the distil-
   lation section and piping the wastewater to a separator.

2. Steam Stripping of wastewaters from the separator to remove
   organics, followed by filtration and recycle as boiler feed
   water.

Following these modifications, the resulting raw waste loads are as follows:

	Plant 1	Plant 2		
	Sample Period #1	Sample Period #1	Sample Period #2	Sample Period #3
PROCESS FLOW				
liter/kkg	74	6,260	6,260	6,260
gal/M lb	8.9	750	750	750
BOD_5 RWL				
mg/liter[1]	7	6	16	10
kg/kkg[2]	0.001	0.04	0.10	0.07
COD RWL				
mg/liter[1]	78	59	50	30
kg/kkg[2]	0.006	0.24	0.31	0.19
TOC RWL				
mg/liter[1]	4	13	16	11
kg/kkg[2]	0.0005	0.08	0.1	0.07

[1]Raw waste concentrations are based on unit weight of pollutant per unit
volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit
weights of product.

Product: Vinyl Chloride

Process: Thermal Cracking of Ethylene Dichloride

Process RWL Category: B

Chemical Reaction:

$$C_2H_4Cl \longrightarrow C_2H_3Cl + HCl$$

Ethylene Dichloride	Vinyl Chloride

This product/process was investigated in Phase 1 of this study, and the detailed process description and process flow diagram can be found in EPA's document, EPA 440/1-73/009 (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) published December, 1973.

Process RWL calculated from flow measurements and analyses of wastewater samples obtained in Phase 2 survey period are shown in the following tabulation:

|	
PROCESS FLOW liter/kkg gal/M lb	17
BOD_5 RWL mg/liter[1]	105
kg/kkg[2]	0.015
COD RWL mg/liter[1]	814
kg/kkg[2]	0.116
TOC RWL mg/liter[1]	50
kg/kkg[2]	0.007

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Product: Acetic Esters (Ethyl Acetate, Propyl Acetate, Butyl Acetate)

Process: Batch or continuous esterification of appropriate alcohol with Acetic Acid catalyzed by Aqueous Sulfuric Acid

Process RWL Category: C (if continuous), D (if batch).

Chemical Reactions:

$$ROH \quad + \quad CH_3COOH \quad \xrightarrow{\text{H}_2\text{SO}_4} \quad CH_3COOR \quad + \quad H_2O$$

<div align="center">
alcohol   acetic acid   acetic ester
</div>
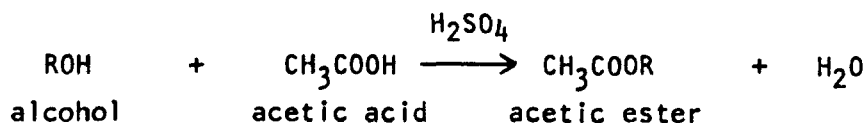
where

R is Ethyl (CH_3CH_2-),
     Propyl $(CH_3CH_2CH_2-)$,
or Butyl $(CH_3CH_2CH_2CH_2-)$

Typical Material Requirements:

Basis	1000 kg Ethyl Acetate	1000 kg Butyl Acetate
Ethyl Alcohol (95%)	620 kg	--
Butyl Alcohol	--	713 kg
Acetic Acid (100%)	688 kg	550 kg
Sulfuric Acid (66°Be')	15 to 150 kg	2,708 kg

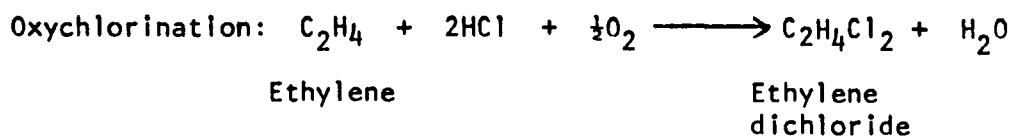Acetic acid esters are used mainly as solvents; the shorter the alcohol, the faster-boiling the solvent. Ethyl acetate is a low-boiling solvent for lacquers, and the various propyl and butyl acetates are popular medium-boiling solvents used mainly in surface coatings. In all cases, acetic acid is esterified with ethyl, propyl, or butyl alcohol in the presence of aqueous sulfuric acid to form the respective acetate. When the reaction is carried out continuously in acqueous solution, it is considered to be in Category C, while batch type processes are considered to be in Category D.

The process plant visited during the field data collection program included manufacturing facilities in ethyl, propyl, and butyl acetates. The acetates were produced in a semi-continuous manner in two independent systems. Since there were only two systems, only two different acetates could be manufactured simultaneously. At the time of the visit, ethyl acetate was being produced in one system and propyl acetate in the second.

The facilities normally are operated continuously for a period of from 1 to 6 weeks. When it is desired to change production (turnaround, e.g. from ethyl acetate to butyl acetate), the reaction stills are washed. Production may then be resumed. Thus, all three acetates are manufactured in two independent facilities by alternating production within each facility.

Ethyl acetate is produced by the esterification of acetic acid and ethyl alcohol in the presence of a catalyst such as sulfuric acid. A flow diagram for the process is shown in Figure 4-19. The reaction is reversible and eventually reaches an equilibrium at about a 67 percent conversion to ethyl acetate. In order to obtain high yields, the reaction must be forced to completion by removing the water formed and employing one reactant in excess. There are many modifications of the process, but all operate on the same general principle; that is, acetic acid is reacted with an excess of ethyl alcohol in the presence of catalytic amounts of sulfuric acid.

The process is carried out either batch by batch or in a continuous manner, depending on the nature of the raw materials and the size of operation. The main variable is acetic acid concentration, which may range from very dilute (about 8 percent) to concentrated (about 100 percent). Generally, 95 percent ethyl alcohol and 50 to 66 Be' sulfuric acid are used. The ratio of reactants varies according to the process used and the type of equipment available. For a batch process, the reactants may be mixed in the following proportions: 10 parts by weight of 8 percent acetic acid, 10 parts by weight of 95 percent ethyl alcohol, and 0.33 part by weight of 50 to 66°Be' sulfuric acid.

The continuous process may be used for any acid concentration, but it is particularly applicable to the utilization of dilute acetic acid, such as that obtained from ethyl alcohol by fermentation. Acetic acid, excess 95 percent ethyl alcohol, and about 1 percent of 66°Be' sulfuric acid are mixed and continuously passed through a preheater to an esterifying column. The column and other equipment are generally constructed of copper. The mixture is allowed to reflux, and a suitable amount of distillate is withdrawn from the top of the column, which is held at about 80°C.

The distillate, containing about 70 percent alcohol, 20 percent ester, and 10 percent water (the acetic acid is consumed in the esterifying column) is run to a separating column. Here the mixture is refluxed, and a ternary azeotrope (83 percent ethyl acetate, 9 percent ethyl alcohol, and 8 percent water) is removed from the top of the separating column at approximately 70°C.

This homogeneous mixture is run to a proportional mixer, where it is blended with (approximately) an equal volume of water. The mixture is allowed to settle in a decanter, where the two layers that form are separated. The bottom aqueous layer, containing small amounts of alcohol and ester, is recycled to the lower part of the separating column, where the ester and alcohol are removed in the constant-boiling ternary mixture taken overhead. A wastewater stream is continuously drawn off as bottoms from the separating column. This stream is necessary to provide a route for removal of water from the process. It includes stoichiometric water from the esterification reactions, dilution water which may be present in the feedstocks, decanter water, and condensed stripping stream used in all three distillation columns.

The top layer in the decanter contains about 93 percent ethyl acetate, 5 percent water, and 2 percent ethyl alcohol. This layer overflows to a drying column, where a sufficient amount of the ester is distilled to carry over all the water and alcohol present. This overhead material is returned to the separating column for recovery of the ester and reuse of the alcohol.

Ethyl acetate is withdrawn as bottoms from the drying column and either run to storage or redistilled. The latter is generally necessary to remove copper salts formed in the copper columns. Other impurities such as higher-boiling esters may also be present, depending on the purity of the raw materials. The yield of ethyl acetate is 90 to 100 percent based on acetic acid. Batch process yields are about 95 percent.

During the sampling visit, propyl acetate was being produced in a manner analogous to that described in detail for ethyl acetate. During the actual production runs, the only continuous contact process wastewater stream from either unit was the aqueous bottoms from the separating column. Process RWL calculated from flow measurements and the analysis of these streams are indicated in the following tabulation:

	Ethyl Acetate	Propyl Acetate
PROCESS FLOW		
liter/kkg	1,290	1,190
gal/M lb	155	142
BOD$_5$ RWL		
mg/liter[1]	38	7
kg/kkg[2]	0.049	0.008
COD RWL		
mg/liter[1]	79	10
kg/kkg[2]	0.102	0.012
TOC RWL		
mg/liter[1]	26	4
kg/kkg[2]	0.034	0.005

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
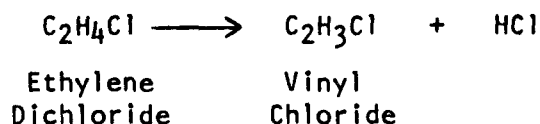[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Based on the previous process description, the raw waste concentrations and subsequent loadings appear quite low for Category C processes. This may be partially explained by the fact that each of the three distillation

columns in the process utilizes direct steam sparging to volatilize organic materials and drive them overhead. It may be that the samples were taken during a period when nearly all of the organics in the decanter water were being effectively steam stripped in the separating column.

Although the recycle of decanter water and overheads from the drying column for recovery of unreacted alcohol and product esters is considered good operating practice, it is questionable whether such low organics concentrations in the separating column bottoms can be maintained on a steady-state basis. It should be also noted that both the ethyl and propyl units were operating respectively at 87.5% and 90.5% of original design capacity. Under such conditions, each unit may be able to provide sufficient hold-up so that a bottoms stream which is relatively free of organics may be withdrawn for limited periods of time.

There are also non-continuous waste streams associated with process turn-arounds when production shifts from one ester to another. Organic residues from the esterifying column may amount to approximately 3 kg/kkg of ester product on a cumulative basis. These organic residues contain no appreciable water and are burned in an incinerator.

In addition, the esterifying columns are normally washed with a detergent or cleaning agent during production turnarounds. This wastewater is highly concentrated in organics and amounts to an additional 3 liter/kkg of esters on a cumulative basis.

Although it is clear that these concentrated organic streams would add to the process RWL, it is not possible to specify quantitative values for pollution parameters such as BOD_5, COD, etc. It is also questionable that the RWL's calculated are truly representative of the process.

Non-contact wastewaters include cooling water flows. Cooling water is circulated throughout the reaction, refining, and stripping stills. A loop system is employed. Make-up water for the entire plant is approximately 78,000 liters/kkg of esters (20,000 gal/M lb). Most of this loss results from evaporation in the cooling towers. A small flow is bled from the esters units to prevent a chloride build-up. This wastewater flows to the dilute stream and eventually to the wastewater treatment faciliites.

Condensate from the entire plant is piped back to a condensate return system for boiler feed water. The total quantity of condensate is approximately 2,000 kg/kkg of ester. Condensate from the various processes cannot be segregated, but it is estimated that condensate from ester production is less than 1 percent of the pollution abatement systems.

The process RWL presented for these two acetic acid esters are not considered to be representative of the process. Therefore, no effluent limitations are proposed.

FIGURE 4-19

ETHYL ACETATE VIA ESTERIFICATION OF
ACETIC ACID AND ETHANOL
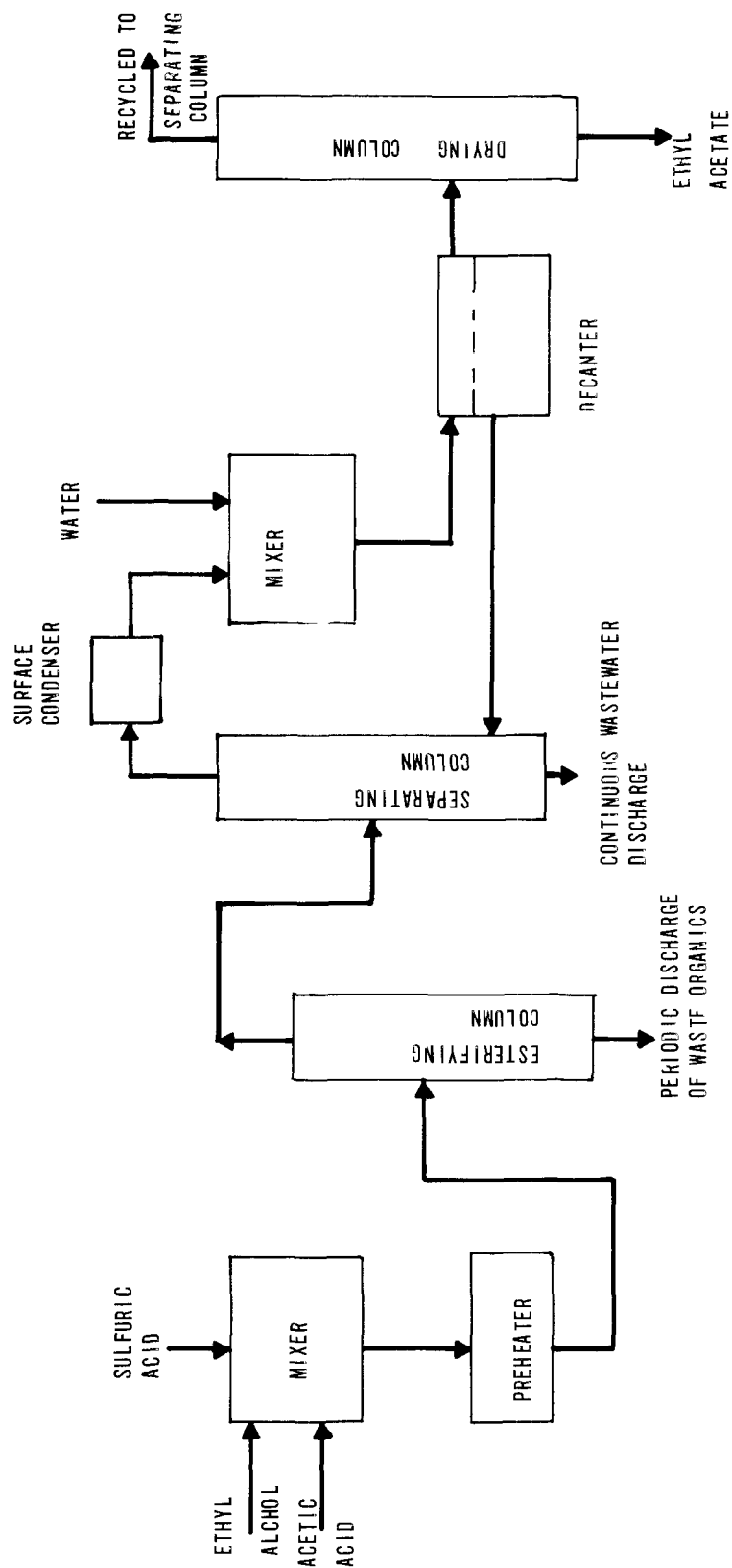
Product: Acrylonitrile

Process: Ammonoxidation of Propylene

Process RWL Category: C

Chemical Reaction:

$$2\ CH_2CHCH_3\ +\ 2\ NH_3\ +\ 3\ O_2\ \longrightarrow\ 2\ CH_2\,CHCN\ +\ 6\ H_2O$$

propylene   Ammonia   acrylonitrile
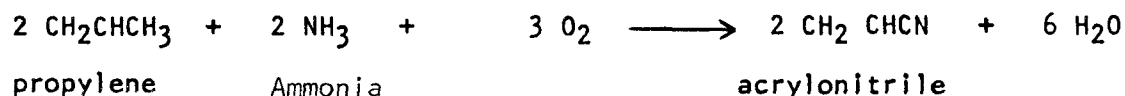
Acrylonitrile is used in the manufacture of acrylic fibers, Acrylonitrile-Butadine-Styrene (ABS) and Stryene-Acrylonitrile (SAN) resins, and nitrile rubber.

A typical process flow diagram for the manufacture of acrylonitrile via ammonoxidation of propylene is shown in Figure 4-20.

Approximately stoichiometric proportions of air, ammonia, and propylene are introduced into a fluid-bed reactor at 15 psig and 750-925°F. One attractive feature of the process is that it is not necessary to use polymerization-grade propylene. The contact time is several seconds, and once-through flow is used because conversion of propylene is practically complete after a single pass.

The catalysts originally developed were oxides of bismuth, cobalt and molybdenum, and molybdates of bismuth and cobalt. However, the use of a newly developed depleted-uranium catalyst is described as considerably enhancing acrylonitrile yield at the expense of the by-products.

The reactor effluent is neutralized with sulfuric acid to remove unconverted ammonia. The quenched liquid stream from the neutralizer proceeds to a steam stripper to recover some of the reacted products. The overhead from the neutralizer goes to an absorption column, in which the stream is washed with water to produce an unabsorbed stream of inert gases and a solution of acetonitrile, acrylonitrile, and HCN.

The solution is then stripped of the dissolved products, which are fractionated to remove pure HCN and then sent to the main purification section. First, a main fractionator produces an overhead consisting of wet acrylonitrile, and a bottoms stream of wet acetonitrile. The overhead is treated first by extractive distillation, and then by conventional fractionation to remove undesirable light and heavy ends, to produce pure acrylonitrile. The bottoms from the main fractionator can be fractionated in a two-column system to produce pure acetonitrile.

Although the actual ammonoxidation reactions is vapor-phase, the process was considered within Category C because of the aqueous separation and purification train.

The major water pollution sources of this process are the wastewater dis-
charged from the steam stripping columns as shown in the process flow
diagram. Process RWL calculated from flow measurements and analyses
of the waste streams are indicated in the following tabulation:

	Plant 1			Plant 2	Plant 3	Plant 4
			Sampling	Periods		
	#1	#2	#3	#1	#1	#1
PROCESS FLOW						
liter/kkg	3,920	3,920	3,920	6,590	4,010	2,820
gal/M lb	471	471	471	790	480	338
BOD$_5$ RWL						
mg/liter[1]	18,000	18,700	19,300	3,330	13,900	--
kg/kkg[2]	71.7	73.3	75.8	21.9	55.5	--
COD RWL						
mg/liter[1]	57,400	60,300	60,700	21,100	36,200	41,100
kg/kkg[2]	229	237	238	139	145	116
TOC RWL						
mg/liter[1]	25,600	24,000	25,100	8,700	15,300	19,100
kg/kkg[2]	102	94.2	98.6	57.3	61.2	53.9

[1]Raw waste concentrations are based on unit weight of pollutant per unit
volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit
weight of product.

The foregoing data indicate that the RWL of Plant 1 is higher than that of
Plants 2, 3, or 4. This difference is attributed to the discharges by
Plant 1 of light hydrocarbons removed as the overhead from the acetonitrile
purification column into the sewer lines. The analytical results from the
sampling survey also reveal that, in addition to the pollution parameters
shown in the above tabulation, the concentration of parameters such as
nitrogen, sulfate, and cyanide are at levels hazardous to the biological
pretreatment process.

An average of all the RWL data was considered as BPCTCA. It should be
noted that all of the plants surveyed use deep-well injections to dis-
pose of wastes from the manufacture of acrylonitrile. The effluent
limitations developed for this process would be applicable only if deep-
well injection becomes unfeasible.

The alternative routes for the manufacture of acrylonitrile include:
1) catalytic dehydration of ethylene cyanohydrin; 2) catalytic reaction
of acetylene and hydrogen; and 3) catalytic reaction of propylene with
nitric oxide. However, present practice concentrates exclusively on the
ammonoxidation of propylene.

FIGURE 4-20

ACRYLONITRILE——AMMOXIDATION OF PROPYLENE
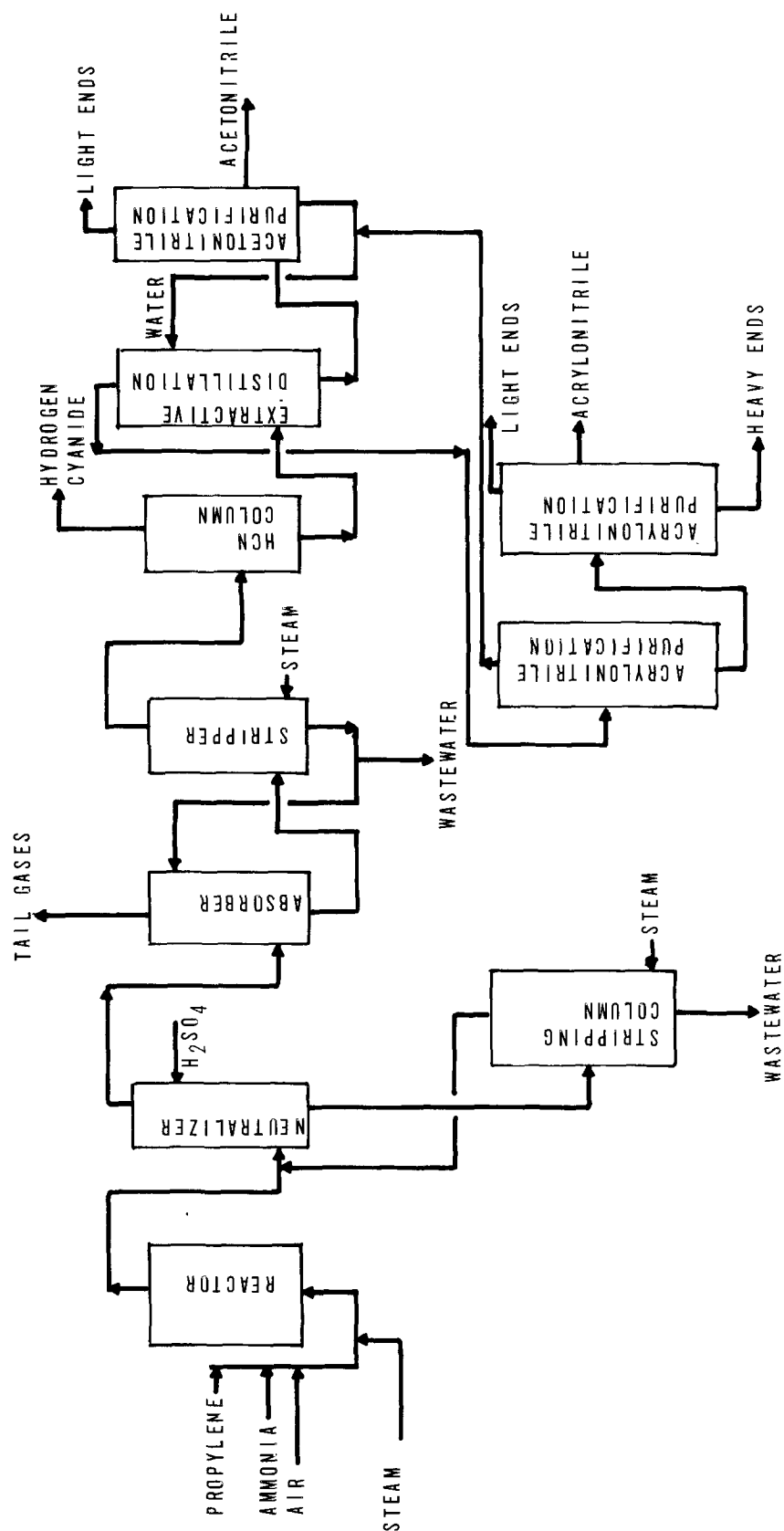
Product: p-Aminophenol

Process: Catalytic Reduction of Nitrobenzene

Process RWL Category: C

Chemical Reactions:

$$C_6H_5NO_2 \quad + \quad 2\ H_2 \quad \xrightarrow[\text{catalyst}]{\overset{H_2SO_4}{}} \quad C_6H_4(OH)NH_2 \quad + \quad H_2O$$

nitrobenzene   metal catalyst   p-aminophenol
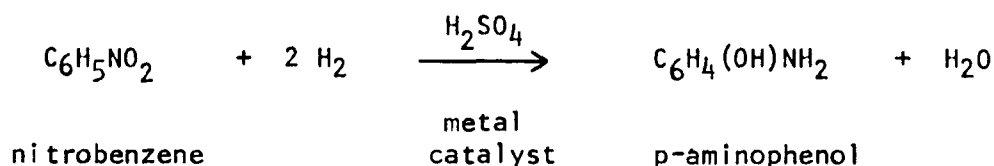
Typical Material Requirements:

Basis	1000 kg p-Aminophenol
Nitrobenzene	1800 kg
Sulfuric Acid	1550 kg
Surfactant	20 kg
Anhydrous Ammonia	500 kg
Toluene	80 kg
Hydrogen Gas	
Nitrogen Gas	
Antioxidants	
By-Products	
Aniline	220 kg

p-Aminophenol is versatile in its use as a dye intermediate, as it can be used in the preparation of disperse, nitro, acid, mordant, direct, sulfur, and oxidation dyes. It is also widely used as a photographic developer. The by-product aniline produced during the reaction also has wide uses in the dye, drug, rubber, plastics, and animal-feed industries.

Production of p-aminophenol is based upon the reduction of nitrobenzene with hydrogen in the presence of aqueous sulfuric acid and a metal-containing catalyst (platinum, palladium, or mixtures of the two), as shown in Figure 4-21. The raw materials (nitrobenzene, deionized water, hydrogen gas, sulfuric acid, surfactants, and the metal catalyst) are fed into a reactor at a temperature ranging from about 60° to 120°C. Prior to completion of the reaction, the reduction of the nitrobenzene is interrupted for catalyst recovery and recycle. During the catalyst recovery step, a distinct interface forms between the reaction products and the catalyst-containing nitrobenzene. The nitrobenzene layer is then separated and can be employed in a subsequent reduction step.

The reaction products proceed to a purification and isolation step. Additional materials (anhydrous ammonia, toluene) are added to facilitate separation of the by-product aniline from product p-aminophenol. After isolation of the aniline, solvent is recovered and recycled to the purification and isolation step.

Following purification, the p-aminophenol is dried and packaged for sale.

The major pollution sources of the process are the wastewaters generated during the aniline recovery step and the p-aminophenol drying step. These wastewaters are collected and passed through two evaporators connected in series. This evaporation process separates the very concentrated ammonium sulfate wastes for landfill disposal. It was claimed by the plant which was visited during the sampling survey that the evaporation process *should be considered as pollution abatement facilities rather than as* part of the manufacturing process. However, separate samples as influent to and effluent from the evaporation process were sampled, and the RWL's are presented in the following tabulation. Also included in the RWL calculations are the wastewater resulted from floor, tank washes, and pump seal leakages.

| FLOW | Influent to Evaporators | | Effluent from Evaporators |
	Sample Period #1	Sample Period #2	Sample Period #1
liter/kkg	15,000	15,000	12,600
gal/M lb.	1,800	1,800	1,510
BOD_5 RWL			
mg/l [1]	59,300	59,300	3,300
kg/kkg [2]	890	886	41.6
COD RWL			
mg/l [1]	115,000	101,000	5,850
kg/kkg [2]	1,725	1,508	73.7
TOC RWL			
mg/l [1]	33,600	27,100	1,730
kg/kkg [2]	505	407	21.7

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The process RWL based on the influent to the evaporators was considered as BPCTCA. The effluent from the evaporators (aqueous condensate) is

combined with wastewaters from other processes and treated in an activated sludge plant prior to discharge to surface waters.

Non-contact wastewaters include cooling tower blowdown and boiler condensate. Each of these wastestreams is bled continuously for the control of dissolved solids. The streams are combined with the treated process wastewaters and eventually discharged to a receiving stream.

p-Aminophenol can also be prepared conveniently by the Beehamp method of reducing p-nitrophenol in the presence of iron filings in an acid medium. Alternatively, the product may be prepared by catalytic hydrogenation of p-nitrophenol, by treatment of phenylhydroxylamine with an acid catalyst, (such as sulfuric acid), by reduction of azoxybenzene in acid solution, and by treatment of p-chlorophenol with ammonia.

FIGURE 4-21

PARA-AMINOPHENOL CATALYTIC REDUCTION OF NITROBENZENE
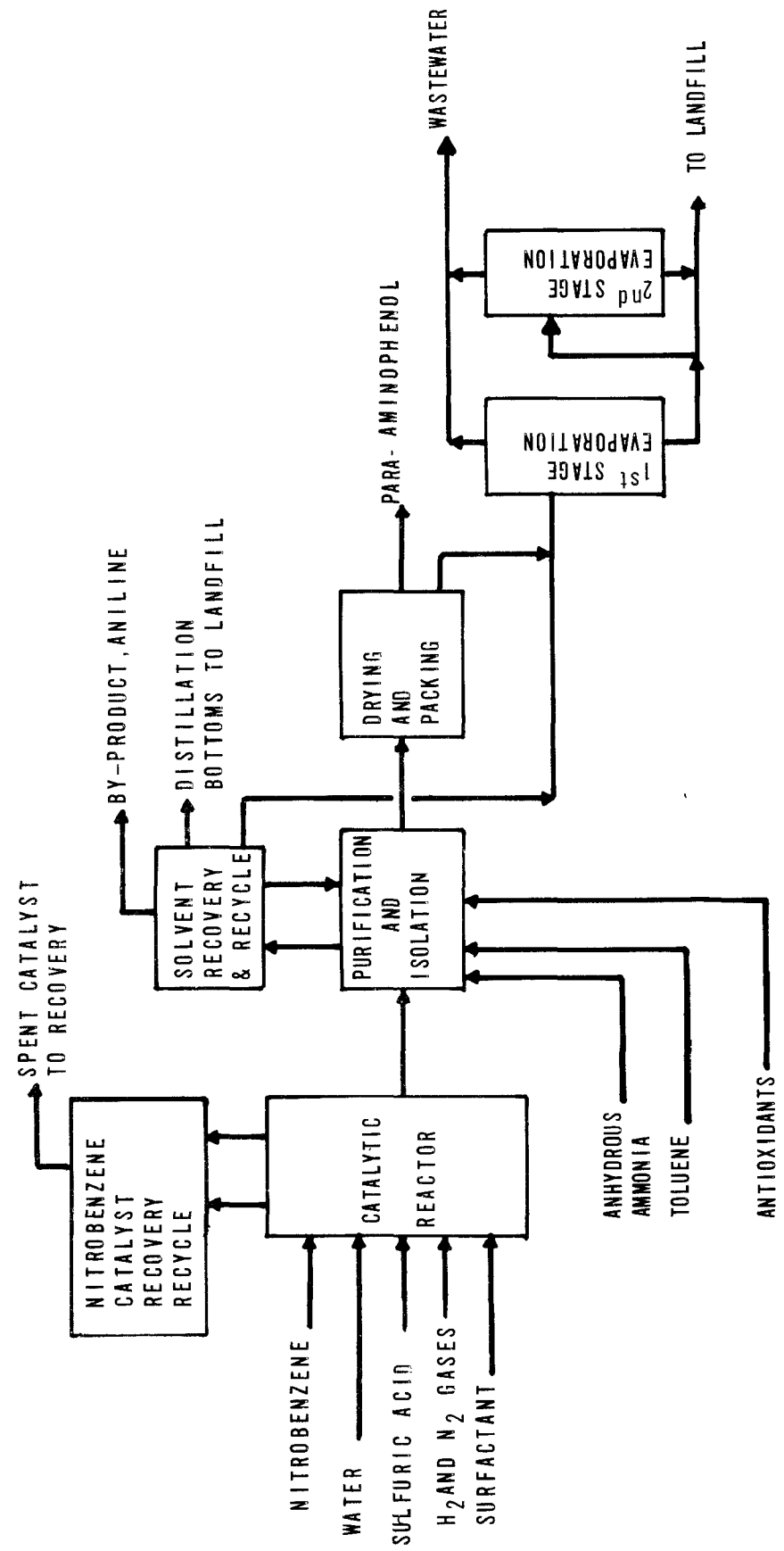
Product: Calcium Stearate

Process: Neutralization of Stearic Acid

Process RWL Category: C

Chemical Reactions:

$$2\ C_{17}\ H_{35}\ COOH\ +\ 2\ NaOH\ +\ CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2\ Ca\ +\ 2\ NaCl\ +\ 2\ H_2O$$

| | sodium | calcium | | | |
| stearic acid | hydroxide | chloride | calcium stearate | | |
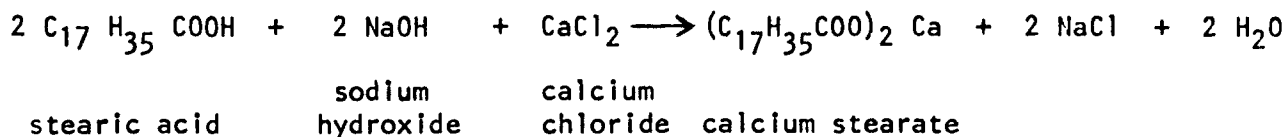
Calcium stearate belongs to a group of water-insoluble metallic soaps. Their water insolubility differentiates them from ordinary soap, and their solubility or solvation in organic solvents accounts for their manifold uses. The precipitation process is the classical method of preparing metallic soaps, including calcium stearate. It is now used primarily in making high melting-point soaps which precipitate as light, fluffy powders and can be recovered by filtration.

Raw materials for the production of calcium stearate including stearic acid, sodium hydroxide, and calcium chloride. A flow diagram of the process is presented in Figure 4-22. The feedstocks are fed continuously into a reactor, where a two-stage precipitation process takes place. In the first reaction, an alkali soap is formed by reacting the stearic acid with caustic soda. In the second step, the alkali soap is treated with a water solution of the calcium chloride to precipitate the calcium stearate. Sodium chloride remains dissolved in the mother liquor. The resulting slurry, containing about 10 percent of calcium stearate, is continuously fed to a filtration step for solids concentration. Vacuum filters are employed, and the filter cake is subsequently washed. The partially dried filter cake is then placed in tray dryers, where the remaining water is removed. The dried soap may then be ground and separated to produce a powder of uniform particle size.

The major water pollution sources of the process are wastewater discharged from the filtration step and from the "Battery-Limit" clean-up water. Multiple wastewater samples were obtained during the plant visit in the survey period. Process RWL calculated from flow measurements and the analyses of these streams (subjected to probability analyses of occurrence) are presented in the following tabulation:

	10% Occurrence	50% Occurrence	90% Occurrence
PROCESS FLOW			
liter/kkg	54,100	54,100	54,100
gal/M lb	6,460	6,460	6,460
BOD$_5$ RWL			
kg/kkg[1]	13.2	13.8	14.4
COD RWL			
kg/kkg[1]	30.2	32.8	35.5
TOC RWL			
kg/kkg[1]	22.4	23.1	23.9

[1]Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

The high flow of the waste stream can be explained by the fact that a considerable quantity of water is utilized during the filtration step to wash the solid cake. The analytical results also indicate high concentrations of calcium and chloride in the waste streams; these are attributed to excess raw material required by the reaction and to the reaction by-product, salt.

The 50 percent occurrence shown in the RWL data above was considered as BPCTCA. The wastes from calcium stearate manufacture are discharged to the local municipal sewer systems.

FIGURE 4-22

CALCIUM STEARATE - NEUTRALIZATION OF STEARIC ACID
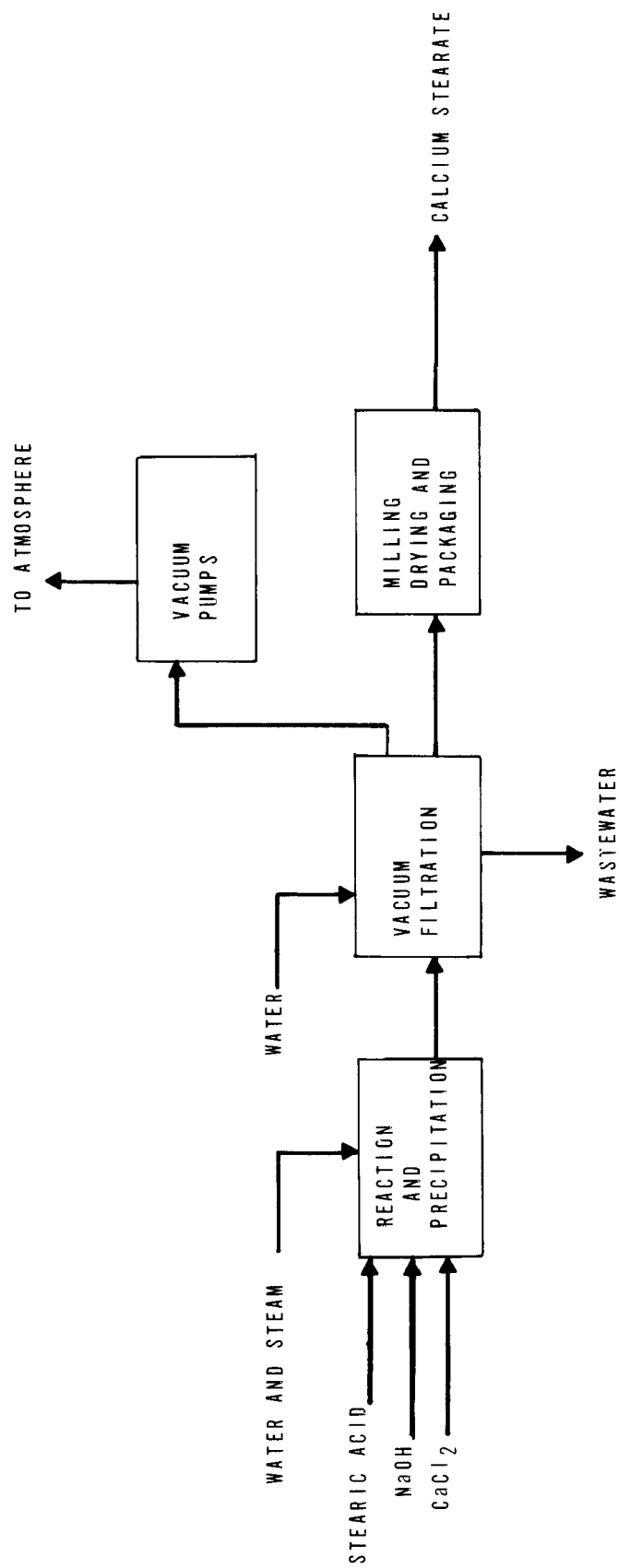
Product: Caprolactam

Process: UBE-Inventa Caprolactam Process

Process RWL Category: C

A schematic flow diagram illustrating the UBE-Inventa process is presented in Figure 4-23. The overall process plant can conveniently be divided into three sections:

1. Cyclohexanone
2. Hydroxylamine
3. Caprolactam

Cyclohexanone Section

The reaction to produce cyclohexanone and cyclohexanol by the oxidation of cyclohexane is represented by the following equations:

$$C_6H_{12} + \tfrac{1}{2} O_2 \longrightarrow C_6H_{11}OH$$

cyclohexane   cyclohexanol

$$C_6H_{12} + O_2 \longrightarrow C_6H_{10}O + H_2O$$

cyclohexane   cyclohexanone
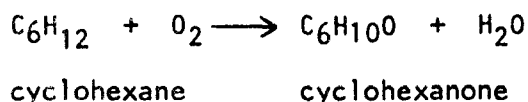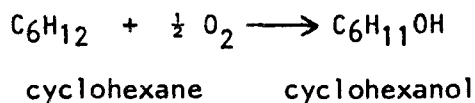
Approximately equal quantities of the hexanol and hexanone are formed. This process is characterized by use of air as the oxidant. As shown in Figure 4-23, fresh feed and recycle cyclohexane are first delivered to the cyclohexane mix tank and then passed in a fixed quantity through a surface pre-heater to the oxidation reactor. The reaction takes place at a pressure of 10 atmospheres and a temperature of 160°C. The reaction does not require a catalyst and is usually carried out in a series of continuously-stirred tank reactors rather than the single oxidizer shown in Figure 4-23.

The oxidant air is compressed and sparged into the oxidizer by a circulation gas blower. The gases leaving the oxidizer are cooled (by pre-heating the cyclohexane feed) and sent to a condenser. The gaseous phase from the condenser is vented through an off-gas scrubber used to recover unreacted cyclohexane vapor. The liquid phase from the condenser is recycled and combined with cyclohexane in the mix tank. An aqueous layer is drawn from the mix tank to remove stoichiometric water of reaction.

The liquid effluent from the oxidizer is combined with the bottoms from the off-gas scrubber. Cyclohexanone recovered later in the process is used to absorb cyclohexane in this scrubber.

Condensed steam-jet water (from vacuum distillations later in the process) is added to the reaction mixture prior to entering the acid wash column. The overflow from the acid wash column is separated into an aqueous and organic phase in a liquid/liquid separator. The aqueous layer drawn from the separator is called "Acid Water" because it contains significant concentrations of adipic and hydroxy caproic acid.

Aqueous caustic soda is added to the organic phase from the separator prior to entering the saponification column. The process to saponify the reaction liquor from cyclohexane oxidation is represented by the following equations:

$$RCO - OC_6H_{11} + NaOH \longrightarrow RCOONa + C_6H_{11}OH$$

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$
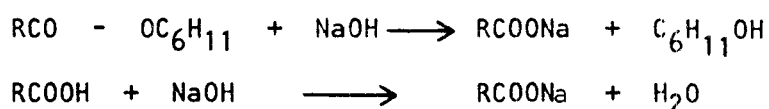
Saponification is necessary to remove by product esters and acids formed in the relatively non-selective oxidation reaction.

The saponified liquor is separated into heavy and light phases in the saponification separator. The heavy phase is sent to a steam distillation column, where contact steam is used to recover cyclohexanol by stripping. The column overhead is combined with the light phase from the saponification separator. The bottoms from the column contains high concentrations of sodium salts of organic acids as well as excess free caustic. This material, called "Caustic Water", is combined with the "Acid Water" for neutralization prior to disposal by deep-well injection.

The light spaonification liquor is fed to a distillation column, where cyclohexane is distilled overhead for recycle. The bottoms from the cyclohexane recovery column are fed to the light-ends column, where low-boiling components are distilled overhead. These by-products are burned as fuel. The feed to the light-ends column also contains crude cyclohexanone produced by the dehydrogenation of cyclohexanol later in the process.

The bottoms obtained by removal of the low-boiling components are fed to the cyclohexanone column, where cyclohexanone is fractionated. The distillate from the top of this column is 99 percent refined cyclohexanone, which is stored in the refined cyclohexanone tank.

The bottoms from the cyclohexanone column are fed to the cyclohexanol column. In this column, cyclohexanol is separated from high-boiling components. These high boilers are taken off as bottoms and burned as fuel.

The refined cyclohexanol is taken overhead and sent to the dehydrogenation reactor. The process to obtain cyclohexanone by dehydrogenation of the refined cyclohexanol is represented by the following reaction:

$$C_6H_{11}OH \longrightarrow C_6H_{10}O + H_2$$

cyclohexanol   cyclohexanone
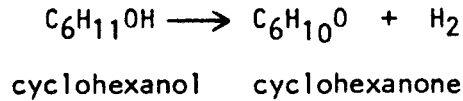
This reaction takes place at about 380°C by passing cyclohexanol vapor over a Zn-Ca catalyst. The cyclohexanone produced is recycled to the light-ends column, and the hydrogen is vented.

Hydroxylamine Section

Ammonia gas is mixed with air and fed to the ammonia oxidizer, where oxides of nitrogen are formed by the following reactions:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

nitric oxide

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

nitrogen dioxide
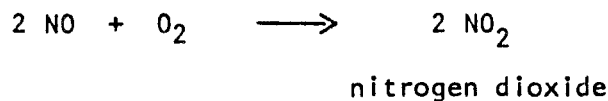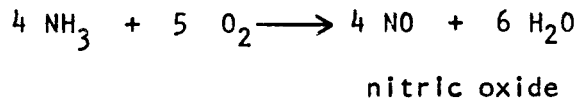
The oxides of nitrogen are fed to the nitroso absorption column, where they are absorbed by ammonium carbonate and converted to ammonium nitrite.

$$NO + NO_2 + (NH_4)_2\ CO_3 \longrightarrow 2\ NH_4\ NO_2 + CO_2$$
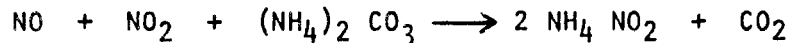
Off gases (mainly nitrogen) are cooled and vented from the nitroso absorption column.

Aqueous ammonia is added to the ammonium nitrite and mixed in the nitrite tank. The mixed solution then enters the SO_2 absorption column, where it is converted to disulfonate by contact with SO_2 gas flowing in parallel. This reaction proceeds as follows:

$$NH_4NO_2 + 2\ SO_2 + NH_3 + H_2O \longrightarrow NOH(SO_3NH_4)_2$$

The disulfonate is fed to the hydrolysis tank, where it is hydrolized to the amine.

$$NOH\ (SO_3NH_4)_2 + 2\ H_2O \longrightarrow NH_2\ OH \cdot \tfrac{1}{2}\ H_2SO_4 + \tfrac{1}{2}\ H_2SO_4 + (NH_4)_2\ SO_4$$
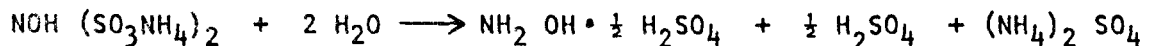
The aqueous mixture of hydroxylamine, sulfuric acid, and ammonium sulfate is stored in the amine tank prior to the reaction with the refined cyclohexanone in the oxime reactor.

Caprolactam Section

The oximation reaction to produce cyclohexanone oxime by adding cyclohexonone to the amine is represented by the following equation:

$$C_6H_{10}O + NH_2OH \cdot \tfrac{1}{2}\ H_2SO_4 + NH_3 \longrightarrow C_6H_{10}NOH + \tfrac{1}{2}\ (NH_4)_2\ SO_4 + H_2O$$
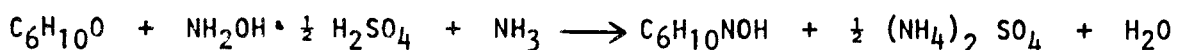
An aqueous ammonia solution is added to the oxime reactor, along with the hydroxylamine and cyclohexanone, to satisfy the requirements of this reaction.

The effluent from the oxime reactor is sent to a liquid/liquid separator, where the aqueous phase (containing ammonium sulfate) is drawn off from the organic phase (containing cyclohexanone oxime). The ammonium sulfate solution is sent to a crystallization and drying process to recover ammonium sulfate crystals for sale as fertilizer. The oxime is sent to the rearrangement reactor.

The reaction to produce caprolactam by Beckmann's rearrangement and to neutralize the oleum used in this process, is represented according to the following equation:

$$C_6H_{10}NOH + H_2SO_4 + 2 NH_3 \longrightarrow (CH_2)_5 NHCO + (NH_4)_2 SO_4$$

The oxime undergoes Beckmann's rearrangement in the presence of oleum catalyst in the rearrangement reactor. The effluent mixture of caprolactam and H_2SO_4 is fed to the neutralization tank, where the acid is neutralized with an aqueous ammonia solution. The caprolactam solution and ammonium sulphate solution obtained by neutralization are cooled and separated in the crude lactam vessel; both of these solutions are aqueous. The crude caprolactam solution is sent to the crude lactam tank. Part of the aqueous ammonium sulfate is recycled back to the neutralization vessel to prevent a violet rise in temperature from the heat of neutralization. The remainder of this solution is sent to a series of solvent extraction columns to recover additional caprolactam.

In order to remove light impurities, the caprolactam solution from the crude lactam tank is steam stripped in the purification column. The overhead condensate from this distillation column is discharged as wastewater. The bottoms from the column, called "caprolactam oil", are sent to a three-stage countercurrent solvent extraction unit for further purification.

The "caprolactam oil" is fed to the third column, where it countercurrently contacts the bezene solvent fed to the first column. The aqueous ammonium sulfate solution formed in the neutralization reaction is fed to the top of the first extraction column. Condensed steam-jet water from vacuum evaporators used later in the process is combined with the ammonium sulfate solution prior to entering the first extraction column. Aqueous raffinate solution from the second column also enters the top of the first column. The benzene solvent entering the bottoms absorbs caprolactam from both aqueous streams entering the top. The benzene and caprolactam extract phase is taken overhead while the aqueous ammonium sulfate phase is drawn off as bottoms. This ammonium sulfate, freed from lactam, is delivered to the ammonium sulfate recovery unit. The benzene-caprolactam extract leaving the third column is cooled and sent to a liquid-liquid separator. The heavy liquid is recycled to the third extractor, while the light liquid (containing caprolactam and benzene) is sent forward to the solvent recovery column.

The next processing step is to remove impurities in the lactam by rectification. The distillation of the lactam must be done minimizing the heating time at a low temperature. Consequently, thin-layer, falling-film type vacuum evaporators and fractionators, which feature a short residue time and a small pressure drop, are used.

The lactam solution is fed to the Stage I evaporator, where low-boiling materials are distilled off. The lactam flowing from the bottom is fed to the Stage II evaporator. Forerun materials, near the lactam boiling point, are evaporated in this stage, and the vapors obtained are fractionated in a distillation column (Stage II fractionator). The distillate foreruns are combined with the light ends and burned as fuel. A portion of this material is also used as a solvent in the final batch stills used to strip additional caprolactam from process residues.

The bottom product from the Stage II evaporator, is fed to the Stage III evaporator, where pure lactam is distilled off. The bottoms are discharged to the Stage IV evaporator and fractionator, where pure lactam and high boiling materials are separated. The pure lactam distilled from Stages III and IV is condensed and sent to the Pure Lactam Tank.

The bottoms product of the Stage IV evaporator is mixed with a portion of the intermediate fraction and then charged to a batch still, where any lactam present is recovered. The distilled lactam is fed back to the Stage II fractionator. The batch still residue is removed by water washing and either incinerated or discharged as wastewater.

One manufacturer utilizing the UBE-Inventa cyclohexane process was surveyed during the field data collection program. The manufacturer actually operates two process plants which run in parallel. Process raw waste loads (RWL) were calculated using both historical data provided by the manufacturers and the analytical results from field sampling. This information is shown in Table 4-1. A separate tabulation is provided for each of the two plants.

It should be noted and clearly understood that the RWL's shown in Table 4-1 are based only on wastewater discharged to the process plant sewers. It is apparent that significant quantities of waste materials (i.e., ACID WATER, CAUSTIC WATER, light and heavy ends, etc.) shown in Table 4-1 are disposed of by deep-well injection or by burning. It should also be noted that approximately 4.5 kg. of by-product ammonium sulfate are formed for each kg. of finished caprolactom. The ammonium sulfate is sold to fertilizer manufacturers and is not shown in Table 4-1.

The ACID WATER and CAUSTIC WATER discussed previously and shown in Table 4-1 would drastically increase the process RWL if the injection well could no longer be used for this disposal. Typical compositions provided by the manufacturer for these waste streams are listed in the following tabulations.

Caustic Water		Acid Water	
Free NaOH	4.5%	Adipic Acid	11%
Organic Carbon	14.5%	Hydroxy Caproic Acid	9%
Total Na	10.0%	Other Acids and Diols	15%
Acid Salts	24.8%	Water	65%
Anone, Anol	0.5%		
Water	63%		

One alternative disposal method would be incineration of the ACID WATER. The CAUSTIC WATER, however, can not be burned because of its alkaline composition.

The previous discussions also indicated that other waste streams in the Cyclohexanone and Caprolactam Sections are concentrated and incinerated. Steam-jet condensates from the vacuum evaporators are recycled to the process. It was, therefore, concluded during Phase I of this study that the RWL shown for Plants I and 2 in Table 4-1 should be considered as minimum values commensurate with BADCT for this process.

Table 4-1

Raw Waste Load Based on UBE-Inventa Caprolactam Process

All Raw Waste Load Quantities are Based on Finished Caprolactam Product

	Plant 1	Plant 2			
		Flow lit/kkg	BOD kg/kkg	COD kg/kkg	TOC kg/kkg
Cyclohexanone Section					
Acid Water / Caustic Water	2800 kg/kkg to Disposal Well[1]	1644 kg/kkg to Disposal Well[1]			
Light Ends Col. Overhead / Cyclohexanol Col. Btms.	139 kg/kkg Burned[1]	98.6 kg/kkg Burned[1]			
Aq. Cond. from Cyclohexane Mix Tank / Miscellaneous Run-off	To Sewer	1,250.	0.22	0.46	0.20[2]
Hydroxylamine Section					
Miscellaneous Run-off	To Sewer	3,090.	0.013	0.38	0.08[2]
Caprolactam Section					
Foreruns and Light Ends / Aq. Cond. from Solvent Recovery	30.5 kg Carbon/kkg Burned[1]	36.0 kg Carbon kkg Burned[1]			
Wash Water & Residue from Batch Stills	15.1 kg Carbon/kkg to Sewer[1]	4.3 kg Carbon/kkg Burned[1]			
Aqueous Waste from Ammonium Sulfate Recovery, Condensed Steam Jet Water (Not Recycled), Miscellaneous Run-off	To Sewer	6,780.	1.40	3.16	0.94[2]
Total (Based on Wastewater to Sewer)	Flow: 18,800 liters/kkg[1] BOD: 11.2 kg/kkg[1] Total Carbon: 30.3 kg/kkg	11,120.	1.63	4.00	1.22[2]

[1] Based on Historical Data Supplied by Manufacturer

[2] Based on Field Sampling

FIGURE 4-23

CAPROLACTAM. UBE INVENTA CAPROLACTAM PROCESS
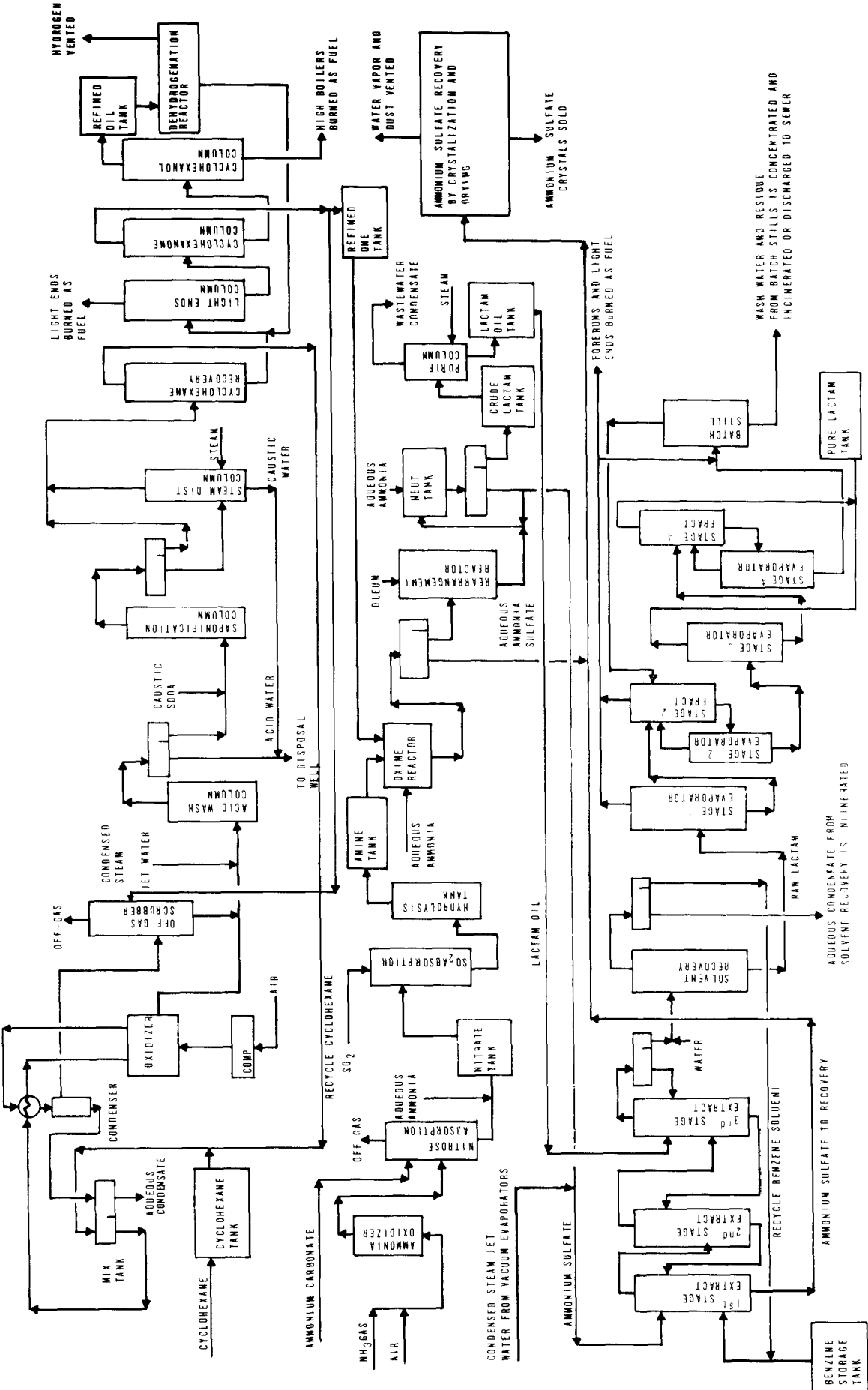
Product: Caprolactam

Process: DSM Caprolactam Process

Process RWL Category: C

A second caprolactam manufacturer surveyed utilizes the Dutch States Mines (DSM) process. A schematic flow diagram for this process is shown in Figure 4-24. Cyclohexanone is prepared in two stages: 1) oxidation of cyclohexane to cyclohexanol; 2) catalytic dehydrogenation of cyclohexanol to cyclohexanone.

Cyclohexane is first oxidized with air in the presence of a cobalt catalyst. The major oxidation product is cyclohexanol, with some cyclohexanone produced as a co-product. Oxidation by-products such as acetic acid, adipic acid, and cyclohexanol esters are also formed.

Off gases from the oxidizers are scrubbed with kerosene prior to venting. Unreacted cyclohexane is subsequently recovered for recycle in a stripper. The process operates at a cyclohexane conversion of less than 10 percent, so that recovery of unreacted cyclohexane is an important part of the process.

The liquid effluent from the reactor is sent to a decanter where the aqueous phase is removed as wastewater. The organic phase is combined with the cyclohexane stripper overhead.

This mixture is then combined with aqueous saponified liquor (containing free caustic) and sent to a neutralization tank. The effluent from this tank is decanted. A heavy layer containing saponified acids, and esters are drawn off and sold. This stream is similar in nature to the combined "ACID WATER" and "CAUSTIC WATER" from the Inventa process. Its only value is for recovery of dibasic acids such as adipic acid. This can be done by lowering the pH and extracting the organic acids with a solvent such as methanol.

The light layer from the decanter is sent to the cyclohexane recovery column. The column overhead is condensed and separated into aqueous and organic layers. The organic layer is cyclohexane, which is recycled to the reactor; the aqueous layer is discharged.

The bottoms from the cyclohexane column are sent to the saponification column, where an excess of caustic and water are needed. The effluent from the saponification column is decanted into heavy saponified liquor, which is sent back and mixed with the reactor effluent, and a light organic layer. The light layer is sent to a series of distillation columns, which remove light ends, cyclohexane, and cylcohexanol respectively. The cyclohexanol is sent to a catalytic dehydrogenation reactor to produce cyclohexanone. The reactor effluent is sent back to the light-ends column.

The overhead from the light-ends column is burned in a flare. Hydrogen from the dehydrogenation reactor is passed through a seal pot containing water and is vented. Water from the seal pot is discharged to the sewer.

Refined cyclohexanone is combined with ammonium hydroxide and hydroxylamine sulfate in the oxime reactor to produce cyclohexanone oxime. The hydroxylamine sulfate is produced by ammonia oxidation similar to the Inventa process.

It should be noted that DSM has also developed an alternative process to produce cyclohexanone oxime which minimizes by-product ammonium sulfate. This process utilizes hydroxylamine phosphate oxime (HPO) and produces an amine which may be fed directly to the rearrangement reactor. The process has been integrated into the total manufacturing scheme so that the rearrangement reaction can utilize oxime feed from either the conventional oxime reactor or HPO.

Excess sulfuric acid in the effluent from the rearrangement reactor is neutralized with ammonium hydroxide in the neutralization reactor. The reaction mixture is then sent to a benzene solvent reactor, in which the crude lactam is absorbed in benzene and separated from aqueous ammonium sulfate. The aqueous salt solution is combined with that from the oxime reactor and sent to a recovery plant to produce crystals for use in fertilizer.

The lactam/benzene extract is mixed with water and sent to a solvent recovery column. The overhead mixture of benzene and water is decanted, with benzene recycled to the extractor and extract water discharged.

An aqueous lactam solution is drawn off as bottoms from the solvent recovery column. The lactum is then purified by cation exchange followed by hydrogenation. The ion exchange resin beds are regenerated by backwashing with water and acid. The backwash wastewater is discharged.

The purified lactam is dried in a vacuum evaporator, with the water recycled to the neutralization reactor. Product caprolactam is withdrawn from the bottom of the evaporator.

Process RWL's for the DSM caprolactam process are presented and discussed at the conclusion of the following section which describes the DSM process for manufacturing cyclohexanone oxime.

FIGURE 4-24

CAPROLACTAM-DUTCH STATE MINES CAPROLACTAM PROCESS
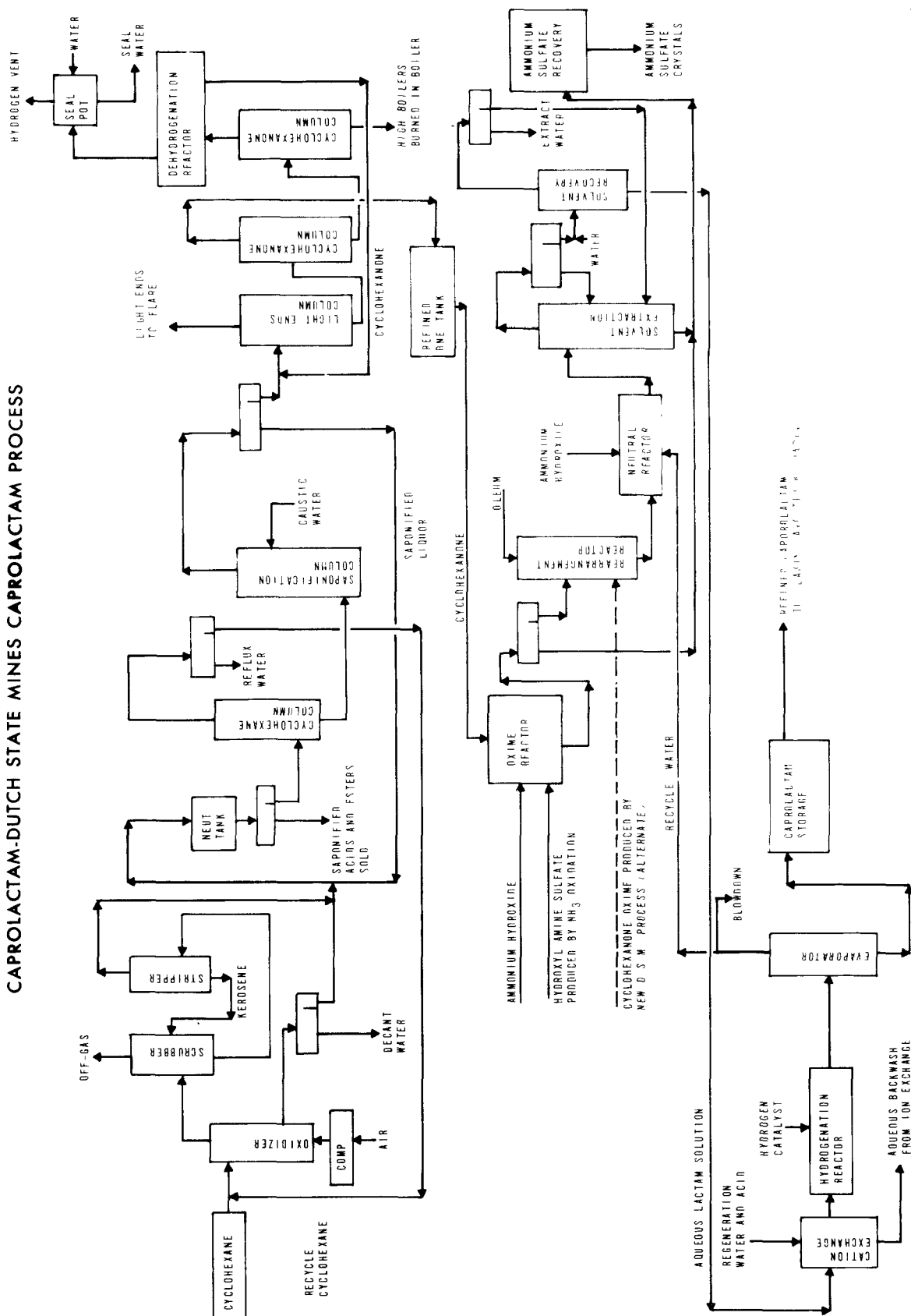
Product: Cyclohexanone Oxime

Process: DSM Cyclohexanone Oxime Process

Process RWL Category: C

Dutch States Mines has developed a new process for manufacturing cyclo-
hexanone oxime without by-product ammonium sulfate. This process has
been integrated into the overall caprolactam production scheme to pro-
vide cyclohexanone oxime feed directly to the rearrangement reactor as
shown by the dashed line in Figure 4-24.

The basic chemistry for the new process is shown in the reactions listed
below:

1. $4NH_3 + 5 O_2 \longrightarrow 4 NO + 6 H_2O$

2. $2 NO + O_2 \longrightarrow 2 NO_2$

3. $3 NO_2 + H_2O \longrightarrow 2 HNO_3 + NO$

4. $NO_3^- + 2 H^+ + 3H_2 \longrightarrow NH_3OH^+ + H_2O$

5. $NH_3OH^+ + C_6H_5O \longrightarrow C_6H_5NOH + H^+ + H_2O$

6. $H^+ + H_2PO_4^- \longrightarrow H_3PO_4$
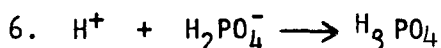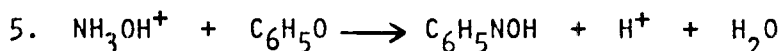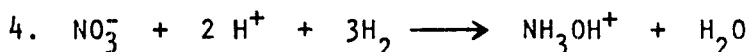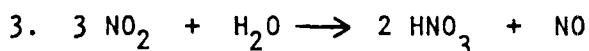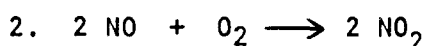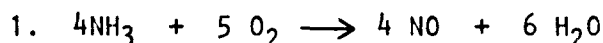
A simplified flow sheet for the process is shown in Figure 4-25. The
first processing step is the oxidation of ammonia with air to nitrogen
dioxide (equations 1 and 2). The gases from the oxidizer are then ab-
sorbed in the recirculated aqueous process solution in the nitrogen gas
absorber. Nitrogen is vented as off-gas from the absorber.

The liquid effluent from the absorber is a buffered aqueous solution of
nitric acid (equation 3), phosphoric acid, and ammonium nitrate. This
mixture is passed to the HPO reactor, where hydroxylamine is produced
(equation 4).

The HPO reactor is a column sparged with compressed hydrogen gas. Un-
used hydrogen gas is separated from the catalyst suspension (palladium
metal on carbon), and recycled by means of a compressor.

The aqueous hydroxylamine solution from the HPO reactor is sent to a
series of stirred tank oximation reactors, where it countercurrently
contacts cyclohexanone in the presence of toluene. Cyclohexanone oxime
is produced as shown in equation 5. Hydrogen ions liberated by the
oximation reaction are accepted by the phosphoric acid buffer system
(phosphate ions in equation 6). The oximation occurs at a pH of 1 to 2.
Due to the countercurrent flow, nearly quantitative conversion of cyclo-
hexanone is obtained.

Product cyclohexanone oxime is drawn from the oximation cascade (left-hand side of Figure 4-25), as a mixture of oxime, water, and toluene. This product mixture is contacted with additional toluene in the oxime extractor. The aqueous bottoms from the oxime extractor is drawn off as wastewater.

The oxime-toluene solution from the oxime extractor is sent to the oxime rectifier, where refined cyclohexanone oxime product is drawn off as bottoms. This material can be used directly in the rearrangement reaction to produce caprolactam.

The overhead from the oxime rectifier is sent to a decanter, where reflux water is drawn off. The separated toluene layer is split, and part is recycled to the oxime extractor; the remainder is sent to the process liquid extractor.

In this extractor, the toluene contacts aqueous process liquid leaving the oximation cascade (right hand side of Figure 4-25). The organic phase from the extractor is mixed with fresh cyclohexanone and sent to the oximation reactors. The process liquid leaving the oximation section must be purified thoroughly to protect the catalyst in the hydroxylamine reactor. To achieve this, the liquid is extracted with toluene and subsequently stripped with steam in the process liquid stripper. Passage through the stripping column also removes water formed during the preparation of hydroxylamine and oxime (equations 4 and 5).

The aqueous process solution is then recirculated to the nitrous gas absorber. Hydrogen and nitrate ions are restored in the process liquid by production of nitric acid (equation 3).

Calculated process RWL's for Oxanone, Caprolactam, and HPO Sections of the DSM plant are shown on Tables 4-2 and 4-3. The data shown here have also been combined to provide a total RWL for the integrated DSM caprolactam process (bottom of Table 4-3).

Examination of the data indicates that the backwash from the cation exchange resin beds in the Caprolactam Section of the DSM process is a major waste source not found with the Inventa process. The DSM route uses chemical treatment by ion exchange and hydrogenation to purify the product lactam, while the Inventa process uses an extensive vacuum distillation train for purification. It is not clear as to whether the physical purification used with the Inventa process could be substituted for the chemical method used by DSM. The impurities to be removed may be significantly different.

The new HPO process incorporated in the DSM scheme also produces a significantly higher RWL than the hydroxylamine section of the Inventa process. However, this must be evaluated considering the fact that by-product ammonium sulfate formation is minimized.

It is therefore recommended that the DSM waste loads shown in Tables 4-2 and 4-3 be considered as commensurate with BPCTCA for this process.

Table 4-2

Process Raw Waste Load Based on DSM Process

Oxanone Section	RWL Based on Cyclohexanone	
	Flow (liters/kkg)	COD (kg/kkg)
Saponified Acids & Esters	Sold for Product Recovery	
Light Ends Column Overhead Cyclohexanol Col. Btms.	Burned in Flare or Steam Boilers	
Decant Water from Oxidation Reactor	358	5.37
Reflux Water from Cyclohexane Column	478	8.35
Hydrogen Seal Water	239	6.78
Flare Condensables	No Data Available	
Total (Based on Wastewater to Sewer)	1075	20.5

Caprolactam Section	RWL Based on Caprolactam	
	Flow (liters/kkg)	COD (kg/kkg)
Extraction Wastewater	394	0.39
Backwash from Cation Exchange Resin Beds	1,730	37.1
Blowdown from Recycle Process Water	No Data Available	
Total (Based on Wastewater to Sewer)	2,120	37.5

Table 4-3

Process Raw Waste Load Based on DSM Process

Hyam Phosphate Oxime (HPO) Section	RWL Based on Cyclohexanone Oxime	
	Flow (liters/kkg)	COD (kg/kkg)
Aqueous Reflux from Cyclohexanone Oxime Rectifier	25.5	0.011
Stripper Overhead Condensate	1146	3.43
Wastewater from Oxime Extractor	509	1.02
Miscellaneous Run-off	229	1.83
Total (Based on Waste Water to Sewer)	1910	6.29

Average Raw Waste Load for Total Plant
Based on Finished Caprolactam Product

Plant Section	Flow (liters/kkg)	BOD (kg/kkg)	COD (kg/kkg)
Oxanone, HPO, and Caprolactam Process Wastewaters	7057	39.1	78.1
Hydrogen Seal Water, Drainage From Oxanone, HPO, and Capro.	6113	3.2	6.6
Ground Drainage Product Loading	630	0.5	0.9
Utilities Blowdown, Salt Drainage	15,268	4.3	7.4
Total (Based on Water to Sewer)	29,100	47.1	93.0

FIGURE 4-25

CYCLOHEXANONE OXIME-DUTCH STATE MINES CYCLOHEXANONE OXIME PROCESS
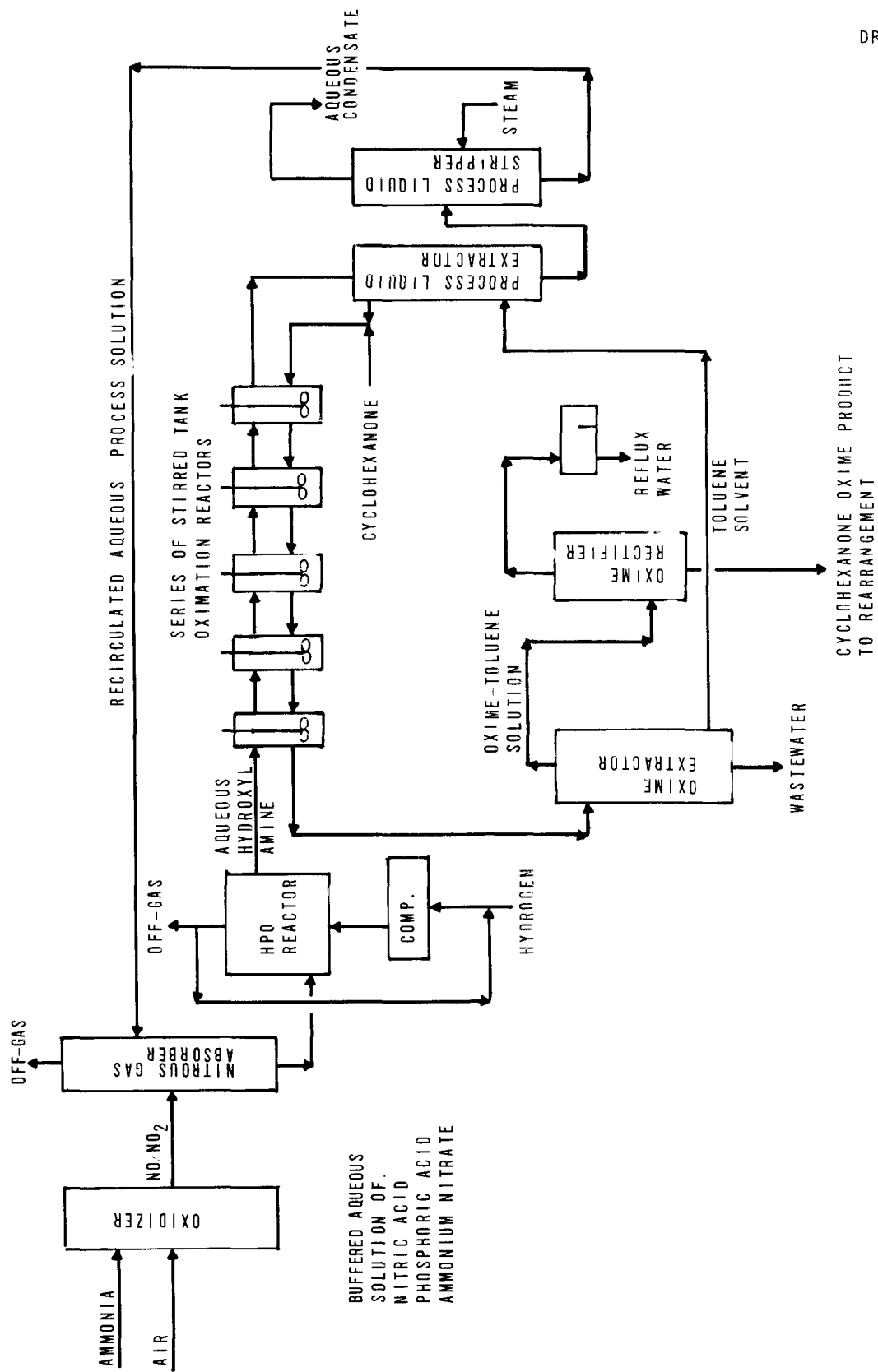
Product: Cresol (Synthetic)

Process: Methylation of Phenol

Process RWL Category: C

Chemical Reaction:

$$C_6H_5OH + CH_3OH \longrightarrow CH_3C_6H_4OH + H_2O$$

phenol   methanol   cresol
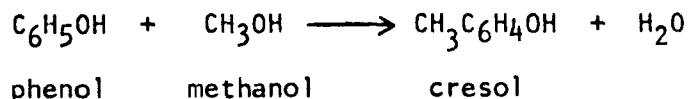
Cresol (cresylic acid) is an isomeric mixture (o-, m-, and p-cresol) obtained by refining the phenolic constituents present in coal tar, refining the petroleum acids formed during the thermal and catalytic cracking of petroleum, or by producing cresols syntheticly. Cresols are used primarily as raw materials for the production of phenolic resins, tricresylphosphate, disinfectants, and solvents.

The facility visited during the field survey produced an iosmeric mixture of cresols by the methylation of pheonol. Figure 4-26 is a process flow diagram of this production technique.

The first step in the process is the preparation of the reactor feed. Fresh and recycled methanol and phenol are mixed in a weight ratio close to 2.5:1. The mixed stream is then vaporized, and condensing Dowtherm vapors are used to vaporize and heat the feed to 300°C. The reaction is carried out at atmospheric pressure in a mixed-bed reactor which contains activated alumina catalyst. The heat of reaction is removed by passing liquid Dowtherm through the tubes imbedded in the fixed bed of the reactor. (The heat of reaction is approximately 20 K cal/mole.) Some of the heat evolved by the reaction will be taken up as sensible heat by the reactants, which are heated from 300°C to the reaction temperature of 350°C. The contact time in the reactor to the point when 52 percent of the phenol is alkylated is less than 30 seconds. A typical distribution on a water-free basis is given below.

	Weight %
Phenol	48
o-Cresol	30
m- and p-Cresol	12
2, 6-Xylenol	15
Anisoles and Hexamethylbenzene	5

The vapors leaving the reactor are condensed and cooled to about 25°C, and then sent to a phase separator. The vapor space is provided with a vent in order to periodically remove any noncondensables (CO_2, CH_4) which might be produced in the reactor. The weight percent of water in

the liquid phase is below 10 percent. Consequently, an aqueous phase
will not appear, because the water will stay in the organic phase. The
solubility level of water in phenol is close to 34 gms/100 gms phenol at
25°C. The presence of cresols and xylenol will undoubtedly decrease the
solubility limit, but the decrease is not expected to be sufficient to
form a separate aqueous phase.

The liquid phase is sent to an extraction column in which benzene (con-
taining some methanol) is circulated countercurrent to the liquid product
stream. The phenol, cresols, xylenols, and by-products are transferred
to the benzene phase, while the water and the methanol form an aqueous
phase.

The aqueous phase is then sent to a methanol recovery column, in which
methanol is removed as the distillate, while water (with small amounts
of phenol) remains as bottoms. The methanol is recycled to the reactor
feed-preparation section, while the water is discharged. The organic
phase, containing benzene and the reactor products, is sent to the ben-
zene recovery column, where this solvent is distilled overhead and re-
cycled to the extraction unit. This column is operated at atmospheric
pressure, with an overhead temperature close to 75°C. Cooling water is
used in the condenser, and condensing Dowtherm vapors are used in the
reboiler.

The bottoms stream leaving the solvent recovery still is sent to the
distillation column, in which anisole and light by-products are removed
in the overhead. Phenol is recovered in a subsequent distillation step
and recycled to the reactor section. The bottoms from the phenol re-
covery column are then sent to the product recovery section. In the
first column, o-cresol is recovered as distillate; in the second, a m-
and p-cresol isomer mixture is distilled overhead. The bottoms are sent
to the 2, 6-xylenol column, in which this co-product is distilled off,
while the bottoms containing the heavier by-products (such as hexamethyl-
benzene) are sent to organics disposal.

The major water pollution source is the water stream withdrawn as the
bottom of methanol recovery column. Process RWL's calculated from flow
measurements and analyses of the wastewater samples are indicated in the
following tabulation:

PROCESS FLOW

liter/kkg	2,090
gal/M lb.	250

BOD_5 RWL

mg/liter[1]	14,300
kg/kkg[2]	297

COD RWL

mg/liter[1]	303,000
kg/kkg[2]	631

TOC RWL

mg/liter[1]	10,400
kg/kkg[2]	217

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

The analytical results also indicate that phenol concentration in the waste stream is at a level hazardous to biological treamtent processes. The waste stream can either be pretreated with lime to form calcium phenolate before being discharged into biological treatment processes or can be steam stripped to reduce the phenol concentrations.

The process RWL shown above is considered as BPCTCA. The waste from the plant is discharged to the municipal treatment plant.

FIGURE 4-26

CRESOLS, SYNTHETICS-METHYLATION OF PHENOL
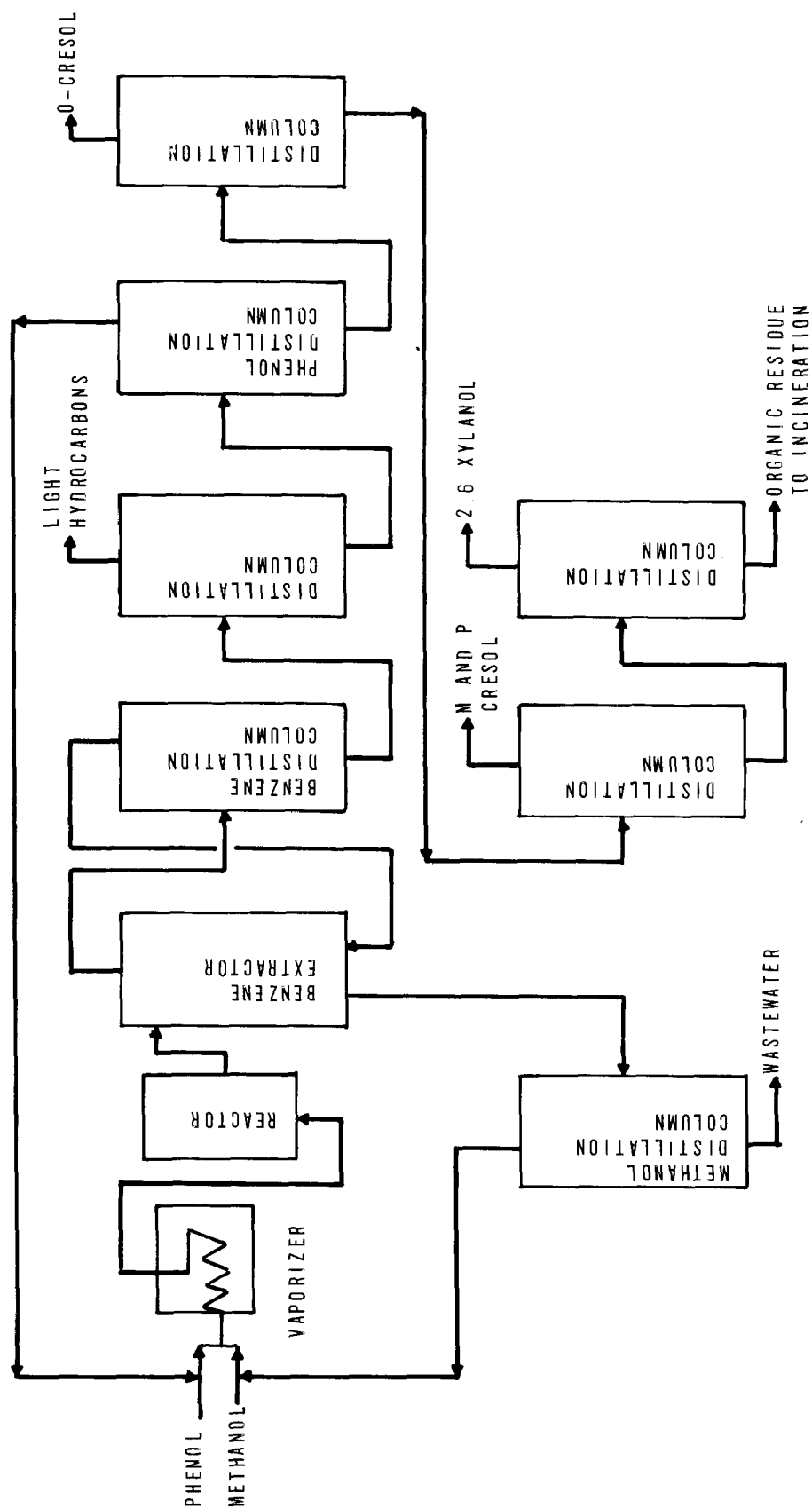
Product: Formic Acid

Process: Hydrolysis of Formamide

Process RWL Category: C

Chemical Reaction:

$$2 \text{ HCONH}_2 + \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ HCOOH} + (\text{NH}_4)_2\text{SO}_4$$

	sulfuric		formic	ammonium
formamide	acid		acid	sulfate
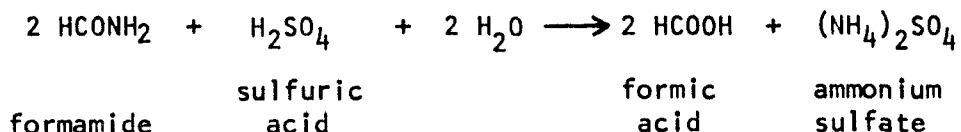
The main application for formic acid outside the United States is as a coagulant for natural rubber latex; domestically, over half of the total is used instead of sulfuric acid in high-temperature acid textile dyeing, and to some extent in leather tanning.

A process flow diagram for the manufacture of formic acid via hydrolysis of formamide is shown in Figure 4-27.

A feed stock, formamide, is stoichiometrically mixed with water and concentrated sulfuric acid in a pre-mixer, where the hydrolysis reaction occurs. The mixture of reaction products is then sent to a series of vacuum stills where ammonium sulfate in the form of a solid powder is withdrawn as the bottom of a still. The crude formic acid vapor taken as the overhead from the still is condensed by passing through a heat exchanger and led to a storage tank before being discharged into a purification still. The product formic acid is then taken as the overhead from the purification still, while the residue in the still is periodically flushed.

The major water pollution source of the process is the contact water utilized for the water eductor which is used to pull vacuum for the distillation columns. Although the residue withdrawn as the bottom of the formic acid purification still is periodically flushed into sewer lines, this stream can be disposed of through incineration and is therefore not included in the raw waste load calculation. Process RWL's calculated from the waste flow measurements and analytical results of the sampling program were subject to analysis for probability of occurrence. The following tabulation presents the results of the analysis.

	Probability Occurrence		
	10%	50%	10%
PROCESS FLOW			
liter/kkg		135,000	
gal/M lb.		16,000	
BOD$_5$ RWL			
mg/liter[1]	0	7.8	20
kg/kkg[2]	0.0	1.05	2.75
COD RWL			
mg/liter[1]	6.7	33	60
kg/kkg[2]	0.9	4.5	8.1
TOC RWL			
mg/liter[1]	0	10	24
kg/kkg[2]	0.0	1.4	3.2

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per one thousand unit weight of product.

The high flows and low concentrations shown are from the water educator used in the process. The 50 percent occurrence from the data above was considered as BPCTCA. It should be noted that the ammonium sulfate by-product is not considered in the RWL calculations. If this product could not be disposed of by fertilizer manufacturers (or other non-aqueous means), the process RWL would increase tremendously. The process wastes considered are discharged directly to surface receiving waters.

Most of the formic acid produced in the U.S. is obtained as a by-product from the manufacture of acetic acid via butane oxidation. Some of it, however, is made by absorbing CO either in caustic soda, followed by neutralization or in methanol, at high pressure, followed by conversion to formamide and hydrolysis.

FIGURE 4-27

FORMIC ACID-HYDROLYSIS OF FORMAMIDE
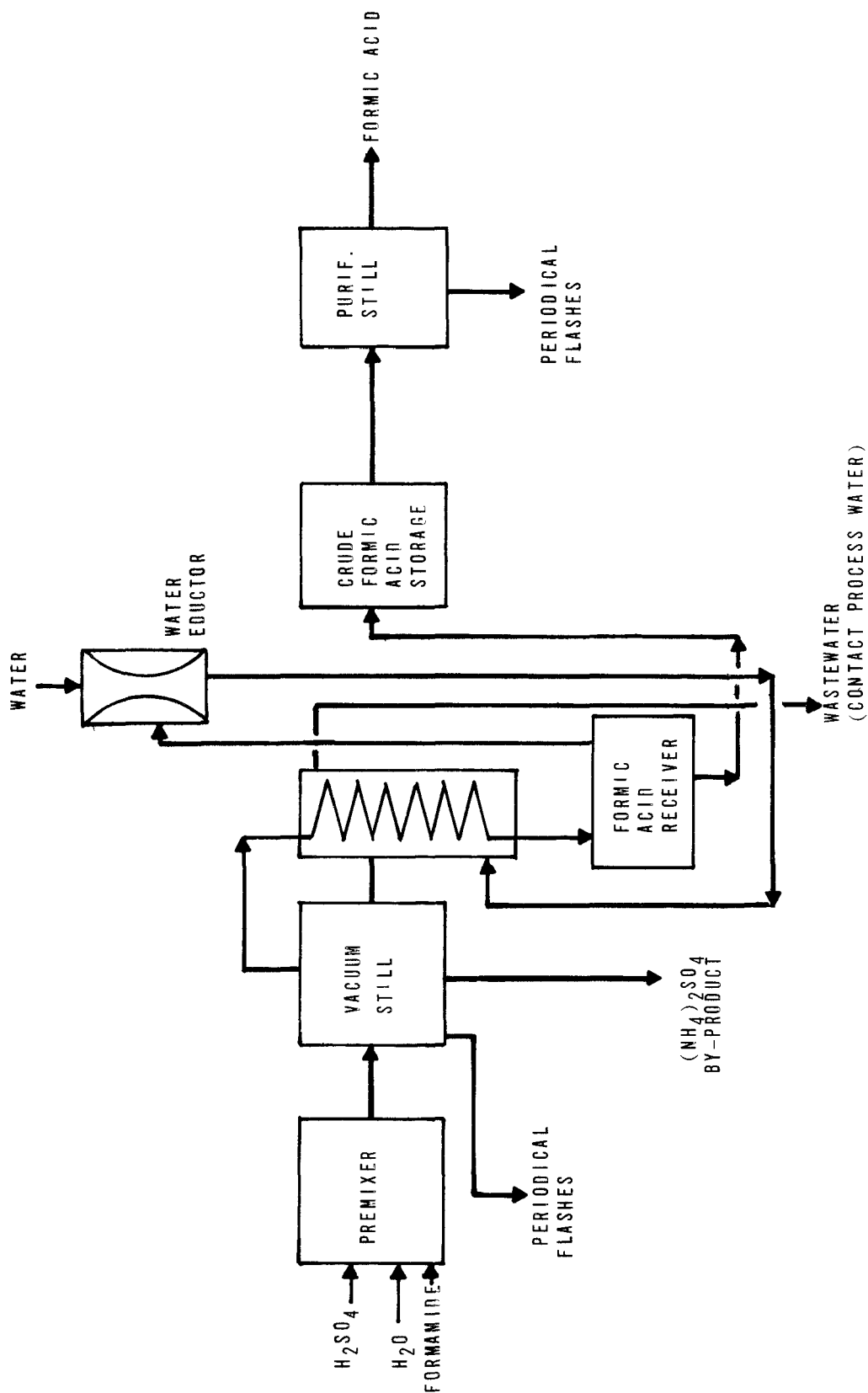
Product: Hexamethylene Tetramine

Process: Synthesis with Ammonia and Formaldehyde

Process RWL Category: C

Chemical Reactions:

$$6HCHO \quad + \quad 4NH_3 \quad \longrightarrow \quad (CH_2)_6N_4 \quad + \quad H_2O$$

<table>
<tr><td>formaldehyde</td><td>ammonia</td><td>hexamethylene
tetramine</td></tr>
</table>
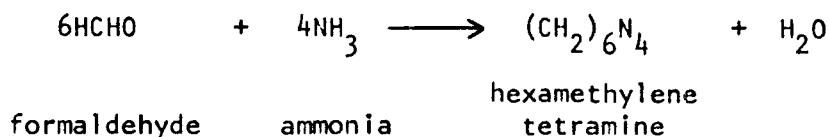
Two manufacturing plants were surveyed during the field data collection
program. Flow diagrams designated Plant 1 and Plant 2 are shown in
Figures 4-28 and 4-29.

Both plants combine aqueous formaldehyde and ammonia in a liquid phase
reactor to produce an aqueous solution of hexamethylene tetramine. The
reaction shown above produces about 0.8 kg of water per kg of hexamethylene,
and can be run with either an excess of ammonia or formaldehyde in the
reaction mixture. The ammonia is used preferably in a substantially an-
hydrous state, in either gaseous or liquid form initially. In view of
the high exothermic nature of the synthesis reaction, the desired control
and stabilization of the reaction temperature is somewhat more readily
achieved if the ammonia is introduced in liquid form so as to take ad-
vantage of the cooling resulting from its vaporization.

Reaction temperatures of 20-75°C constitute the range specified for manu-
facture of hexamethylene tetramine. The reaction is conducted at es-
sentially atmospheric pressure, although slightly superatmospheric pres-
sures may be employed for operating convenience. The production of
hexamethylene tetramine is carried out in the liquid phase in the presence
of an aqueous solution of the product as a rule. No catalyst is employed
in the reaction of ammonia with formaldehyde to give hexamethylene tetramine.

In both plants the liquid effluent from the reactor is concentrated in a
vacuum evaporator, where water from the reactor and formaldehyde feed-
stock are drawn off. In Plant 1, the overhead from the evaporator is
sent to a vapor-liquid separator with the liquid phase recycled to the
evaporator; the water vapor from the separator is passed through a non-
contact surface cooler and then sent to a second vapor-liquid separator;
and condensate is drawn off from this second separator and discharged to
the sewer as wastewater.

A steam jet is used to draw vaccum on the evaporator. Water vapor from
the second separator is drawn off into the steam line as shown in
Figure 4-28. The steam and water vapor then pass through a jet and are
subsequently vented to the atmosphere.

The concentrated liquid effluent from the evaporator is sent to a centri-
fuge where solid crystals of hexamethylene are separated. The centrate
is recycled to the evaporator

Hexamethylene crystals from the centrifuge are dried by hot air and
pulverized before being shipped off in bags or drums. Air from this
part of the process is cleaned using dry dust collectors.

A sampling program covering several weeks' operation at Plant 1 was con-
ducted. The data on process RWL are summarized below on a probability
basis

	Process RWL Plant 1			
	Flow (liters/kkg)	BOD₅ (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
30% Occurrence	3,920	4.6	18.8	4.5
50% Occurrence	3,200	9.2	29.4	9.8
70% Occurrence	5,200	15.7	40.0	15.1

It should be noted that the RWL data presented from Plant 1 do not in-
clude the additional flows and pollutant loads from carry-over into the
cooling jet vacuum system an appreciation for the magnitude of these
quantities can be gained in sampling the process used in Plant 2.

A flowsheet for this process is shown in Figure 4-29. The liquid ef-
fluent from the reactor is sent to a pH conditioner and evaporator oper-
ated on the sorbet water jets operating in a similar fashion to a baro-
metric condenser drew vacuum on both units. Water from both jets is
collected in a barometric sump. The warm water from the barometric sump
is circulated through a forced draft evaporative cooling tower, with the
cool water recycled to the vacuum jets.

Acid is added to the water in the cooling tower to react with
excess ammonia present. This is done to control the ammonia vapors
which would be stripped with the water vapor produced by evaporation
in the tower. Ammonium sulfate is produced by the reaction between am-
monia sulfuric acid

Water must be taken from the tower because the evaporation loss is
sufficient to carry off the water formed in the chemical reaction to
produce hexamethylene and the water present in the aqueous formaldehyde
solution. It is also necessary to control the level of dissolved solids
present in the recirculating contact cooling water.

A small wastewater stream is discharged from a wet scrubber used with
the dryer for the hexamethylene crystal. The following tabulations sum-
marize the RWL contribution from both the scrubber discharge and cooling
water blowdown.

	Process RWL Plant 2			
	Flow (liter/kkg)	BOD₅ (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
Cooling Tower Blowdown	550	71.5	116	42.7
Scrubber Blowdown	490	11.7	112	28.3
Total RWL	6,040	83.2	228	71.0

These data, from Plant 2, are significantly higher, both with respect to flow and loading, than those obtained from Plant 1. The flow and loadings attributed to the wet scrubber in Plant 2 are not sufficient to explain the difference between the two plants. Instead, the difference relates back to the fact that Plant 1 does not condense the steam used to draw vacuum on the evaporator. Although Plant 1 uses a surface condenser ahead of the vapor-liquid separator, there may be significant carryover of contaminants to the steam jet. These contaminants are then vented to the atmosphere with the uncondensed steam. The data shown for Plant 2 also may not fully show the magnitude of this difference in that the flow from the cooling tower represents a blowdown and does not include evaporation losses.

The manufacturer at Plant 2 indicated that the water circulation rate between the cooling tower and barometric condensers is approximately 73,900 liters/kkg of hexamethylene. Flows greater than this would be required if a once-through system were employed.

The RWL data from Plant 2 were considered as BPCTCA. These wastewaters are discharged to a municipal treatment plant, as are the wastes from Plant 1.

FIGURE 4-28

HEXAMETHYLENE TETRAMINE —SYNTHESIS WITH AMMONIA AND FORMALDEHYDE

PLANT 1
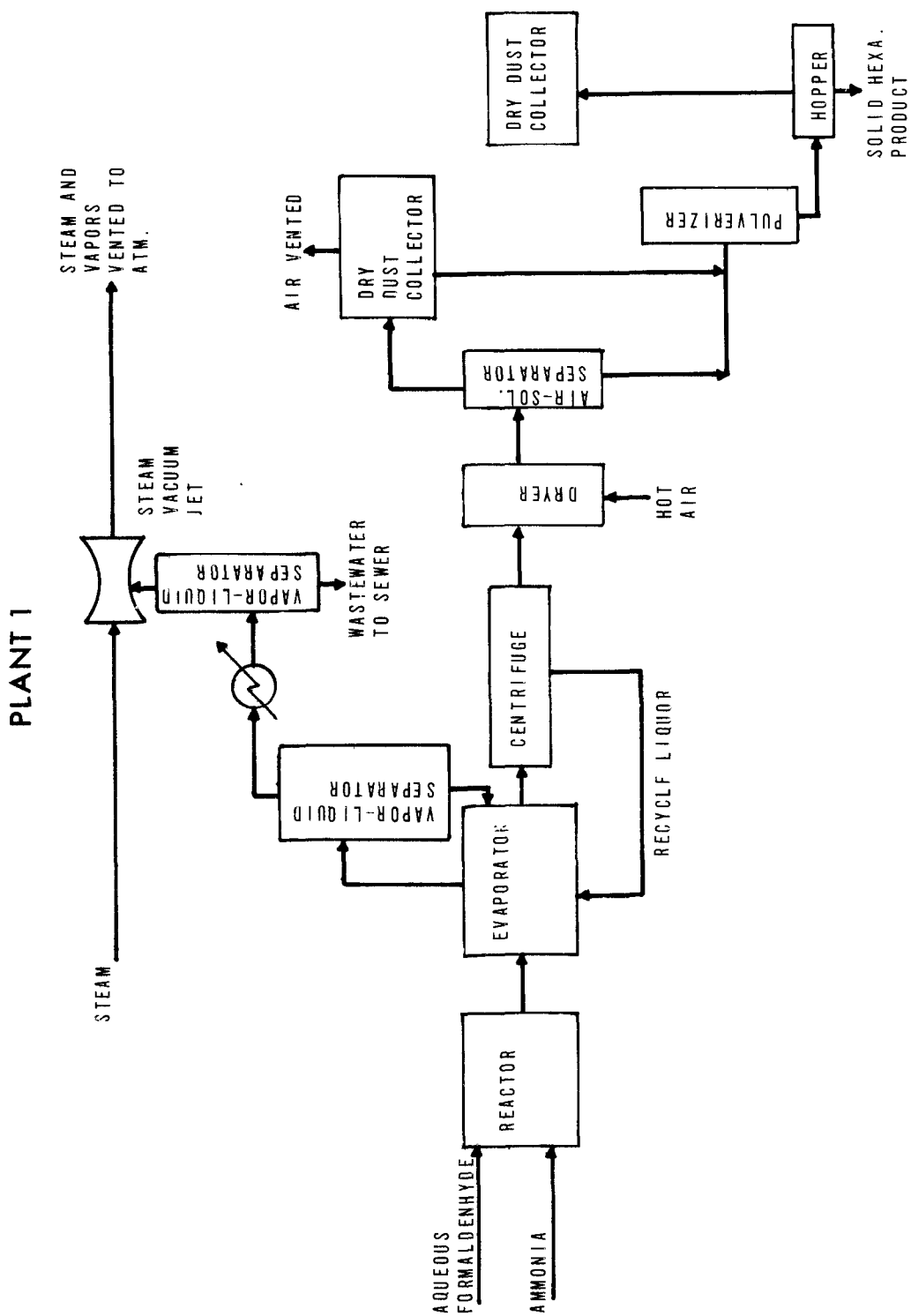
FIGURE 4-29

HEXAMETHYLENE TETRAMINE — SYNTHESIS WITH AMMONIA AND FORMALDEHYDE PLANT 2
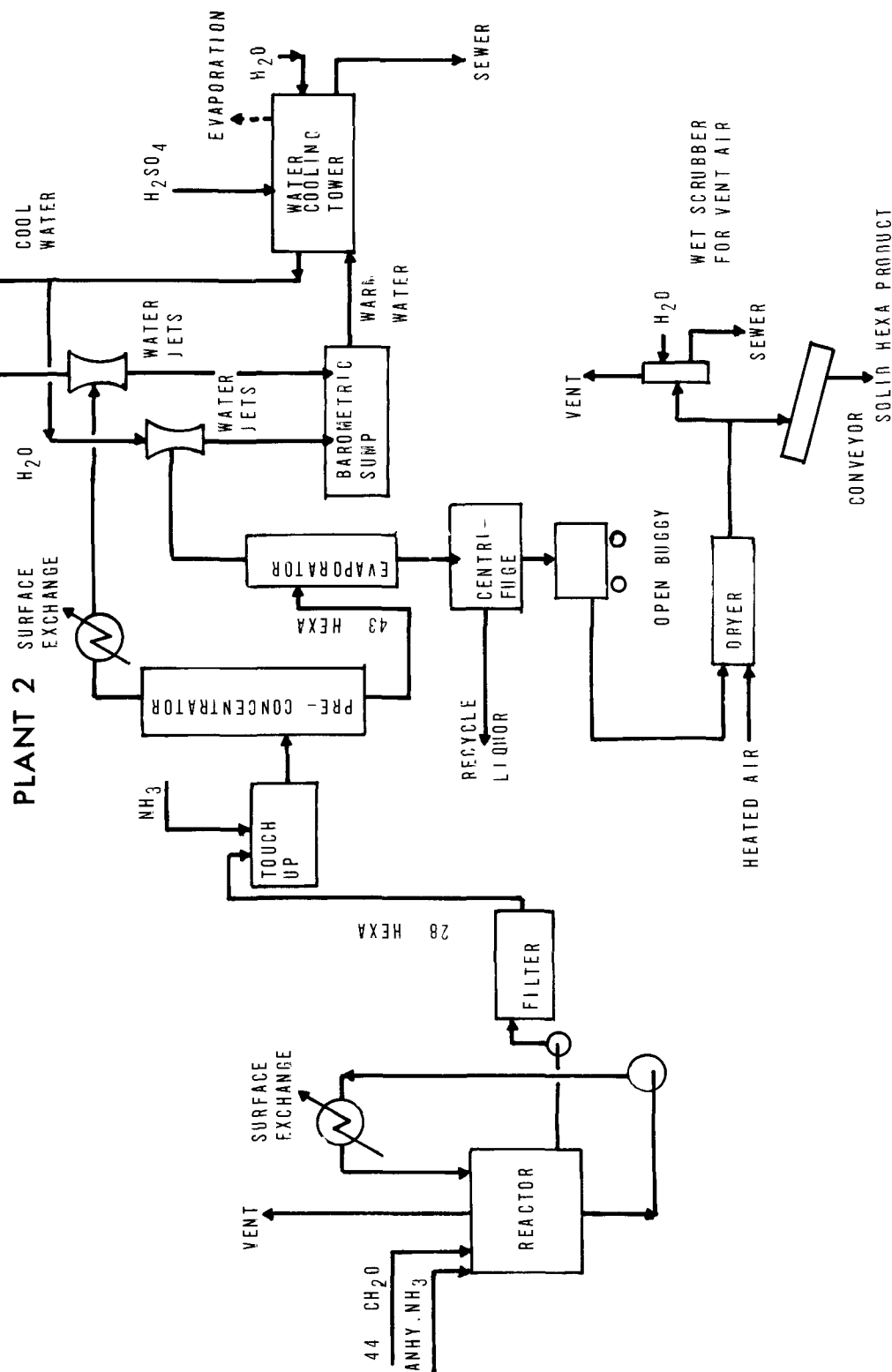
Product: Hydrazine Solutions

Process: The Raschig Process

Process RWL Category: C

Chemical Reactions:

$$NaOH + Cl_2 \longrightarrow NaOCl + HCl$$

$$\text{sodium}$$
$$\text{hypochloride}$$

$$NaOCl + NH_3 \longrightarrow NH_2Cl + NaOH$$

$$\text{chloramine}$$

$$NH_2Cl + NH_3 \longrightarrow N_2H_4 + HCl$$
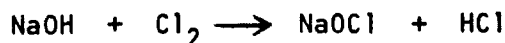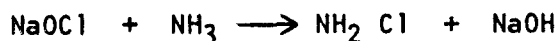
$$\text{hydrazine}$$

The principal use for hydrazine is as a military missile fuel where anhydrous hydrazine is required. Hydrazine also has a number of non-military applications. The most important of these is maleic hydrazine, a plant-growth regulator used for tabacco suckering and tree pruning. Other uses include wash-and-wear finishes, pharmaceuticals, anti-oxidants used in foam, hydrazine monobromide, and soldering flux.

A process flow diagram for the manufacture of hydrazine hydrate is shown in Figure 4-30.

Sodium hydroxide and chlorine are mixed in a reactor system to produce sodium hypochloride. Glue is added to the solution as an inhibitor until the mix is viscous; a dilute solution of ammonia (5 to 15 percent) is added until a molar ratio of $3NH_3$ to 1 hypochlorite is obtained. This mixture forms chloramine which, when reacted with anhydrous ammonia in a ratio of 20:1 to 30:1, produces hydrazine. The temperature reaches $130^{\circ}C$.

The effluent from the hydrazine reactor is fed to an ammonia removal still where excess ammonia is taken off overhead and recycled back to the reactors. The tails are fed to an evaporator where concentrated sodium chloride is removed. The vapors from the evaporator are fractionated to yield (as bottoms) a commercial grade of hydrazine hydrate.

Anhydrous hydrazine may be produced from hydrazine hydrate by extractive distillation. Hydrazine salts are produced by neutralizing hydrazine hydrate with the appropriate acid and then dehydrating the resulting slurry. The salts produced are hydrazine hydrobromide, hydrazine hydrochloride and hydrazine sulfate.

The wastewater stream from this process is a sodium chloride solution from the crystallizing evaporator. Process RWL calculated from the flow measurements and analyses of the wastewater obtained in the sampling survey are indicated in the following tabulation. The extreme high chloride concentration is the wastewater results in an inhibitory effect on the BOD_5 test and, consequently, the analytical results show a high COD/BOD_5 ratio. The low TOC is due to the lack of organic carbon involved in the process.

PROCESS FLOW

liter/kkg	30,300
gal/M lb.	3,630

BOD_5 RWL

mg/liter[1]	300
kg/kkg[2]	9.09

COD RWL

mg/liter[1]	3,800
kg/kkg[2]	115

TOC RWL

mg/liter[1]	-
kg/kkg[2]	-

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weight of product.

The process RWL shown above was considered as BPCTCA. The salt stream is combined with other plant wastewaters in a settling pond to remove suspended solids. The effluent from the pond is discharged to surface waters.

FIGURE 4-30

HYDRAZINE HYDRATE-THE RASCHIG PROCESS
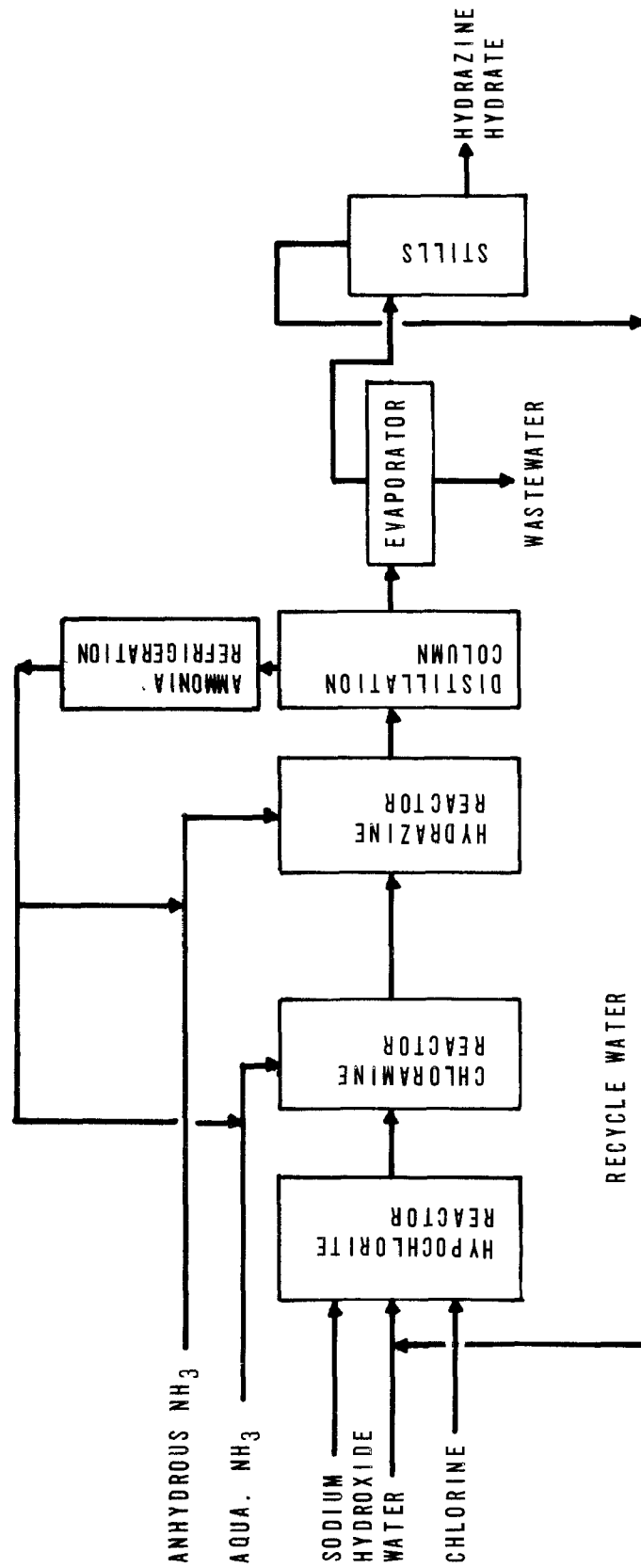
Product: Isobutylene

Process: Extraction with Sulfuric Acid from a Mixture of C_4 Hydrocarbons

Process RWL Category: C

High-purity isobutylene is required for applications such as the pro-
duction of butyl rubber and the alkylation of aromatics. In the U.S.,
the most common process for manufacturing pure isobutylene is extraction
with 65 percent sulfuric acid. The feedstock is usually a mixed C_4 cut
from a refinery. The process is continuous and is characterized by ex-
tensive contact between water (as H_2SO_4) and hydrocarbons. As such, it
is assigned to process Category C (Aqueous Phase Reactions). It should
be noted that regeneration of the sulfuric acid absorbent is considered
as an integral part of the process.

A flow diagram for the extraction process is shown in Figure 4-31. A
mixed C_4 hydrocarbon feedstock is drawn from the feed tank and passed
through two-stage countercurrent absorbers using 65 percent H_2SO_4. The
extract from the rich-stage absorber contains sulfuric acid and iso-
butylene. Steam is injected into the extract to flash off light hydro-
carbons in the extract vent drum. The liquid phase is sent from the vent
stream to the acid regenerator, where isobutylene is separated from sul-
furic acid by heating. The heat is supplied by contact steam injected
into the bottom of the tower.

Dilute sulfuric acid (45 percent) is withdrawn from the bottom of the
regenerator and recycled after reconcentration. The regenerator off-gas,
containing isobutylene and light polymer plus t-butyl alcohol, is scrub-
bed with caustic and water washed prior to being stored in the crude
isobutylene storage tank.

Alcohol by-product is withdrawn from an accumulator between the caustic
scrubber and water scrubber. The bottoms from the water scrubber are
reused as make-up on the caustic scrubber. The aqueous bottoms from the
caustic scrubber are discharged through an alcohol stripper, which re-
moves alcohol by injection of contact steam. The stripper alcohol is
passed back through the caustic scrubber.

Final purification of isobutylene is accomplished in a drying tower,
where water is discharged overhead, and a rerun tower, which takes iso-
butylene at greater than 99 percent purity overhead.

The only continuous contact wastewater stream and significant source of
water pollution associated with the isobutylene flow in the process
(shown by darkened lines in the flow diagram) is the alcohol stripper
bottoms. Aqueous batch dumps are also taken periodically from:

1. The C_4 hydrocarbon feed tank.
2. Knockout drums following the water scrubber.
3. The crude isobutylene tank.

The overhead water from the drying column amounts to a very small intermittent discharge.

The remaining process contact wastewater streams are associated with by-product and recycle streams and sulfuric acid regeneration. Unabsorbed normal C4 hydrocarbons from the lean-stage absorber may be scrubbed with caustic before being used in other processes, or merely stored if subsequent processing also involves the use of sulfuric acid (as is done in the process plant sampled). The aqueous bottoms from the normal C4 holding tank contain residual acid and are drained periodically.

The hydrocarbon vapors from the rich extract vent drum may contain some isobutylene along with normal C4 hydrocarbons absorbed by the sulfuric acid. These vapors are passed through a vent gas scrubber where they are first scrubbed with caustic and then with water. The overhead vapors from the vent gas scrubber are passed through a knock-out drum where entrained water from the scrubber is periodically drained. The vapors are then recycled to the C4 feed tank. The aqueous bottoms from the vent gas scrubber are discharged through the alcohol stripper.

The dilute sulfuric acid from the regenerator is reconcentrated from 45 percent to 65 percent by vacuum evaporation. The evaporators are equipped with steam heated calandrias (shell and tube surface heat exchangers) which evaporate excess water. This water is actually condensed contact stripping steam used in the acid regenerator to separate the absorbed isobutylene from sulfuric acid.

The overhead vapors from the vacuum evaporator are drawn through a surface condenser, which utilizes non-contact cooling water. The surface condensate is discharged through a pipe which has its discharge end submerged in a hot well which is divided by internal baffles. The remaining vapors are condensed in a series of barometric condensers associated with the steam jet vacuum system.

Reconcentrated 65 percent sulfuric acid is drawn from the vacuum evaporator and recycled to the process. Aside from unabsorbed normal butylenes, the principal by-products of this process are di-isobutylene and tertiary butyl alcohol. The former is formed by six polymerization reactions and the later from the hydrolysis of t-butyl sulfate.

Process RWL for isobutylene extraction are summarized in the following tabulation:

PROCESS FLOW

liter/kkg	20,400
gal/M lbs.	2,440

BOD_5 RWL

mg/liter[1]	669
kg/kkg[2]	13.6

COD RWL

mg/liter[1]	3,150
kg/kkg[2]	64.1

TOC RWL

mg/liter[1]	633
kg/kkg[2]	12.9

[1]Raw waste concentrations are based on unit
weight of pollutant per unit volume of con-
tact process wastewaters.
[2]Raw waste loadings are based on unit weight
of pollutant per 1,000 unit weights of product.

This process RWL data was considered as BPCTCA. The wastes from this
process are combined with those from other processing areas and treated
by the activated sludge process before discharge.

FIGURE 4-31

ISOBUTYLENE—EXTRACTION FROM C₄ HYDROCARBONS WITH SULFURIC ACID
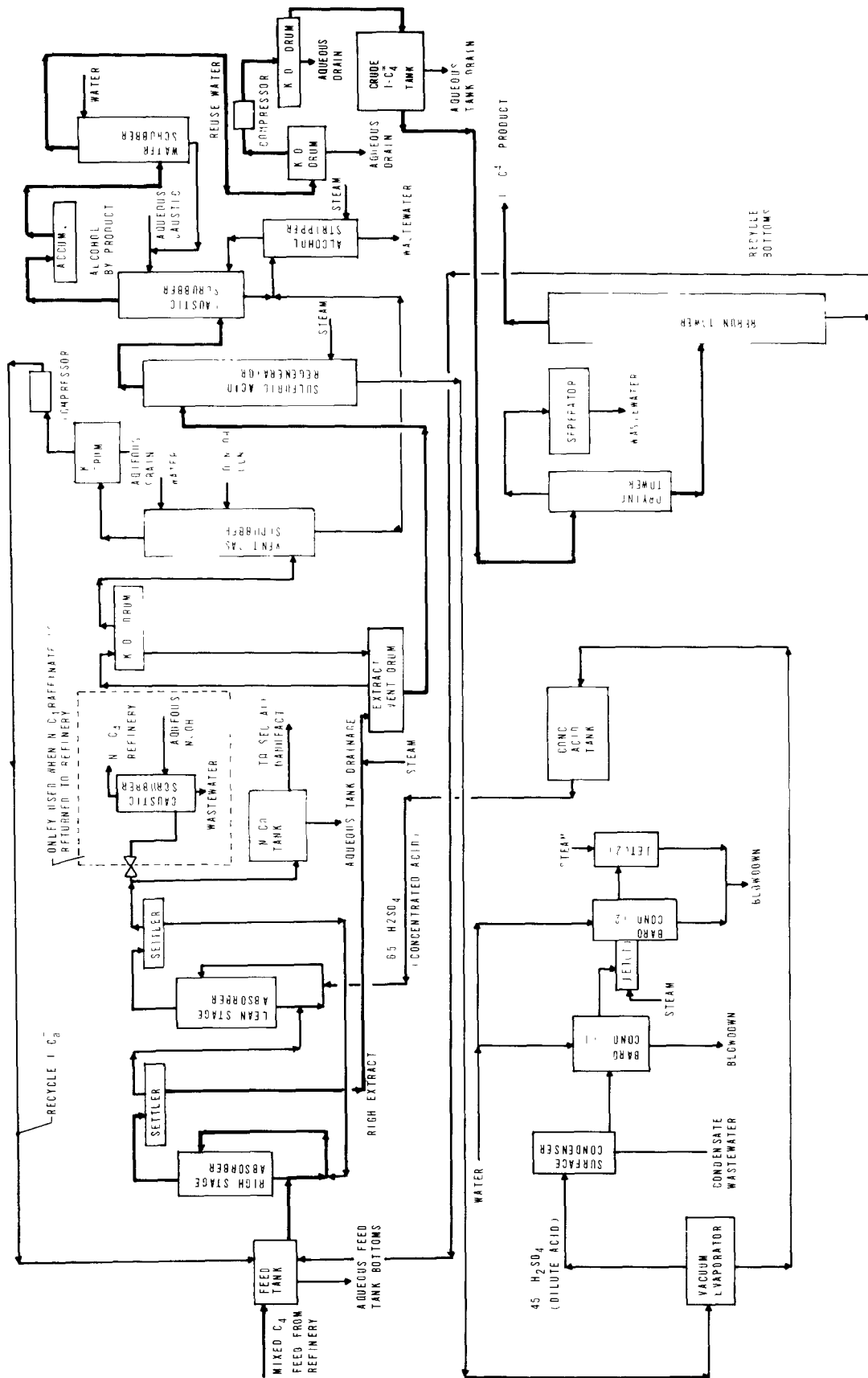
Product: Isopropanol

Process: Continuous hydrolysis of propylene

Process RWL Category: C

Chemical Reactions:

$$CH_2CH_2CH = CH_2 \ + \ 75\% \ H_2SO_4 \ \longrightarrow \ CH_3CHCH_3 \ + \ H_2O \ \longrightarrow \ CH_3CHCH_3 \ + \ H_2SO_4$$

propylene
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ HSO₄ $\quad\quad\quad\quad\quad\quad\quad\quad$ OH

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ iospropyl
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ hydrogen $\quad\quad\quad\quad\quad\quad$ iospropyl
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ sulfate $\quad\quad\quad\quad\quad\quad\quad\quad$ alcohol
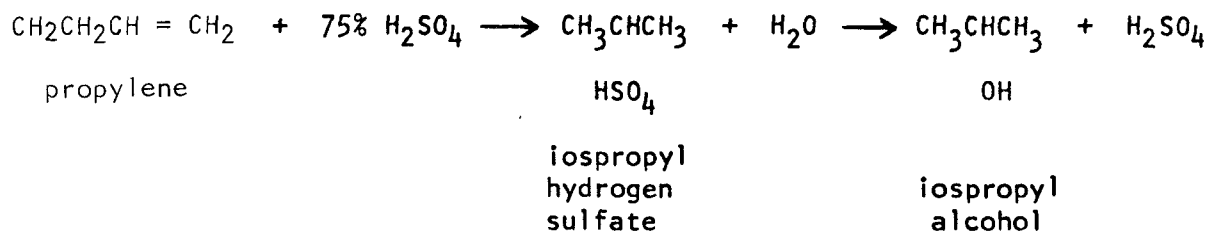
Typical Material Requirements

	100 kg isopropanol (87% isopropanol azeotrope)
Propylene	820 kg
75% sulfuric acid	<1.0 kg
25% caustic	6.5 kg
Benzene	<1.0 kg

Isopropanol is widely used in two major areas: feedstocks for the pro-
duction of other organic chemicals, and solvents. Organic chemicals which
employ isopropanol as a raw material include acetone, glycerine, isopropyl
acetate, amines, and hydrogen peroxide. The largest single use for iso-
propanol, which accounts for nearly one-half the total production, is
the manufacture of acetone by catalytic dehydrogenation.

As a solvent, isopropanol is used mainly for gums, shellac, and synthetic
resins, competing on a price-performance basis with ethanol. It is also
used widely as a rubbing alcohol.

The process plant visited during the sampling program was operated con-
tinuously except for occasional equipment washings. Since there is con-
tact with aqueous waters the process belongs to Category C. The flow diagram
for the process is shown in Figure 4-32.

The liquid propylene feedstock (65 percent) combined with recycled hydro-
carbons, is absorbed in 75 percent sulfuric acid to form a solution of
diisopropyl sulfate and isopropyl acid sulfate. The reaction takes place
at approximately 400 psig and 140°F. The sulfated hydrocarbon solution
is converted to an acid solution of isopropyl alcohol, ether, and polymer
by hydrolysis reactions with the addition of dilution water in the
hydrolyzer-stripper. Hydrolyzed reaction products are steam-stripped
from the acid and the vapors are condensed following neutralization with
a caustic solution.

Dilute acid is returned for reconcentration. The liquid products are then charged to a distillation column, where isopropyl alcohol is separated from isopropyl ether. The ether goes overhead while remaining isopropanol is extracted with recycled water and returned to the crude storage tank; the ether is then distilled and stored for subsequent sale. The isopropanol from the other distillation column is charged to the isopropanol (87 percent azeotrope) distillation column and then to storage. If a dry isopropanol is required, the azeotropic mixture is broken with benzene.

During the sampling visit, isopropanol was being produced at the normal rate; thus the wastewaters are considered to be typical of the everyday operation. The major sources of wastewater include pump seals and miscellaneous drips, the crude isopropanol waterwash scrubber, the crude isopropanol caustic scrubber, the isopropanol azeotrope distillation step, and the organic (benzene) recovery step. Process raw waste loads calculated from flow measurements and the total pollutant loadings are indicated in the tabulation below:

	Sample Period #1	Sample Period #2
PROCESS FLOW		
liter/kkg	2,537	2,537
gal/M lb	304	304
BOD$_5$		
mg/liter[1]	400	386
lb/M lb[2]	1.01	.979
COD		
mg/liter[1]	1,123	1,132
lb/M lb[2]	2.85	3.13
TOC		
mg/liter[1]	508	530
lb/M lb[2]	1.29	1.34

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

Waste streams included in the above calculations are continuous. However, there are occasional washings which were not sampled during the plant visit. The organic stripper is cleaned with water once per month. The

cleaning procedure requires approximately 100,000 gallons of water, equivalent to only 4 gallons per M lbs of product. Although it is not possible to specify quantitative values for pollution parameters such as BOD_5, COD and TOC for this stream, it is believed that this stream can either be ignored for the RWL calculations or disposed of by incineration. Therefore, the RWL presented in the above tabulation can be considered as representative of the process. Another discontinuous source of waste is the yearly cleaning of the absorption tower which yields approximately 1000 lbs of carbon tar to landfill disposal.

Non-contact wastewaters include cooling water flows. The process uses approximately 100 kg of once-through cooling water per kg of product. The treatment of the intake cooling water consists of bar screening and chlorination. Boiler blowdown is an additional non-contact flow. The blowdown is added to the cooling water return system. Hot phosphate softening is employed to treat the boiler feedwater.

The process RWL data presented were considered as BPCTCA. The wastes from this plant are neutralized and discharged to the local municipal treatment plant.

FIGURE 4-32

ISOPROPANOL- HYDROLYSIS OF PROPYLENE
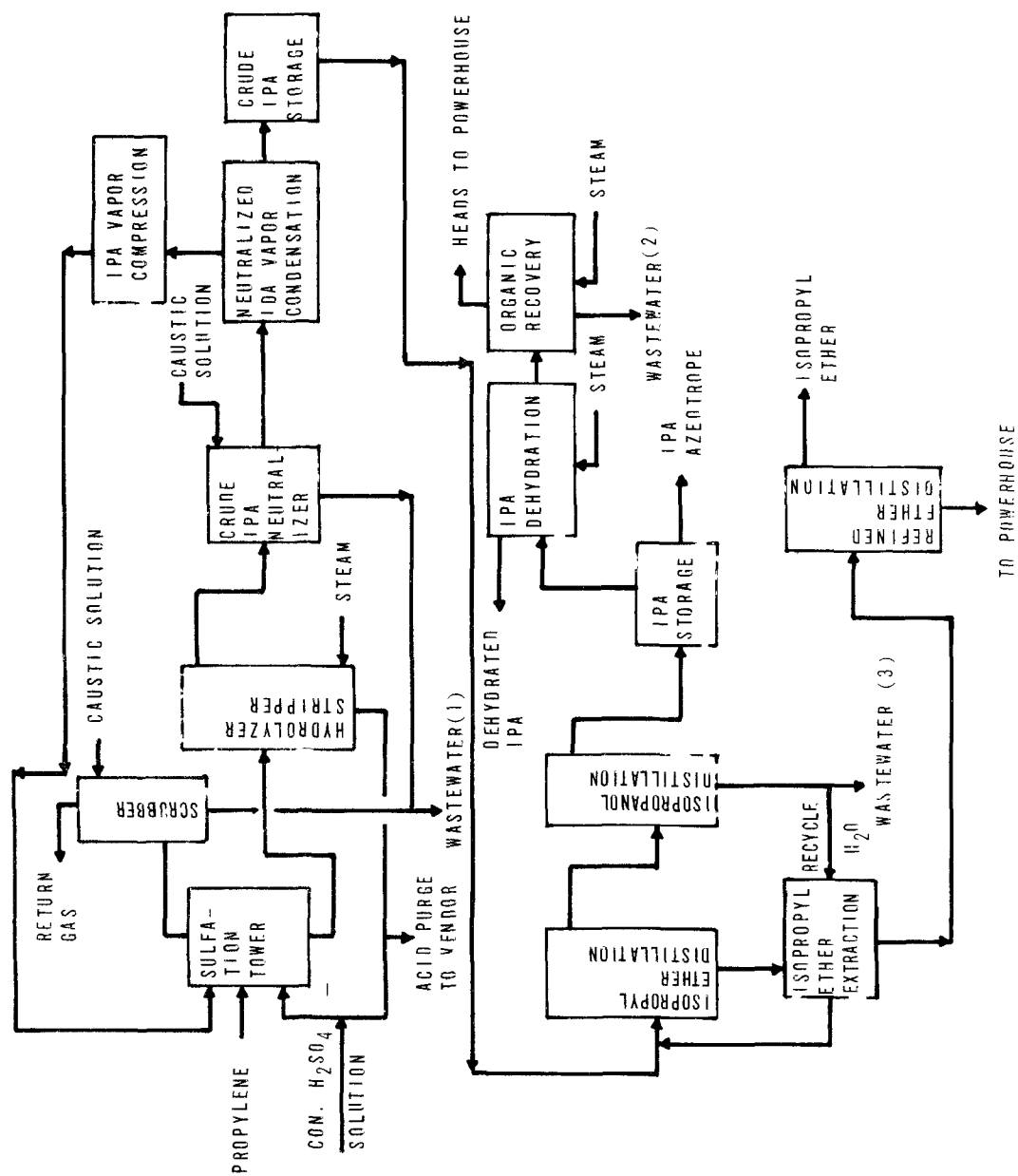
Products: Organic Solvents Complex

Processes:

Isobutylene - Sulfuric Acid Extraction (Category C)
Sec-Butyl Alcohol - Sulfonation & Hydrolysis (Category C)
Methyl Ethyl Ketone - Dehydrogenation of Sec-Butyl Alcohol (Category B)
Acetone - Dehydrogenation of Isopropyl Alcohol (Category B)
Methyl Isobutyl Ketone - Acetone Co-Product (Category B)
Isophorone - Acetone Co-Product (Category B)
Mesityl Oxide - Acetone Co-Product (Category B)

The historical data on wastewater flows and total carbon loss, shown in
Table 4-4, were provided by a manufacturer producing the chemicals listed
above. The data are based on weekly composite samples and were normalized
to reflect total weekly production for the complex.

Based on 27 weeks operation, the arithmetic average (mean) wastewater flow
was 3,900 liters/kkg total production (467 gallons/1,000 lbs) with a
standard deviation of 1,201 liters/kkg (144 gallons/1,000 lbs). The
average total carbon loss was 23.9 kg/kkg with a standard deviation of
10.5 kg/kkg. These data are presented for orientation with no intention
to develop effluent limitations relating to this type of chemical complex.

The manufacturing personnel at this facility were very cooperative during
the sampling survey and each individual process plant appeared to be well
operated with respect to both housekeeping and control measures relating
to water pollution. The spread in the historical data provided can there-
fore be interpreted to be typical of the spread in RWL which will occur
in a well run process plant.

Table 4-4

Historical RWL Data for Organic Solvent Complex

Flow gal/1000 lbs	% Occurrence	Total Carbon lb/1000 lbs	% Occurrence
322.300	3.570	8.190	3.570
337.200	7.140	9.630	7.140
342.200	10.710	10.830	10.710
348.400	14.290	10.840	14.290
356.000	17.860	12.770	17.860
362.600	21.430	15.240	21.430
372.900	25.000	17.400	25.000
381.000	28.570	17.700	28.570
386.000	32.140	18.140	32.140
415.600	35.710	19.140	35.710
416.400	39.290	21.240	39.290
432.600	42.860	21.280	42.860
432.900	46.430	23.240	46.430
435.700	50.000	23.310	50.000
446.100	53.570	23.340	53.570
453.000	57.140	23.380	57.140
466.500	60.710	25.520	60.710
485.600	64.290	26.560	64.290
490.800	67.860	27.180	67.860
502.000	71.430	27.570	71.430
504.900	75.000	27.810	75.000
508.200	78.570	30.110	78.570
513.400	82.140	34.350	82.140
533.700	85.710	37.870	85.710
535.000	89.290	38.690	89.290
893.500	92.860	45.360	92.860
933.900	96.430	49.670	96.430

Product: Oxalic Acid

Process: Nitric Acid Oxidation of Carbohydrates

Process RWL Category: C

Chemical Reaction:

$$C_6H_{12}O_6 \ + \ 6HNO_3 \longrightarrow 3HOOCCOOH \ + \ 6NO \ + \ 6H_2O$$

	nitric		nitric	
glucose	acid		acid	
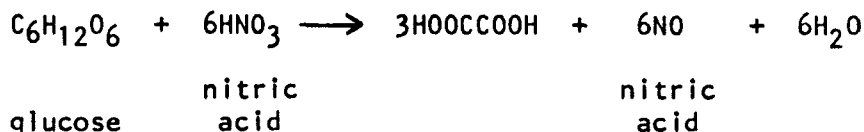
Typical Material Requirements:

Basis: 1 ton oxalic acid dihydrate

Glucose (60 percent)	2,112 lbs
Nitric Acid (90 percent)	5,135 lbs
Sulfuric Acid (100 percent)	116 lbs

The uses for oxalic acid center around its calcium-ion removal and re-
ducing properties; it is used as a laundry "sour", as a bleach for re-
moving iron stains from a variety of materials, and in cleaning compounds.
It also finds use in automobile radiator cleaners, leather tanning and
manufacture, chemical processing, photography, medicinals, dyes, and
inks.

Figure 4-33 is a process flow diagram of oxalic acid production via
nitric acid oxidation of carbohydrates. Carbohydrates (in the form of
corn starch), vanadium catalyst, steam, sulfuric acid, and nitric acid
are added to the reactor. The reaction time is twelve hours and the re-
actors are sequenced so as to continuously provide products for the re-
mainder of the processing equipment. Spent nitric acid is withdrawn from
the reactor and recovered. The reaction products go to a vacuum crystal-
lizer followed by a wringer. The liquid effluent from the wringer goes
to a liquid-solid separation step, in which the solids are recycled to
the crystallizer while the liquid proceeds to an evaporator; the dis-
charge from the evaporator is recycled to the reactor. The crude oxalic
acid crystals from the wringer are redissolved and then filtered. The
solids from the filter are disposed by landfill while the oxalic acid is
recrystallized under vacuum conditions; the crystals proceed to a second
wringer; and the liquid from this wringer undergoes a liquid-liquid
separation step, along with liquid from the previous crystallization
step. Some liquid is recycled to the crystallizer, while the remaining
portion proceeds to a second liquid-liquid separation step. Some of the
liquid is recycled to the reactor and the remainder goes to an evaporator.
The discharge from the evaporator is recycled to the liquid-liquid sepa-
rator. The oxalic acid crystals from the wringer are dried and then
packaged for sale.

The wastewaters from this process consist exclusively of barometric condenser effluents. This effluent was sampled and its flow measured. The process RWL calculated from the flow measurements and the analyses of the samples are indicated in the tabulation below:

PROCESS FLOW

liter/kkg	436,000
gal/M lb	52,300

BOD$_5$ RWL

mg/liter[1]	3
kg/kkg[2]	1.31

COD RWL

mg/liter[1]	10
kg/kkg[2]	4.36

TOC RWL

mg/liter[1]	3
kg/kkg[2]	1.31

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The high flows and low concentrations seen above are caused by the vacuum system associated with the process. These data were considered as BPCTCA. The wastes from the process are discharged to a municipal treatment plant.

The alternate route in the manufacture of oxalic acid is via sodium formate. Sodium formate is produced by the reaction of solid sodium hydroxide and carbon moxoxide at 200°C and 150 psi in an autoclave. After the reaction is completed, the pressure is reduced and the temperature is raised to 400°C. The sodium formate is converted into sodium oxalate, which is then precipitated by calcium hydroxide to form calcium oxalate. Calcium oxalate is further acidified by sulfuric acid to form oxalic acid.

FIGURE 4-33

OXALIC ACID-NITRIC ACID OXIDATION OF CARBOHYDRATES

Product: Pentaerythritol

Process: Aldehyde Condensation

Process RWL Category: C

Chemical Reactions:

$$4HCHO + CH_3CHO + NaOH \longrightarrow C(CH_2OH)_4 + HCOONa$$

| formaldehyde | acetaldehyde | sodium hydroxide | pentaerythritol | sodium formate |
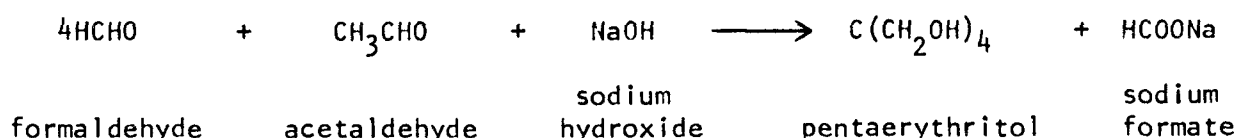
The most important end use of pentaerythritol is in the manufacture of alkyl resins, in competition with glycerol. Next in importance are pentaerythritol resin esters, which are used in floor polish and in flexographic inks. Other applications of pentaerythritol esters are in the manufacture of fire-retardant paints, use as high pressure lubricants, and production of PVC plasticizers of low volatility suitable for use in wire insulation.

A typical process flow diagram for producing pentaerythritol by aldehyde condensation is shown in Figure 4-34.

To a solution of formaldehyde (20 to 30 percent by weight) is added either 50 percent sodium hydroxide or 50 to 80 percent calcium hydroxide slurry while the temperature is maintained at 15 to 20°C. With suitable agitation, 99 percent liquid acetaldehyde is slowly added under the surface of the formaldehyde-alkali solution. Since the reaction is exothermic, external cooling is used to maintain the reaction temperature between 20 and 25°C. The mole ratio of formaldehyde to acetaldehyde generally used is between 4.5:1 and 5.0:1. A ratio of 1.0 to 1.5 moles of hydroxyl ion per mole of acetaldehyde appears to be the optimum amount of condensing agent. The temperature of the reaction mixture is held at 25° to 30°C for several hours and is then raised to about 60°C until the free aldehyde content is less than 0.1 percent. Numerous side reactions occur simultaneously, mostly other condensations and autocondensations.

The crude reaction mixture is distilled, with tops (mainly formaldehyde) going back to the reactor and bottoms transferred to the neutralizing tank, where an acid is added to neutralize the excess alkali and to effect removal of the metallic ion of the condensing agent. If sodium hydroxide is used, formic acid may be added to reduce the pH of the solution to 7.8 to 8.0 and subsequently to remove the sodium ion present as sodium formate. If calcium hydroxide is the condensing agent, sulfuric acid or oxalic acid, either alone or conjunctively, may be employed to precipitate the calcium ion as calcium sulfate or calcium oxalate. The calcium salt is removed by filtration.

The solution is then evaporated to a specific gravity of about 1.27. It is chilled to crystallize pentaerythritol, and the resulting slurry is filtered. The mother liquor goes to a recovery system, where it is reworked. If sodium hydroxide acted as the condensing agent, the sodium ion is removed as sodium formate during this operation. If the calcium process is used, the calcium ion is removed in the previous step by filtration.

The filter cake contains pentaerythritol and polypentaerythritols. The latter materials are formed by side reactions and are a mixture of ether-linked polymers such as dipentaerythritol and tripentaerythritol. Other by-products found in the reaction liquors include both linear and cyclic formals of the various pentaerythritols. The amounts of these poly-pentaerythritols and formals formed vary with reaction procedures and may be kept at a minimum under proper reaction conditions. The filter cake is then redissolved in hot water and passed through an ion-exchange purification unit which removes the last traces of formic acid. The concentration of this solution is sufficient; thus another evaporation step is unnecessary. Deionization is followed by vacuum crystallization, filtration, and drying. The yield is a technical product containing about 11 percent dipentaerythritol. Some producers treat part of the product further to obtain both products in pure form.

The major pollution sources of the process are residue from the distillation column and mother liquors withdrawn from filtration units. The condensates from the steam jets which are used to pull vacuum are recycled back to the process, and are not considered wastewaters. The process RWL calculated from the flow measurements and analyses of wastewater samples obtained in the sampling period are presented in the following tabulation:

PROCESS FLOW

liters/kkg	10,200
gal/M lbs	1,220

BOD_5 RWL

mg/liter[1]	38,100
kg/kkg[2]	390

COD RWL

mg/liter[1]	155,000
kg/kkg[2]	1,580

TOC RWL

mg/liter[1]	81,200
kg/kkg[2]	830

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2]Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The above process RWL are considered as BPCTCA. The wastewater from this process is combined with other wastes for treatment in an activated sludge plant. The plant effluent is discharged to solar evaporation ponds.

FIGURE 4-34

PENTAERYTHRITOL —ALDEHYDE CONDENSATION
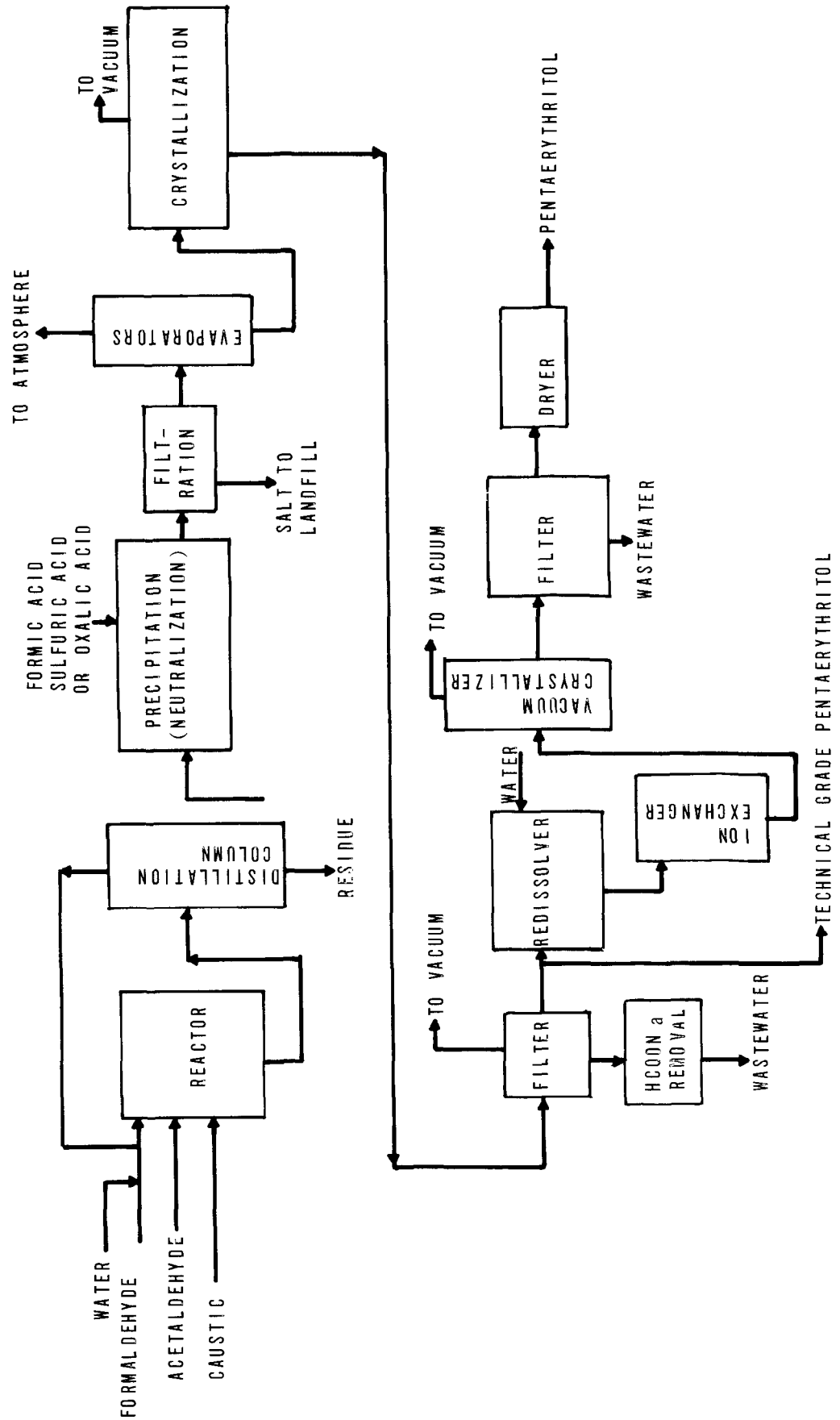
Product: Propylene glycol

Process: Hydrolysis of propylene oxide

Process RWL Category: C

Chemical Reactions:

$$CH_3CH\overset{}{\underset{O}{\diagdown}}CH_2 \quad + \quad H_2O \quad \longrightarrow \quad CH_3CHOHCH_2OH$$

Propylene   water   propylene glycol
oxide
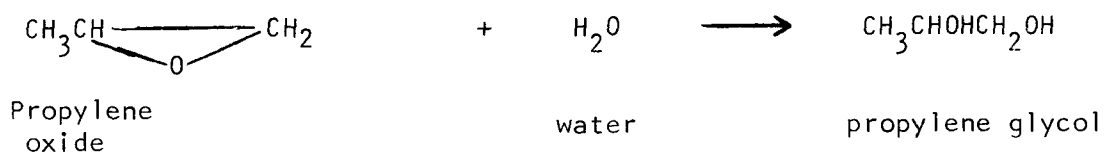
Propylene glycol is by far the most widely used difunctional alcohol for the manufacture of unsaturated polyesters. This end use consumes nearly one-half of the propylene glycol produced in the United States.

Propylene glycol is also used as a cellophane plasticizer. This market is relatively new, since propylene glycol is a substitute for ethylene glycol, which has recently been deemed toxic. Toxicity regulations also determine the use of propylene glycol in tobacco. Miscellaneous outlets for propylene glycol include uses as a binder for cork bottle caps, as a humectant in cosmetics, and as an intermediate for propylene carbonate.

Production of propylene glycol is based on the liquid-phase hydrolysis of propylene oxide, and is shown as a flow diagram in Figure 4-35. The hydrolysis reaction occurs at an elevated temperature and pressure in the presence of a sulfuric acid catalyst.

By selection of the ratio of feedstock propylene oxide to water, 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 formation of undesirable by-products.

Reaction products are passed from the reactor to a series of evaporation and drying towers to remove excess water. This excess vapor is often discharged to the atmosphere, although it could be recycled to the reactor.

After passing through the drying operation, the crude propylene glycol is sent to a series of fractionators. The first tower removes water and traces of the light ends. Mono-propylene glycol is then separated, condensed, and stored as an industrial grade product. The bottoms from the mono-propylene glycol tower are sent to the crude di-propylene glycol storage facilities.

Crude di-propylene glycol is then vacuum-distilled. The tops are recycled to the reactor hydrolyzer to dry the materials further and to recover glycol product. Bottoms leaving this first column are further distilled. Food-grade di-propylene glycol is obtained as bottoms from the second distillation step; the tops are then further distilled to separate additional mono-propylene glycol. Both light and heavy ends are waste products.

Wastewaters from the production of propylene glycol are generated during the evaporation-drying operation and the distillation processes. Steam ejectors and barometric condensers are employed in most of the distillation columns. During the plant visit, samples of these contact process wastewaters were obtained. Process raw waste loads calculated from flow measurements and analyses of these streams are indicated in the tabulation below:

PROCESS FLOW

liter/kkg		5,500
gal/M lb.		660
BOD_5	RWL	
	mg/liter[1]	3
	kg/kkg[2]	.016
COD	RWL	
	mg/liter[1]	10
	kg/kkg[2]	.055
TOC	RWL	
	mg/liter[1]	1
	kg/kkg[2]	.006

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

These RWL values are not considered to be truly indicative of the process because all of the steam from the ejectors is discharged to the air and is not condensed. For this reason, it is not possible to recommend effluent limitations for this process.

RWL data obtained from a plant survey are summarized in the following
tabulation. Since the plant surveyed is designed strictly for manufac-
turing of one plasticizer (diethyl phthalate), it requires less frequent
reactor clean-up. Consequently, both flow and RWL of this process are
not as high as expected.

PROCESS FLOW

	liter/kkg	653
	gal/Mlbs	78.3
BOD_5 RWL	mg/l [1]	82,600
	kg/kkg [2]	53.9
COD RWL	mg/l [1]	127,000
	kg/kkg [2]	82.6
TOC RWL	mg/l [1]	51,200
	kg/kkg [2]	33.4

[1] Raw waste concentration are based on unit
weight of pollutant per unit volume of
contact process wastewaters.

[2] Raw waste loadings are based on unit weight
of pollutant per 1000 unit weights of product.

These data were considered as BPCTCA.

FIGURE 4-35

PROPYLENE GLYCOL-HYDROLYSIS OF PROPYLENE OXIDE
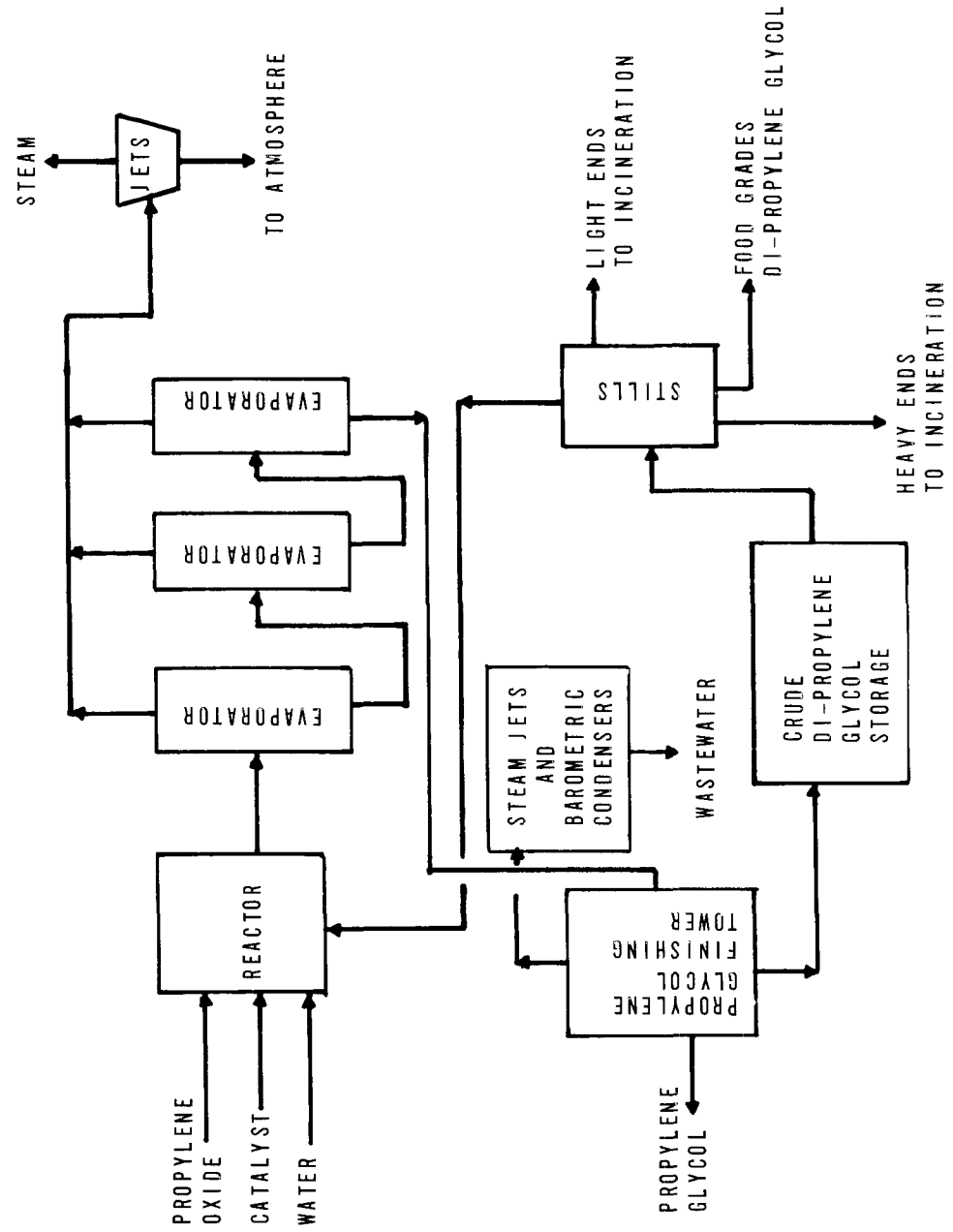
Product: Propylene oxide

Process: Chlorohydrin Process

Process RWL Category: C

Chemical Reactions:

$$C_3H_6 \quad + \quad HOCl \longrightarrow HOCH_2CH_2CH_2Cl$$

propylene   hypochloric acid   propyl
                                     chlorohydrin

$$2\ HOCH_2CH_2CH_2Cl \quad + \quad Ca(OH)_2 \longrightarrow 2\ CH_3CH \overset{}{\underset{O}{\diagdown\diagup}} CH_2 \quad + \quad CaCl_2 \quad + \quad 2\ H_2O$$

   propyl   lime   propylene oxide   calcium   water
chlorohydrin   chloride
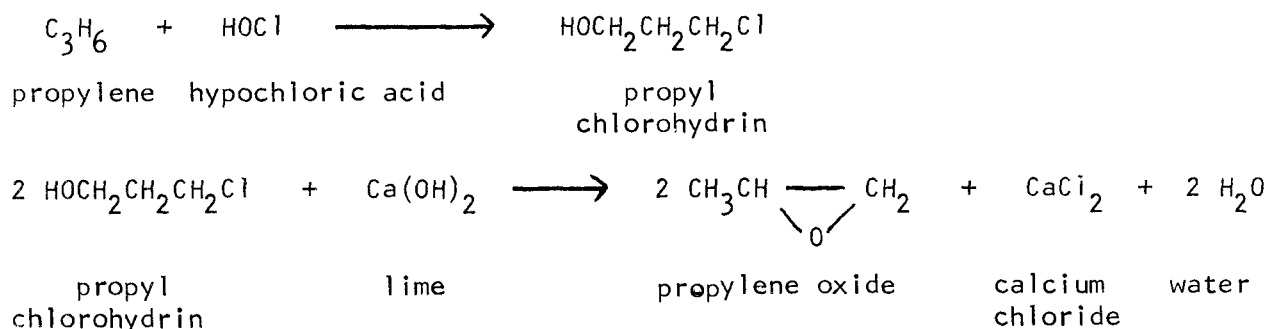
The most important outlet for propylene oxide is in the manufacture of
propylene glycol. It is also used during the production of polyethers,
or which are in turn used in the manufacture of urethane forms and elast-
omers.

The manufacture of propylene oxide from propylene is similar to that of
ethylene oxide by the chlorohydrin route. In fact, many propylene oxide
manufacturing facilities are converted ethylene oxide plants which were
rendered obsolete by the advent of direct oxidation. In recent years,
considerable research has been undertaken to discover a viable process
for making propylene oxide without using chlorine. A number of alter-
natives have been developed, including epoxidation of propylene by means
of a hydroperoxide and direct oxidation of propylene.

Production of propylene oxide by the chlorhydrin process involves a
reaction between propylene and chlorine, and the process flow sheet is
shown in Figure 4-36. The raw materials are fed into a reactor and
water is added. The reaction products are primarily chlorohydrin and
dischlorohydrin. Vent gases from the reactor are passed through a
water scrubber. A second stage caustic scrubber is also employed to
neutralize potential acid carry-over in the off-gases.

Following the caustic scrubbing, the gases are passed to an oil absorption
unit where propylene dichloride is selectively concentrated and recovered.
(An activated carbon adsorption system may be substituted for the oil
absorption unit). Other gases, such as propylene and propane are often
vented to a fuel gas supply. At some installations, pure propane may
be recovered in a dehydrator (activated alimina).

Reaction products, containing mainly propyl-chlorohydrin, are sent to
a saponification reactor. A lime slurry is fed into the reactor along
with live steam. In the reactor, propyl-chlorohydrin is converted to
propylene oxide. Dichlorohydrin is also converted to propylene dichloride,
which may be recovered as a by-product. Following the lime addition,
the products are passed through a stripper. The products (propylene oxide
and propylene dichloride) are separated from unreacted lime and calcium
chloride. The unreacted lime solution is passed through a clarifier
from which the underflow, containing unreacted lime, is recycled back
to the saponitrication reactor; the overflow is discharged as wastewater.

The product lime is then passed through a recovery tower, where propylene
oxide is separated. The underflow, containing propylene dichloride, is
sent to a stream stripper where propylene dichloride is separated from
other impurities. The propylene dichloride is combined with the propylene
dichloride separated from the off-gases. Bottoms from the stripper con-
stitute a second major waste stream.

Production facilities for propylene oxide were visited during the
sampling period, and samples of the contact process wastewaters were
obtained. Process raw waste loads calculated from flow measurements and
analyses of these wastewaters are indicated in the tabulation below:

	Plant 1		Plant 2	Plant 3
	Sample Period #1	Sample Period #2	Sample Period #1	Sample Period #1
PROCESS FLOW				
liters/kkg	60,000	50,200	69,300	66,000
gal/M lb.	7,150	6,020	8,300	7,910
BOD_5 RWL				
mg/liter[1]	290	575	480	578
kg/kkg[2]	17.2	28.9	33.2	38.1
COD RWL				
mg/liter[1]	2,480	2,740	1,680	2,580
kg/kkg[2]	148	138	116	170
TOC RWL				
mg/liter[1]	310	320	365	385
kg/kkg	18.6	16.0	25.3	25.4

NOTE: [1]Raw waste concentrations are based on unit weight of pollutant
per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per
1000 unit weights of product.

A plant average of the values presented above was considered as BPCTCA. The wastewaters from all three plants are combined with wastes from other processes and pumped to settling basins from which they are discharged to surface receiving waters. The high flows may be partially explained by the fact that a large quantity of water is required in the reactor and also in the many scrubbers. Furthermore, a large quantity of stichiometric water is formed during the reaction.

It is possible that both pollutant loadings and flows may vary at other production facilities. The pollutant loadings may be greatly increased if propylene dichloride is not recovered following separation of the propylene oxide. At such an installation, the flows would probably be lower since the propylene dichloride stripper would not be required.

An additional feature of the process plant visited during the sampling period which may differ at other installations relates to the recycling of unreacted lime. A clarifier had been installed to remove lime and calcium chloride from the wastewater. These materials were then recycled to the reaction products, thus reducing the total flow and the pollutant loadings. This was considered as part of the process since required materials were recycled.

FIGURE 4-36

PROPYLENE OXIDE CHLOROHYDRIN PROCESS
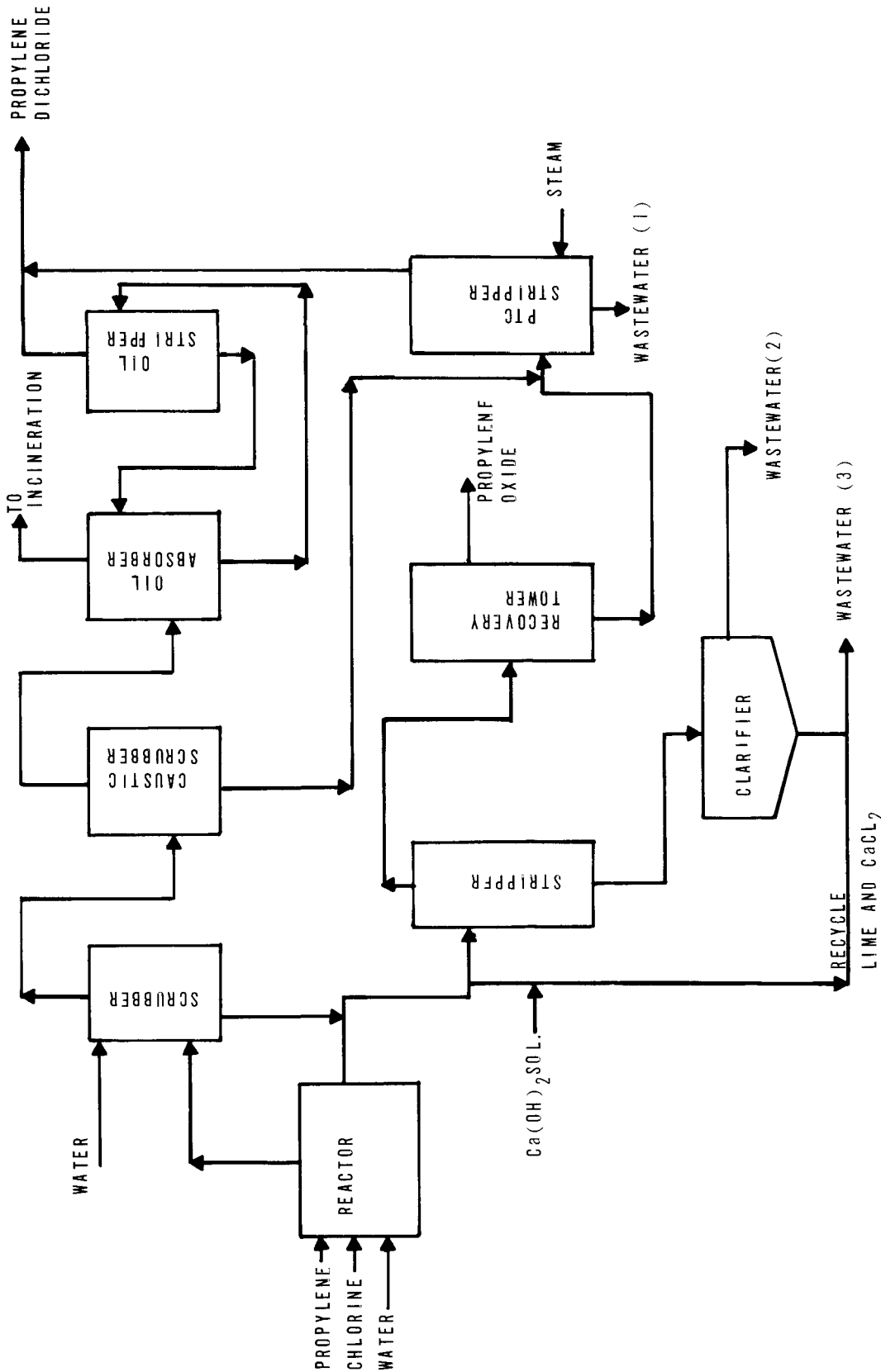
Product: Saccharin

Process: Synthesis from Phthalic Anhydride Derivatives

Process RWL Category: C

Saccharin is the imide of the mixed anhydride of o-carboxylbenzenesulfonic acid. It is a powerful sweetening agent, having a sweetness from 550 to 750 times cane sugar. Saccharin has no food value and is used only when it is desirable to reduce the consumption of carbohydrates.

A continuous process for the manufacture of saccharin from phthalic anhydride derivatives is shown in Figure 4-37.

The phthalic anhydride derivatives along with water and a 50 percent sodium hydroxide solution enter the reactor. A metal catalyst is used during the reaction. The fumes leaving this reactor are hydrochloric acid vapor, nitrogen, and sulfur dioxide. These fumes are scrubbed with water and sodium hydroxide. The resultant wastewater flows to a neutralization tank, where caustic is added to raise the pH to approximately 6.5

The product mixture from the first reactor is then chlorinated in the second reactor; and the fumes from this reaction include chlorine, hydrochloric acid, and water vapor. These fumes are also piped to the aforementioned caustic scrubber. A portion of the metal catalyst is removed from the second reactor for regeneration. The catalyst is treated with sodium hydroxide and then filtered. The filtrate goes to the neutralizer, while the catalyst is recycled to the first reactor.

The products from the second reactor are then reacted with NH_3 in the third reactor, with any unreacted ammonia vented to an absorber where the ammonia is absorbed with water and returned to the third reactor. An organic solvent is used to extract the product saccharin from the reaction mixture. The raffinate stream from the extraction operation is first neutralized and then distilled to recover the solvent. The extractive phase is steam stripped to recover solvent, which is condensed at a scrubber and recycled back to the third reactor. The aqueous solution leaving the stripper is precipitated by the addition of hydrochloric acid. The precipitate is further concentrated by filtration and crystallized under vacuum conditions and then dried to produce saccharin. The filtrate is neutralized by a caustic solution prior to its discharge to the sewer.

The major water pollution sources of the process are the wastewaters from caustic scrubber, catalyst filtration unit, solvent recovery still, product filtration unit, and barometric condenser. Process RWL's calculated from flow measurements and analyses of the wastewater streams are presented in the following tabulation. The analytical results also indicate that, in addition to the parameters shown in the tabulation, pollution parameters such as nitrogen, sulfate, chloride, and metals are at levels hazardous to the biological treatment process.

PROCESS FLOW
    liter/kkg   269,000
    gal/M lb   32,200

BOD$_5$ RWL
    mg/liter[1]   945
    kg/kkg[2]   254

COD RWL
    mg/liter[1]   3,270
    kg/kkg[2]   879

TOC RWL
    mg/liter[1]   1,430
    kg/kkg[2]   384

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

FIGURE 4-37

SACCHARIN — SYNTHESIS FROM PHTH LIC ANHYDRIDE DERIVATIVES
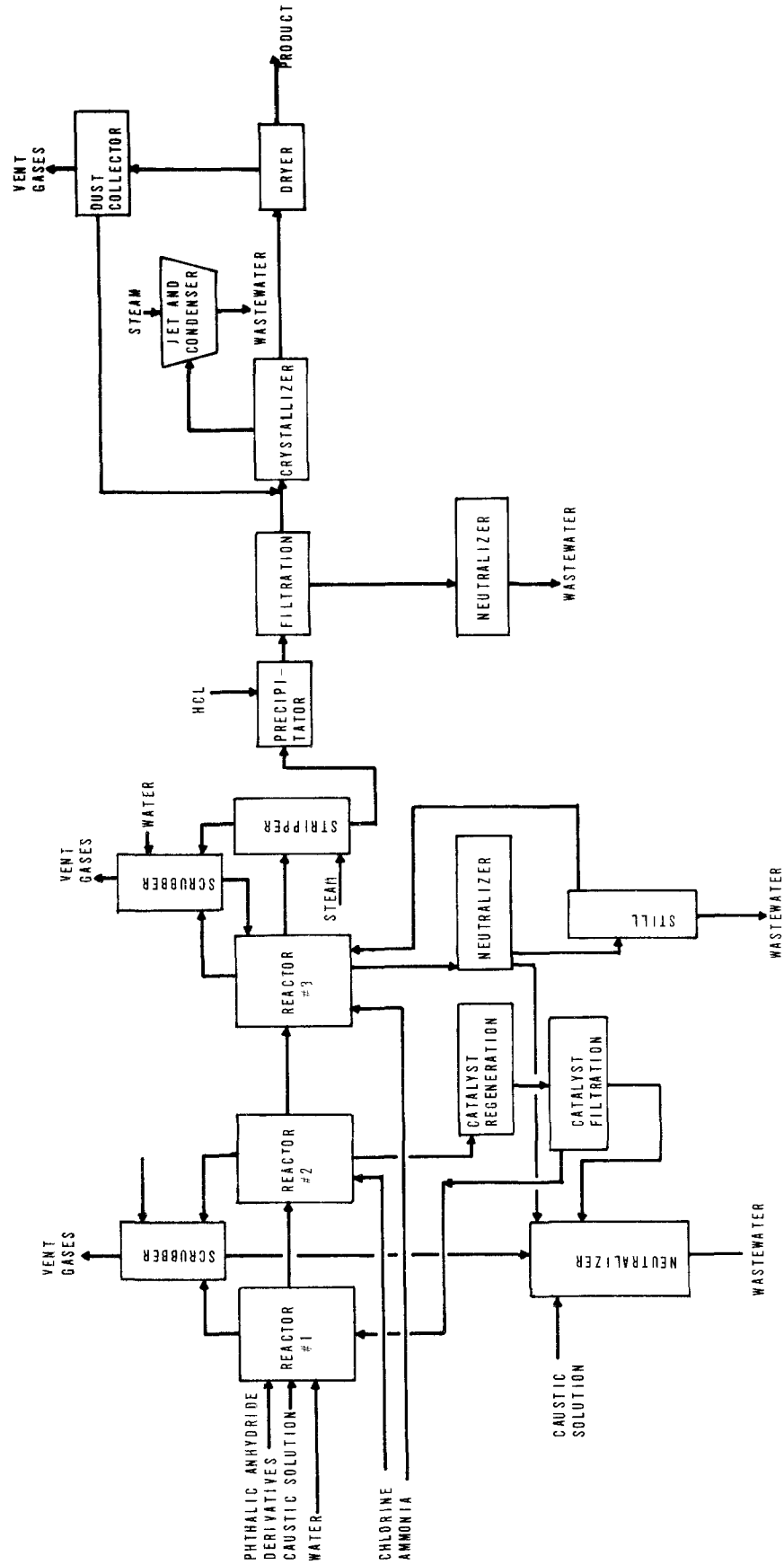
Product: Secondary Butyl Alcohol

Process: Sulfonation and Hydrolysis of Mixed Butylenes

Process RWL Category: C

Chemical Reactions;

$$CH_3CH = CHCH_3 \ + \ H_2SO_4 \ \longrightarrow \ CH_3CH_2CHCH_3$$

Butene-2	Sulfuric Acid	Sec-Butyl Sulfate

$$CH_3CH_2CHCH_3 \ + \ H_2O \ \longrightarrow \ CH_3CH_2CH(OH)CH_3 \ + \ H_2SO_4$$
$$HSO_4$$

Sec-Butyl Sulfate	Water	Sec-Butyl Alcohol	Sulfuric Acid
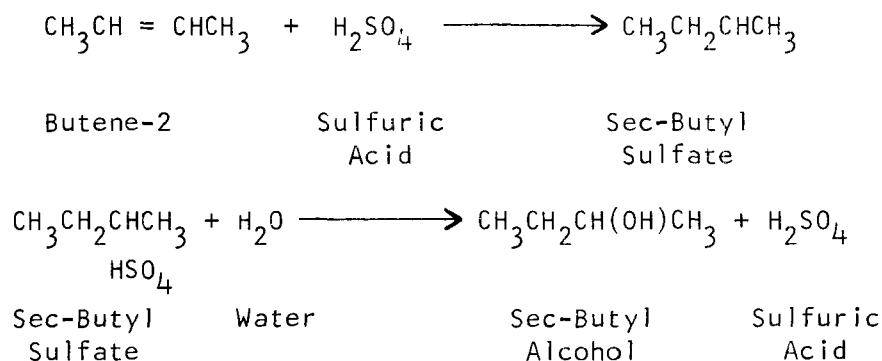
Secondary butyl alcohol is made from mixed butylenes. However, because of its alternate uses, isobutylene is normally extracted from the C_4 feedstock prior to the manufacture of secondary butyl alcohol. This is also done to prevent the formation of excessive quantities of tertiary butyl alcohol from isobutylene.

Normal butylenes are first absorbed by concentrated sulfuric acid (75 percent) to form isobutyl sulfate. This is subsequently hydrolyzed with water to secondary butyl alcohol and dilute sulfuric acid. A flow diagram for the process is shown in Figure 4-38. The extensive requirements for contact water usage make this continuous process typical of Category C. The reconcentration of sulfuric acid for recycle is considered an integral part of the process. It should also be noted that this process for secondary butyl alcohol is analogous to that used to produce isopropyl alcohol from propylene.

As shown in Figure 4-38, the normal C_4 hydrocarbon feed is passed into multiple countercurrent absorbers using 75 percent sulfuric acid. The absorption and the isobutyl-sulfate-forming reaction are strongly exothermic and require large volumes of non-contact cooling water.

The rich extract from the first-stage absorber is passed through an olefin soaker, which acts as an absorption stage for the recycle C_4 olefins that have not been converted to secondary butyl alcohol.

The mixture of sulfuric acid and isobutyl sulfate is combined with hydrolysis water and enters the hydrolysis generator, where crude secondary butyl alcohol and regenerated C_4 olefins go overhead and dilute acid is taken off as bottoms. The acid is sent to regeneration by vacuum evaporation, while the alcohol and olefins are separated in a combination

scrubber-stripper. The hydrolysis reaction is also highly exothermic and requires large quantities of non-contact cooling water.

Direct-contact steam is injected into the bottom of the stripping section of the scrubber-stripper to remove the more volatile olefins and alcohol from the excess hydrolysis water. This aqueous waste stream is withdrawn as bottoms and combined with other aqueous wastes as shown in Figure 4-38. Product secondary butyl alcohol as a 70 percent alcohol/30 percent water mixture is drawn off as a side stream and C_4 olefins are taken overhead. These olefins are scrubbed with water to recover any entrained alcohol in the olefin scrubber, with the aqueous bottoms returned to the scrubber-stripper. The regenerated C_4 olefins are then returned to the process via the olefin soaker described previously. The olefin recycle line is equipped with a knockout drum to remove water entrained from the olefin scrubber.

The unextracted C4 raffinate is taken from the fourth-stage absorber, combined with aqueous caustic, and sent to a scrubber-stripper. Caustic addition is necessary to neutralize excess acid from the absorbers.

Contact steam is injected into the lower section of the raffinate scrubber-stripper to drive saturated C_4 hydrocarbons overhead. The aqueous bottoms contains a di-isobutylene by-product, which is decanted from the water layer in a settler.

The saturated C_4 hydrocarbons are then sent to a rerun tower to remove additional dimer by-product. The rerun tower bottoms contains both water and dimer, which are separated by decantation in a second settler. The organic dimer layer from both settlers is combined, as are the aqueous layers.

The major wastewater streams associated with the flow of hydrocarbons within the process (shown by darkened lines in Figure 4-38) are:

1. Crude secondary butyl alcohol scrubber-stripper bottoms
2. Water layer from regenerated olefin knockout drum
3. Water layer from raffinate scrubber-stripper bottoms
4. Water layer from rerun tower bottoms
5. Water layer from rerun tower overhead

Except for the second stream, all of these wastewaters are combined and sent to a holding drum. This tank discharges to the wastewater treatment plant, with a small drawoff to provide a seal for the process flare stock.

The weak acid bottoms from the hydrolysis generated are reconcentrated by multi-stage vacuum evaporation. Normally, three evaporators in series are used to bring the acid concentration back to 75 percent strength. However, during the sampling program, only two were in service, with the final stage down for cleaning. This type of operation is possible by pulling a higher vacuum on the first two evaporators.

The overhead vapors from the first evaporator are drawn through a surface condenser which utilizes non-contact cooling water. The non-condensible vapors are entrained in two barometric condensers operating with steam jet vacuum pumps in series. The second- and third-stage evaporators are also equipped with this condenser-steam jet arrangement.

Apart from dehydrogenation to butadiene, secondary butyl alcohol production is the main end use for normal butylenes. Secondary butyl alcohol itself is used mainly as a solvent or to make secondary butyl acetate or methyl ethyl ketone. It should be noted that the alcohol product is obtained as an aqueous solution in this process. The product is really an azeotropic binary mixture drawn as a side stream from the crude secondary butyl alcohol scrubber-stripper. It contains approximately 70 wt percent (36 mole percent) alcohol and 30 wt percent (64 mole percent) water, and is withdrawn at a minimum boiling point of approximately 90°C. Dehydration of the alcohol is accomplished in subsequent processes, and this wastewater is not included in the wasteload computed for the alcohol process.

During the field data collection program, two plants utilizing the previously described process were sampled. The following brief tabulation summarizes the RWL for each plant:

	Plant 1	Plant 2
PROCESS FLOW		
liters/kkg	64,900	626
gal/M lb		
BOD$_5$ RWL		
mg/liter[1]	374	22,800
kg/kkg[2]	24.3	14.2
COD RWL		
mg/liter[1]	3,280	62,000
kg/kkg[2]	213	38.8
TOC RWL		
mg/liter[1]	665	38,300
kg/kkg[2]	43.2	23.9

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

FIGURE 4.38

SEC—BUTYL ALCOHOL—SULFONATION AND HYDROLYSIS OF MIXED BUTYLENES
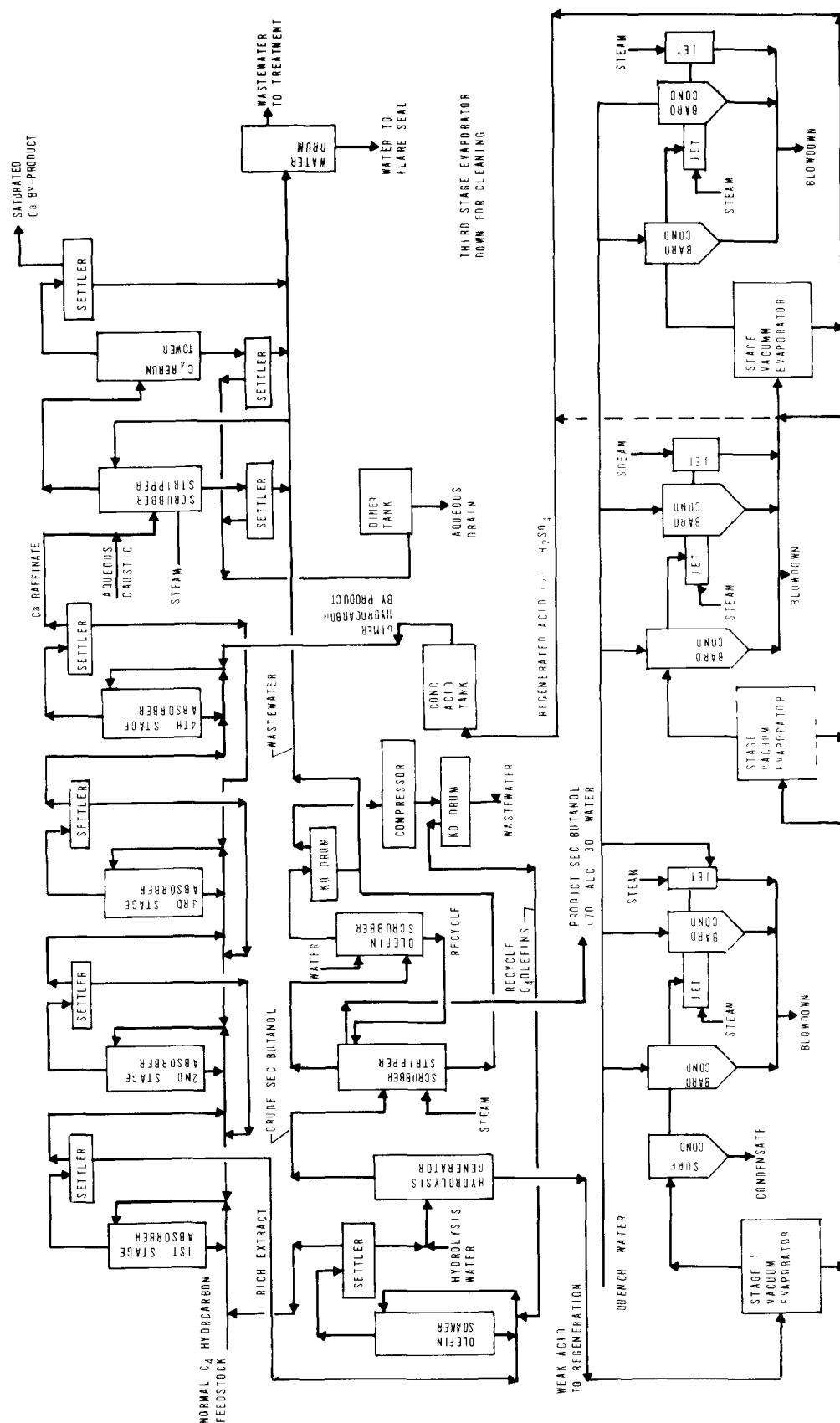
Product: Citric Acid

Process: Fermentation of Molasses

Process RWL Category: D

Reaction:

$$C_{12}H_{22}O_{11} \text{ or } C_6H_{12}O_6 \quad + \quad H_2O \longrightarrow C_6H_8O_7 \quad + \quad CO_2 \quad + \quad H_2O$$

sucrose   or dextrose   water $\longrightarrow$ citric   carbon   water
                                                          acid   dioxide
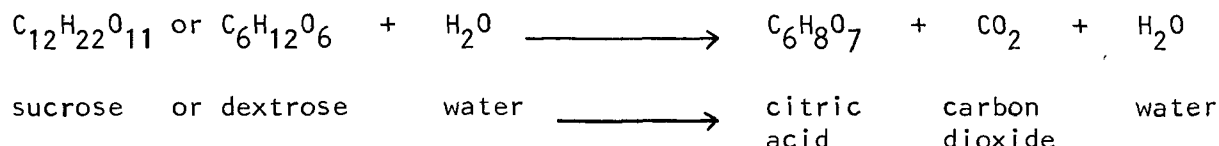
Typical Material Requirements

                                                1000 kg citric acid

Molasses   4000 kg
Nutrients   5 to 15 kg
Sulfuric Acid (95%)   7000 kg
Lime   5000 kg

Citric acid is one of the widely employed organic acids. Its major use is
as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs.
Another important use of citric acid is in the medicinal field, including
the manufacture of citrates and effervescent salts. There are a few in-
dustrial uses, including citric acid as a sequestering agent, and acetyl
tributyl citrate as a vinyl resin plasticizer.

Except for small amounts produced from citrus fruit wastes, citric acid is
manufactured by aerobic fermentation of crude sugar or molasses. The fer-
mentation changes sugar, a straight-chain compound, into a branched chain.

Production of citric acid may proceed in either of two methods: fermentation
in shallow pans, or fermentation in aerated tanks. Both processes may be used
simultaneously as shown in Figure 4-39. In the tray process, a sugar solution
is placed in the trays, and air is circulated for 9 to 12 days over hundreds
of shallow, pure-aluminum trays. The trays are placed in a closed cabinet
provided with facilities for sterilization, ventilation, and temperature control.
After the fermentation, the mycelium is removed from the broth by screens
or filters, and the spent mycelium is washed and disposed. Mycelium wash-
water containing citric acid is combined with acid separted in the filtration
step. The citric acid then passes through an oxalic acid recovery stage.
(Oxalic acid is available for recovery only from the tray process.) The
addition of calcium sulfate precipitates calcium oxalate. Addition of sul-
furic acid recrystallizes the calcium sulfate, and the solids are removed by
filtration. Hydrous oxalic acid is then crystallized under a vacuum pulled by
a barometric condenser.

After removal of the oxalic acid, the broth is combined with the liquor pro-
duced in the deep tanks. The essential steps of the deep tank process are
similar to the tray process, but a different type of mycelium culture is
grown and oxalic acid is not generated as a by-product. Molasses and water
are first introduced into the deep fermentation tanks. Air is introduced to
maintain aerobic conditions and to keep the tank contents well mixed. The
fermentation process is complete after approximately 4 to 9 days at 30 to
32° C. The tanks are then emptied and partially filled with boiling water
to sterilize them prior to the next batch. The crude liquor is filtered to
remove the mycelium, and the broth is combined with the broth produced in the
tray processes.

Citric acid is recovered from the broth by precipitation with calcium hydrox-
ide. The solution is then passed through a series of filters for removal of
the crystalized calcium citrate. Both filtrate and washwater used during the
filtration process are discharged as waste. The calcium citrate is then chem-
ically reacted with sulfuric acid to form calcium sulfate and citric acid.
The calcium sulfate is removed by filtration to purify the citric acid. Some
of the filter cake is recycled to the oxalic acid precipitation process, while
the remainder is wasted. The crude citric acid is then concentrated from
30 to 60 percent in a double-effect evaporator equipped with two-stage steam
jet to pull the vacuum. Barometric condensers are employed following the
steam jets. Since the citric does not vaporize, the only loss in the evaporator
is by entrainment; thus, entrainment separators are used prior to the con-
densers.

The crude crystals are redissolved in water during the finishing step. Treat-
ment processes, including granular activated carbon, are employed to remove
trace heavy metals and color. The white liquid is then crystallized
(utilizing a barometric condenser), dried, and packaged for sale.

To determine the raw waste load, samples of the various wastestreams were
obtained. These wastestreams included tray and deep tank wash waters, filtrate
from the calcium citrate filtration step, and barometric wastewaters from the
purification steps. A wastewater stream (barometric condenser wastewater) re-
sulting from the purification of oxalic acid was included in the raw waste load;
thus, production is expressed as the combined total of oxalic and citric acids
in their anhydrous forms. Process raw waste loads calculated from flow
measurements and the analyses of these streams are indicated in the following
tabulation:

	Oxalic plus Citric Acids (Anhydrous form)
Process Flow	
liter/kkg	477,000
gal/M lb.	57,200
BOD_5 RWL	
mg/liter[1]	690
kg/kkg[2]	328

Oxalic plus Citric Acids (Anhydrous form)

COD	RWL		
	mg/liter[1]		1,380
	kg/kkg[2]		657
TOD	RWL		
	mg/liter[1]		507
	kg/kkg[2]		242

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The foregoing data were considered as BPCTCA. The wastes from this plant are discharged to surface water without treatment.

The analytical results also indicate that, in addition to the parameters shown in the tabulation, pollution parameters such as sulfate, nitrogen, chloride, calcium, magnesium, and zinc are at levels hazardous to biological treatment processes. Proper pretreatment to reduce the aforementioned parameters is necessary before the wastestreams can be discharged into any biological treatment unit.

Non-contact wastewaters include cooling water and stream condensate. The total cooling water usage is approximately 107,000 gallons per 1000 lbs. of product. A large quantity of the cooling water is employed in tube-and-shell heat exchangers. The total steam usage (live plus reboiler) is estimated to be 15,500 lbs. per 1000 lbs. of product.

FIGURE 4-39
CITRIC ACID-OXALIC ACID-FERMENTATION OF MOLASSES

DRAFT
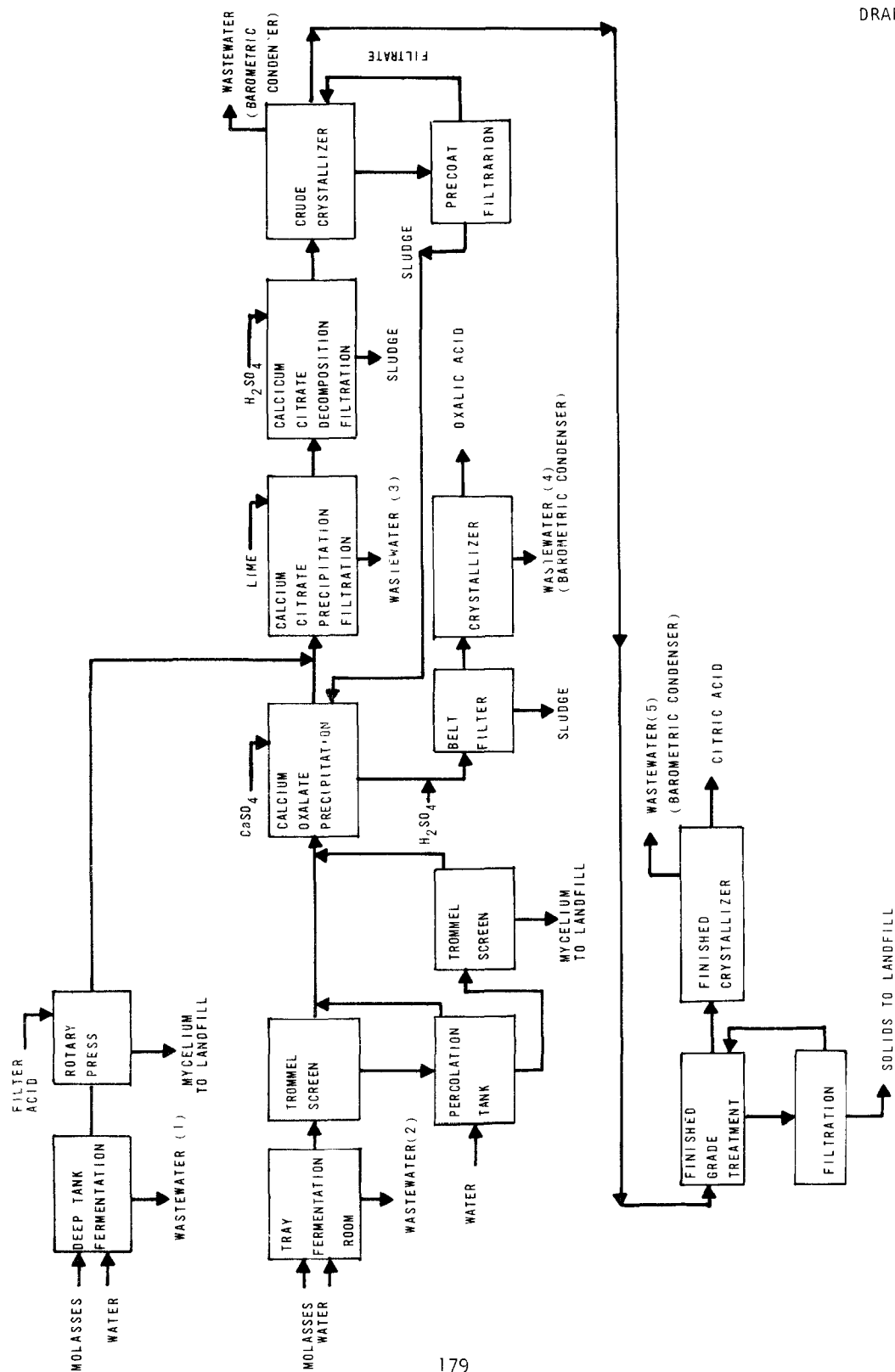
Products: Citronellol and Geraniol

Process: Distillation of Citronella Oil

Process RWL Category: D

Chemical Structure:

$$(CH_3)_2 \quad C = CH - (CH_2)_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2CH_2OH$$

citronellol

$$(CH_3)_2 - C = CH(CH_2)_2 - C = \underset{\underset{CH_3}{|}}{C}HCH_2OH$$
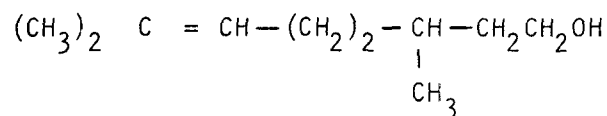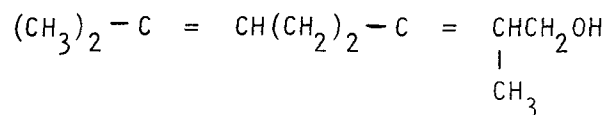
Geraniol

Citronellol and Geraniol are used as odorants in perfumery. Natural geraniol is produced by the distillation of citronella oil; citronellol is made by limited hydrogenation of geraniol. Figure 4-40 is a process flow diagram of geraniol and citronellol production. Citronella oil, the raw material, is vacuum distilled to separate citronellol. The remaining citronella oil components undergo a three-stage potassium hydroxide washing prior to entering into the vacuum steam distillation step, followed by a vacuum distillation. In this step, geraniol heavies and citronellol are recovered; the geraniol fraction is washed with a caustic solution and then water, and the geraniol terpene fraction undergoes boration and washing prior to being rerun through the vacuum distillation step.

As shown in Figure 4-40, the major wastestreams from the process are vacuum jet condensates and wastewater from product washes. The following tabulation summarizes the RWL calculated for the process:

Flow	10,000 liters/kkg
BOD_5	58.1 kg/kkg
COD	111 kg/kkg
TOC	37.7 kg/kkg

The foregoing values were considered as BPCTCA. These wastes are discharged to a sewage treatment plant.

FIGURE 4-40

CITRONELLOL AND GERANIOL-CITRONELLA OIL DISTILLATION
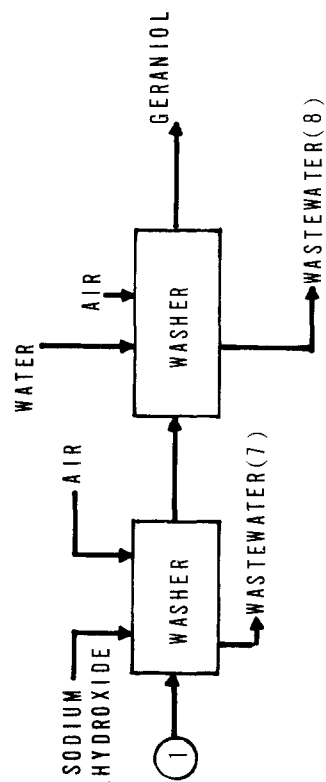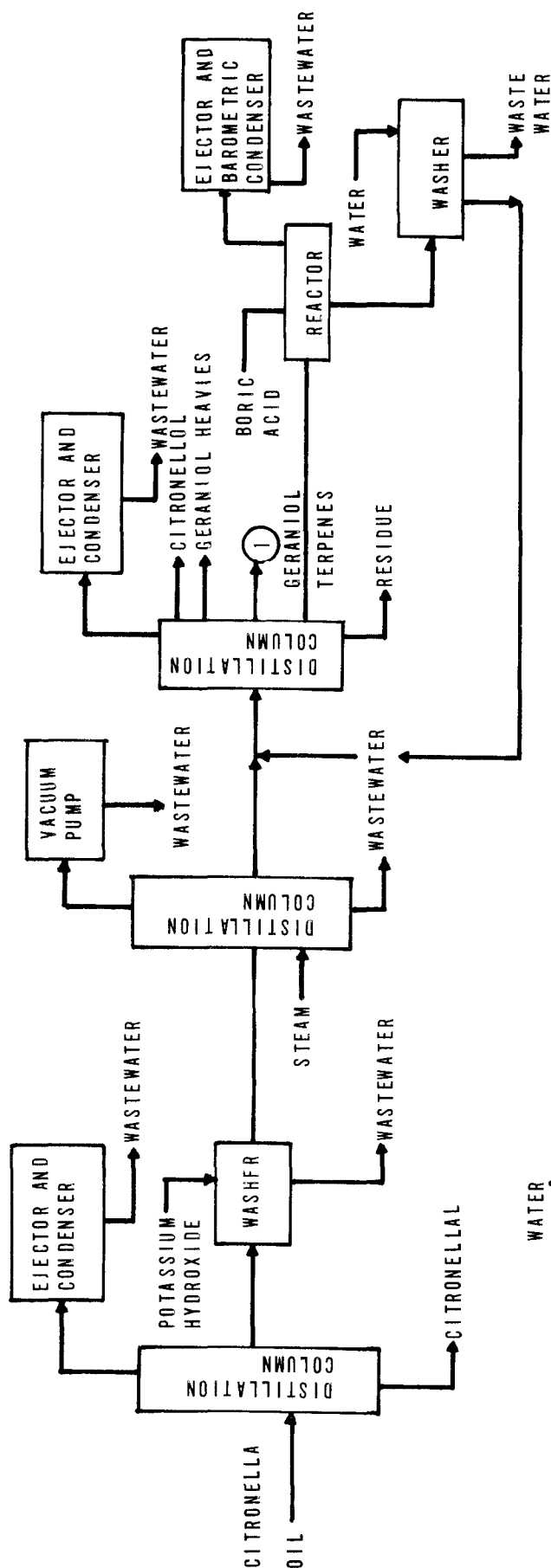
Product: Dyes and Dye Intermediates

Process: Batch Chemical Reactions

Process RWL Category: D

Dyes may be defined as intensely colored substances which, when applied to
a substrate, impart color to this substrate by a process which, at least
temporarily, destroys any crystal structure of the colored substances.
The dyes are retained in the substrate by adsorption, solution, and mechanical
retention, or by ionic or covalent chemical bonds. Pigments, on the other
hand, are usually applied in vehicles (although the substrates themselves
may serve as vehicles, e.g., in the mass coloration of polymeric materials),
and retain, to some degree, their crystal or particulate structure.

The color of a dye is due to electronic transitions between molecular
orbitals of the molecule, the probability of these transitions determining
the intensity of the color. The energy differences between the orbitals
determine whether the "color" falls in the visible range of the electro-
magnetic spectrum and, if it does, the precise shade or hue. Only organic
molecules of considerable complexity, containing extensive conjugated
systems and polar or semipolar substituents, are useful as dyes.

Much of the complexity of present-day dye technology arises from the great
diversity of materials to be dyed, such as foods, drugs, cosmetics, waxes,
greases, solvents, plastics, rubber, photographic film, leather, fur, paper,
and, primarily, textiles. In the textile field, the introduction of syn-
thetic fibers, such as cellulose acetate, nylon, polyester, acrylics, cellulose
triacetate, and polypropylene, as well as the more stringent fastness re-
quirements and the continuous-dyeing techniques, have presented the dye manu-
facturer and dyer with new problems. These problems cannot be separated
from one another; for example, the new polyester fibers are sometimes dyed
by a continuous heat-treatment process requiring new dyes with a new fastness
property, sublimation fastness; and a special physical form. Dispersed dyes,
for instance, are more hydrophobic than those used previously for cellulose
acetate; they must be nonvolatile (i.e. must not sublime off the fiber during
the heat treatment) and must have a physical form, either powder or paste, which
gives rapid and stable dispersions in the dye bath.

Dye intermediates are derived from a wide variety of aromatic organic com-
pounds, such as benzene, naphthline, anthracene, higher polycyclic derivatives,
and hetrocyclics. The United States Tariff Commission lists some 230 com-
pounds under the heading "cyclic intermediates", of which more than 210
are used in the dye industry. Many of the large-volume intermediates have
a principal use outside the dye industry. For example, about 60% of the
aniline produced is used in the rubber industry, and practically the entire
phenol and phthalic anhydride production is consumed by the plastics industry.
Originally, however, all three of these materials were dye intermediates ex-
clusively.

The dyes themselves are usually much more complicated than the inter-
mediates from which they are derived. Some dyes are mixtures, while
others (such as aniline and sulfur colors) are still of unknown structures.
Therefore, systematic chemical names are rarely used. Almost all dyes
also have a multiplicity of trade names in addition to their common
names. Despite the diversity of trade names, a certain amount of rationality
can be found in these names. Thus, most may be considered to be divided
into three parts, as in the example of Cibacete/Brilliant Blue/BG. The
first part usually gives the particular dyeing class,and, from this trade
name, we learn that the dye is a disperse dye intended for application
on acetate. Cibanone would be the same manufacture's designation for a
vat dye of high fastness. The second part of the name is obviously the
color, and the third part (BG in this case) refers to the shade. Often the
letters subdivide the numerous reds, oranges, blues, and greens into bluish
(B), greenish (G), yellowish (Y) (Y or G for the German "gelb"), and
reddish (R) shades. A number in front of these letters indicates their depth,
as in the name "Crystal Violet 6B". Other letters show other properties;
thus, K stands for cold dyeing (the German "kalt"), L for lightfastness,
N for new, CF for copper free (as in the case of goods to be vulcanized),
A for acetate left unstained, W for washfastness, and S for sublimation fast-
ness. Strength and physical form are designated at times by such terms as
Conc. (concentrated), Dbl. Pst. (double-strength paste), Pdr. (powder), etc.

Dyes have been classified by a wide variety of schemes. Classes based on
usuage and application are useful to the dyer and also to the dye manufacturer
who must supply the demands of the dye user. However, this type of classi-
fication results in groups containing a great diversity of chemical structures.
Table 4-5 is arranged according to a usage classification and indicates
briefly the major substrates, method of application, and representative
chemical types. A second type of classification based on chemical structure
has also been used in the industry. Table 4-6 is arranged according to
chemical classification, giving typical examples of the characteristic
structural units and the application dying classes which fall in each chemical
group. Tables 4-7 and 4-8 show U.S. production and sales of dyes of usage
and chemical classifications.

The primary source of organic raw materials for the dye industry has traditionally
been products recovered from the fractional distillation of coal tar; hence
the name "coal-tar dyes" is frequently used in place of the more correct
"synthetic dyes." Coal tar is a by-product of the gasification (or car-
bonization) of coal, the primary purpose of which is the production of coke
for steel manufacture and coal gas for industrial and domestic heating. The
coal tar is refined by distillation, and from over 300 products which have been
isolated and characterized the most important for the dye industry are benzene,
toluene, xylene, naphthalene, anthracene, acenaphthene, pyrene, pyridine,
carbazole, phenol, and cresols.

The petroleum industry is now supplying an increasing proportion of the primary
raw materials, notably benzene, toluene, xylene, and more recently, naphthalene.

In addition ot the organic materials above, a great variety of inorganic chemicals are used in the dye industry. These include sulfuric acid and oleum for sulfonation, nitric acid for nitration, chlorine and bromine for halogenation, caustic soda potash for fusion and neutralization, and sodium nitrate for diazotization, as well as hydrochloric acid, sodium carbonate, sodium sulfate, sodium sulfite, sodium sulfide, aluminum chloride, sodium dichromate, manganese dioxide, iron powder, and many others.

The great number of intermediates used to manufacture dyes and, where their use is confined to dyes, the comparatively small tonnages involved make manufacture by continuous process uneconomical. Anthraquinone, produced from anthracene by catalytic air oxidation, is one of the very few intermediates used solely by the dye industry that is made by a continuous process. Other large-volume intermediates (e.g., aniline, phthalic anhydride, and phenol) are also manufactured by continuous process but, as mentioned previously, the bulk of production is used in other industries.

The batch processes for the production of dyes and intermediates are carried out in reaction kettles made from cast iron, stainless steel, or steel, often lined with rubber, glass (enamel), brick, carbon blocks, or stainless steel. These kettles have capacities ranging from 500 to 10,000 gallons and are equipped with mechanical agitators, thermometers, condensers, etc, depending upon the nature of the operation. Products are transferred from one piece of equipment to another by gravity flow, pumping, or by blowing with air or inert gas. Plate and frame filter-presses, filter boxes, and centrifuges are used for the separation of solid products from liquids. Where possible, the intermediates are used for the subsequent manufacture of other intermediates or dyes without drying. Where drying is required, air or vacuum ovens (in which the product is spread on trays) and rotary dryers are used. Less frequently used are drum dryers (flakers) and spray dryers, although the latter are becoming increasingly important.

Most of the material handling is manual, and labor costs represent a significant part of the final dye price. Automatic process control, based on feedback from temperature, redox potential, and pH measurement, is finding increasing use in the industry.

The actual manufacture of intermediates and dyes proceeds by a series of chemical reaction steps. The major steps and associated chemical reactions typical of each are listed as follows:

Step 1 -   Addition of Functional Groups to Raw Materials

The attachment of one or more chemical groups onto the aromatic hydrocarbon raw material. Typical reactions include sulfonation, nitration, halogenation, and oxidations. Normally, the starting raw material (such as benzene, toluene anthracene, etc.) is reacted in the presence of aqueous sulfuric or nitric acid.

Step 2 -   Replacement of Functional Groups on
             Intermediates Produced in Step 1

             The replacement of the functional groups intro-
             duced in Step 1 by other groups of higher reactivity
             which cannot be introduced directly. The starting
             materials for this step may be the intermediates
             produced in Step 1 or intermediates purchased from
             another manufacture. Typical reactions include:
             caustic fusion, to replace a sulfonic acid group
             by a hydroxyl group; replacement of a sulfonic
             acid group by an amino group by reaction with
             ammonia and replacement of halogen atoms by
             hydroxyl or amino groups.

Step 3 -   Further Modification of Functional Groups
             On Intermediates from Step 2

             This step involves the further modification or
             development of functional groups on the inter-
             mediates produced in Step 2 (or purchased inter-
             mediates). There can be few generalizations about
             these reactions, as each particular case depends
             on the specified end product required. Examples
             of these reactions include alkylation of functional
             groups by reactions of the intermediate with an
             alcohol, acylation with organic acid chlorides
             or anhydrides, and other rearrangements.

Step 4 -   Combination of Two or More Intermediates to
             Form a Dye

             In this step, two or more intermediates are com-
             bined to form a product having a skeletal, if not
             complete, dye structure. Typical reactions include
             diazotization and coupling, condensations, and di-
             mirization. It should be noted that many of these
             products may themselves also be intermediates in the
             synthesis of dyes of greater complexity.

When defining the production of dyes and intermediates at a specific plant,
it must be understood that some manufactures purchase the intermediates
associated with Steps 1, 2, and 3, so that Step 4 may be the only chemical
reaction processing done at the plant. Other manufacturers carry out Steps
1,2,3, and 4 in the synthesis of a dye product. Although the final quantities
of dye product sold at each plant might be the same, the actual production
activity (as measured by intermediates production) would be drastically
different.

It should also be noted that production schedules vary drastically in dye plants.

Both the types and specific quantities of dyes and intermediates which are manufactured change on a week-to-week basis.

Because of the nature of the batch operations, it was not possible to isolate dye products according to chemical or usage classification for the development of production based raw waste load data. Instead, the entire plant was sampled for periods up to one month. Wastewater flows and analyses were developed on a 24-hour composite basis. Production for the corresponding period was defined to include all dyes and intermediates which were separated within the establishment during the sampling period. A commodity was considered separated when it was isolated from the reaction mixture and/or when it was weighed, analyzed, or otherwise measured.

It should be noted that in some cases it was not possible to differentiate between production as 100% active ingredients and as standardized material. The difference between these two relates to the quantity of inert diluent which is added to some dyes prior to shipment to the user. The raw waste load data to be presented subsequently are based primarily on standardized material. The ratio of standardized material to 100% active ingredients can be as high as 10 to 1. This means that if the raw waste loads were based on 100% active ingredients, the data reported should be increased by a factor of ten (depending on the specific plant.)

The following tabulation summarizes the raw waste load data obtained from six plants sampled during both phases of this study.

Process RWL for Dyes and Intermediates

Plant	Flow	BOD5	COD	TOC
	(lit./kkg)	(kg/kkg)	(kg/kkg)	(kg/kkg)
1. (10% occurrence)		5	50	40
(50% occurrence)	795,000	79	1,850	790
(90% occurrence)		156	3,700	1,580
2. (10% occurrence)		17	104	25.0
(50% occurrence)	205,000	62	212	57.0
(90% occurrence)		106	318	89.5
3. (10% occurrence)		278	1,060	350
(50% occurrence)	185,000	602	1,595	502
(90% occurrence)		930	2,155	656
4. (sampled 3 days)	32,800	-	195	205
	32,800	1.18	19.5	5.24
	32,800	-	189	49.2

Process RWL for Dyes and Intermediates (continued)

Plant	Flow (lit./kkg)	BOD_5 (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
5. (sampled 2 days)	114,000	220	1,075	450
	114,000	126	652	269
6. (sampled 1 day)	175,000	59	175	60
Mean (based on 90% Plants 1,2,3)	395,000	397	2,060	775

Only Plants 1, 2, and 3 were used to compute the mean RWL shown, as each plant was sampled for 1 month (30 days.) In such case, the 90% occurrence value was used. This is a value greater than 27 of the 30 RWL values computed during the sampling period for each plant. The use of this value is justified because of the extremely high variability shown by the dye plants.

Table 4-5

Usage Classification of Dyes

Class[1]	Major Substrates[2]	Method of Application	Major Chemical Types	Remarks
Acid	Wool,[2] silk, nylon, and polyacrylic	Applied usually from neutral to acid dyebaths	Azo, including premetallized dyes, anthraquinone, triphenyl-methane, azine, xanthene, nitro, and nitroso	The very important premetallized dyes are members of this class
Azoic dyes and components (ingrain)	Cotton,[2,3] (also silk, wool, and fur) and blacks on acetate and polyester	Fiber impregnated with coupling component and treated with solution of stabilized diazonium salt	Azo	
Basic	Cotton,[2,3] leather, paper, wool, silk, polyacrylics, and other synthetics	Dyed on tannin mordanted cotton, directly on other materials	Triarylmethane, azo, azine, xanthene, thiazine, poly-methine, oxazine, and acridine	"Cationic Dyes"
Direct	Cotton,[2,3] paper, and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Disazo, trisazo, and polyazo as well as a small number of phthalocyanine, stilbene, oxazine, and thiazole	Second most important class of dyes
Disperse	Cellulose acetate, triacetate, nylon, polyacrylic, and polyester	Fine aqueous dispersions often applied by high temperature "pressure" or lower temperature "carrier" dyeings. On cloth padded dye may be baked on or "thermofixed"	Simple azo, anthraquinone, and nitroarylamine	New fast-growing field of dyes important for synthetic fibers
Reactive	Cotton,[2,3] wool, silk, and nylon	Fixation on the fiber under alkaline conditions	Azo, anthraquinone, phthalo-cyanine, and stilbene	New class first introduced in 1956 bonds chemically to the fiber
Mordant	Wool,[2] silk, nylon, and anodized aluminum	Applied in conjunction with chelating salts of Al, Cr, and Fe	Anthraquinone, azo, oxazine, triphenylmethane, nitroso, and xanthene	
Solvent	Organic solvents examples are inks, gasoline, lacquers, wood stain, cosmetics, plastics, and wax	Dissolution in the appropriate solvent or medium	Azo, triphenylmethane, anthraquinones, and copper phthalocyanine derivatives	
Sulfur	Cotton	Dissolved in water (with the addition of sodium sulfide for the insoluble types) exhausted with Glauber's salts	Sulfur dyes	
Vat	Cotton[2,3] and wool	By vatting (dye solubilized by reduction with sodium hydrosulfite), exhaustion on the fiber and reoxidation	Anthraquinone, polycyclic quinones, and indigo	
Optical Brighteners[4]	All Fibers, soaps, detergents, oils, paints, and plastics	From aqueous solution or dispersion or by incorporation in the mass	Stilbene, dibenzothio-phenes, azoles, coumarin, and pyrazine	

[1] For Food, Drug, and Cosmetic dyes see Colors for foods, drugs, and cosmetics
[2] Indicates major use.
[3] Includes all other cellulosic fibers and viscose.
[4] See Brighteners, optical.

Table 4-6

Chemical Classification of Dyes

Class	Dyeing Classes	Remarks
Nitroso	Acid, disperse, mordant	Dyed as a metal chelate
Nitro	Acid, disperse, mordant	
Azo monoazo disazo trisazo polyzao	Acid, direct, mordant, disperse, basic, reactive	A large and varied class produced almost without exception by the coupling of a diazotized aromatic amine to a phenol, amine, pyrazolone, or other coupling component
Azoic	Azoic	Insoluble dye formed directly on fiber from soluble components by diazotization and coupling
Stilbene	Direct, reactive	Class also includes mixtures of indeterminate constitution made for example by condensation of nitro stilbene compounds and aromatic amines
Diphenylmethane (ketone imine)		
Triarylmethane	Basic, acid, mordant	Brilliantly colored dyes of only moderate lightfastness
Xanthene	Basic acid, mordant	Pure, bright hues
Acridine	Basic (sulfur)	Basic dyes used chiefly on leather, also for antiseptics
Quinoline	Acid, basic, direct, disperse	Used for cotton, paper, and more recently in disperse dyeing
Methine and Polymethine		Important in photography
Thiazole	Direct, basic, reactive (sulfur)	
Indamine and indophenol		Intermediates for photographic and sulfur dyes
Azine	Acid, basic, oxidation (sulfur)	The first commercially important synthetic dye, Perkin's Mauve belongs to this class
Oxazine	Basic, mordant direct (sulfur)	
Thiazine	Basic, mordant vat (sulfur)	
Sulfur	Sulfur, vat	Obtained by heating a variety of organic compounds with sulfur or polysulfides to give disulfide or sulfoxide bridges
Aminoketone and hydroxyketone		The natural dye logwood is included in this class
Anthraquinone	Acid, mordant, vat, dispersed, basic, direct, reactive	Condensed polycyclic quinonoid dyes of great importance
Indigoid	Vat, acid	Derivatives of indigo and thioindigo
Phthalocyanine	Acid, direct, azoic, vat, sulfur, basic reactive	Only blue or green dyes and pigments (of high lightfastness) are found in this class
Oxidation bases	Incompletely characterized oxidation products from amines, diamines, and aminophenols	Aniline Black is a member of this class

Table 4-7

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

Class of Application	Production in 1,000 lbs.	Sales		Unit Value $/lb.
		Quantity in 1,000 lbs.	Value in $1,000's	
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 4-8

U. S. Production and Sales of Dyes
by Chemical Classification 1964

		Sales		
Chemical Class	Production in 1,000 lbs.	Quantity in 1,000 lbs.	Value in $1,000's	Unit Value $/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.

Products: Fatty Acids and Primary Derivatives

Process RWL Category: D

Fatty acids are organic acids characterized by a straight chain carbon structure terminating in a single carboxyl group. The carbon structure may contain only saturated carbon atoms or may contain one or more double bonds.

In general, the saturated acids having 12 to 18 carbon atoms are of major commercial concern. Their uses tend to reflect their stability or lack of easy reactivity at any point along the chain except at the carboxyl position. Saturated acids, including those saturated by hydrogenation, comprise about one-third of all fatty acids commercially produced.

Acids of reduced hydrogen content, having one or more double bonds between carbon atoms along the chain, constitute the other main fatty acid family of high commercial importance. The unsaturated acids of the ethylenic family are made up of a number of separate series of the following compositions:

$$C_nH_{2n-2}O_2 \quad \text{(monoethenoic)}$$

$$C_nH_{2n-4}O_2 \quad \text{(diethenoic)}$$

$$C_nH_{2n-6}O_2 \quad \text{(triethenoic)}$$
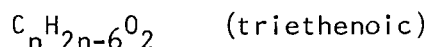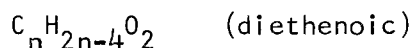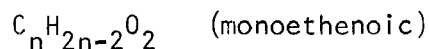
The chemical reactivity and utility of unsaturated fatty acids in various polymeric or "drying" reactions is determined in part by the number of double bonds along the carbon chain. These double bonds also introduce different properties arising from the location along the chain, i.e., conjugated and nonconjugated fatty acids. A different structure also results from a reversed positioning of those parts of the molecule on either side of the double bond, known as cis and trans isomerism.

To avoid confusion of terms, it is necessary to distinguish between fatty acids as defined by the organic chemist and fatty acids as commercially produced and sold. The term "stearic acid" is an example of this confusion.

Here the commercial product name has priority, going back to the splitting of tallow for the manufacture of hard, high-melting candles, before individual acids of definite composition have been isolated or defined.

Historically, commercial stearic acid has been a crystalline combination of the chemist's palmitic and stearic acids in a 55 to 45% ratio, respectively, with some small percentage of unsaturated acids. This ratio is that which naturally occurred in the mixed acid derived from splitting tallow, after most of the liquid acids were removed by the original pressing method. The liquid acids so removed are known as oleic acid, or red oil.

Other commercial acids have been identified by origin - for instance, coconut fatty acid or cottonseed fatty acid - in terms reflecting the characteristic ratio in which the component acids exist when released from the glycerides of these oils. Fractionation to separate or to enrich the wanted acids, however, has made identification by origin obsolete as a means of characterizing many of today's acids. Blends and "cuts" are offered to meet particular market demands, such as drying characteristics in paint firms. Composition expressed in terms of component acids as the chemist defines them is now finding its way more and more into product descriptions and specifications.

Table 4-9 lists 15 of the most important commercial fatty acids, along with their composition in terms of specific constituent acids.

In addition to the saturated and unsaturated acids, primary derivitives based upon acids modified by amination, esterification, ozonation, and polymirization are considered within the context of this study. Also, the processing assiciated with the recovery and purification of by-product glycerine is considered. The relation between glycerine and fatty acid production will become apparent during subsequent discussions. However, at this point it should be clearly noted and understood that the production of other products (such as soaps) from fatty acids is not considered within the context of this study.

Raw materials for the production of fatty acids fall into three groups:

    1. Tall oil derived from Kraft papermaking.
    2. Animal tallow and grease.
    3. Vegetable oils and soap stocks.

As a raw material for fatty acid production, crude tall oil ranks first in volume. Crude tall oil is a mixture of rosin acids and free fatty acids (in addition to a large percentage of water and impurities) and is a by-product of kraft papermaking. Most of the crude tall oil is fractionated, and the separated rosin acids and tall oil fatty acids are sold directly to consumers after purification. The fatty acids derived directly from tall oil can be used in the manufacture of primary derivitives such as dimers, polyamides, nitriles, primary amines, di-fatty tertiary amines, and fatty quatenary ammonium chloride. The major constituents of tall oil fatty acid are oleic acid and linolenic

TABLE 4-9

Some Examples of Commercial Fatty Acids Showing Typical Percentage of Constituent Acids

Typical commercial fatty acids	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic	Arachidic	Behenic	Oleic	Linoleic	Linolenic
C-atoms	6	8	10	12	14	16	18	20	22	18	18	18
Double bonds	0	0	0	0	0	0	0	0	0	1	2	3
Stearic acid (T.P. type)					1	50	48			6		
Stearic acid (S.P. type)						51	43			5		
High palmitic					2	75	20			4		
Solid fatty acid (Hydrogenated tallow type)					1	35	59					
Solid fatty acid (Hydrogenated vegetable type)						29	68			2		
Solid fatty acid (Hydrogenated fish type)					10	35	28	15	10	2		
High lauric acid (Distilled coconut)		1	7	49	17	9	2			6	2	
Oleic acid (red oil) (Distilled)					2	7	2			79	10	
Oleic acid (Multiple distilled)					3	5	1			85	6	
Animal fatty acid (Distilled)					4	25	15			50	4	2
Vegetable fatty acid (Distilled cottonseed)					1	24	2			33	39	1
Vegetable fatty acid (Distilled soybean)						11	4			29	51	5
Vegetable fatty acid (Fractionated soybean)										39	60	1
Tall oil fatty acid						2				51	47	
Distilled linseed fatty acid						6	3			19	24	47

acid which contain two and three double bonds respectively (see Table 4-9).
It should be noted that the production of tall oil fatty acid involves
only distillation of free acids and is simpler than the processes used to
manufacture fatty acids from animal and vegetable sources.

There are four main types of animal fats: edible tallow, inedible tallow,
lard and inedible grease. Inedible tallow and grease are important raw
materials as a primary source of stearic and oleic acids. These materials
are supplied to fatty acid manufacturers from meat packing plants and
rendering plants. It should be noted that fatty acid production is a
relatively small part of the tallow market, with the major end use of
tallow being in the production of soap.

Coconut oil (obtained by crushing coconuts) is an important vegetable
raw material for fatty acid and fatty ester production, because of its
high C_8, C_{10}, and C_{12} content. Although soybean oil and cottonseed
oil are produced in huge quantities, they are not often used for fatty
acid manufacture because of their high costs. However, by-products
from the refining of these oils for other end uses are used in the manu-
facture of fatty acids. These by-products are called "soap stocks" or
"foots" and vary in composition, depending on the refining process by
which they are produced.

It should be noted that fatty acids are present in animal and vegetable
sources as glycerides. Tall oil, which is not a glyceride, is the only
raw material which contains high concentrations of free fatty acids.

The three-pronged glycerol linkage, typical of all fats, must be severed
in the production of all fatty acids derived from animal and vegetable
sources. The chemical reaction for this cleavage involves the following
hydrolysis:

$$
\begin{array}{c}
\overset{O}{\overset{\|}{R-C-O-CH_2}} \\
| \\
\overset{O}{\overset{\|}{R-C-O-CH}} \\
| \\
\overset{O}{\overset{\|}{R_2-C-O-CH_2}}
\end{array}
\; +3H_2O \longrightarrow
\begin{array}{c}
CH_2-OH \\
| \\
CH -- OH \\
| \\
CH_2--OH
\end{array}
\; + \;
\begin{array}{c}
R--COOH \\
R_1-COOH \\
R_2-COOH
\end{array}
$$

Fat (triglyceride)   Glycerine   Fatty acids
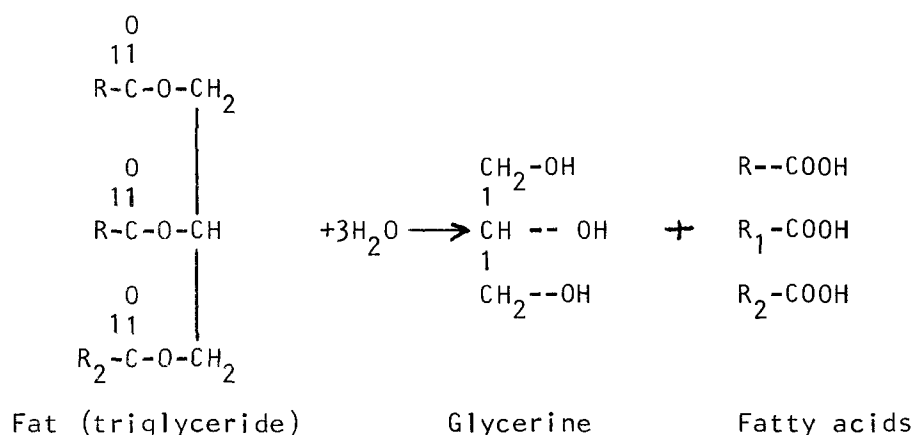
The products of the reaction are crude glycerine and fatty acids.

Depending upon the nature of the feedstock and the desired end-product
fatty acids, different combinations of the following processing steps may
be found in a fatty acid plant:

1. Pretreatment For Purification Of Feedstock
2. Saponification/Acidulation Of Feed Or Products
3. Hydrogenation Of Feed Or Product Acids
4. Hydrolysis Of Feed (Fat Splitting)
5. Distillation Of Product Acids
6. Distillation For Glycerine Recovery
7. Separation Of Saturated And Unsaturated Acids

The following paragraphs briefly describe each of these processing steps.
A generalized process flow diagram showing their interrelation is pre-
sented in Figure 4-41.

Pretreatment

Many of the impurities present in the feedstock will decompose, volatilize,
or contaminate the product acids and must be removed. Water-soluble salts
will deposit on heating surfaces. Mineral acid will attack the fatty
acid upon heating and attack the equipment as well. Water-washing and
drying of feedstock containing these impurities are essential.

Feed stock containing gums, proteinaceous material, calcium, and iron
soaps should also be acid-washed. Acid-washing is generally performed
in lead-or monel-lined tanks. A common method is to treat a charge of
melted fat at about 140°F with 2 to 4% sulfuric acid in a fairly con-
centrated (30 to 50%) solution, with good agitation for about 1 hr., after
which the charge is heated to 200°F with open steam. After settling,
the acid water is drawn off, and the charge is washed with water to remove
the mineral acid. Acid washing breaks up calcium and iron soaps that act
as catalysts, forming ketones, or that remain as soap in still bottoms.
Sulfuric acid removes proteins and other organic impurities.

Acid-washing also removes impurities that hinder hydrolysis. Bleaching
with acid clays is effective in removing oxidized acids and impurities
that hinder splitting and/or hydrogenation.

Saponification/Acidulation

In special cases where the feedstock is by-product "soap stock" or "foots"
produced in the caustic refining of vegetable oils, the saponification of
the feed followed by acidulation is a convenient means of manufacturing
fatty acids. It has an advantage in the handling of raw refinery foots
because very little additional caustic soda is required to complete the
saponification before the acid treatment. Completely saponified foots

upon acidulation yield raw material satisfactory for distillation. Although more expensive than the other methods using water, it gives practically 100% conversion and avoids the use of high temperatures. The splitting of fatty acids from waxes and sperm oil is done by complete saponification, using anhydrous alkali, followed by steam distillation to remove the high molecular weight alcohols and by subsequent splitting of the soap with sulfuric acid.

Hydrogenation

Hydrogenation is the process of adding hydrogen to materials that are deficient in hydrogen, e.g., oleic acid requiring one molecule of hydrogen to form the C_{18} saturated acid. Either the glyceride or the fatty acid can be hydrogenated. The process is essentially the same, with the exception that the acid must be processed in a corrosion-resistant apparatus, usually stainless steel.

Refined oils and fats and fatty acids that have been properly distilled are hydrogenated with little difficulty; but impure materials or mixtures of fatty acids and neutral oil, such as acidulated foots, are hydrogenated only after they have been specially treated, and then usually with difficulty.

Hydrogen addition to the unsaturated groups occurs only when it is activated by means of a catalyst. Reduced nickel, the usual hydrogenation catalyst, is made by reducing nickel salts, i.e., formate, carbonates, or the aluminum nickel alloy.

Hydrogenation is done in both batch and continuous processes. The batch process, which is older and not as generally used today, uses a vessel that is equipped with a top-entering agitator and a means for heating and cooling and that is built to operate at pressures of from 25 to 250 psi (in some instances up to 500 psi and higher). The nickel catalyst is added to the pre-dried charge in amounts varying from about 0.05 to 0.5%. The vessel is purged several times with hydrogen and then brought up to reaction temperature with steam. Once reaction starts, however, it is exothermic, and cooling is required to prevent overheating of the catalyst and the stock. The exothermic heat is significant, and the absorption of 1 lb-mole of hydrogen releases about 40,000 Btu, requiring generous amounts of cooling surface as well as good agitation. Good agitation is also required to keep replenishing the reaction with hydrogen gas. Reactors in use today vary in size from those holding a few pounds to large ones holding 50,000 lbs.

Continuous methods for the hydrogenation of all classes of chemicals have been developed in recent years, especially in connection with petrochemicals and for petroleum processing in general. The fat and fatty acid industries have been much slower in developing and using continuous

methods, owing perhaps to the wide variety of products produced, the relatively smaller volumes, and the need for modifying the product by partial and selective hydrogen addition.

Hydrolysis

Hydrolysis or splitting is the process of reacting the fat with water to form glycerine and fatty acid. A series of three hydrolysis steps is required to obtain free acid and free glycerine, and it is believed that they are homogeneous reactions taking place mainly in the fat phase, as the solubility of water in a fat is greater than the solubility of fat in water.

It is necessary only to mix fat with water to cause some hydrolysis, but the reaction is very slow. When sulfuric acid is added to a fat, the sulfonated products formed increase the solubility of water in fat, and hydrolysis takes place at a faster rate. Solubility is further increased by the use of an alkaline catalyst, i.e., zinc oxide, magnesium hydroxide, or calcium oxide.

A major development in hydrolysis techniques was made by Twitchell, who developed the sulfonic acid catalyst bearing his name. As the solubility of water in fat increases very rapidly at high temperatures, high-pressure autoclaves, both of the batch and continuous type have been developed.

Commercial fat splitting is carried out by several processes, each of which has advantages and disadvantages; the selection depends upon the type of raw material, the size of the operation, and the number of kinds of raw materials handled.

A. Twitchell Process

The Twitchell process, developed in 1890, is still used to some extent in the United States. It is carried out in a lead- or Monel-lined tank at atmospheric pressure; the charge consists of the fat mixed with about 50 wt.% of water, 1% of the sulfonic acid catalyst, and 0.5% sulfuric acid. The misture is boiled with open steam for 16 to 24 hr, allowed to settle, and the sweet water is drawn off and replaced with fresh water. The boiling is continued until a split of about 95% is reached. The overall split depends upon the glycerol concentration of the sweet water.

By countercurrent use of water, it is possible to obtain high splits and high concentrations of sweet water, usually 10 to 15%. The advantages of the Twitchell operation are in the relatively simple equipment and the use of low

temperatures. Low-temperature operation is highly desirable
for splitting stocks containing multiple unsaturation. Dis-
advantages are the length of time required, high steam con-
sumption, and poisoning of the catalyst, which necessitate
the pretreatment of most stocks, especially the lower-
grade variety.

B. Batch Autoclave

Batch autoclaving is a very old method, which, as originally
developed, used a closed cylindrical pressure vessel with
agitation provided by open-steam injection with a continuous
vent. The usual temperatures are about 365°F, equal to
about 150 psi. About 2% lime, zinc, oxide, and so forth,
are used; the amount of water is about 50 wt.% of fat. The
degree of split reaches an equilibrium at about 90%; to
obtain a higher split, the glycerine water must be replaced
with fresh water.

This catalytic autoclave process is suitable for all types
of fats and has the advantage over the Twitchell process
of a shorter reaction period and the production of lighter
colored fatty acid because of the absence of air. A more
recent development in autoclave splitting is the use of
higher temperatures and higher pressures requiring no
catalyst. This process is usually carried out using
mechanical agitation, with the temperature held at about
450°F under a pressure of 450 psi. Splitting is rapid,
and there is no catalyst to remove. Its disadvantage
is the effect of high temperature on stocks having a
high degree of unsaturation.

C. Continuous Countercurrent Splitting

Over the past 30 years, several companies have designed
and built successful continuous hydrolyzers, which have
replaced the older methods. Fat enters near the base of
the hydrolyzer and passes upward through a sparger pipe
near the top. Steam from the high-pressure steam boiler,
at 750 psi, is injected at two locations, the top ad-
dition into a water-distributing tray and the lower
addition through a sparger pipe near the fat-water inter-
face.

The fat rises slowly through the column in a continuous
phase while the water drips through it, constantly re-
placing the glycerine-laden water that is in the solution
in the fat. At the bottom of the tower, the glycerine
water collects and is removed continuously to maintain
a constant interface level near the base of the tower.

The fatty acid leaves the top of the tower through a
pressure control valve set to maintain about 720 psi,
sufficiently high to prevent vaporization of water at
the required operating temperature, usually about 250
to 260°C.

The fat must be under pressure for about 2 hr to reach
a split of 96 to 99%, although the time required may
vary, depending upon the type of fat and quantity of
water used. It is usual practice to remove sweet
water with a concentration between 12 to 20% glycerine.

Continuous splitting has the advantage of yielding
high splits and more concentrated glycerine solutions
than any other process. It has a high capacity and
short reaction time and requires less room, less
process inventory, and less labor. It does, however,
restrict flexibility in changing stocks. The high
temperatures, as mentioned above, have the advantage
of speeding up the hydrolysis reaction; however, it
has a real disadvantage when handling highly un-
saturated fat, such as fish oil, because these oils
tend to polymerize.

Recovery and Purification of Glycerine

The dilute (10-20 wt.%) glycerine solution ("sweet water) may be concen-
trated by stripping water overhead in an evaporator or distillation column.
In most operations, non-contact steam is used to drive off the water to an
approximate 80% glycerine concentration. The non-contact steam may be
condensed and used in the hydrolysis reactor. The separated water vapor
and some glycerine are normally condensed in a barometric condenser and
discharged. Additional treatment steps for purification of glycerine
water may include filtration, ion exchange, and activated carbon adsorption

Distillation

Distillation as a means of purifying fatty acid has been in use for the
better part of a century. It is an economical and successful method of
producing high-purity fatty acids, but it is beset with many problems
because fatty acids have high boiling points and decompose when held at
elevated temperatures. The early distillers soon discovered that pro-
cessing temperatures must be held at about 250°C maximum to limit decom-
position. At higher temperatures, fatty acids first lose water, forming
anhydrides, and later, under continued heating, break down into ketones
and hydrocarbons. Unsaturated fatty acids polymerize, forming dimers,
trimers, and so forth.

The early stills were operated at atmospheric pressure and large quantities of injected steam were used to maintain the temperature at 250°C. As better equipment became available, the stills were operated at lower and lower pressures until today most fatty acid stills operate at pressures of between 5 and 50 mm Hg abs. At low pressures, fatty acids will distill without injected steam, but it is usually desirable to use some injected steam because even a small amount will aid in preventing the formation of anhydrides. When stills are operated at pressures lower than the vapor pressure of the available cooling water, it is necessary to provide a steam compressor in addition to the ordinary air pumps to maintain desired operating pressures.

Fatty acid stills now in general use may be classified into three general types: 1) those for semicontinuous batch operation; 2) those for continuous simple distillation; and 3) those for continuous fractional distillation. If only a decolorizing step is necessary (one that removes the unhydrolyzed oil, polymers, and high-boiling color bodies), a simple distillation will produce satisfactory distillate. If considerable amounts of odor bodies (low-boiling unsaponifiable matter and compounds that cause color reversion) are present, some means of fractionally concentrating these "low boilers", either by fractional distillation or fractional condensation, is required. If the component acids must be separated, an efficient fractionating still is necessary.

Separation Processes

Separation of tallow fatty acids into solid (saturated) and liquid (unsaturated) components cannot be accomplished by the fractionation methods previously described because major components have the same chain length and an insignificant difference in molecular weight. Two major separation processes have achieved commercial significance in the separation of solid saturated acids from liquid unsaturated acid, namely, the panning and pressing method and solvent crystallization.

The panning and pressing process at one time accounted for a major portion of the total production of stearic and oleic acids. The idea of pressing liquid fatty acids from solid fatty acids probably occurred from observing the production of lard oil. In fact, equipment used for the pressing of grease to yield lard oil was initially used for the separation of fatty acids. This method is used for the separation of animal fatty acids to produce commercial stearic and oleic acids. Simply, this method involves the crystallization of solid or saturated fatty acids in a solvent of liquid or unsaturated fatty acids. In consequence, the solid (saturated) fatty acids must exhibit a reasonably good crystal formation so that the liquid acids may be easily and efficiently expressed.

In the production of commercial stearic acid, the optimum crystal
structure is attained when the saturated acids of the fatty acid
mixture have a composition of 55% palmitic acid and 45% stearic acid.
Limited variation in this ratio may be tolerated in actual practice,
but the variation in normal animal fats is suffient so that blending
is necessary to secure a proper crystalline structure. Fatty acid
mixtures of a non-crystalline structure may be partially separated
by the pressing method.

In the panning and pressing operation properly prepared melted fatty
acids are cascaded into rectangular aluminum trays, which are stacked
in racks in cold-storage rooms. Cooling takes place very slowly to
assure the formation of large and well-defined crystals. Cooling by
mechanical refrigeration to a final temperature of 35°F is attained
in a cold-storage room in about 6 to 8 hr. The solidified cakes of
fatty acids are removed from the trays, wrapped in burlap or cotton
cloths, and stacked in vertical hydraulic presses. Metal sheet
separators are placed between every two layers of wrapped cakes to
serve as stabilizers to conduct the expressed oleic acid to a trough
at the edge of the press. Pressure is very slowly applied to the
stack of cakes until a maximum of approximately 3000 psi is attained.
The expressed oleic acid amounts to about 50 to 60% of the original
fatty acids. Depending upon the temperature of the cakes of fatty
acid during pressing, the titer of the oleic acid will range from
6 to 10°C.

The pressed cakes, now referred to as "cold pressed cake", are melted,
again cascaded into racks of aluminum trays in an open room, and al-
lowed to solidify at room temperature. The solidified cakes are placed
in hair mat slings suspended between steam-heated hollow metal plates
in a horizontal ram press. Application of pressure and heat removes
most of the oleic acid along with a small portion of the solid acids,
resulting in a mixture of fatty acids known as "hot press oil". The
pressed cake from this "hot pressing operation" is called "double-
pressed" stearic acid. It contains about 5 to 8% oleic acid and has
a titer of approximately 54 to 55°C. In much the same manner "triple-
pressed" acid is produced with the additional production of hot press
oil. Triple-pressed stearic acid contains from 1 to 3% oleic acid
and has a titer of approximately 55 to 56°C. The hot press oil has
a composition of saturated and unsaturated acids similar to the feed-
stock and is therefore mixed with the incoming fatty acid feed. As
a result, about 40% of the fatty acids in this process is being recycled.

The panning and pressing method is gradually being replaced by the
newer solvent methods, as has countercurrent extraction by immiscible
solvents.

Solvent processes utilizing a liquid-to-liquid extraction method, i.e., depending on the selective action of a solvent on the liquid fatty acid, have been proposed, but the mutual solubility of mixed fatty acids in solvents results in an inefficient separation. This has limited the commercial use of these methods.

Separation methods involving the crystallization of one-component fatty acids from a solvent solution of a mixture of fatty acids eliminate, to ' a large extent, the effect of mutual solubility. Solvent crystallization methods may be applied to the separation of most fatty acid mixtures, provided the component acids can be selectively removed in a solid state, from a solvent solution of the mixture.

Of the many solvent crystallization separation methods proposed, the Emersol Process has the most commercial installations. This process involves the controlled crystallization of fatty acids from a polar solvent to achieve a separation of solid fatty acids from liquid fatty acids. Separation of saturated acids or of triglycerides may also be accomplished. One of the best illustrations of the application of this process is in the separation of animal fatty acids to yield commercial stearic acid and oleic acid.

Animal fatty acids are dissolved in 90% methanol to yield a 25 to 30% concentration. The methanol solution of the fatty acids is pumped continuously to a multitubular crystallizer fitted with agitator scraper blades and cooled to about -15°C. Cooling is accomplished by circulating refrigerated methanol through the jackets of the crystallizer tubes. During chilling the solid fatty acids crystallize from the solvent solution to form a slurry that is fed to a rotary vacuum filter. The solid acids filter to form a cake that is continuously washed with fresh 90% methanol and then discharged from the filter. This filter cake containing approximately 40 to 60% methanol is melted and pumped to a solvent recovery still in which the solvent is removed from the fatty acids and returned to the system. The solid acids are discharged from the still ready for finishing and packaging operations into commercial stearic acid.

The filtration containing the liquid acids is passed through a heat exhanger to a solvent recovery still. The discharged liquid acids from the still are ready for finishing and packaging into commercial oleic acid. Reported capacities of the Emersol units range from 2000 to 5000 lb of fatty acids per hour. At present, there are a total of seven units in operation in the United States, Great Britain, Holland, and Australia.

Certain other separation methods, although not yet commercial, have interesting possibilities. A solvent crystallization process for separating tallow fatty acids using hexane as a solvent has been employed. Much has

been published on the separation of fatty acid mixtures by use of urea
or thiourea complexes. Urea or thiourea adducts or complexes of fatty
acids have varying degrees of stability, depending on the carbon chain
length and configuration of the molecule. This difference in adduct
stability is the basis for obtaining a separation of the fatty acids.

Recovery of Fatty Acids From Tall Oil

When non-glyceride feedstocks such as tall oil are used, a different
process from that shown in Figure 4-41 must be used.

In the production of tall oil fatty acids and rosin by fractional dis-
tillation, crude tall oil is passed through a vaporizer into a fraction-
ating column where the volatile rosin and fatty acids are separated
from higher-boiling and nonvolatile impurities, which are drawn off as
pitch. The vapor enters the fractionation column and is separated into
three fractions: (1) rosin that is taken off at the bottom of the
column, (2) a fatty acid containing from 1 to 5% rosin near the top of
the column, and (3) a heads fraction overhead, containing a high per-
centage of low-boiling fatty acids (mainly palmitic), unsaponifiables,
and color bodies. The fatty acid fraction is then passed into a third
column where it is further stripped of rosin, unsaponifiables, and
color and odor bodies to yield a product with a rosin content of 0.3
to 2.0% and unsaponifiables content of 0.3 to 1.5%. The fraction con-
taining 25 to 35% rosin, taken off at the bottom of this column, is
either sold as such or refractionated. By taking fatty acids off at
the second column or at various points on the third column, the rosin
content of the fatty acids can be varied.

The fractionation of tall oil presents a number of problems. Both the
fatty acids and the rosin have low vapor pressures and are subject to
decomposition on heating. Either very high vacuum or vacuum with the
addition of superheated steam is needed to keep the temperature low
enough to prevent damage to the products. Overheating must be pre-
vented during vaporization by creating high flow velocities in heaters
and vaporizers, and entrainment must also be prevented. The equipment
is, therefore, specifically designed for the purpose. Various types of
fractionating trays, grid trays, sieve trays, and bubble-cap trays
are used; all of them have certain advantages and disadvantages and
unless they are carefully chosen and designed for the purpose, will
fail to produce the desired results.

Different operating schemes are used by the various producers, employing
single and multiple tower system. A two-tower system can produce excel-
lent results by refractionating the fatty acids. This raises the operat-
ing cost but the investment cost for the plant is lower.

For the purposes of this study, the previously described unit operations and chemical conversions are defined to be the basic steps necessary to produce fatty acids. Field sampling was used to establish raw waste loads for plants encompassing these steps. Because of the batch or semi-continuous nature of the operations, it was not possible to break out the total RWL according to individual step sources. Rather, combined waste streams from the acid production areas were sampled in most cases. A total of 6 plants were sampled. Table 4-10 indicates the specific operations relating to acid and derivatives production. Table 4-11 summarizes the RWL data related to acid production for 5 plants, and presents an arithmetic average for these operations. It should be noted that the RWL data presented in Table 4-11 are based on samples taken after gravity separation of fatty acids from the wastewater. It is common practice to recycle the skimmed material back to the acid pretreatment section of the plant for recovery.

Table 4-12 summarizes the raw waste loads calculated from production of primary derivatives. As with acid production, it was not possible to develop separate RWL's for specific derivatives because of the batch nature of the operations. The data shown relate to groups of processes in operation during the sampling program. Associated primary derivative products include esters, amines, nitriles, dimers and trimers, polyamides, and fatty quaternary ammonium chloride. An average RWL value for these processing operations is provided in Table 4-12. Again, it should be noted that the values are based on samples taken after gravity separation of free oil and in-process survey steps, except as noted.

The average values shown in Tables 4-11 and 4-12 were considered as BPCTCA. The plants surveyed discharge both to surface waters and to municipal treatment plants.

TABLE 4-10

CHEMICAL CONVERSIONS AND UNIT OPERATIONS CONTRIBUTING TO PROCESS RAW WASTE LOADS FOR THE MANUFACTURE OF FATTY ACIDS AND

PRIMARY DERIVATIVES (BASED ON PLANTS SURVEYED)

Plant 1

Acid Production
1. Acid Washing
2. High Pressure Fat Splitting
3. Glycerine Recovery and Purification
4. Solvent Separation of Fatty Acids
5. Hydrogenation of Fatty Acids

Derivatives
1. Dimerization & Trimerization [1]
2. Ozonation
3. Esterification
4. Ammination

[1] Wastewater included with acid product.

Plant 2

Acid Production
1. Pretreat. by Filt. and Acid Wash
2. Hydrogenation of Tallow
3. Hydrolysis by Twitchell Proc.
4. Glycerine Recovery
5. Distillation of Fatty Acids
6. Separation of Acids by Pressing

Plant 3

Acid Production
1. Saponification
2. Acidulation
3. Hydrogenation
4. Fat Splitting
5. Glycerine Recovery (b)
6. Distillation

(b) Wastewater from Glycerine Recovery Sampled Separately.

Derivatives
1. Esterification (c)
2. Ammination (c)

(c) Esters & Ammine Sampled Separately

Plant 4

Acid Production
1. Pretreat. by Filt.
2. Hydrogenation
3. Fat Splitting
4. Glycerine Recovery
5. Distillation

Derivatives
1. Esterification

Plant 5 (d)

Acid Production
1. Hydrogenation
2. Fat Splitting
3. Glyceride Recovery
4. Distillation

Derivatives
1. Esterification
2. Ammination

(d) Production Units for Acids & Derivatives could not be sampled separately.

Plant 6 (e)

Acid Production
1. Distillation from Tall Oil

Derivatives
1. Dimerization & Trimerization
2. Ammination

(e) Only production units for derivatives were sampled.

TABLE 4-11

PROCESS RWL ASSOCIATED WITH MANUFACTURE OF FATTY ACIDS (ALL RWL BASED ON SAMPLES TAKEN AFTER GRAVITY SKIMMING FREE FATTY ACIDS FROM WASTEWATER)

		Flow (lit./kkg)	BOD (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
Plant 1	(1 day)	10,300 (a)	12.7	44.3	4.89
	(1 day)	10,300 (a)	18.5	52.5	10.3
Plant 2	(1 day)	63,900	12.8	23.6	4.41
Plant 3	(1 day)	3,700 (b)	11.7	37.3	10.6
	(1 day)	45,500 (c)	14.6	41.6	14.3
Plant 4	(1 day)	65,900	21.5	5.8	1.2
Plant 5	(1 day)	12,100 (d)	15.6	42.4	13.6
	(1 day)	12,100 (d)	37.5	53.2	18.9
Average		28,000	18.1	37.6	9.8

(a)   RWL includes wastewater from dimerization

(b)   RWL does not include wastewater from glycerine recovery

(c)   RWL based only on glycerine recovery (i.e., gased on glycerine)

(d)   RWL includes small contribution from derivatives

TABLE 4-12

PROCESS RWL ASSOCIATED WITH MANUFACTURE OF PRIMARY DERIVATIVES FROM FATTY ACIDS (NOTE RWL BASED ON SAMPLES TAKEN AFTER GRAVITY SKIMMING FREE OIL INDICATED BY ASTERISK)

	Flow (lit./kkg)	BOD (kg/kkg)	COD (kg/kkg)	TOC kg/kkg
Plant 1* (1 day)	4,590	16.5	32.6	9.75
(1 day)	4,590	17.0	41.3	14.7
Plant 3				
Esters (1 day)	127,000[1]	26,500	54,700	13,600
Amines (1 day)	18,800[2]	495	1,070	245
Plant 4* (1 day)	8,920	28.6	14.7	5.7
Plant 6* (1 day)	5,700	9.82	23.0	3.73
Average (Exclude Plant 3)	6,400	18.0	27.9	8.47

[1] Sample taken prior to methanol recovery

[2] Sample from blowdown on recirculating system

FIGURE 4-41

GENERALIZED PROCESS FLOW DIAGRAM ILLUSTRATING THE

MANUFACTURE OF FATTY ACIDS FROM GLYCERIDE FEEDSTOCKS
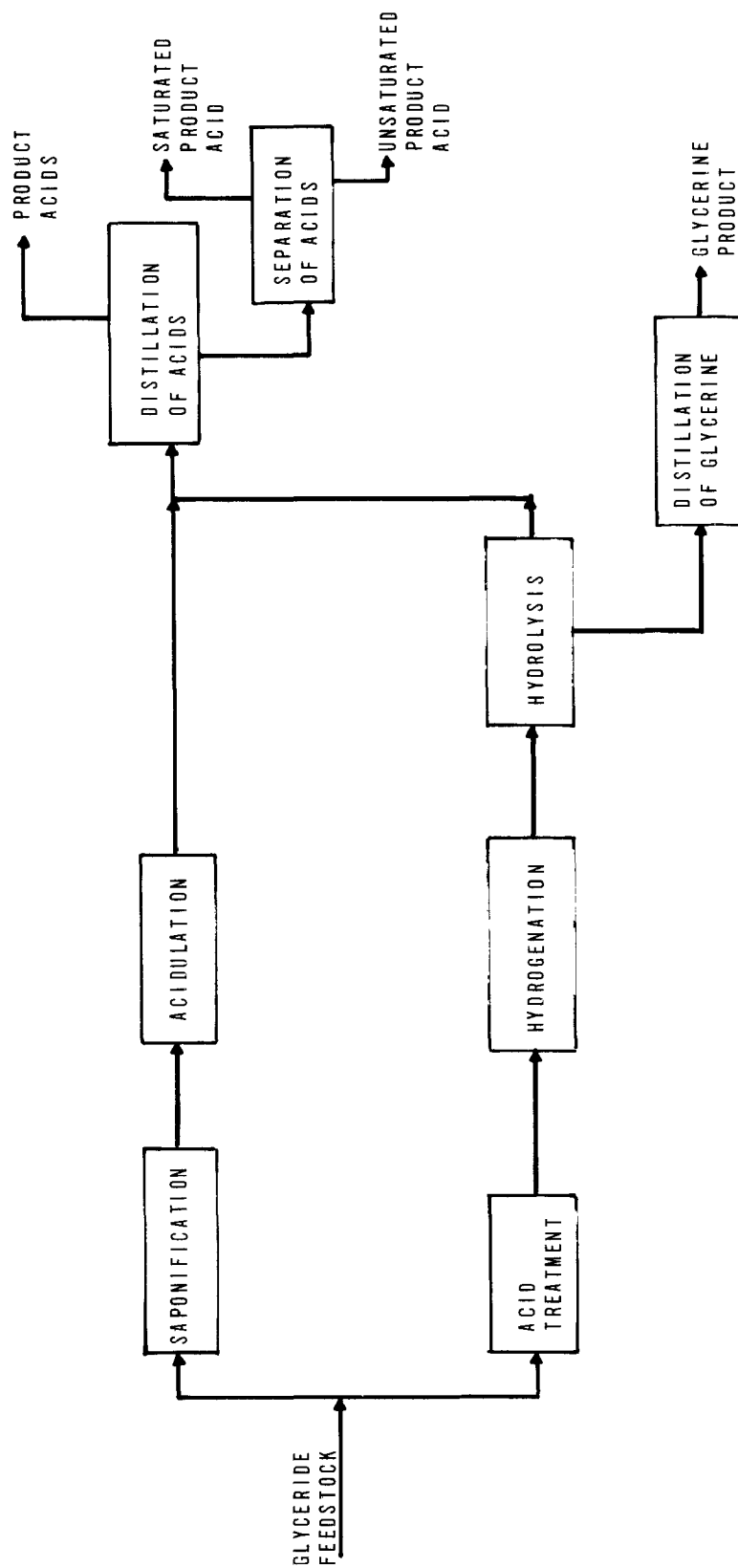
Product: Ionone and Methylionone

Process: Condensation and Cyclization of Citral

Process RWL Category: D

Chemical Reactions:

$$Citral + Acetone \xrightarrow{NaOH} pseudo\text{-}Ionone$$

$$pseudo\text{-}Ionone \xrightarrow{H_2SO_4} \alpha\text{-}Ionone + \beta\text{-}Ionone$$
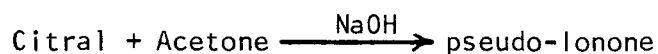
Ionones and methylionones are used in perfumery and flavors; the beta ionone isomer is an intermediate in the manufacture of vitamin A.

The production of ionones and methylionones involves two steps. First, the pseudo-ionone is prepared by the condensation of citral obtained from lemongrass oil; the condensation reaction uses either acetone or methyl ethyl ketone to produce pseudo-ionone or pseudo-methylionone. Second, these pseudo-ionones are cyclized with an acid catalyst. Commercial ionones are generally mixtures of the alpha and beta isomer, with one form predominating, although separations are sometimes made through bisulfite compounds.

A typical process flow diagram for producing ionone/methyl-ionone is shown in Figure 4-42. Citral, acetone/methyl ethyl ketone, sodium hydroxide, and organic solvent are put into the first batch reactor. The solvent from this reaction step is recycled, and the product vapors are condensed and stored in a receiver. The crude product from the receiver is then distilled to remove the heavy-end residues and washed with caustic solution to obtain pseudo ionone (or pseudo-methylionone).

These materials are fed into the second reactor, where cyclization is accomplished via a carbonium ion reaction with H_3PO_4, H_2SO_4, or BF_3 as catalyst. The reaction products proceed through a series of washing tanks, where the products are quenched with sulfuric acid and then washed by water, caustic solution, and acid solution.

After the washing steps, the product mixture is discharged into a series of distillation columns, where the organic solvent and heavy-end residue are recovered and withdrawn from the main product stream. The product vapor leaving the last distillation column is condensed and sent to a liquid-liquid separator for removal of water.

The major water pollution sources of this process are wastewaters from the various washing steps and from periodic reactor washings. During the sampling visit, pseudo-ionone was being produced; hence the wastewater samples obtained at the facility reflect ionone production RWL. However, the RWL of methyl-ionone is believed to be of the same order of magnitude as that of ionone. Process RWL's calculated from flow measurements and the analyses of the wastewater streams are indicated in the following tabulation:

PROCESS FLOW

| liter/kkg | 9,370 |
| gal/Mlb | 1,120 |

BOD_5 RWL

| mg/l [1] | 2,450 |
| kg/kkg [2] | 23 |

COD RWL

| mg/l [1] | 10,000 |
| kg/kkg [2] | 94 |

TOC RWL

| mg/l [1] | 3,520 |
| kg/kkg [2] | 33 |

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of product.

The analytical results also indicate that, in addition to the parameters shown in the tabulation, pollution parameters such as pH, sulfate, oil, and chloride are at levels hazardous to biological treatment processes.

These data, shown above, were considered as commensurate with BPCTCA. The wastes from this plant are discharged to a municipal treatment plant.

FIGURE 4-42

IONONE/METHYLIONONE-CONDENSATION AND CYCLIZATION OF CITRAL
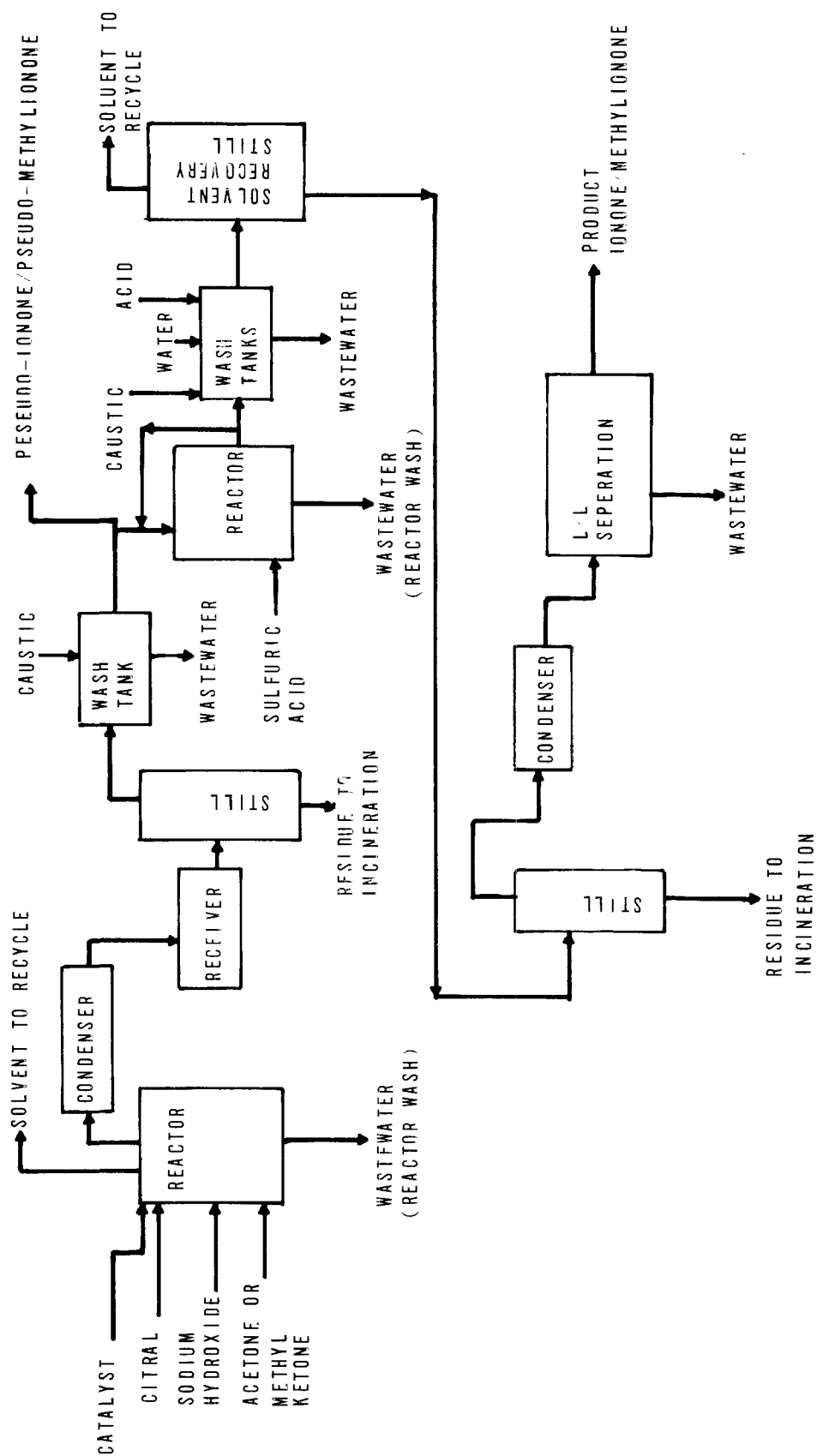
Product: Methyl Salicylate

Process: Esterification of Salicylic Acid with Methanol

Process RWL Category: D

Chemical Reactions:

$$(C_6H_4OH)\ COOH\ +\ CH_3OH\ \longrightarrow\ (C_6H_4OH)\ COOCH_3\ +\ H_2O$$

salicylic acid methanol   methyl salicylate
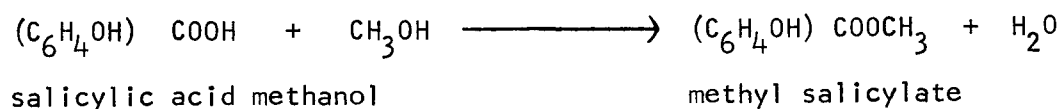
Methyl salicylate, the methyl ester of salicylic acid, also known as "oil of wintergreen" is used as a flavoring compound in mouthwash and certain food products.

The esterification of salicylic acid is carried out in the presence of a catalyst (such as sulfuric acid) and a solvent (such as methylene dichloride or ethylene dichloride). Ethylene dichloride is generally preferred, but the choice of the solvent depends to some extent upon the boiling point of the desired ester. A flow diagram for the methyl salicylate manufacturing process is shown in Figure 4-43, and the general procedure is described in the following paragraphs.

For each mole of salicylic acid, 3 moles of commercial methanol, 300 ml ethylene dichloride and 15 ml of concentrated sulfuric acid are used. The mixture is refluxed in the reactor for 6 to 15 hours.

Progress of esterification is usually, but not invariably, indicated by the development of cloudiness and separation of an upper layer containing water, methanol, and sulfuric acid. When the reaction is complete, the mixture is cooled, and the bottom ethylene dichloride layer is washed successively with water, sodium bicarbonate solution, and again with water. The ethylene dichloride layer, which contains the product stream, is then distilled in vacuum or at atmospheric pressure, and the residue methyl ester is further purified by distillation or crystallization before being packaged for subsequent sale.

The aqueous upper layer formed in the reactor is recycled to the distillation operation for recovery of methanol. The water generated in the washing steps is discharged into a lizuid/liquid separator, from which the organic phase is recycled back to washing towers.

The major water pollution sources of the process are the waste streams
resulting from the washing steps. The steam jets used in pulling the
vacuum for distillation are discharged directly into the atmosphere
in the facilities visited and do not contribute to any pollution load-
ing in the contact wastewaters. Samples were obtained in the survey
period for analyses, but unfortunately, flow rates were not provided
by the manufacturer, and no RWL's are listed.

FIGURE 4-43

METHYL SALICYLATE — ESTERIFICATION OF SALICYLIC ACID
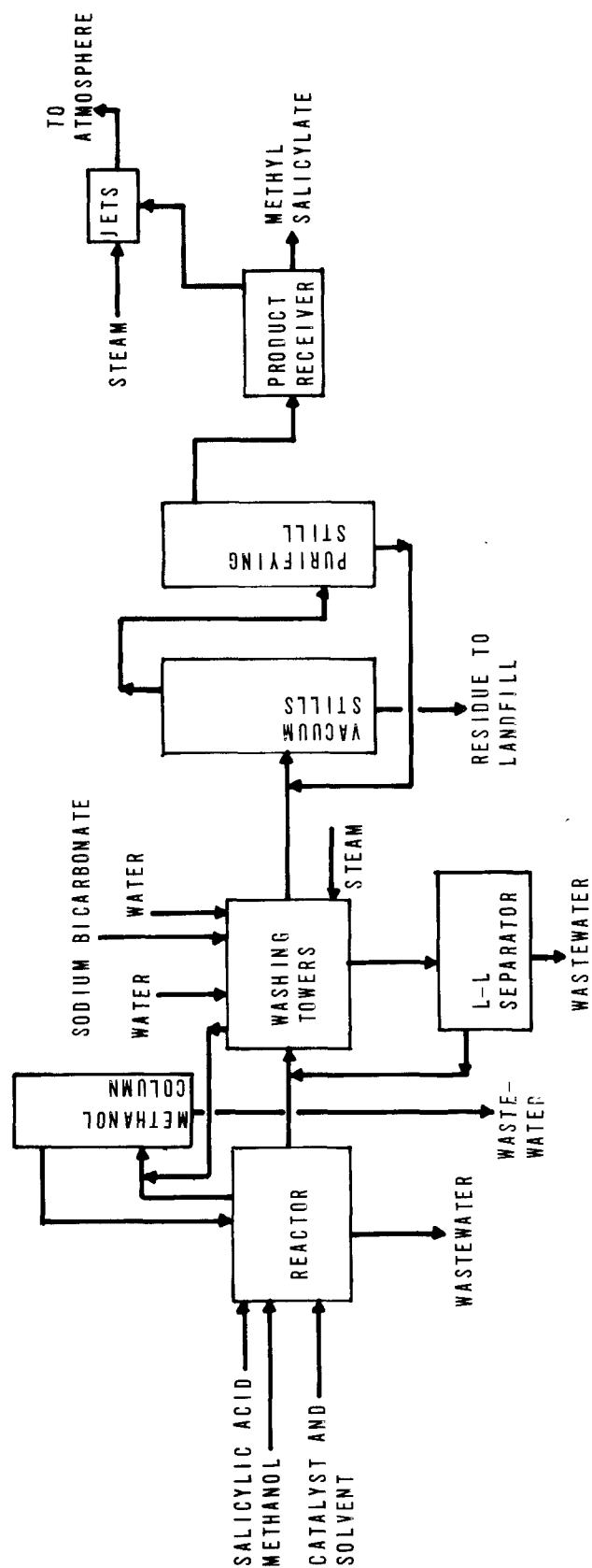
Products: Miscellaneous Batch Chemicals
            Intermediates
            Dyes
            Rubber Chemicals
            Pigments
            Pharmaceuticals

Process: Numerous Batch Processes (Batch Chemicals Complex)

Process RWL Category: D

The RWL data presented and discussed in the following paragraphs were
obtained by sampling the total effluent from a large chemical plant.
This plant manufactures thousands of chemicals within the five general
classifications indicated above. In such a case, it is impossible to
sample each of the process operations on an individual basis. It should
also be noted that it will be impossible to effectively develop effluent
limitations for such a facility using specific limitations relating to
each specific batch process. A facility of this nature can be addressed
only in terms of its total aggregate production.

Daily 24-hour composite samples were taken over a period of 9 days, fol-
lowed by three, 5-day composite samples over the next 15 days. The measured
flows and concentrations were put on a production basis by means of a
weekly production activity report supplied by the manufacturer. The RWL
data obtained in this manner are summarized in Table 4-13.

The RWL data shown in Table 4-13 represent the total raw waste from the
plant. Examination of the data based on the nine consecutive 24-hour
composite samples indicates significant variation. For example, the
calculated mean   for BOD is 20.4 kg/kkg of product, with high and low
values of 27.4 and 11.9 during the nine-day period.

It is significant to note that the three 5-day composite samples show
approximately the same range of variability. The calculated average
BOD raw waste load for the three periods is 24.1 kg/kkg, with high and
low values of 35.8 and 14.1 respectively.

This type of variation may be caused principally by the fact that in
this type of chemical plant it is impossible to relate production data
to the exact sampling periods, and, consequently, calculated ratios
will always have this type of error present.

Production at a batch chemical complex involves the startup and shut-
down of thousands of discrete batch processing operations on a day-to-
day basis. Although the plant maintains a materials inventory, this

is usually updated only on a monthly basis. In this particular case, the manufacturers expended considerable effort to provide weekly production figures based on changes in the materials inventory.

However, it was still necessary to divide each of the weekly total aggregate production quantities by seven to approximate a daily production figure. In the case of the 24-hour composite sample data, it was this production figure which was divided into the product of the corresponding daily flows and pollutant concentrations to calculate the RWL. Similar difficulties occurred with the 5-day composite samples in that sampling periods did not match the periods for which production quantities were developed.

In light of these difficulties, it would be informative to examine some of the possible results which may occur in the application of effluent limitations to this type of facility. The average of the nine 24-hour composite RWL provides a number comparable in accuracy to many of the RWL values assigned to other processes in this study. The BOD and COD RWL values relating to this plant (from Table 4-13) are:

Average of Nine 24-hour Composite Samples

BOD	20.4 kg/kkg
COD	77.2 kg/kkg

In later sections of this report, reduction factors based on the performance of end-of-pipe treatment systems are developed. These numbers were uniformly applied to the RWL developed for each sub-category of process. The reduction factors for BPCTCA relating to BOD and COD are 92% and 69% respectively. If these reductions are applied to the average RWL for the batch chemical complex indicated above, the following effluent limitations will result:

$$BOD = (20.4)(0.08) = 1.63 \text{ kg/kkg}$$

$$COD = (77.2)(0.31) = 23.9 \text{ kg/kkg}$$

It should be noted and clearly understood that adjustment factors based on treatment plant variability must then be applied to the above values. The adjusted effluent limitations in terms of a maximum value for any one day are indicated as follows:

Parameter	BPCTCA Effluent Limitation	Daily Adj. Factor	Max.for Any One Day
BOD	1.63 kg/kkg	4.5	7.34 kg/kkg
COD	23.9 kg/kkg	3.4	81.3 kg/kkg

It is possible to compare the actual treated effluent discharged by the plant with the maximum one-day values, utilizing the data presented in Tables 4-14 and 4-15.

Table 4-14 presents data on the performance of the activated sludge treatment plant associated with the batch chemical complex during the same period covered by the RWL sampling. Table 4-15 presents the calculated effluent discharged from the complex on a production basis. The effluent values shown in Table 4-15 were obtained by multiplying the BOD and COD raw waste load values from Table 4-13 by the corresponding reduction factors in Table 4-14.

Examination of the data presented indicates that in no case were the BOD and COD effluents greater than the Maximum Values for Any One-Day presented above. An examination of the data presented in Tables 4-13 and 4-14 shows that the variability in the actual treatment plant performance (as % reduction) was less than that taken into account in developing the daily adjustment factor for treatment plant performance. Thus, the variability correction associated with the treatment plant cancelled much of the variability exhibited by the process plant.

Obviously, this simple example does not prove that there may be gross inequities resulting from the application of production-based effluent limitations derived from a very limited data base. However, it does indicate that such limitations can serve as a meaningful basis for negotiations in the development of an NPDES permit.

It is recommended that large batch chemical complexes which produce a great number of specific commodities be approached in the manner illustrated here. This should be done on an individual basis. In these cases, it should be incumbent upon the manufacturer to develop production-based RWL data for presentation to EPA. The time period should preferably be longer than was possible for sampling during this study project.

A reduction factor (such as 92% for BOD) can then be applied to the RWL to determine a production-based limitation. This limitation should then be adjusted for variability depending upon the sampling period.

Table 4-13

RWL Data for Batch Chemical Complex

Sample Period	Flow L/kkg	BOD (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
24 hr. composite	65,300	19.6	63.5	17.0
" "	74,800	16.5	68.4	19.5
" "	90,100	27.0	90.1	23.4
" "	89,300	27.4	96.4	29.9
" "	71,300	23.8	83.9	22.1
" "	113,000	27.4	99.4	29.2
" "	68,800	11.9	55.3	17.9
" "	70,400	13.0	60.4	23.9
" "	78,700	16.9	77.0	23.6
Average	80,100	20.4	77.2	22.9
5-day composite	70,600	22.4	80.9	27.1
" "	65,500	14.1	76.6	27.1
" "	100,000	35.8	144.	40.1
Average	78,700	24.1	100.5	31.4

Table 4-14

Treatment Plant Performance Data for Batch Chemical Complex
Treatment Plant Utilizing the Activated Sludge Process

	BOD			COD			TOC		
	Inf. mg/l	Eff. mg/l	% Red.	Inf. mg/l	Eff. mg/l	% Red.	Inf. mg/l	Eff. mg/l	% Red.
24-hr. comp.	300.	29.	90.3	972.	311.	68.0	260.	75.	71.1
24-hr. comp.	220.	21.	90.5	914.	295.	67.7	260.	67.	74.2
24-hr. comp.	300.	18.	94.0	1000.	310.	69.0	260.	79.	69.6
24-hr. comp.	307.	14.	95.4	1080.	270.	75.0	335.	68.	79.7
24-hr. comp.	333.	14.	95.8	1176.	333.	71.7	310.	104.	66.5
24-hr. comp.	243	15.	93.8	882.	363.	58.8	259.	104.	59.8
24-hr. comp.	173.	9.	94.8	804.	314.	60.9	260.	83.	68.1
24-hr. comp.	185.	17.	90.8	860.	350.	59.3	340.	125.	63.2
24-hr. comp.	215.	35.	83.7	980.	420.	57.1	300.	109.	63.7
5-day comp.	318.	25.	92.1	1147.	330.	71.2	385.	90.	76.6
5-day comp.	215.	32.	85.1	1171.	278.	76.3	415.	91.	78.1
5-day comp.	358.	23.	93.6	1439.	272.	81.1	400.	64.	84.0

NOTE: These performance data were obtained during December from a plant located
in the Northeatern U. S. The high removal efficiencies indicate that
treatment technology is available to design a highly efficient biological
treatment facility which will operate satisfactorily during winter conditions.
Historic performance data from this plant are reported in Table 7-2 as
Plant No. 3

Table 4-15

Effluent Discharged From Batch Chemical Complex
After Biological Treatment

Sample Period	BOD (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
24-hour composite	1.90	20.3	4.91
" "	1.57	22.0	5.03
" "	1.62	27.9	7.11
" "	1.26	24.1	6.07
" "	1.00	23.7	7.40
" "	1.70	41.0	11.7
" "	0.62	21.6	5.71
" "	1.20	24.6	8.80
" "	2.75	33.0	8.57
BPCTLA Effluent Limitation Maximum for any one day	7.34	81.3	

Product: Monosodium Glutamate (MSG)

Process: Batch Fermentation of Beet Sugar Molasses

Process RWL Category: D

Chemical Reaction:

Fermentation (Glutamic Acid Production)

Beet Sugar + Bacteria Culture + O_2 + NH_3 $\longrightarrow$
(sucrose)

NH_2-CH-COOH + H_2O + CO_2 + Bacteria Mass
    |
    CH_2-CH_2-COOH
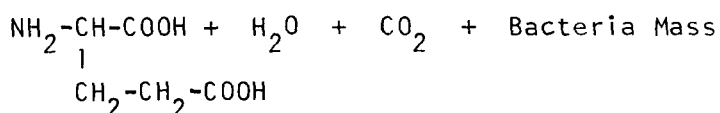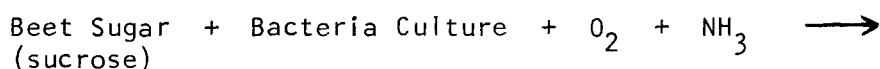
glutamic acid

MSG Conversion and Neutralization

NH_2-CH-COOH + NaOH $\longrightarrow$ NH_2-CH-COOH + H_2O
    | |
    CH_2-CH_2-COOH CH_2-CH_2-COONa
                                         mono sodium glutamate
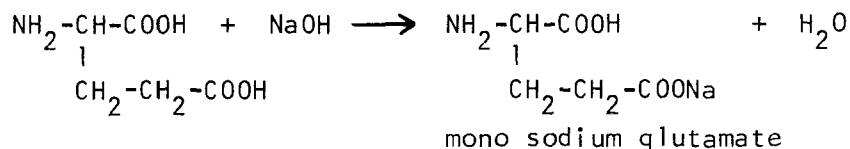
Typical Raw Materials

    Beet Sugar Molasses
    Ammonia (NH_3)
    Bacteria Culture
    Nutrient Salts
    Compressed Air
    Diatomeceous Earth Filter Aid
    Hydrochloric Acid (HCl)
    Sodium Hydroxide (NaOH)
    Steam
    Cooling Water
    Bleaching Activated Carbon

Monosodium Glutamate (MSG) is an amino acid salt which is used as a
flavor enhancer. MSG is produced by the conversion of Glutamic Acid (GA)
with caustic. There are several routes to obtaining the GA, including
hydrolysis of Steffen's Waste Liquor with caustic or acid, acid hydrolysis
of wheat and corn gluten, and fermentation of a carbohydrate.

The process visited during the field data collection program was the fermentation of beet molasses (sucrose) to produce glutamic acid. This fermentation reaction is a batch reaction; subsequent separation processes and the conversion of the glutamic acid to monosodium glutamate are done on a semi-continuous basis (refer to Figure 4-44).

The aerobic fermentation of the sugar beet molasses occurs in a jacketed vessel, which is either steam-heated or water-cooled to maintain temperature. The cooling water may be recirculated without organic pickup. The pH of the fermenting liquor is monitored and controlled by ammonia addition. The added ammonia also supplies the amino group in the product formulation and supplements the nitrogen content of the raw molasses for bacteria culture growth. The surplus air from the fermentation vessels contain odorous compounds; therefore, these gases are sent to the boilers for air makeup, and the odorous materials are thermally destroyed.

At the completion of the fermentation reaction, the bacteria cell mass (cell cream) is separated via centrifuges and discarded (point No. 2); this cell mass represents the most significant part of the raw waste load. The high pollutant loading and commensurate high substrate content of this waste stream make it a prime candidate for by-product recovery and sale if a market can be found.

The clarified centrate is heat treated to precipitate miscellaneous proteinaceous material. The precipitated material and any fugitive cell mass are then removed via vacuum filtration. The resulting sludge is cyclone classified to recover most of the filter aid material. The waste stream (point B, appcor cyclone overflow) is characterized as heavily contaminated with inert and organic suspended solids. Intermittent discharge of filter precoat material impacts considerably on the RWL for all parameters measured (point No. 3).

The clarified filtrate (glutamic acid solution) is concentrated via a two-stage evaporation process. The condensate of the first effect is recycled as water make-up to the fermentation process. The second-stage vapors are condensed in barometric contact condensers. The barometric condenser system is serviced with recirculated cooling-tower water. The blowdown (point No. 7) from this cooling-tower system was found to be highly contaminated with materials exerting a significant biochemical oxygen demand.

The concentrated glutamic acid (GA) solution is treated with concentrated hydrochloric acid to a pH of 3.2, the isoelectric point of GA. The GA is crystallized out of solution, filtered, and washed. The wash water,

which represents the major blowdown of impurities from the system, is recovered and sold as an animal feed supplement, "Dynaferm". The primary constituent of Dynaferm is GA, but it also contains many other salts and proteinaceous impurities which escape the heat coagulation/ filtration treatment. This stream was not sampled during the data- gathering survey, but its recovery and sale probably impact very favorably in reducing the RWL.

The GA crystals are then solubilized and partially converted to MSG with caustic. The GA/MSG solution is decolorized with activated carbon. The spent carbon is recovered and thermally regenerated; this represents a significant in-process pollution control measure because the color bodies and other adsorbed impurities are oxidized in the regeneration furnace. There are three small water discharges (points No. 4, 5 and 6) which do not significantly impact on the RWL.

Potential odors in the exhaust gases from the carbon regeneration facilities are oxidized via a thermal afterburner. The three discharges (point D) from the carbon regeneration are significant in volume but contribute little of any of the pollutants monitored during the survey.

Further downstream processing includes: pH adjustment, filtration, MSG crystallization, and separation of water and GA. These streams are recycled in order to retain valuable product and by-product materials.

The results of combining the two grab composites of all major contributing sources to wastewater discharges yielded values which compare to 62% and 11% BOD_5 occurrence probability of the historical data; this indicates that the samples are representative of the MSG production facility surveyed.

The RWL can be reduced significantly from those levels of pollutants measured during the data-gathering survey. The approach with the greatest potential for reducing the RWL is the recovery and sale of cell cream (point No. 2) for animal feed. It is not possible to mark the impact of cell cream recovery precisely, but it is estimated that approximately 20 to 50 percent of the suspended solids RWL could be removed. A somewhat similar impact on the organic and oxygen-demanding parameters would also be experienced. The prospects for recovery of this material depend on the development of nearby markets and favorable economics.

The recovery of the precoat wastewater (point No. 3) is also an attractive alternative to discharge. This material, soluble and suspended, could be recirculated to achieve almost total recovery.

The RWL for MSG production during the survey and the estimated impact on RWL in regard to recovery of cell cream and precoat wastes are shown in the following tabulation:

Process Flow	Sample Period #1	Sample Period #2	RWL After Reduction
liter/kkg	67,000	67,000	62,200
gal/Mlb	8,030	8,020	7,460

BOD

	Sample Period #1	Sample Period #2	RWL After Reduction
mg/l[1]	1,510	1,020	980
kg/kkg[2]	101	68.4	61

COD

	Sample Period #1	Sample Period #2	RWL After Reduction
mg/l[1]	4,060	4,410	3,600
kg/kkg[2]	272	296	224

TOC

	Sample Period #1	Sample Period #2	RWL After Reduction
mg/l[1]	1,360	1,350	1,090
kg/kkg[2]	91.4	90.5	67

SS

	Sample Period #1	Sample Period #2	RWL After Reduction
mg/l[1]		2,260	305
kg/kkg[2]		151	19

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of products.

FIGURE 4-44

SODIUM GLUTAMATE — FERMENTATION OF BEET SUGAR MOLASSES

DRAFT
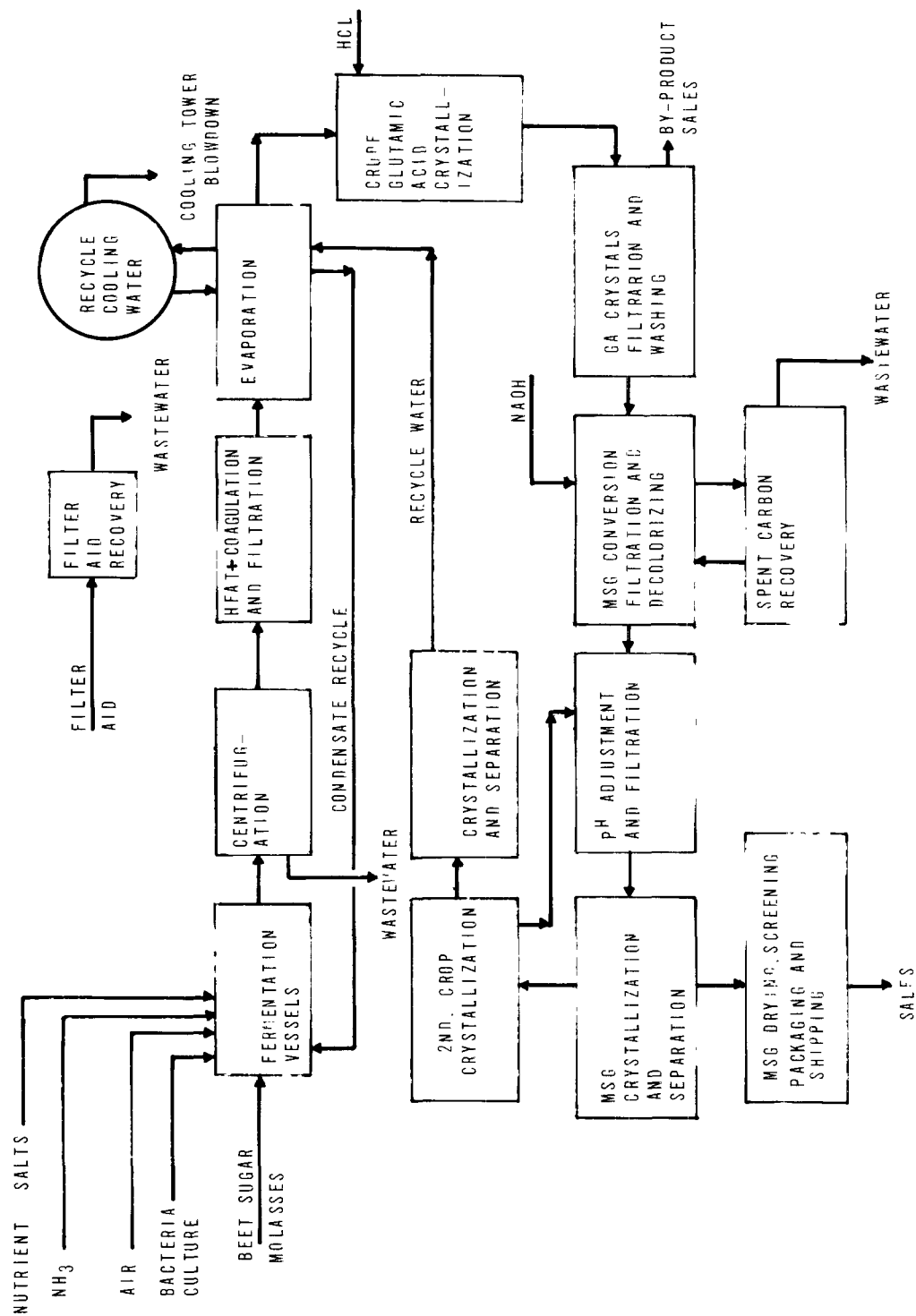
Product: Naphthenic Acid

Process: Extraction and Acidification of Caustic Sludge from Petroleum
           Refinery

Process RWL Category: C

Chemical Structure: Naphthenic acids are cyclo-paraffinic organic acids
                      and usually are mono-carboxylic

The term naphthenic acids is applied to the mixture of carboxylic acids
obtained from the alkali washes of petroleum fractions. They are com-
plex mixtures of normal and branched aliphatic acids, alkyl derivates of
cyclopentane- and cyclohexane-carboxylic acids, and cyclopentyl and cyclo-
hexyl derivates of aliphatic acids. Naphthenic acids are used chiefly in
the form of metallic salts which are soluble in oils and organic solvents.
Copper naphthenate is an excellent fungicide for wood and canvas treating;
the lead, manganese, zinc, and iron salts are used as dryers (oxidation
catalysts) for paints and varnishes.

The napthenic acids are present in the caustic sludge primarily as sodium
napthenates. Figure 4-45 is a process flow diagram of naphthenic acid
recovery. The caustic sludge, which has been used to scrub the light
distillate crude oil fractions, is treated with water and an alcohol
soap solvent. The resulting oil and soap phases are separated; the oil
phase is stripped with the oil going to fuel and the solvent recovered
overhead; the soap phase is treated with an oil solvent, and another oil-
phase/soap-phase separation takes place. The oil phase is recycled to
the caustic sludge, while the soap phase is treated with an acid. The
naphthenic acids are then separated from the solvent.

The solvent proceeds to a stripper where it is recovered as the overhead
and sent to solvent storage; the bottoms from this column are quenched
with water and discharged to the sewer. The extracted naphthenic acids
go to a stripper, where solvent is taken overhead and sent to storage;
the bottoms from the stripper are vacuum distilled. The bottoms from
the vacuum still are sent to fuel, while the naphthenic acids are re-
covered.

Process RWL calculated from flow measurements and the analyses of waste-
water streams are indicated in the following tabulation. In addition,
the sulfate concentrations in the wastewaters are extremely high and are
hazardous to biological treatment processes.

PROCESS FLOW

liter/kkg	39,800
gal/M lb	4,760

BOD_5 RWL

mg/liter[1]	3,550
kg/kkg[2]	141

COD RWL

mg/liter[1]	7,500
kg/kkg[2]	298

TOC RWL

mg/liter[1]	2,630
kg/kkg[2]	104

[1]Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2]Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

These data were considered as BPCTCA.

The process plant visited during the field data collection program used direct-contact cooling to reduce the temperature of the bottoms stream from the soap stripper. The substitution of non-contact cooling would reduce the water requirements for this process by approximately 75 percent. However, the raw wasteload would not be appreciably affected.

FIGURE 4-45

NAPHTHENIC ACID - EXTRACTION AND ACIDIFICATION

OF CAUSTIC SLUGE FROM PETROLEUM REFINERY
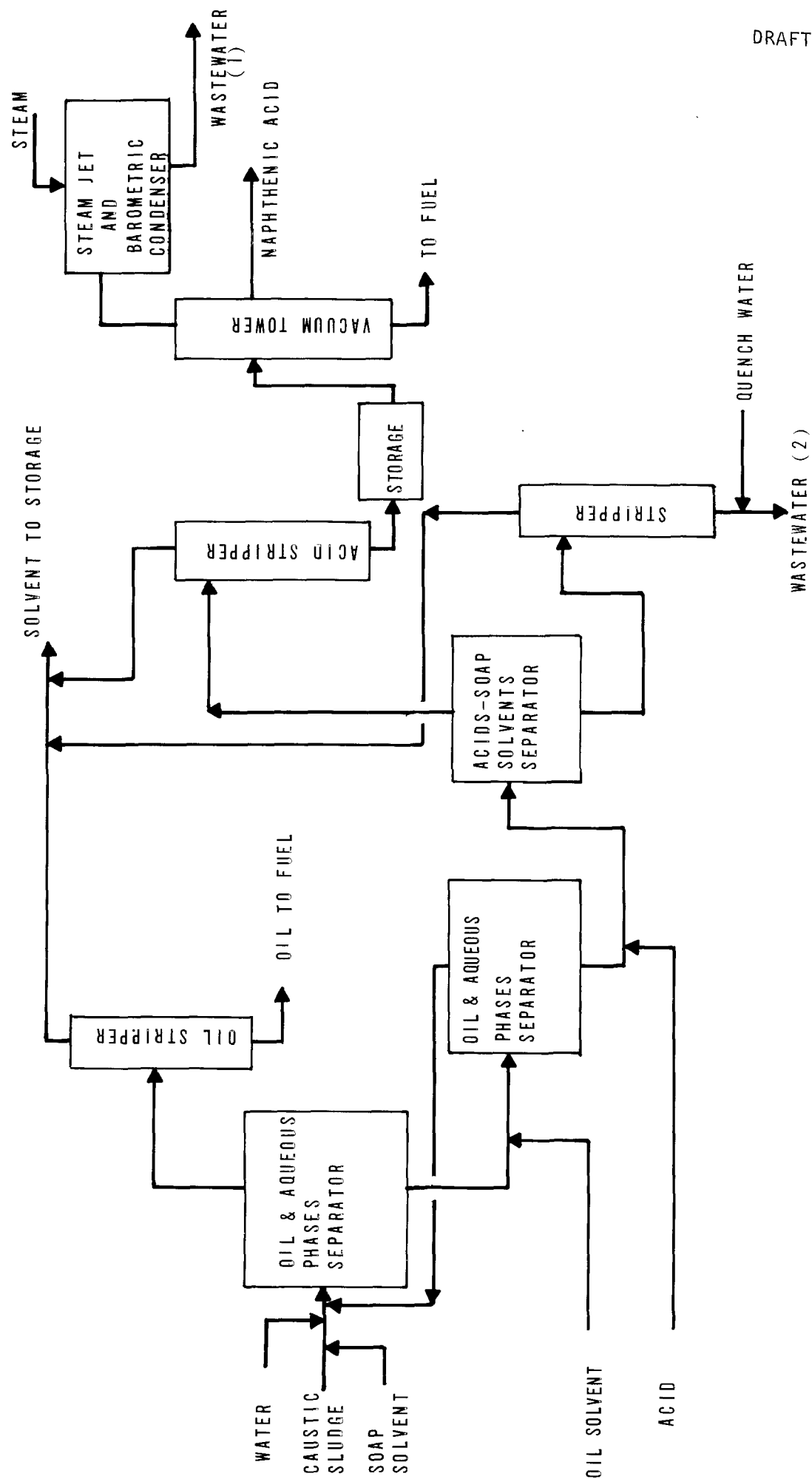
Product: o-Nitroaniline

Process: Ammonolysis of o-Nitrochlorobenzene

Process RWL Category: D

Chemical Reaction:

$$NO_2C_6H_4Cl \ + \ NH_3 \ (excess) \ \xrightarrow{\ H_2O\ } \ NO_2C_6H_4NH_2 \ + \ NH_4Cl$$

          o-nitrochlorobenzene Ammonia   o-Nitroaniline + ammonium chloride
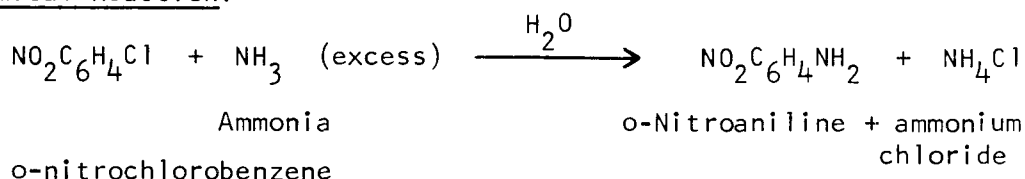
The manufacture of o-nitroaniline is similar to that of p-nitroaniline, which is described in the next section. A typical process flow diagram is shown in Figure 4-46.

The o-nitrochlorobenzene and ammonia enter the batch reactor, and o-nitroaniline is formed. The excess ammonia in the reaction mixture is distilled off the absorbers, from which ammonia is recycled back to the reactor. The aqueous stream from the distillation step goes to a washing operation and proceeds to dehydration and refining operations. Both the dehydration and the refining steps are performed under vacuum conditions, and steam jets with barometric condensers are generally used in pulling the vacuum for the operation. The refined o-nitroaniline may be used directly or it may be further transformed into a flake.

The major water pollution sources of the process are wastewaters withdrawn from the scrubber in the ammonia-recovery system, from the washing step, and the condensates from barometric condensers. Process RWL's calculated from flow measurements and analyses of the wastewater streams are indicated in the following tabulation. The analytical results also indicate that waste streams contain high concentrations of nitrogen and chloride which are hazardous to biological treatment processes.

PROCESS FLOW

liter/kkg	269,000
gal/M lb	32,200

BOD_5 RWL

mg/l[1]	61
kg/kkg[2]	16

COD   RWL

mg/l[1]	391
kg/kkg[2]	105

TOC   RWL

mg/l[1]	115
kg/kkg[2]	30.9

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.

[2] Raw waste loadings are based on unit weight of pollutant per 1000 unit weights of products.

FIGURE 4.46

ORTHO-NITROANILINE—AMMONOLYSIS OF ORTHONITROCHLOROBENZENE
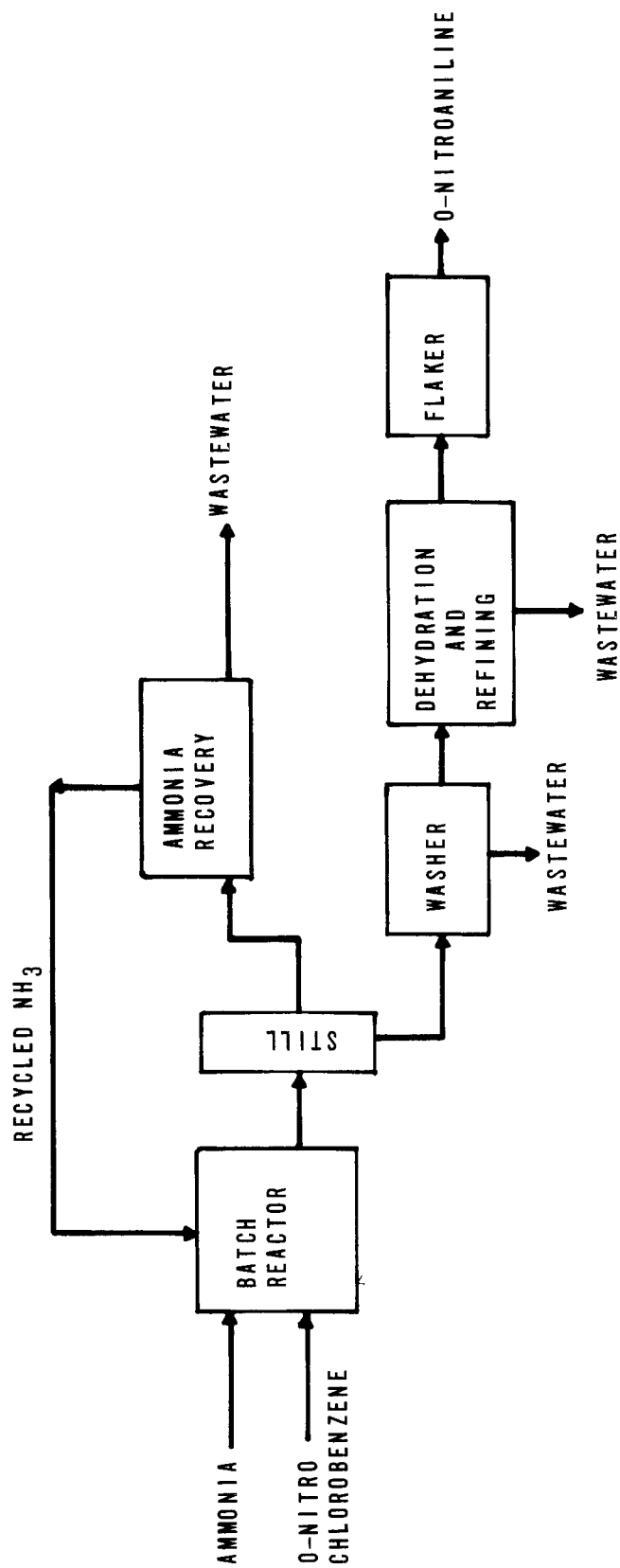
Product: p-Nitroaniline (PNA)

Process: Ammonolysis of p-Nitrochlorobenzene

Process RWL Category: D

Chemical Reactions:

$$NO_2C_6H_4Cl \quad + \quad NH_3 \text{ (excess)} \quad \xrightarrow{H_2O} \quad NO_2C_6H_4NH_2 \quad + \quad NH_4Cl$$

Ammonia

p-nitrochlorobenzene   p-nitroaniline   ammonium chloride
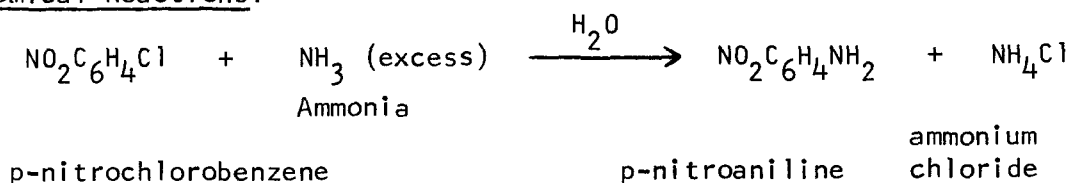
p-Nitroaniline is an important intermediate for dyes and pigments and also for the preparation of numerous antioxidants and antiozonants of the N-substituted p-phenylenediamine type.

A typical process flow diagram for batchwise manufacturing of p-nitroaniline is shown in Figure 4-47.

p-Nitroaniline is manufactured by heating p-nitrochlorobenzene with aqua ammonia at 175°C under pressure. A jacketed autoclave provided with efficient stirrers should be used as the reactor. Molten p-nitrochlorobenzene is added to aqua ammonia (28%) and heated gradually; the temperature is increased over a period of 3 hours to 175°C at a pressure of 530-580 psi, and these latter conditions are maintained for 16 hours to complete the reaction.

Some of the ammonia gas is then vented to an absorption system, and the excess ammonia in the reaction mixture is distilled off to absorbers, from which it is recycled back to the reactor. The aqueous reaction mixture is passed through a pressure filter and sent to wooden crystalizing tubs, where the p-nitroaniline separates as a finely divided, canary-yellow crystalline mass. After cooling to 30°C, the solid product (averaging 99% purity) is removed by centrifuging. The centrate passes through an elaborate system of catch boxes to cool it to room temperature, and additional product settles out. This is recovered periodically by siphoning the water from the catch boxes.

The solid cake leaving the centrifuge is then passed through drying and packaging steps to obtain final product. Dust collectors and scrubbers are used in the drying steps to remove the dust in the vent gases.

The major pollution sources of this process are wastewaters withdrawn
from scrubbers, filtration units, and the crystallization unit. Process
RWL's calculated from flow measurements and analyses of the wastewater
streams obtained in the survey period are shown in the following tabula-
tion. The analytical results also indicate that, in addition to the
parameters shown in the tabulation, pollution parameters such as nitrogen,
chloride, calcium are at levels hazardous to biological treatment processes.

PROCESS FLOW

liter/kkg	39,100
gal/M lb	4,680

BOD_5 RWL

mg/l[1]	65
kg/kkg[2]	2.55

COD   RWL

mg/l[1]	2,030
kg/kkg[2]	79.1

TOC   RWL

mg/l[1]	570
kg/kkg[2]	22.2

[1]Raw waste concentrations are based on unit
weight of pollutant per unit volume of
contact process wastewaters.
[2]Raw waste loading are based on unit weight
of pollutant per 1000 unit weights of product.

These data are considered as BPCTCA.

Continuous processes can also be employed for ammonolysis of p-nitrochloro-
benzene. In such a process, preheated aqueous ammonia is forced through
an inlet pipe to the bottom of the vertical reaction cylinder, then passes
upward through an annular space, and overflows through a central outlet
pipe leading to a still, where excess ammonia is stripped off before the
product is crystallized. The space above the overflow pipe provides a
vapor space to absorb fluctuations of the internal pressure. The lower
part of the cylinder, where the major part of the reaction occurs, is
provided with packing and is constructed of stainless steel to minimize
corrosion. The operating pressure is about 1200 psi.

FIGURE 4-47

PARA-NITRO ANILINE—AMMONOLYSIS OF PARA - NITROCHLOROBENZENE
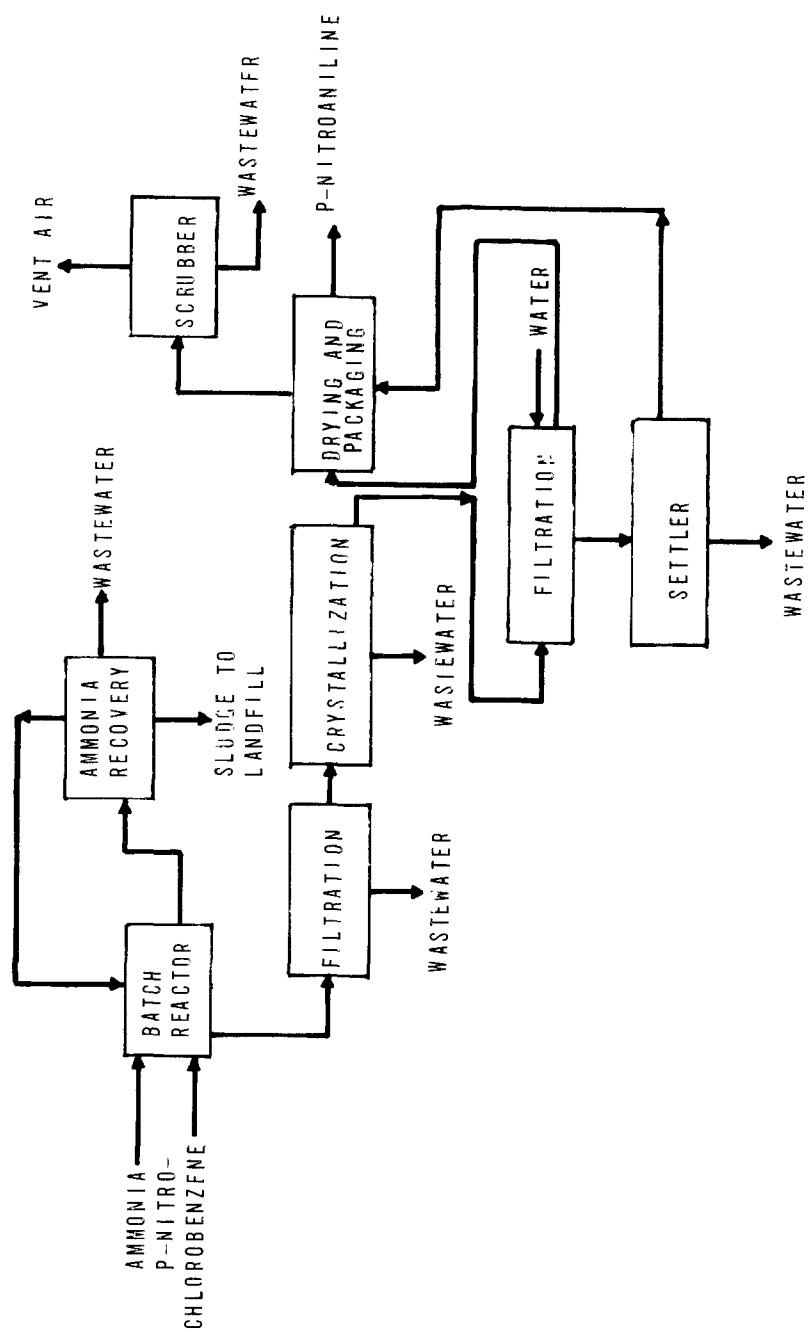
Product: Pentachlorophenol

Process: Chlorination of Phenol

Process RWL Category: D

Chemical Reaction: $C_6H_5OH + 5Cl_2 \longrightarrow C_6Cl_5OH + 5HCl$
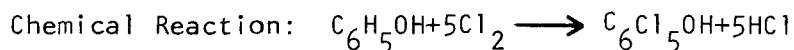
Pentachlorophenol is widely used as a wood preservative, especially in such applications as residential construction where creosote would be undesirable. It is also used as a fungicide in paint and adhesives, and in paper mills.

Although pentachlorophenol can be manufactured by continuous processes, it is generally produced by batch reaction in the facility visited in the survey period. A simplified process flow diagram for the production of pentachlorophenol via the chlorination of phenol is shown in Figure 4-48.

Phenol and chlorine are fed to the reactor, where the chlorination reaction occurs. The product of the first step of the reaction is trichlorophenol, which is further chlorinated to form pentachlorophenol.

The product mixture leaving the second reactor is discharged into a quench vessel, in which the gases are separated from the molten product stream. The gases proceed to the HCl absorber and caustic scrubber, while the liquid stream is solidified in a flaker. The solidified pentachlorophenol is then passed into a rotary kiln for glazing.

The major water pollution sources of this process are the waste streams generated at the caustic scrubber, flaker, and glazing units. Process RWL's calculated from flow measurements and analyses of the samples obtained in the survey period are shown in the following tabulation.

	Sampling Period #1	Sampling Period #2
PROCESS FLOW		
liter/kkg	2,960	2,560
gal/M lb	354	354
BOD$_5$ RWL		
mg/l [1]	330	306
kg/kkg [2]	0.975	0.906
COD RWL		
mg/l [1]	5,740	6,020
kg/kkg [2]	17	17.9
TOC RWL		
mg/l [1]	768	781
kg/kkg [2]	2.27	2.31

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per one thousand unit weight of product.

The analytical results also indicate that parameters such as chloride, phenol, and sulfate are at levels hazardous to biological treatment processes. The low BOD_5 values shown in the foregoing tabulation are possibly caused by the interferences of these biological-inhibitory pollutants.

The demand for pentachlorophenol in the U.S. is approximately 40 million pounds per year, of which 15 million pounds are used in mixtures with creosote. Pentachlorophenol can also be made by caustic fusion of hexachlorobenzene, which is a cheaper route but gives a product contaminated with NaCl.

FIGURE 4-48

PENTACHLOROPHENOL- CHLORINATION OF PHENOL
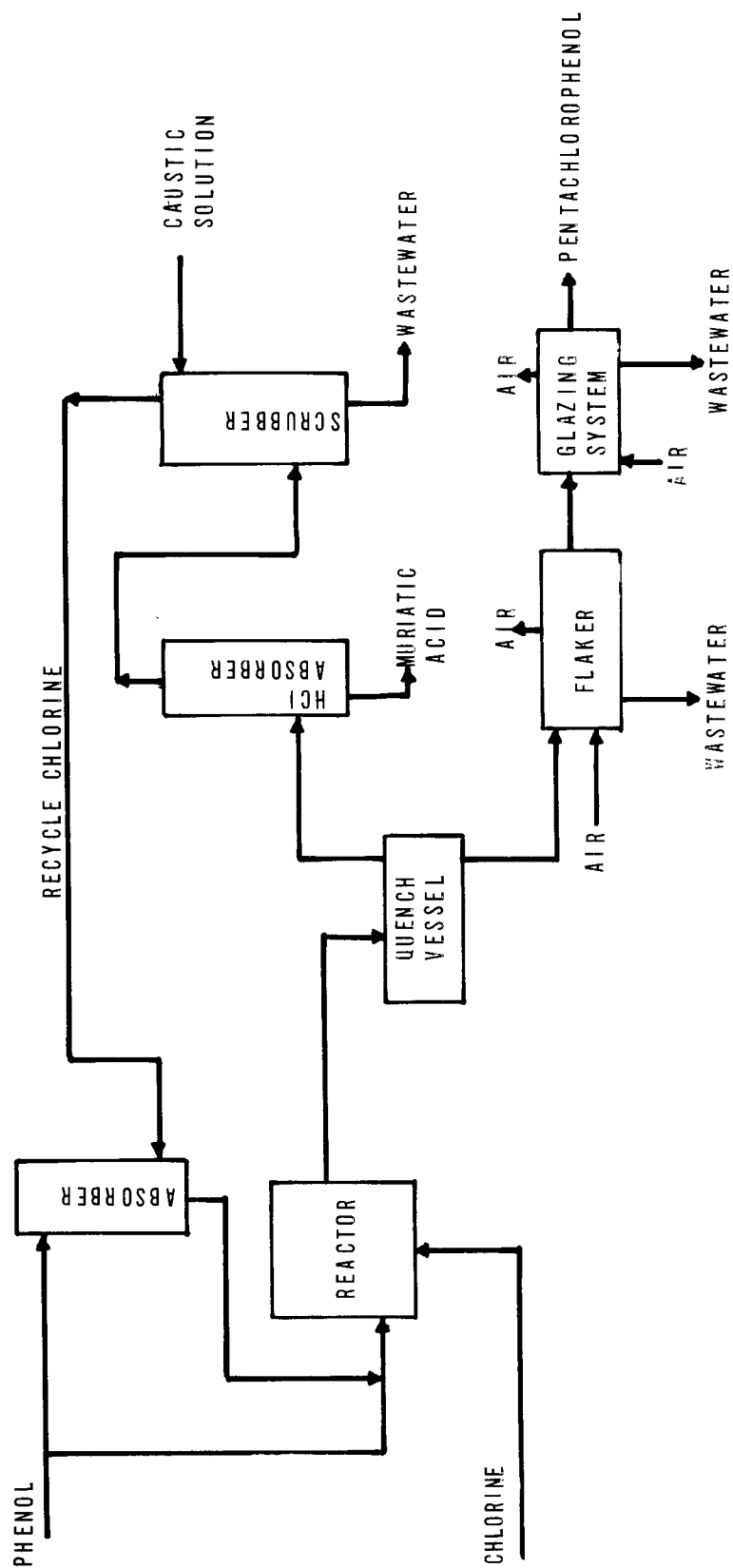
Product: Pigments

Process RWL Category: D

Pigments are various organic and inorganic insoluble substances. They
are used in surface coatings, and also in the ink, plastic, rubber, ceramic,
paper, and linoleum industries to impart color. A large number of pigments
are produced because different products require a particular choice of
material to give maximum coverage, economy, opacity, color, durability,
and desired reflectance.

Organic pigments may be subclassified into toners and lakes. Toners are
insoluble organic dyes that may be used directly as pigments because of
their durability and coloring power. Toners are used in paints, printing
inks, and wallpapers, and especially for the pigment printing method for
textiles, employing pigments of metal phthalocyanines and other types.
Lakes result from the precipitation of organic colors, usually of synthetic
origin, with salts of Ca, Ba, Cr, Al, or phosphomolybdic acid. The dye
molecule frequently contains -OH or -SO₃H groups. Such lakes, when ground
in oil or other media, form the pigments of many of our paints and inks.
Some basic dyes are used for the tinting of paper in a water-dispersed
form or phosphomolybdic (or tungstic) acid lakes. Wallpapers are fre-
quently colored with lakes from basic dyes containing a sulfonic group.
The use of pigments in the "dope" before spinning rayon, acetate, and
synthetic fibers is growing rapidly and is producing excellent colors
of outstanding all-around fastness.

One facility visited during the field survey produced toners for the pigment
printing of textiles. Figure 4-49 is a process flow diagram for the manu-
facture of this product. Hydrochloric acid, sodium nitrite, water, an
amine, and sulfamic acid are put into the first reactor. The coupler is
prepared in the second reactor; this entails the addition of a coupling
agent, sodium hydroxide, water, and steam. The reaction products from
both reactors then proceed to a third reactor, where they are combined
with acetic acid, sodium acetate, and water. The pigment which forms
in this reactor is filtered. The solid phase is recovered as the pigment
dye, while the mother liquor is discharged into the sewer.

Samples were obtained on two successive days to characterize the waste-
water from this process. The samples for the two days indicate that the
characteristics of the wastewater are quite variable, attributable mainly
to the batch nature of the operation. The second plant produced lakes
for use in paints.

The following tabulation of process RWL, calculated from flow measurements
and the analyses of the wastewater stream, includes data obtained for both
plants.

	Plant 1 (Toners)		Plant 2 (Lakes)
	1st Day	2nd Day	
PROCESS FLOW			
liter/kkg	313,000	313,000	1,000,000
gal/M lb	37,500	37,500	
BOD$_5$ RWL			
mg/l [1]	3,000	640	1,470
kg/kkg [2]	940	200	
COD RWL [1]			
mg/l [2]	11,300	1,000	4,930
kg/kkg	3,520	315	
TOC RWL			
mg/l [1]	750	570	819
kg/kkg [2]	235	178	

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weight of product.

The average of the two plants was considered as BPCTCA.

FIGURE 4-49

PIGMENT DIAZOTIZATION AND COUPLING
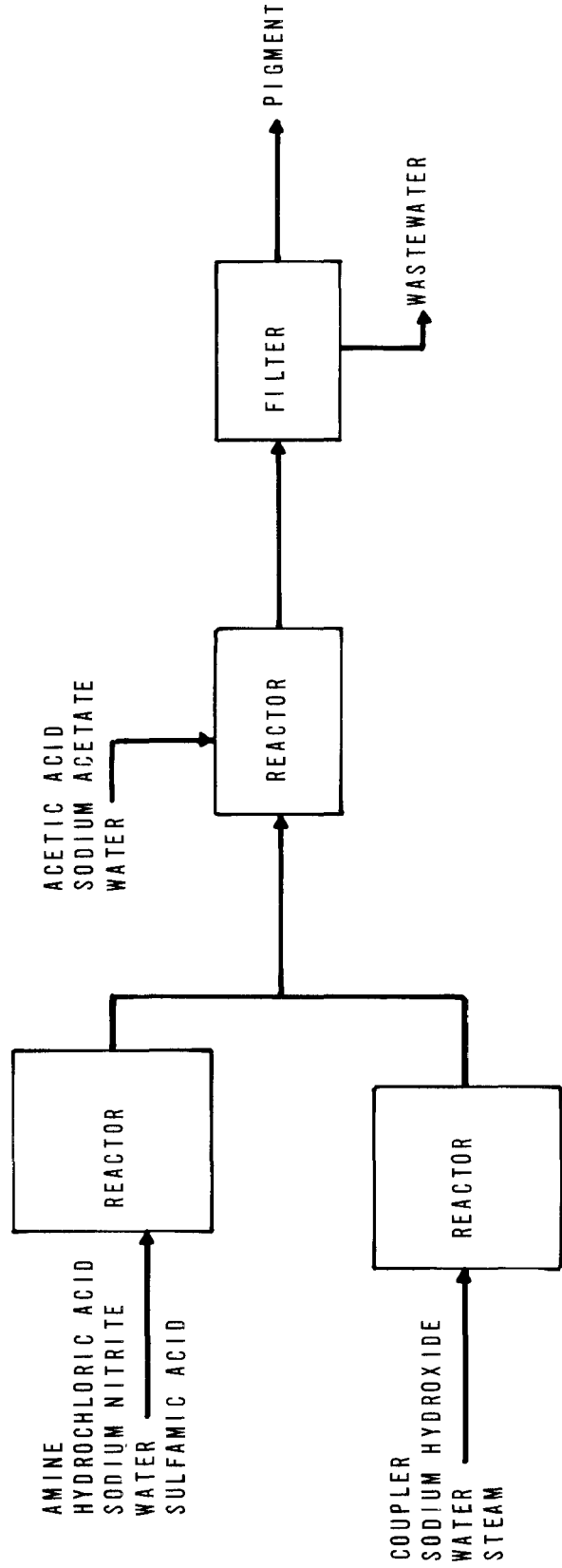
Product: Plasticizers

Process: Condensation of Phthalic Anhydride

Process RWL Category: D

Plasticizers are organic chemicals that are added to synthetic resins to improve workability during fabrication, to modify the natural properties of these resins, and to develop new improved properties not present in the original resins. This type of chemical is manufactured by liquid-phase batch reactions.

A generalized process flow diagram is shown in Figure 4-50, while the overall chemical reaction is given below:

$$C_6H_4C_2O_3 \quad + \quad 2ROH \quad \longrightarrow \quad C_6H_4C_2O_2(OR)_2 \quad + \quad H_2O$$

phthalic anhydride   alcohol   phthalate
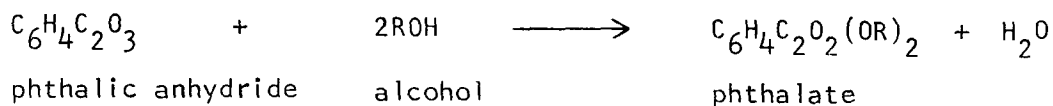
Feed materials, an alcohol and an anhydride, along with acid catalyst, are fed into a reactor. The esterification is carried out at a pressure of about 10 psig and at temperatures ranging from 104 to 356°F, for six to 20 hours, depending on the feed and the desired product. The reactor effluent is either sent directly to a wash tank or passed through a filter press to remove solids, depending on whether activated charcoal or a catalyst neutralizer is being added to the reactor.

Caustic soda (or soda ash) is used in the wash tank to remove unreacted acid and anhydride. Wastewater from the washing is sent to a series of settling tanks before being discharged to the sewer. Oil removed in the settling tanks is recycled back to the reactor.

The plasticizer stream from the wash tank flows to a stripper, where any remaining alcohol is taken overhead and recycled to the batch reactor. The main stream from the stripper is further polished by an activated carbon filter to obtain 99.5+% purity plasticizer.

Because the feed materials and desired products change, a large quantity of water for intermittent reactor clean-up is required. This clean-up water is the major source of wastewater pollution. The other two waste-water streams are wash water from the wash tank and backwash water from the filters. A high RWL for this type of operation is expected because of high loss of organics during the wash operations.

FIGURE 4-50

PLASTICIZERS—CONDENSATION OF PHTHALIC ANHYDRIDE
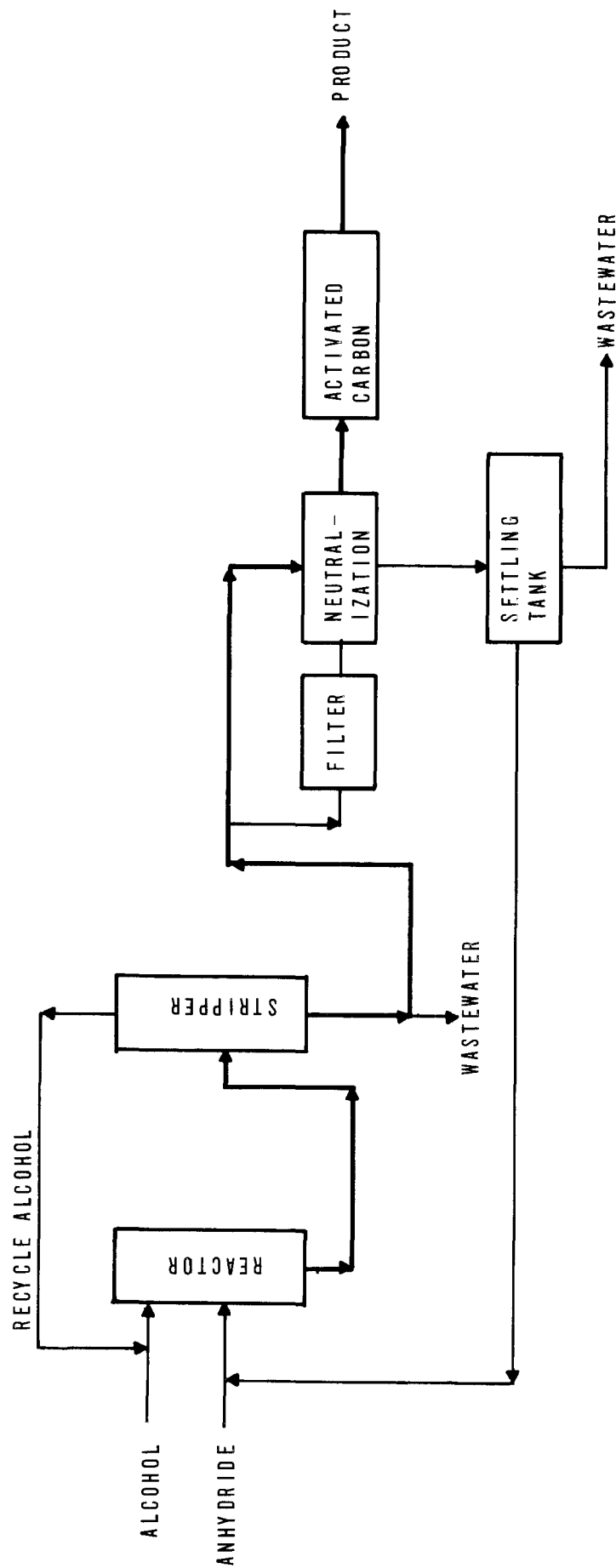
Product: Tannic Acid

Process: Extraction of Natural Vegetable Matter

Process RWL Category: D

Tannic Acid, a glucoside of gallic acid, can be obtained by extraction of natural vegetable matter with water. The water extract is then concentrated and upon drying yields technical tannin, which is used as a mordant in dyeing and as a source of gallic acid. Extraction of nutgalls with alcohol or other bleachings, or extraction with mild reducing agents (such as sodium bisulfite) and evaporation of the extract yield medicinal grade tannin. Tannic acid is commonly used for burns, as an astringent, in gargles, and to precipitate proteins in wineries and breweries.

Figure 4-51 shows a typical flow diagram for tannic acid manufacture. The raw materials (natural nutgalls) are fed into the preparation section and ground into small pieces. The ground material is then batchwise extracted with an organic solvent. The slurry raffinate phase is diluted with water, put through a steam stripper for solvent recovery, and discharged into the sewer. The extract phase, a mixture of organic solvent, extracted material, and a small amount of water, is steam stripped for removal of the solvent. The solvent is then condensed and recycled to the extraction step.

The steam-stripped aqueous solution containing tannic acid is cooled and passed through a filter press for removal of suspended solids. The filtrate (containing tannic acid) is concentrated in an evaporator before final drying and packaging. The evaporation step employs steam jets to pull a vacuum, and the gases are subsequently condensed in barometric condensers. Waters from the barometric leg are recycled to the cooling towers for reuse.

The major pollution source of the process is the slurry waste stream withdrawn as the bottom of the raffinate stripper. The intermittent reactor washings, as well as "battery limits" clean-up, also contribute to the RWL of the process. The amounts of contaminants were estimated to be 5 percent of that of the major waste stream. The results of the sampling survey are summarized in the following tabulation.

Process Flow	Tannic Acid		
	Sample Period #1	Sample Period #2	Sample Period #3
liter/kkg	10,000	10,000	10,000
gal/M lb	1,200	1,200	1,200
BOD_5 RWL			
mg/l[1]	16,100	14,700	15,100
kg/kkg[2]	161	147	151
COD RWL			
mg/l[1]	109,000	99,400	112,000
kg/kkg[2]	1,093	995	1,120
TOC RWL			
mg/l[1]	14,000	16,800	21,000
kg/kkg[2]	140	168	210

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

The water from the barometric condensers in the evaporation step was not included in the foregoing RWL calculations. Since the organics in the evaporation step are not volatile, the pollutant loading in the barometric water is low. Furthermore, this water has been totally recycled for re-use in the process.

The analytical results indicate that the high RWL of this process is attributable to the high suspended organic vegetable matter present in the slurry stream. The removal of suspended solids from this stream can substantially reduce the RWL of the process. As was indicated during the sampling survey, the following three possible methods for removal/disposal of suspended solids are being investigated.

1. Filtration and landfill disposal of Suspended Solids (SS).
2. Filtration and incineration of SS.
3. Filtration and recycle of SS into other industrial and/or agricultural uses.

The RWL of the process should be based on the amounts of contaminants in the filtrate, and is subject to further investigation.

Non-contact cooling water is employed in the solvent recovery area and prior to filtration. The total quantity of non-contact cooling water is estimated to be approximately 641 lbs per lb of product.

FIGURE 4-51

TANNIC ACID EXTRACTION OF NATURAL VEGETABLE MATTER
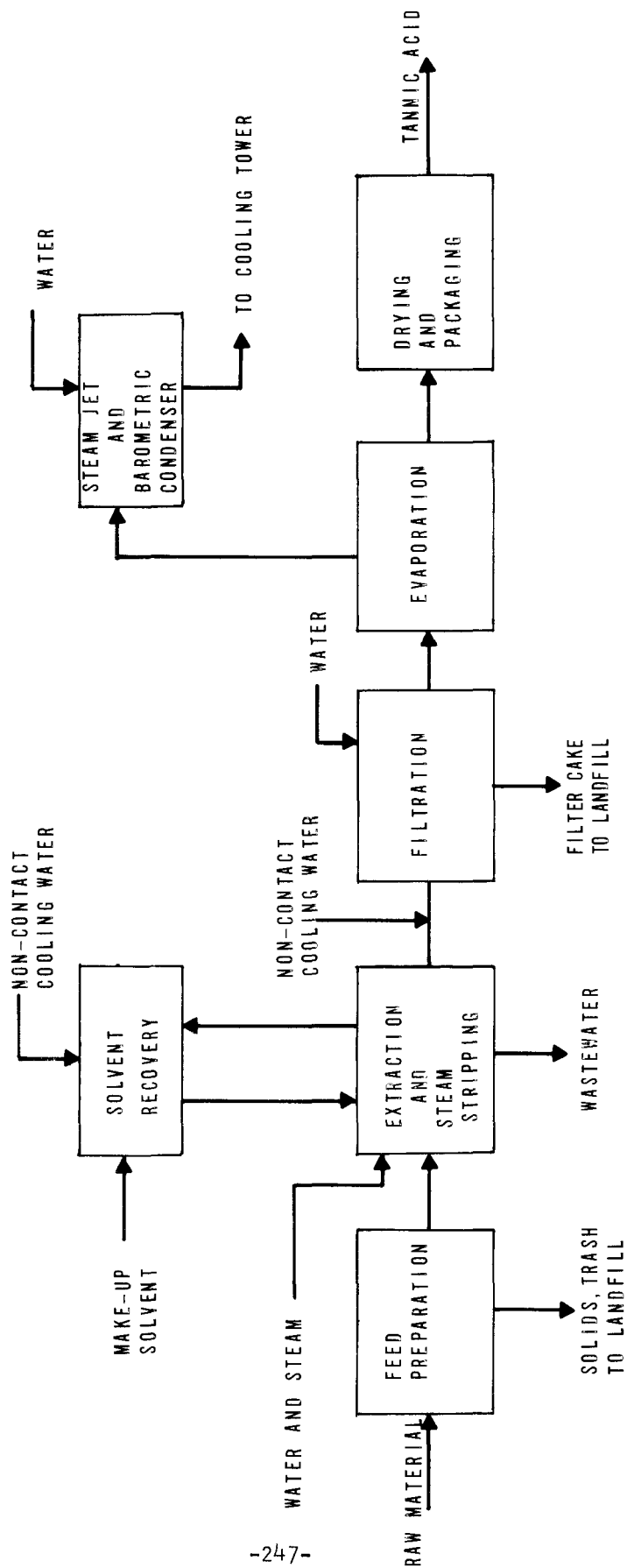
Product: Vanillin

Process: Alkaline oxidation of spent sulfite liquor

Process RWL Category: D

Chemical Reactions:

Spent sulfite liquor + O_2 + NaOH $\longrightarrow$ C_6H_3 (OCH$_3$) (CHO) OH

(lignosulfonic acid)   vanillin
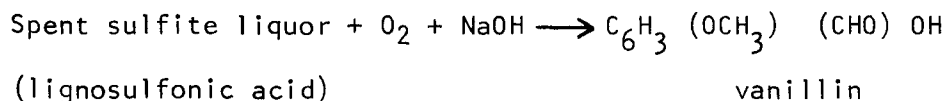
Vanillin is one of the most widely used food flavors. It is also used in perfumery and in the deodorizing of manufactured goods. During the plant visit, company representatives indicated that approximately one-third of the vanillin produced at this plant is used for flavor manufacture, with the remaining two-thirds used for perfumes and other miscellaneous items.

A typical process flow diagram for the manufacture of vanillin is shown in Figure 4-52.

Waste sulfite liquor containing about 15 percent sulfite solids (mainly lignosulfonic acid), supplied by paper mills, is treated with lime in a series of three tanks. In the first stage (pH = 10.5) calcium sulfate (principally) precipitates; in the second, the pH is increased to 12.0 to precipitate calcium lignosulfonate; in the third a further excess of lime is added. Thickened liquors from the third stage are then reused as a supplementary lime source in the first tank. The precipitated calcium lignosulfonate from the second tank is filtered under vacuum, and redissolved in a caustic soda solution to yield a solution containing 3.5 percent lignin solids and 10 percent caustic soda.

The alkaline solution is then pumped to a falling-film contactor countercurrent to a carefully controlled flow of air, which oxidizes the sulfonate to sodium vanillate. In one application of the process, the oxidation reaction is carried out at 1,500 psi and 225°C. Residence time of the liquid in the contactor is of the order of 4 minutes, with an overall liquor-oxygen ratio of 0.01 volume of liquor per volume of air (STP). At this rate, an 18 to 20 percent conversion of lignin to vanillin is effected, and overoxidation is minimized. Because the reaction is exothermic, the temperature of the effluent liquor rises to about 250°C. The vanillate from the oxidizer is then extracted with organic solvents, such as birtanol or isopropanol, by a conventional one- or two-stage countercurrent process. Both the extracted and raffinate phases are steam stripped to recover, respectively, organic solvents and vanillate, which are then recycled back to the process line. The vanillate separated from the organic solution is further purified by vacuum extractive distillation followed by acidification. Vanillin is then recovered by vacuum crystalization, centrifuging, and vacuum tray-drying.

The air oxidation process described has replaced a former process in which nitrobenzene was used as the oxidizing agent. Also, a Canadian plant has installed an air oxidation process similar to that described, but with lime replacing caustic as the alkaline agent. Other differences are the use of carbohydrate-free waste sulfite liquor from an alcohol plant, the use of toluene as the extracting agent, and vacuum distillation to separate vanillin from contaminating by-products.

The major pollution sources of the process are waters discharged from the pretreatment of sulfite solution, the raffinate stripper, the centrifuge filtration, and the steam jets connected with the barometric condensers. Additional process wastewaters are generated during spills and washings. Process RWL's calculated from the flow measurements and analyses of the aforementioned waste streams are presented in the following tabulation.

|	Sample period #1	Sample period #2
PROCESS FLOW		
liter/kkg	133,000	133,000
gal/Mlb	15,900	15,900
BOD$_5$ RWL		
mg/l[1]	17,900	17,500
kg/kkg[2]	2,380	2,320
COD RWL		
mg/l[1]	118,000	116,000
kg/kkg[2]	15,600	15,400
TOC RWL		
mg/l[1]	30,400	29,900
kg/kkg[2]	4,030	3,960

[1] Raw waste concentrations are based on unit weight of pollutant per unit volume of contact process wastewaters.
[2] Raw waste loadings are based on unit weight of pollutant per 1,000 unit weights of product.

The high raw waste loads shown in the tabulation may be explained by the fact that spent sulfite liquor is a waste product from paper mill operations containing 15 to 20 percent lignosulfonic acid. The reaction realizes a maximum of 15 to 20 percent yield, and the remaining unusable spent sulfite liquor must be discharged as a waste. The analytical results also indicate that, in addition to the parameters shown in the tabulation, pollution parameters such as dissolved solids, sulfate, and phenol concentrations are at levels hazardous to biological treatment processes.

No effluent limitations are proposed for this process because it is utilized by only one manufacturer in the United States.

The primary non-contact wastewater flows are cooling tower and boiler blowdown. Samples of the boiler blowdown have been taken, and the flow has been estimated. Samples of the cooling tower blowdown were not taken, because typical analyses were available and the flows are highly variable. The cooling tower make-up averages approximately 120 gpm and the cooling water makes approximately 3 cycles. A phosphate corrosion inhibitor and a biocide are added to the make-up.

FIGURE 4-52

VANILLIN — ALKALINE OXIDATION OF SPENT SULFURIC LIQUOR
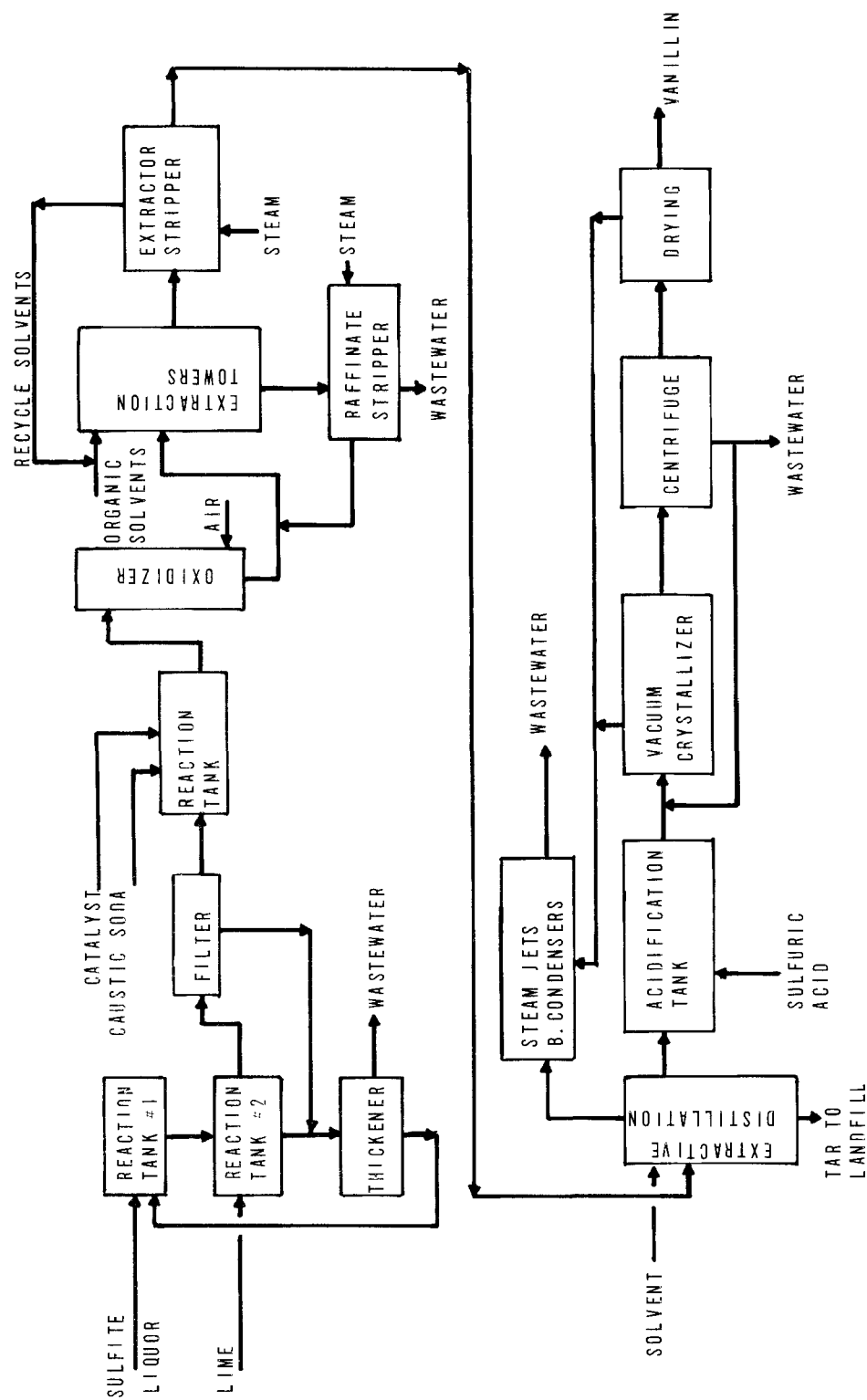
SECTION V

WASTE CHARACTERIZATION

The process RWL data obtained for each of the 54 Secondary Organic Products were discussed previously in Section IV - Industry Categorizations. These descriptions related the raw waste flows and loadings to specific sources such as chemical conversions and unit operations within each product/process grouping. The discussions in this section relate the single net of RWL values assigned to each product/process grouping, and compare waste loadings and concentrations between product/process groupings.

Tables 5-1, 2, 3, and 4 list the single set of BPCTCA-RWL values which has been assigned to each product/process grouping. These values include the following parameters:

> Contact Process Wastewater Flow (liters/kkg of product)
> BOD Raw Waste Load (kg BOD/kkg of product)
> COD Raw Waste Load (kg COD/kkg of product)
> TOC Raw Waste Load (kg TOC/kkg of product)

Although the sampling data indicate that in some cases there is considerable variation between two manufacturers who nominally operate the same process and between different time sampling periods for the same manufacturers, it was necessary to specify one set of values for each product/process grouping. This was done in the most equitable manner possible from the data available. Rather than arbitrarily choosing the lowest observed value for each product/process grouping, an effort was made to choose values which were considered consistent with BPCTCA in-process technologies.

The RWL data for each product/process grouping shown in Tables 5-1, 2, 3, and 4 have been inserted in the major process Subcategories A, B, C, and D. For orientations, concentrations have been calculated for the BOD parameters by dividing the BOD loading by the corresponding contact process wastewater flow. Examination of these data indicates quite a large spread in flows, loadings, and resulting concentrations.

It should be noted that the BOD concentrations shown are based on wastewaters coming directly from the process and do not necessarily represent the waste concentrations which a treatment plant would accept. If the plant manufactured a single product which generated concentrated wastes, these may be diluted with contaminated cooling wastes and steam condensate or other non-contact waters prior to biological treatment depending upon concentrations and economic considerations. In a multi-product plant, the concentrated wastewater could be diluted with less concentrated

Table 5-1

Major Subcategory A BPCTCA Process Raw Waste Loads

Product	Process Description	Flow L/kkg	BOD₅ (BPCTCA Process Raw Waste Loads)		COD		TOC	
			kg/kkg	(mg/L)	kg/kkg	(mg/L)	kg/kkg	(mg/L)
Cumene	Alkylation of Benzene by Propylene	0.334	<0.0001	(<300)	<0.0001	(<300)	<0.0001	(<300)
p-Zylene	Isomerization, Crystallization, and Filtration of Mixed Xylenes	44.3	0.01	(226)	0.025	(564)	0.007	(158)

Table 5-2

Major Subcategory B BPCTCA Process Raw Waste Loads

Product	Process Description	Flow L/kkg	BOD₅ (BPCTCA Process Raw Waste Loads)		COD		TOC	
			kg/kkg	(mg/L)	kg/kkg	(mg/L)	kg/kkg	(mg/L)
Adiponitrile	Chlorination of Butadine	9,770.	19.2	(1,970)	135.	(13,800)	44.	(4,500)
Benzoic Acid and Benzaldehyde	Catalytic Oxidation of Toluene With Air	2,840.	25.6	(9,010)	50.8	(17,900)	19.6	(6,900)
Chlorinated Methanes	Chlorination of Methyl Chloride & Methane Mixture	2,820.	0.22	(78)	0.94	(333)	0.37	(131)
*Chlorobenzene	Chlorination of Benzene	-	-	-	-	-	-	-
Chlorotoluene	Chlorination of Toluene	525.	0.24	(2)	1.82	(15)	0.24	(2)
Diphenylamine	Deamination of Aniline	121,000.	0.087	(165)	0.313	(595)	0.228	(433)
Hexamethylene Diamine	Hydrogenation of Adiponitrile	1,700.	60.8	(35,800)	114.	(67,100)	41.7	(24,500)
Hexamethylene Diamine	Ammonolysis of 1,6 - Hexanediol	1,100.	4.0	(3,640)	11.7	(10,600)	2.5	(2,270)
Maleic Anhydride	Oxidation of Benzene	4,430.	263.	(59,400)	440.	(99,300)	138.	(31,200)
Methyl Chloride	Esterification of Methanol with Hydrochloric Acid	12,000.	17.7	(1480)	62.7	(5,230)	12.8	(1,070)
Methyl Ethyl Ketone	Dehydrogenation of Sec. - Butyl Alcohol	1,050.	37.5	(35,700)	103.	(98,100)	40.2	(38,300)
Perchloroethylene	Chlorination of Chlorinated Hydrocarbons	5,400.	0.44	(81)	2.83	(524)	0.17	(31)
*Phthalic Anhydride	Oxidation of Naphthalene	All	Waste	All	Waste	Incinerated		
Phthalic Anhydride	Oxidation of o-Xylene	594.	0.128	(215)	0.642	(1,080)	0.02	(34)
Tricresyl Phosphate	Condensation of Cresol and Phosphorus Oxychloride	28,000.	1.12	(40)	11.4	(407)	1.96	(70)

*Not placed in Subcategory

Table 5-3

Major Subcategory C BPCTCA Process Raw Waste Loads

Product	Process Description	Flow L/kkg	BPCTCA Process Raw Waste Loads					
			BOD5		COD		TOC	
			kg/kkg	(mg/L)	kg/kkg	(mg/L)	kg/kkg	(mg/L)
*Acetic Esters								
Ethyl Acetate	Esterification of Ethyl Alcohol with Acetic Acid	1,294.	0.049	(38)	0.102	(79)	0.034	(26)
Propyl Acetate	Esterification of Propyl Alcohol with Acetic Acid	1,186.	0.009	(8)	0.012	(10)	0.005	(4)
Acrylonitrile	Ammoxidation of Propylene	4,210.	60.	(14,300)	179.	(42,500)	78.	(18,500)
p-Aminophenol	Catalytic Reduction of Nitrobenzene	15,000.	888.	(59,200)	1,620.	(108,000)	456.	(30,400)
Calcium Stearate	Neutralization of Stearic Acid	54,100.	13.8	(255)	32.8	(606)	23.1	(427)
Caprolactam	DSM Caprolactam Process	29,100.	47.1	(1,620)	93.0	(3,200)	-	-
Cyclohexanone Oxime	Hydroxylamine Process	1,910	-	-	6.29	(3,290)	-	-
Cresol, Synthetic	Methylation of Phenol	2,090.	297.	(142,000)	632.	(302,000)	217.	(104,000)
Formic Acid	Hydrolysis of Formamide	134,000.	1.05	(7.8)	4.5	(34)	1.4	(10)
Hexamethylene Tetramine	Synthesis with Ammonia	6,040.	83.3	(13,800)	229.	(37,900)	71.0	(11,800)
Hydrazine Solutions	The Raschig Process and Formaldehyde	30,300.	9.09	(300)	115.	(3,800)	0.182	(6)
Isobutylene	Extraction from a Mixture of C_4 Hydrocarbons	20,400	13.6	(668)	64.1	(3,140)	12.9	(632)
Isopropanol	Hydrolysis of Propylene	2,540.	0.995	(392)	2.99	(1,180)	1.32	(520)
*Organic Solvent Complex		3,640	-	-	-	-	23.3	(6,400)
Oxalic Acid	Nitric Acid Oxidation of Carbohydrates	437,000.	390.	(38,200)	4.36	(10)	1.31	(3)
Pentaerythritol	Aldehyde Condensation	10,200.	390.	(38,200)	1,590.	(156,000)	830.	(81,400)
*Propylene Glycol	Hydrolysis of Propylene Oxide	5,500.	0.016	(3)	0.055	(10)	0.006	(1)
Propylene Oxide	Chlorohydrin Process	63,500.	31.5	(496)	143.	(2,250)	22.7	(357)
Saccharin	Synthesis from Phthalic Anhydride Derivatives	269,000.	253.	(9,400)	879.	(3,270)	384.	(1,430)
Sec. Butyl Alcohol	Sulfonation and Hydrolysis of Mixed Butylenes	32,800.	19.3	(588)	126.	(3,840)	33.1	(1,010)

*Not Placed in Subcategory

Table 5-4

Major Subcategory D BPCTCA Process Raw Waste Loads

Product	Process Description	Flow L/kkg	BOD5 kg/kkg	(mg/L)	COD kg/kkg	(mg/L)	TOC kg/kkg	(mg/L)
Citric Acid	Fermentation of Molasses	477,000	328.	(688)	657.	(1,380)	242.	(507)
Citronellol and Geraniol	Citronella Oil Distillation	10,100.	58.1	(5,750)	111.	(11,000)	37.7	(3,740)
Dyes and Dye Intermediate	Batch Manufacture	395,000.	397.	(1,010)	2,060.	(5,220)	775.	(1,960)
Fatty Acids	Hydrolysis of Natural Fats	28,000.	18.1	(646)	37.6	(1,340)	9.8	(350)
Fatty Acid Derivatives		6,400.	18.	(2,810)	27.9	(4,360)	8.47	(1,320)
Ionone and Methylionone	Condensation and Cyclization of Citral	9,370.	23.0	(2,450)	94.0	(10,000)	33.0	(3,520)
*Methyl Salicylate	Esterification of Salicylic Acid with Methanol	–	–	–	–	–	–	–
*Miscellaneous Batch Chemicals								
Monosodium Glutamate	Fermentation of Beet Sugar Molasses	67,000.	84.7	(1,260)	284.	(4,240)	91.	(1,360)
Naphthenic Acid	Extraction and Acidification of Caustic Sludge from Petroleum Refinery	39,700.	141.	(3,550)	298	(7,510)	104	(2,620)
o-Nitroaniline	Ammonolysis of o-Nitrochlorobenzene	269,000.	16.9	(63)	105	(390)	30.9	(115)
p-Nitroaniline	Ammonolysis of p-Nitrochlorobenzene	39,100.	2.55	(65)	79.1	(2,020)	22.2	(568)
*Pentachlorophenol	Chlorination of Phenol	2,960.	0.941	(318)	17.5	(5,910)	2.29	(774)
Pigments	Diazotization and coupling of amine, sulfuric, etc.	658,000.	385	(585)	3,422	(5,200)	513	(780)
Plasticizers	Condensation of Phthalic Anhydride	650.	53.9	(82,900)	82.6	(127,000)	33.4	(51,400)
Tannic Acid	Extraction of Natural Vegetable Matter	10,000.	153	(15,300)	1,070.	(107,000)	173.	(17,300)
*Vanillin	Alkaline Oxylation of Spent Sulfite Liquor	134,000.	2,313.	(17,300)	15,400	(115,000)	3,960.	(29,600)

*Not placed in Subcategory

wastes from other processes. The point to be kept in mind here is that calculated concentrations for individual product/process groupings can not be correlated with real situations in existing process plants unless a complete case study, considering the total mix of processes which are operated, is developed for each plant.

This same argument extends to hypothetical process effluents obtained by applying a reduction factor to the process RWL. An effluent concentration calculated by dividing the process effluent loading by the process contact wastewater flow is meaningless, because in almost all instances the actual treatment plant which accomplishes the percent removal or waste reduction will be accepting the combined wastes from multiple processes whose overall concentrations are lower because of the inclusion of products/processes of lesser loads and slightly contaminated wastes such as steam condensate, pump seals, etc.

The large spread in RWL within the major process subcategories has led to the establishment of additional subcategories. Tables 5-5, 6, 7 and 8 list the new subcategories which have been derived from the previous major process categories. From the 54 product/process groupings considered in Phase 2, the RWL data from 44 were considered as adequate for the ultimate determination of effluent limitation guidelines. In order to make these guidelines as equitable as possible, 13 new subcategories were considered necessary to subdivide the 44 product/process groupings. This number of groupings was necessary so as not to penalize a product/process which had reached the degree of inplant control commensurate with BPCTCA.

Examination of Tables 5-5, 6, 7, and 8 shows that the new subcategories have been established based on similarities in waste loadings for BOD, COD, and TOC. Effluent limitations were then calculated for each of the new subcategories by applying reduction factors to the calculated mean RWL.

Table 5-5

Subcategory A BPCTCA - RWL

Subcategory A-2	Flow L/kkg	BOD$_5$ kg/kkg	COD kg/kkg	TOC kg/kkg
Cumene	0.334	< 0.0001	< 0.0001	< 0.0001
p-Xylene	44.3	0.01	0.025	0.007

Table 5-6

Subcategories B-3, B-4, B-5 BPCTCA - RWL

Subcategory B-3	Flow L/kkg	BOD$_5$ kg/kkg	COD kg/kkg	TOC kg/kkg
Chloromethanes	2,820.	0.220	0.940	0.370
Chlorotoluene	121,000.	0.24	1.82	0.24
Diphenylamine	526.	0.087	0.313	0.228
Perchloroethylene	5,400.	0.44	2.83	0.170
Phthalic Anhydride (o-Xylene)	594.	0.128	0.642	0.02
Tricresyl Phosphate	28,000.	1.12	11.4	1.96
MEAN	2,340	0.373	2.99	0.498

Subcategory B-4				
Adiponitrile	9,770.	19.2	135.	44.
Benzoic Acid & Benzaldehyde	2,840.	25.6	30.8	19.6
HMDA (hexanediol)	1,100.	4.0	11.7	2.50
Methylchloride	12,000.	17.7	62.7	12.8
MEAN	6,430.	16.6	65.1	19.7

Subcategory B-5				
HMDA (Adiponitrile)	1,700.	60.8	114.	41.7
Maleic Anhydride	4,430.	263.	440.	138.
Methyl Ethyl Ketone	1,050.	37.5	103.	40.2
MEAN	2,390.	120.	219.	73.3

Table 5-7

Subcategories C-3, C-4, C-5, C-6, C-7 BPCTCA - RWL

Subcategory C-3	Flow L/kkg.	BOD_5 kg/kkg	COD kg/kkg	TOC kg/kkg
Cyclohexane Oxime	1,910.	-	6.29	-
Isopropanol	2,540.	0.995	2.99	1.32
MEAN	2,230.	0.995	4.64	1.32

Subcategory C-4				
Formic Acid	134,000.	1.05	4.5	1.4
Oxalic Acid	437,000.	1.31	4.36	1.31
MEAN	285,000.	1.18	4.43	1.36

Subcategory C-5				
Calcium Stearate	54,100.	13.8	32.8	23.1
Caprolactam (DSM)	29,100.	47.1	93.	-
Hydrazine Solutions	30,300.	9.09	115.	-
Isobutylene	20,400.	13.6	64.1	12.9
Propylene Oxide	63,500.	31.5	143.	22.7
Sec. Butyl Alcohol	32,800.	19.3	126.	33.1
MEAN	38,400.	22.4	95.7	23.0

Subcategory C-6				
Acrylonitrile	4,210.	60.	179.	78.
Hexomethylene Tretramine	6,040.	83.3	229.	71.
MEAN	5,130.	71.7	204.	74.5

Subcategory C-7				
p-Aminophenol	15,000.	888.	1,620.	456.
Cresol, Synthetic	2,090.	297.	632.	217.
Pentaerythritol	10,200.	390.	1,590.	830.
Saccharin	26,900.	253.	879.	384.
MEAN	13,500.	457.	1,180.	472.

Table 5-8

Subcategories D-1, D-2, D-3, D-4   BPCTCA - RWL

Subcategory D-1	Flow L/kkg	BOD$_5$ kg/kkg	COD kg/kkg	TOC kg/kkg
o-Nitroaniline	269,000	16.9	105.	30.9
p-Nitroaniline	39,100	2.55	79.1	22.2
MEAN	154,000	9.73	92.	26.5

Subcategory D-2				
Citronellol and Geraniol	10,100.	58.1	111.	37.7
Fatty Acids	28,000.	18.1	37.6	9.8
Fatty Acid Derivatives	6,400.	18.	27.9	8.47
Ionone and Methyl Ionone	9,370.	23.	94.	33.
MEAN	13,500.	29.3	67.6	22.2

Subcategory D-3				
Plasticizers	650.	53.9	82.6	33.4
MEAN	650.	53.9	82.6	33.4

Subcategory D-4				
Citric Acid	477,000.	328.	657.	242.
Dyes and Intermediates	395,000.	397.	2,060.	775.
Naphthenic Acid	39,700.	141.	298.	104.
Pigments	658,000.	385.	3,422.	513.
Sodium Glutamate	67,000.	84.7	284.	91.
Tannic Acid	10,000.	153.	1,070.	173.
MEAN	274,000	248.	1,300.	316.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Twenty-eight parameters were examined during the field data collection program. These parameters are listed in Table 6-1, and all field sampling data are summarized in Supplement B.

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

1.   Pollutants of Significance.

2.   Pollutants of Limited Significance.

The rationale and justification for pollutant categorization 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 light of the current knowledge as to their limitations from an analytical as well as from an environmental standpoint.

Pollutants observed from the field data that were present in sufficient concentrations so as to interfere with, be incompatible with, or pass inadequately treated through 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 BOD and TSS.

The reason for expressing the effluent limitations in terms of only one oxygen-demanding parameter is that almost all the biological treatment plants observed during the study were designed on the basis of one controlling design parameter. Survey data indicates that the parameter most widely used was BOD. This is also the argument why multiple effluent limitations are ambiguous. Most of the biological plants surveyed were not designed specifically to remove any parameter but BOD and TSS. Therefore biological treatment plant effluent concentrations reported in subsequent sections for other parameters do not reflect optimal removal kinetics. The use of the BOD parameter is logical since almost all stream assimilation capacities are assessed on the basis of ultimate BOD. It has only been in recent years that effects of refractory organics as measured by COD and TOC have been of concern in water quality analyses.

Table 6-1

List of Pollutants and Indicators of Pollution
Examined for the Organic Chemicals Industry

Chemical Oxygen Demand	Total Dissolved Solids
Biochemical Oxygen Demand	Chlorides
Total Organic Carbon	Hardness - Total
Total Suspended Solids	Total Phosphorus
Oil (Freon extractables)	Calcium
Ammonia Nitrogen	Magnesium
Total Kjeldahl Nitrogen	Zinc
Phenol	Copper
Cyanide - Distillation	Iron
Color	Chromium - Total
Sulfate	Cadmium
pH	Cobalt
Acidity	Lead
Alkalinity	Nickel

Possible biological inhibition associated with the product/processes surveyed will be discussed in the latter part of this Section.

BOD

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

The major objections are as follows:

1. The standard BOD 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 BOD test, seed culture (microorganisms) is added to the BOD bottle. If the seed culture was not acclimated, i.e., exposed to a similar wastewater in the past, then it may not readily biologically degrade the waste. This results in the reporting of a low BOD 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 reviewing agencies to duplicate industrial BOD values unless great care is taken in seed preparation.

3. The BOD test is sensitive to toxic materials, as are all biological processes. Therefore, if toxic materials are present in a particular wastewater, the reported BOD value may very well be erroneous. This situation can be remedied by running a microorganism 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 BOD as 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 BOD 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 wastewater. The use of COD or TOC to monitor the efficiency of BOD removal in biological treatment is possible only if there is a good correlation between COD or TOC and BOD. Under normal circumstances, two correlations would be necessary, one for the raw wastewater and one for the treated effluent. 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 and disadvantages, the BOD parameter should continue to be used as the pollutional indicator for the organic chemicals industry.

COD

Chemical oxygen demand (COD) provides a measure of the equivalent oxygen required to oxidize the organic material present in a wastewater, under acidic 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 and produce erroneous results. In the case of chlorides, this problem can be eliminated with the addition of mercuric sulfate.

Standard Methods for the Examination of Water and Wastewater, the principal reference for analytical work in this field, cautions that aromatic compounds and straight-chain aliphatic compounds, both prevalent in the organic chemicals industry, are not completely oxidized during the COD test. The addition of silver sulfate, a catalyst, aids in the oxidation of the straight-chain alcohols and acids, but does not affect aromatic hydrocarbons. The exact extent of this partial oxidation has not been documented in the literature.

TOC

Total organic carbon (TOC) is a measure of the amount of carbon in the organic material in a wastewater sample. The TOC analyzer withdraws a small volume of sample and thermally oxidizes it at $150^{\circ}C$. The water vapor and carbon dioxide from the combustion chamber (where the water vapor is removed) is condensed and sent to an infrared analyzer, where the carbon dioxide is monitored. This carbon dioxide value corresponds to the total inorganic value. Another portion of the same sample is thermally oxidized at $950^{\circ}C$, which converts all the carbonaceous material; this value corresponds to the total carbon value. TOC is determined by subtracting the inorganic 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 adsorption band of carbon dioxide and can therefore inflate the reported value.

2. The sample volume involved in the TOC analyzer is so small (approximately 40 microliters) that it can easily become contaminated, with dust, for example.

3. Industrial wastes from the organic chemicals industry with low vaporization points may vaporize before 150°C and therefore be reported as inorganic carbon.

TSS

Total suspended solids (TSS) is a measure of the organic and inorganic solids removed when filtered through a preformed glass fiber mat in a Gooch crucible. As in the Phase 1 study, the TSS RWL's for the organic chemicals industry are characteristically low. TSS RWL values for the Phase 2 products surveyed are presented in Tables 6-2 through 6-5. The following is a summary of specific products with significant TSS RWL's:

Subcategory	Product	RWL Concentration mg/L
B	Maleic Anhydride	2,380
B	Chloromethanes	1,170
B	Methyl Chloride	1,380-7,100
C	Hydrazine	1,180
C	Acrylonitrile	630
C	Propylene Oxide	4,520
D	Fatty Acids and Derivatives	57-3,840
D	Sodium Glutamate	2,260
D	Para-nitro-analine	1,430

Since TSS RWL's are not generally significant throughout the industry, it is not meaningful to set an effluent limitation in terms of lbs/1,000 lbs product because the RWL TSS data are so low. The problem is that much of the TSS eventually discharged to surface waters are biological solids which have been produced in the end-of-pipe biological treatment facilities and only a fraction of which are finally removed before discharge. To minimize this problem, the effluent limitations will be based on a concentration value which will be attainable with adequate solids handling facilities. This subject is discussed in detail in Section VII.

Table 6-2

Miscellaneous RWL for Category A

	Phase II Data		Supplementary Phase I RWL Data				
	p-Xylene	Cumene	BTX	BTX	BTX	Ethyl Benzene	Ethyl Benzene
Flow, gal/1,000 lbs	5.25	.04	87.5	52.3	5.56	55.5	39.7
Phenol							
mg/l	.16	14.6	.155	1.98	.2	1.94	1.03
kg/kkg	.00001	Negligible	.00009	.00087	.00001	.00069	.000335
NH_3-N							
mg/l	1.0	3.4	1.27	18.0	142.7	13.2	11.8
kg/kkg	.00005	Negligible	.0010	.00785	.00662	.00546	.00387
TKN							
mg/l	3.12	8.2	4.05	49.3	322.4	18.2	105.5
kg/kkg	.00013	Negligible	.0028	.0215	.0154	.00772	.0355
CN							
mg/l		.02			.818		
kg/kkg		Negligible			.00004		
Sulfate							
mg/l	2.6	12.3	140	5,860	1,400	23.9	12.8
kg/kkg	.00011	Negligible	.0872	2.56	.0649	.0160	.00578
Oil							
mg/l	746	21	251	26	9	55	9
kg/kkg	.0327	Negligible	.709	.011	.0004	.0318	.00298
T-P							
mg/l	4.76	.005	.45	1.112	.033	.079	.0178
kg/kkg	.00021	Negligible	.00035	.00049	.00000	.00004	.00006
Zn							
mg/l	.287	.13	1.49	.116	.343	2.46	30.5
kg/kkg	.00001	Negligible	.00095	.00005	.00002	.00087	.0102
Cu							
mg/l	.44	.05	< .08	.09	.05	.18	21.5
kg/kkg	.00002	Negligible	< .00006	.00004	.00000	.00006	.00721
Fe							
mg/l	2.30	109	1.45	13.8	1.57	2.55	7.9
kg/kkg	.00010	.00003	.00090	.006	.00007	.00096	.00149
Cr-Total							
mg/l	2.50	.01	5.16	.171	.01	1.26	.807
kg/kkg	.00011	Negligible	.00315	.00008	.00000	.00089	.00027
Cd							
mg/l	< .05	.01	< .05	.127	.01	.052	.051
kg/kkg	0	Negligible	< .00005	.00006	.00000	.00003	.00002
TSS							
mg/l	17.3	100	44.5	331	9	61.5	5
kg/kkg	.00076	.00003	.0270	.1445	.0004	.0254	.00172
TDS							
mg/l	162	138	2,045	47,600	21	20,300	13,200
kg/kkg	.0711	.00004	.343	20.8	.00097	6.68	4.44
Cl⁻							
mg/l	32	37	168	3,280	36	4,410	50,800
kg/kkg	.0014	.00001	.103	1.43	.00169	1.48	16.9

Table 6-3

Miscellaneous RWL for Category B

Product	Flow gal/1000 lb	Phenol mg/l	Phenol kg/kkg	NH_3-N mg/l	NH_3-N kg/kkg	TKN mg/l	TKN kg/kkg	CN mg/l	CN kg/kkg
Benzoic Acid via Benzene	340	.16	.00044	<15.3	0.043	33.5	.095	0	0
Maleic Anhydride via Benzene	788	2.10	.014	16.6	.109	16.6	.109	---	---
Maleic Anhydride via Benzene	274	1.47	.0034					---	---
Adiponitrile	1170	.103	.00102	1,940	18.9	3,730	36.4	187	1.83
Chloromethanes	336	.03	.00007	.7	.00191	2.1	.00591	---	---
Chloromethanes	71.6	.035	.00002	1.95	.00116	6.05	.0036	---	---
Chlorotoluene	14,500	.04	.00436	---	---	---	---	---	---
Methyl Ethyl Ketone	156	.01	.00001	<1.4	<.0018	5.2	.0068		
Methyl Ethyl Ketone				2.1	.00167	4.5	.00355		
Diphenylamine	63			15,500	8.15	16,700	8.78		
HMDA (Adiponitrile)	203	.638	.00108	4,540	7.69	4,000	6.78	.638	.00108
HMDA (Adiponitrile)	121	.073	.00073	3,080	3.1	4,400	4.44	16.7	.0202
Hexamethylene Diamene (Hexanediol)	132	.01	.00001	7,630	8.40	9,170	10.10		
Methyl Chloride	1,430	.01	.00011	.1	.0012	1.9	.0230		
Methyl Chloride	101	.07	.00006	1.9	.0016	69.3	.0585		
Methyl Chloride	69.9	.05	.00003	.55	.000325	1.9	.00110		
Perchloroethylene	642	.09	.00048	.2	.00107	4.6	.0247		
Phthalic Anhydride (o-xylene)	71.2	.21	.00013	10.4	.00618	18.8	.0112		
Tricresyl Phosphate	3,350	10.8	.304	3.65	.102	11.8	.344		
Supplementary Phase I RWL Data									
Acetone	276			0	0	1.8	.0041		
Ethylene Dichloride	28.2	.27	.00006	10.4	.0024	17.9	.0042		
Vinyl Chloride	17.0	<.01	0	.7	.00079	4.6	.00066		
Vinyl Chloride	135	.36	.00040	23.5	.143	2.85	.00379		
Styrene	733	1.83	.0112	5.15	.00763	29.8	.182		
Styrene	250	1.13	.00252			12.3	.0364		

Table 6-3
(continued)

Miscellaneous RWL for Category B

Product	Fe mg/l	Fe kg/kkg	Cr-Total mg/l	Cr-Total kg/kkg	Ca mg/l	Ca kg/kkg	TSS mg/l	TSS kg/kkg	TDS mg/l	TDS kg/kkg	Cl^- mg/l	Cl^- kg/kkg
Benzoic Acid via Benzene	.78	.00222	.076	.00022	.10	.00029	118	.334	34,900	98.9	290	.823
Maleic Anhydride via Benzene	101	.665			.42	.0028	17	.109	56,000	371		
Maleic Anhydride via Benzene	30	.069	1.74	.0040	<.05	<.00011	2,380	5.44	53,700	122	18	.0421
Adiponitrile	1.58	.0154	.0973	.000953	.161	.00156	56.3	.55	124,000	1,210	83,400	814
Chloromethanes	14.3	.0403	7.7	.0217	.050	.00014	89	.251	28,300	79.3	3,570	2.12
Chloromethanes							1,170	.702	4,100	2.45	325	39.3
Chlorotolulene									467	56.5		
Methyl Ethyl Ketone	.68	.00054	.05	.00004	.05	.00004					56	.0446
Methyl Ethyl Ketone	.29	.000155	.05	.00003	.05	.00003						
Diphenylamine							8.5	.00447	16	.00842	6,300	17.6
HMDA (Adiponitrile)	.30	.00219	.141	.00024	.05	.000085	53.5	.0905	3,600	6.10	26	.0437
HMDA (Adiponitrile)	1.11	.000113	.053	.000053	.05	.00005	4	.00404	535	.541	489	.492
Hexamethylene Diamene (Hexanediol)	.25	.00028	.027	.00003	.027	.00003	28	.333	29	.0316	5,190	5.71
Methyl Chloride	5.81	.0695	.050	.00060	.052	.00062	7,100	6.001	336	4.01	11,500	137
Methyl Chloride	18.8	.0159	.644	.00054	.050	.00004	1,380	.802	23,500	19.8	2,760	2.330
Methyl Chloride	4.12	.0024	.088	.00005	.215	.000125			117,000	68.1	----	----
Perchloroethylene	5.98	.0321	9.45	.0507	.05	.00027	25.5	.136	1,700	9.20	33,600	180
Phthalic Anhydride (o-xylene)	.5	.0003	4.01	.00238	.01	.00001	29	.0172	541	.321	92	.0547
Tricresyl Phosphate	1.31	.0366	.041	.00115	.041	.00115	4	.110	615	17.2	2,560	71.5
Supplementary Phase I RWL Data												
Acetone	37.7	.0089					14.5	.00341	46,000	10.8	18,900	4.45
Ethylene Dichloride			.05	.00001	.10	.00002						
Vinyl Chloride	2.06	.00029	.06	.00001	.05	.00001	26	.00369	85,200	12.1	18,900	4.45
Vinyl Chloride	13.6	.0153	2.55	.00287	.05	.00006	68	.0766	13,300	15.0	11,300	12.7
Styrene	.33	.00199	.056	.00034	<.05	.00031	8.5	.0504	69.8	.263	7.7	.0472
Styrene	7.9	.00149	.015	.00002	.055	.000025	1,230	.118	42.5	.114	3.5	.0072

Table 6-3
(continued)

Miscellaneous RWL for Category B

Product	Sulfate mg/l	Sulfate kg/kkg	Oil mg/l	Oil kg/kkg	T-P mg/l	T-P kg/kkg	Zn mg/l	Zn kg/kkg	Cu mg/l	Cu kg/kkg
Benzoic Acid via Benzene	36.3	.103	43	.121	.27	.00078	4.19	.012	.06	.00017
Maleic Anhydride via Benzene			482	3.17	137	.902	5.42	.036	2.20	.014
Maleic Anhydride via Benzene			2,020	4.62			.26	.00059	.17	.00039
Adiponitrile	156	1.53	1,270	12.400	12.3	.12	.328	.0032	48	.479
Chloromethanes	349	.98	12	.0335	.678	.00190	5.16	.0145	.19	.00054
Chloromethanes	2,590	10.5	0	.00017	.12	.000075	8.06	.00482		
Chlorotoluene	28.0	3.39	---	---	---	---	---	---	.15	.0182
Methyl Ethyl Ketone	1.20	.0016	441	.576	.005	.00001	.49	.00039	.08	.00006
Methyl Ethyl Ketone	1.0	.00079	280	.222	.02	.00002	.085	.000045	.05	.00003
Diphenylamine	1.0	.00053	18	.0096	1.057	.00056	---	---		
HMDA (Adiponitrile)	5.12	.00869	1,380	2.33	.375	.000635	74.5	.000125	.185	.00032
HMDA (Adiponitrile)	15.7	.0158	1,270	12.3	2.03	.00205	.28	.000283	.05	.00005
Hexamethylene Diamene (Hexanediol)	.538	.00059	36	.0398	.212	.00023	.022	.00002	.08	.00003
Methyl Chloride	3,020	36	460	5.500	.057	.00068	14	.168	.07	.00084
Methyl Chloride	482	8.85	33	.0278	.172	.00015	23.6	.200	26.3	.0223
Methyl Chloride	5,800	446	121	.0707	.039	.00002	33.8	.0198	.125	.000075
Perchloroethylene	6,840	36.6	0	.000445	.0535	.000285	4.05	.022	.06	.00032
Phthalic Anhydride (o-xylene)	106	.0630	6	.00351	1.24	.00074	.72	.00043	.07	.00004
Tricresyl Phosphate	54	1.513	10.5	.297	1.19	.0335	.327	.0914	.07	.00197
Supplementary Phase I RWL Data										
Acetone	3.60	.0083	2,370	5.47	.388	.00090				
Ethylene Dichloride	21.0	.0049	13	.0029	.048	.00001	.11	.00002	.85	.00020
Vinyl Chloride	4.0	.00057	19	.00264	1.36	.00019	.33	.00005	.70	.00010
Vinyl Chloride	145	.163	7	.00744	.059	.00055	2.0	.00226	.205	.00023
Styrene	<4.29	.0265	<29	.181	.027	.00016	.053	.00032	<.05	.00031
Styrene	1.0	.00208	18	.0013	.015	.00001	.135	.00019	.115	.00011

Table 6-4

Miscellaneous RWL for Category C

Product	Flow gal/1000 lb	Phenol mg/l	Phenol kg/kkg	NH3-N mg/l	NH3-N kg/kkg	TKN mg/l	TKN kg/kkg	CN mg/l	CN kg/kkg	Sulfate mg/l	Sulfate kg/kkg	Oil mg/l	Oil kg/kkg	T-P mg/l	T-P kg/kkg
Hexamethylene Tetramine	557	.16	.00072	395	2.39	6,650	32.90			367	2.22	50	.19	1.07	.0044
Hexamethylene Tetramine	384	<.01	<.00002	7,040	22.5	8,260	26.50			<9.3	<.0050	131	.419	.177	.00057
Synthetic Cresols	250	6,500	13.6	2.7	.0057	4.9	.0102	<.02	<.00004	<6.5	<.0136	5,600	11.6	.169	.00035
Sec. Butyl Alcohol	7,780	.38	.025	0	0	3.1	.200			1,280	83.2	408	26.4	.079	.0051
Isobutylene	2,440	.01	.00012	9.4	.190	12.6	.256			1,210	24.50	1,030	20.9	1.07	.0217
Pentaerythritol	1,230	.17	.00178	<1.1	<.012	2.3	.023			2,570	26.20	369	3.77	.081	.00082
Ethyl Acetate	155	0	0	.8	.00104	<2.0	<.00259			1.0	.00129	203	.263	0	0
Propyl Acetate	142	0	0	.7	.00083	1.8	.00213			1.4	.00166	265	.314	.05	.00006
Calcium Stearate	6,460	.014	.00067	.8	.0568	6.0	.322	.0202	.00110	112	6.06	169.2	9.10	.0134	.00072
Hydrazine	3,630			1.0	.0297	11.3	.342			---	---	19	.569	.176	.00533
Isopropanol	304	.01	.00003	1.1	.00281	1.95	.00501			366	.931	15	.0380	.153	.00039
Acrylonitrile	338	2.28	.0064	13,600	38.3	22,000	62.1	270	.755	2,700	64.10	168	.475	.152	.00043
Acrylonitrile	570	.165	.000705	2,600	10.26	4,040	16.9	197	.970	5,300	74.3	135	.657	6.15	.0298
Propylene Glycol															
Propylene Oxide	6,580	1.15	.0381	1.5	.0875	3.8	.209			---	---	98.5	5.45	1.04	.061
Saccharin	32,200	.01	.0032	130.3	35.0	5,980	604			2,060	553			.07	.0189
Formic Acid	16,000	.0056	.00087	1.43	.193	5.07	.686	.02	.00267	4.67	.623	43.4	5.77	.042	.00561
Oxalic Acid	52,300	---	---	3.2	1.41	5.9	2.56	.02	.00873	5.6	2.44			.02	.00873

Table 6-4
(continued)

Miscellaneous RWL for Category C

Product	Zn mg/l	Zn kg/kkg	Cu mg/l	Cu kg/kkg	Fe mg/l	Fe kg/kkg	Cr-Total mg/l	Cr-Total kg/kkg	Cd mg/l	Cd kg/kkg	TSS mg/l	TSS kg/kkg	TDS mg/l	TDS kg/kkg	Cl⁻ mg/l	Cl⁻ kg/kkg
Hexamethylene Tetramine	1.4	.0085	.07	.00032	1.61	.0097	2.02	.012	<.05	<.00023	27	.106	2,320	10.1	40.5	.149
Hexamethylene Tetramine											6	.0192	971	3.11	234	.75
Synthetic Cresols	.19	.0004	<.05	<.0001	6.07	.013	<.05	<.0001	<.05	<.0001	9	.0188	33.5	.0699	1.5	.0034
Sec. Butyl Alcohol																
Isobutylene																
Pentaerythritol	.543	.0055	.20	.0020	8.65	.088	1.44	.0148	.093	.00095	129	1.31	289,000	2,960	868	8.86
Ethyl Acetate	.43	.00056	.77	.001	.55	.00071	<.05	<.00007	<.05	<.00007	1	.00129	66	.085	7	.00917
Propyl Acetate	.07	.00008	3.49	.00414	1.15	.00136	<.05	<.00006	<.05	<.00006	10	.0119	85	.101	3	.00335
Calcium Stearate	.049	.00262	.04	.00221	.108	.00590	.041	.00221	.041	.00221	26.7	1.43	6,020	324	3,870	208
Hydrazine	.13	.00394	.14	.00424	4.30	.130	.15	.00454	.23	.00697	1,180	35.8	118,000	3,590	98,700	991
Isopropanol	2.84	.00722	.17	.000435	2.88	.00731	.051	.00013	.051	.00013	4.5	.0121	2,550	6.46	214	.542
Acrylonitrile	.052	.00002	<.05	<.00014	3.13	.0088	<.05	<.00014	<.05	<.00014	630	1.78	57,200	161	858	2.42
Acrylonitrile	2.10	.00922	.05	.000235	4.24	.0182	.01	.00005	.052	.00024	184	.915	36,500	181	125	.616
Propylene Glycol																
Propylene Oxide	26.6	1.56	.25	.0138	23.9	1.39	.334	.0191	.111	.00614	4,520	263	44,700	2,460	24,800	351
Saccharin	.071	.0190	27.6	7.43	.25	.0665	.051	.0138	.062	.0166	33	8.83	14,500	3,900	5,050	356
Formic Acid	.107	.0142	.08	.0107	.05	.0104	.089	.0119	.05	.00668	6.8	.902	40.9	5.45	6	.792
Oxalic Acid	.01	.00436	.05	.0218	.01	.00436	.1	.0436	.05	.0218	10	4.36	36	15.7	6	2.58

Table 6-5
(continued)

Miscellaneous RWL for Category D

Product	Zn mg/l	Zn kg/kkg	Cu mg/l	Cu kg/kkg	Fe mg/l	Fe kg/kkg	Cr-Total mg/l	Cr-Total kg/kkg	Cd mg/l	Cd kg/kkg	TSS mg/l	TSS kg/kkg	TDS mg/l	TDS kg/kkg	Cl⁻ mg/l	Cl⁻ kg/kkg
Fatty Acids	.104	.0069	.05	.0033	3.06	.202	.05	.0033	.05	.0033	128	8.44	370	24.4	67	4.40
Fatty Acids											780	2.86	61,900	227	84	.308
Fatty Acids & Derivat.	.755	.00913	.075	.00091	3.67	.0445	.65	.0079	.05	.00061	669	8.10	2,630	31.8	61.5	.074
Fatty Acids & Derivat.	.17	.011	.05	.0032	.01	.00064	.05	.0032	.05	.0032	57	3.64	1,150	73.4	4,320	275
Fatty Acids	.31	.0032	1.73	.0178	2.85	.0294	2.37	.0240	.05	.00052	1,560	16.0	1,378	14.2	70	.721
Pentachloro Phenol	.272	.00081	.185	.00054	2.69	.00796	.107	.000315	.15	.00044	155	.46	8,950	26.4	291,000	860
Esters from Fatty Acids	.66	.0059	.05	.00045	21.4	.191	.35	.0031	.05	.00045	3,840	34.2	770	6.88	119	1.06
Methyl Esters											551	69.8	5,720	726	27	3.41
Fatty Acid Derivatives	.79	.00365	.22	.00101	2.71	.0125	3.25	.0149	.05	.00023	211	.970	3,490	16.0	100	.651
Fatty Acid Derivatives	1.60	.0092	.10	.00057	2.13	.012	.05	.0025	.05	.00029	748	4.29	2,400	13.9	71	.408
Naphthenic Acid	.302	.0139	.05	.002	9.23	.366	.05	.002	.05	.002	68.5	2.72	7,690	305	69	2.75
Glycerine	.450	.021	.40	.0182	11.2	.509	.05	.0022	.05	.0022	928	42.2	10,800	490	17	.791
Fatty Acid Amides											494	9.27			326	6.12
Batch Chemicals	1.312	.110	.587	.0442	9.05	.744	1.15	.0988	.05	.00383	42.6	3.28	3,250	261	776	61.4
Tannic Acid	3.52	.0347	.807	.008	28.6	.287	.518	.00519	.035	.00035			108,000	1,080		
Sodium Glutamate											2,260	151,000	1,650	110	85	5.68
Plasticizers (Diethyl Phthalate)	3.95	.00258	97.9	.0640	4.49	.00293	.076	.00005	.151	.0001	101	.0661	94,800	61.9	160	.104
Dyes	.413	.0135	61.6	2.02	5.62	.184	.56	.0184	.06	.00197	121	3.97	42,400	1,390	12,100	398
para-Nitro-Analine	.229	.00892	.11	.00417	5.48	.214	.147	.00574	.073	.00287	1,430	56.1	13,300	520	5,780	226
Miscellaneous Dyes	.580	1.07	.775	1.43	7.62	14.1	12.6	3.28	.050	.0924	99.3	20.4	3,150	646	1,130	215
Azo Dye	.287	.0614	.941	.192	4.58	.940	.572	.136	.049	.0100	270	72.5	2,020	543		
ortho-Nitro-Analine	.068	.0184	.05	.0142	2.79	.751	.05	.0135	.05	.0135	24.5	3.26	348,000	46,300	306	82.3
Vanillin	.517	.0686	7.59	1.00	17.2	2.28	.458	.0607	.186	.0247	78	36.9	41,300	19,700	---	---
Citric Acid	3.30	1.57	.25	.120	2.09	.996	.055	.0264	.05	.0238	124	1.42	85,400	976	15,500	423
Ionone & Methyl Ionone	1.47	.0168	9.31	.106	25.0	.286	.112	.00128	.090	.00102	21	.211	32,600	330	191	2.18
Citronellol Geraniol	.317	.00322	.08	.00081	.98	.00996	.062	.00063	.061	.00062	59	18.4	1,940	606	282	2.86
Pigments	.135	.0423	.26	.207	.85	.266	.05	.0157	.05	.0157					621	194

Table 6-5

Miscellaneous RWL for Category D

Product	Flow gal/1000 lb	Phenol mg/l	Phenol kg/kkg	NH3-N mg/l	NH3-N kg/kkg	TKN mg/l	TKN kg/kkg	CN mg/l	CN kg/kkg	Sulfate mg/l	Sulfate kg/kkg	Oil mg/l	Oil kg/kkg	T-P mg/l	T-P kg/kkg
Fatty Acids	7,900	.02	.00138	1.5	.096	4.6	.303			33.6	2.21	54	3.56	.39	.026
Fatty Acids	440	.55	.00202	121	.447	147	.540			1,400	152	1,190	4.36	129	.474
Fatty Acids & Derivat.	1,450	1.19	.0144	934	11.30	2,430	29.4			1,860	22.5	600	7.25	2.30	.0279
Fatty Acids & Derivat.	7,650	.06	.00383	86.1	5.50	37.6	5.59			280	17.9	68	4.34	.10	.00638
Fatty Acids	1,230	.45	.00461	3.75	.0364	21.2	.218			456	4.69	1,070	11.0	9.53	.0982
Pentachloro Phenol	354	37.6	.112	211.	.624	223	.661	.078	.00023	914	2.70	3	.00753	.038	.000115
Esters from Fatty Acids	1,070	.07	.00059	4.2	.0375	13.4	.119			192	1.71	4,000	35.7	3.3	.029
Methyl Esters	15,200	.33	.042	40	5.07	109	13.8			960	122	4,250	540	1.67	.212
Fatty Acid Derivatives	550	.20	.00088	.55	.0026	15.5	.071			640	2.94	701	3.22	2.01	.0092
Fatty Acid Derivatives	688	.54	.00312	620	3.56	640	3.67			1,640	9.42	470	2.70	18.7	.107
Naphthenic Acid	4,760	8.57	.341	3.7	.147	6.3	.252	.02	.00079	3,230	128	255	10.12	.194	.0077
Glycerine	5,450	10.6	.482	5.5	.248	980	44.5			4,200	191	8	.350	2.48	.113
Fatty Acid Amides	2,250	.04	.00068	7,730	145	7,890	148	.02	.00154	2.4	.045	467	8.77	.02	.00038
Batch Chemicals	9,560	1.83	.19	36.7	2.87	53.7	4.16			1,220	98.6	43.7	3.35	1.90	.156
Tannic Acid	1,200	2.37	.0238	1.8	.0180	350	3.50	.0237	.000303					595	5.96
Sodium Glutamate	8,030	.05	.0035	241	16.1	458	30.6			279	18.7	85	5.69	15.2	1.02
Plasticizers (Diethyl Phthalate)	78.3	.01	.00001	1.1	.00073	3.9	.00258	.04	.00003	2,030	1.33	12,500	8,170	3.29	.00215
Dyes	3,930	.63	.0205	82.1	2.69	126	4.14	.041	.0014	548	18.0	334	10.9	.142	.0047
para-Nitro-Aniline	4,680	7.15	.279	1,590	62.1	1,830	71.5			92.5	3.61	332	12.9	.493	.0193
Miscellaneous Dyes	221,000	16.9	31.2	17.7	31.7	27.9	51.6	.432	.756	1,020	578	74	136	10.5	19.4
Azo Dye	26,200	7.49	1.57	15.0	3.08	32.3	6.63	.085	.018	442	90.7	106	24.8	.53	0.113
ortho-Nitro-Aniline	32,200	7.97	2.14	1,150	310	7,340	976			103	27,700	10	2,600	.531	.143
Vanillin	15,900	147	19.5	4.05	.536	181	24.0			5,330	33.5	72	9.56	.087	.0115
Citric Acid	57,100	.07	.0309	51.8	24.7	91.2	43.5	.026	.0123	2,070	986	19	8.85	.101	.0484
Ionone & Methyl Ionone	1,370	1.04	.0119	44.5	508	53.2	.608	.023	.00026	3,980	45.3	383	4.37	.293	.00335
Citronellol Geraniol	1,220	0.00	0.00	9.3	.0943	11.8	.120	.020	.00020	40.8	0.414	2,630	76.6	.797	.00808
Pigments	37,500	1.81	.565	2.1	.66	13.9	4.33	.026	.00814	564	176	67	20.9	.309	.0967

Pollutants of Limited Significance

The following parameters, which were investigated in particular cases, have significant effects on the applicability of end-of-pipe treatment technologies.

Oil

Oil (Freon extractables) is a measure of the insoluble hydrocarbons and the free-floating and emulsified oil in a particular wastewater sample. Free-floating and emulsified oil are critical to wastewater treatment because they interfere with oxygen transfer. One particular problem of importance is obtaining a representative wastewater 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 RWL's for the major Subcategories A, B, C, and D are presented in Tables 6-2 through 6-5. The following is a summary of specific products with high free or emulsified oils; the remaining high oil RWL's merely reflect the amount of insoluble hydrocarbons which are soluble in Freon:

Subcategory	Product	RWL Concentration
		mg/L
B	Maleic Anhydride	2,020
	Acetone	2,370
C	Isobutylene	1,030
	Synthetic Cresol	5,600
	Secondary Butyl Alcohol	1,280
	Pentaerythritol	2,570
	Methyl Chloride	3,020
D	Fatty Acids and Derivatives	8-4,250
	Citronellol and Geranoil	2,630
	Plasticizers	12,500

Petroleum-based free oil concentrations of 50 mg/L, measured according to the API Method 733-58, have been reported inhibitory to biological treatment.[1] Oils of animal or vegetable origin, e.g., found in the fatty acid industry, have not been reported inhibitory at these levels. However, efficient TSS removal in biological treatment plants requires that the fatty acid industry have highly efficient oil-water separation devices before any type of biological treatment to insure adequate TSS removal.

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[1] All information regarding biological treatment inhibition is quoted from EPA's - Federal Guidelines - Pretreatment of Discharges to Publicly Owned Treatment Works.

Nitrogen

Ammonia nitrogen (NH_3-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 NH_3-N and organic nitrogen present in the sample. Both NH_3 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 anaerobic conditions. The ammonia nitrogen then becomes the nitrogen and energy source for autotrophic organisms (nitrofiers). The oxidation of ammonia to nitrite and then to nitrate has a stoichiometric oxygen requirement of approximately 4.6 times the concentration of NH_3-N. The nitrification reaction is much slower than the carbonaceous reactions, and, therefore, the dissolved oxygen utilization is observed over a much longer period.

The ammonia and TKN RWL data of major significance is summarized below by product and subcategory:

Subcategory	Product	RWL Concentration NH_3-N mg/L	TKN-N mg/L
B	Acrylonitrile	13,600	22,000
	Diphenylamine	15,500	16,700
	Hexamethylene Diamine	7,630	9,170
C	Hexamethylene Tetramine	7,040	8,260
D	Fatty Acids and Derivatives	1-7,730	5-7,890

Ammonia concentrations of 3,000 mg/L have been reported inhibitory to anaerobic sludge digestion.

Phenol ✓

Phenols in wastewater present two major problems: at high concentrations phenol acts as a bactericide; and at very low concentrations, when disinfected with chlorine, chlorophenols are formed, producing taste and odor. Past experience 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 should be given careful consideration in the design. Slug loadings as low as 50 mg/L could be inhibitory to the biological population.

The following are phenol RWL's of significance:

Subcategory	Product	RWL Concentration mg/L
C	Synthetic Cresols	6,500

/ Total Dissolved Solids, Chlorides, Sulfates

Total dissolved solids in organic chemical wastewaters consist mainly of carbonates, bicarbonates, chlorides, sulfates, and phosphates. High chlorides and sulfates in Subcategories C and D are primarily from acid scrubbing or the by-product formation of ammonium sulfate. Sulfate concentrations of 500 mg/L have been reported to be inhibitory to anaerobic digestion, while NaCl concentrations of 10,000 mg/L are reported inhibitory to biological treatment.

The following is a summary of the significant TDS, SO_4, and Cl data from Tables 6-2 through 6-5:

Subcategory	Product	RWL Concentration		
		TDS	SO_4	Cl
		mg/L	mg/L	mg/L
B	Benzoic Acid	34,900	36	290
	Maleic Anhydride	53,700	-	18
	Adiponitrile	124,000	156	83,400
	Chloromethane	28,300	349	-
	Methyl Chloride	117,000	5,800	-
C	Secondary Butyl Alcohol	-	1,280	-
	Isobutylene	-	1,205	-
	Pentaerythritol	289,000	2,570	868
	Acrylonitrile	57,200	2,700	858
	Hydrazine	118,000	-	98,700
	Propylene Oxide	14,500	-	5,050
D	Naphthenic Acid	7,690	3,230	69
	Glycerine	10,800	4,200	17
	Citric Acid	41,300	2,070	15,500
	Ionone	85,400	3,980	191
	Vanillin	348,000	5,330	-
	Dyes	42,400	548	12,100
	Fatty Acid Derivatives	1,400	1,640	71
	Tannic Acid	108,000	-	-
	Citronellol-Geraniol	32,600	40	282
	Plasticizers	94,800	2,030	160

Cyanide

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:

$$H^+ + CN^- \qquad HCN$$

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

Cyanide (as HCN) values of 1.0 mg/L have been reported inhibitory to biological treatment.

The following is a summary of cyanide data which is significant in regard to inhibition of biological treatment:

Subcategory	Product	RWL Concentration[1] mg/L
B	Adiponitrile	187
C	Acrylonitrile	270

[1]Cyanide Titration Procedure

The cyanide results from the previous processes were determined using Standard Method's Cyanide Titration Procedure with and without preliminary distillation. The following is a comparison of results from one plant:

	CN mg/L
Standard Method Titration Procedure	4,870
Standard Method Distillation - Titration Procedure	940

It has been reported that aldehydes combine with HCN to form cyanohydes during distillation and that this complex interferes with the titration procedure. Based on this analytical experience, it is recommended that only the titration procedure be used with these wastewaters.

Heavy Metals ✓

Heavy metals (such as zinc, copper and cadmium) are inhibitory to microorganisms because of their ability to tie up proteins in their key enzyme systems. The following concentrations of heavy metals have been reported as being inhibitory to biological treatment:

Pollutant	Inhibitory Concentration mg/L
Copper	1.0
Zinc	5.0 - 10.0
Cadmium	0.02[1]
Total Chromium	3.0
Iron	5.0[1]

[1]Inhibitory to anaerobic sludge digestion.

The following is a summary of the metals data from Tables 6-2 through Tables 6-5 which is considered significant in regard to inhibition of biological treatment:

Subcategory	Product	Metal RWL Concentration mg/L	
B	Adiponitrile	48	- Copper
	Chloromethanes	14.3	- Iron
		7.7	- Total Chromium
	Methyl Chloride	26.3	- Copper
		0.21	- Cadmium
		18.8	- Iron
		33.8	- Zinc
	HMDA	74.5	- Zinc
	Maleic Anhydride	0.4	- Cadmium
	Perchloroethylene	9.45	- Total Chromium
C	Propylene Oxide	0.1	- Cadmium
		23.9	- Iron
		26.9	- Zinc
	Saccharin	27.6	- Copper
	Hydrazine	0.23	- Cadmium
D	Plasticizers	97.9	- Copper
	Dyes	61.6	- Copper
	Vanillin	17.2	- Iron
	Miscellaneous Dyes	12.6	- Total Chromium

SECTION VII

CONTROL AND TREATMENT TECHNOLOGIES

Control and treatment technologies which are available for the Organic
Chemicals Industry can encompass the entire spectrum of wastewater treat-
ment technology. The selection of a particular technology is dependent
on the technology economics and the magnitude of the final effluent con-
centration. Control and treatment technology may be divided into two
major groupings; namely,

    1. In-plant pollution abatement.
    2. End-of-pipe treatment.

After discussing the available performance data, conclusions will be made
relative to the reduction of various pollutants commensurate with the
following distinct technology levels:

    1. Best Practicable Control Technology Currently Available (BPCTCA).
    2. Best Available Technology Economically Achievable (BATEA).
    3. Best Available Demonstrated Control Technology (BADCT).

To access the economic impact of these proposed effluent limitations on
the industry, model treatment systems have been proposed which are con-
sidered capable of attaining the recommended RWL reduction. It should
be noted and understood that the particular systems chosen for use in
the economic analysis are not the only systems which are capable of at-
taining 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. Various types of end-of-pipe wastewater treatment.
    2. Various in-plant modifications and installation of pollution
        control equipment.
    3. Various combinations of end-of-pipe and in-plant technologies.

The complexity of the Organic Chemicals Industry dictated the use of only
one treatment model for each effluent level. This situation poses some
problems for specific chemicals whose wastewaters are, for example, bio-
logically inhibitory. The use of the biological treatment model for these
chemicals is done only to facilitate the economic analysis and not to be
inferred as a recommended technology.

It is the intent of this study to allow the individual manufacturer within
the Organic Chemicals Industry to make the ultimate choice of what specific
combination of pollution control measures is best-suited to his situation
in complying with the limitations and standards presented in this report.

In-Plant Pollution Abatement

The complexity of the Organic Chemicals Industry precludes the pos of providing a specific list of process modifications or control m which are applicable to all of the Industry's processes.

The elimination or reduction of in-plant pollution depends upon any one of the following factors:

1. New plant process selection to minimize pollution. Present corporate environmental awareness requires that new products and processes be evaluated with regard to their environmental aspects.

2. The modification of process equipment to improve product recovery or to minimize pollution. These areas have been discussed thoroughly in a previous study.[1]

3. Maintenance and good housekeeping practices minimize pollution. The competitive nature of the industry in conjunction with the flammable nature of many of its products requires most producers to operate their plants in the most efficient manner possible. This necessitates good maintenance and housekeeping practices. However, there are other segments of the industry who have minimized maintenance expenditures and whose management does not adequately fund their environmental control staff nor support them in their quest to enforce rigid housekeeping regulations.

4. The age of the plant and process equipment as it impacts on pollution. Poorly maintained process equipment does not warrant consideration under this age consideration. The real problem is that older technology generally pollutes more than new technology. In addition, older plant layouts do not allow for economic modifications to the process equipment to minimize pollution and, in many cases, prohibit segregation of storm and process waters.

    The age problem has its greatest impact on the batch chemicals segment of the Organic Chemicals Industry. However, as of this time, none of the approaches which have been suggested to handle the age factor would be manageable as well as quantifiable. Since

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[1]Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products. U.S. Environmental Protection Agency; EPA 440/1-73/009; December 1973.

many of the older plants are located in the inner cities and discharge to municipally owned treatment plants, it is recommended that age be a factor which may be negotiated for plants classified as point sources.

End-of-Pipe Treatment

As explained previously, the RWL data from the Phase 2 field survey is being handled as a separate report. However, because of the scarcity of treatment plant performance data, it was decided to combine the Phase I and II data for this study. A summary of the types of treatment technology which were observed during both phases are listed in Table 7-1. During the Phase II study, 70 individual plants were surveyed; however, 6 of the 70 plants were previously surveyed during the Phase I study. Table 7-1 has been prepared taking this duplication into consideration. Of the plants surveyed in Phase II which are subcategorized in A, B or C, over 80 percent provide their own waste treatment facilities, while 60 percent of the Subcategory D plants discharge to municipally owned treatment facilities.

Single-Stage Biological Treatment

During the plant survey program, historic wastewater treatment plant performance data were obtained when possible. The data were statistically analyzed, and, when possible, the individual plant performance was evaluated with respect to the original design basis. Subsequent to this evaluation, a group of plants were selected as being exemplary in performance. These particular exemplary plants are indicated in Table 7-2, which is a summary of all of the historic performance data made available by industry for the purposes of the study. The amount of analytical data used in the statistical analyses are indicated in the "data base column" of Table 7-2. The following is a summary of the average reductions capable of exemplary treatment plants:

	COD Removal percent	BOD Removal percent	TOC Removal percent	Effluent TSS mg/l
Exemplary Single- and Multiple-Stage Plants	74	93	79	134
Exemplary Single-Stage Plants	69	92	60	65

The major differences observed in performance from the previous analyses are in the TOC removals. This is because only two historic TOC data points are available.

Table 7-1

Organic Chemicals Study
Treatment Technology Survey

Type of Treatment or Disposal Facility	Number of Plants Observed	
	Phase I	Phase II
Activated Sludge	7	9
Activated Sludge-aerated lagoon	2	0
Activated Sludge-polishing pond	0	1
Activated Sludge-solar evaporation pond	0	1
Trickling Filter-activated sludge	1	0
Aerated lagoon-settling pond	3	1
Aerated lagoon-no solids separation	2	1
Facultative Anaerobic lagoon	4	4
Stripping Tower	1	1
No current treatment - system in planning stage	3	7
To Municipal Treatment Plant	5	23
Deep-well disposal	2	6
Physical Treatment, e.g. API Separator	4	3
Activated Carbon	0	6
Incineration	0	1
TOTAL	34	64

Table 7-2

Historic Treatment Plant Performance
50% Probability of Occurrence

Plant No.	Treatment System	Category	COD % Removal	COD Effluent mg/l	BOD % Removal	BOD Effluent mg/l	TOC % Removal	TOC Effluent mg/l	SS % Removal	SS Effluent mg/l	Data Base Duration (months)	Data Base Performance Period
1[1]	AL	D	75	320	97	10	--	--	--	--	6(Sept-Feb)	daily average
2[1,2]	AS-AL	C	96.4	470	--	--	--	--	--	163	12	daily average
3[1]	AS	D	63	200	93.5	16	--	--	--	55	12	monthly average
4[1]	AS	B	64.2	120	--	15	--	--	--	--	14	monthly average
5[1,2]	TF-AS	B	73.5	83	--	--	--	--	--	--	14	monthly average
6	AL	B-C	--	--	--	291	--	--	--	665	12	weekly average
7	AL	C	--	165	--	9.9	--	--	--	81	12	monthly average
8[1]	AL	B	--	75	--	23.5	--	--	--	24.3	12	monthly average
9[1]	AS	C	--	--	83	152	60	170	--	130	7(Aug-Feb)	daily average
10[1]	AS	B	74.5	80	90.1	20	--	--	--	--	12	weekly average
11[1,2]	AS-AL	C	--	--	99.7	20	97	100	-370	145	12	daily average
12	AS	A-B	85	97	--	59	--	--	--	--	12	monthly average
13	AS	B-C	--	610	--	294	--	295	--	189	14	monthly average
14	AS	B	--	--	73	410	42	780	--	280	14	monthly average
15	AL		--	226	--	63	--	--	--	--	6(July-Dec)	weekly average
16[1]	AS	D	--	--	82.5	362	--	--	--	289	8(Aug-Mar)	monthly average
17[1]	AS	D	67	1,760	--	--	--	--	--	--	6(June-Oct)	daily average
18	AS	D	25.4	1,520	63.6	303	--	--	--	480	12	weekly average
19[1]	AS	D	--	--	97.6	157	--	--	--	--	5(June-Sept)	monthly average
20[1]	AS	C	--	296	98.8	46.9	--	--	--	--	5(June-Sept)	weekly average
Exemplary Plant Average			74	378	93	82.2	79	135	--	134		
Exemplary Single Stage Plants - Average			69		92		60		--	65[3]		

[1] Plants considered to be exemplary in performance.

[2] Multiple-stage biological treatment.

[3] Plant 16 is not included in average.

During the survey program, 24-hour composite samples were obtained in order to verify the plants' historic performance data, as well as to provide a more complete wastewater analytical profile. These results are presented in Table 7-3. The following is a summary of the average reductions capable of being attained by exemplary treatment as verified by composite sampling:

	COD Removal percent	BOD Removal percent	TOC Removal percent
Exemplary Treatment Plants	72	87	58

The TOC removal of 58 percent would seem to substantiate the lower value of 60 percent as previously indicated for the historic values appearing in Table 7-2. As indicated by the TSS removal data, 9 of the 17 plants surveyed had negative TSS removal and over 75 percent of the plants had inadequate solids handling facilities.

The impact of TDS and oil on the TSS levels for the plants surveyed is indicated in Table 7-3. There is a trend indicating that high TDS and oils in the plant effluent contribute to high TSS levels, e.g. note Plants 16 and 18 which treat fatty acid industry wastewaters. However the direct effect of TDS on the TSS is not clear from the sampling data, e.g. Plants 21 and 22 have high TDS and relatively low TSS, while Plant 19 has a high TDS as well as TSS in its effluent. The major problem is that biological sludge in many facilities is not wasted, thereby increasing its TSS effluent levels. Unless one is thoroughly familiar with a particular plant's operation, it is very difficult to interpret TSS data, much less draw conclusions concerning variables affecting sludge settleability. For this reason, recommendations concerning TSS for the technology levels BATEA and BADCT will be based on the performance experience of adequately designed units functioning in other industries.

Multiple-Stage Biological Treatment

During the course of the plant surveys, three plants were observed to have multiple-stage biological treatment. Plant 5 (see Table 7-2) required two-stage treatment for phenol removal, while Plants 2 and 11 required it because of relatively high raw waste loads and rigid water quality criteria. The Phase I recommendation that single-stage biological treatment be considered BPCTCA is further substantiated by the Phase II survey data.

Filtration

Supplemental organics and solids removal is being practiced within the industry in one particular case using a polishing pond. One major

Table 7-3

Treatment Plant Survey Data[1]

Plant No.	Treatment System	Category	COD % Removal	COD Effluent mg/L	Total BOD % Removal	Total BOD Effluent mg/L	TOC % Removal mg/L	TOC Effluent mg/L	TSS % Removal	TSS Effluent mg/L	TDS Effluent mg/L	Oil & Grease Effluent mg/L
2[2]	AS-AL	C	64	2,300	90	427	32	2,710	Negative	4,700	2,300	-
3[2]	AS	D	71	284	73	74	71	132	Negative	62	3,100	1[3]
4[2]	AS	B	57	214	82	13	35	80	40	14	2,900	4[3]
5[2]	TF-AS	B	59	133	92	12	43	61	97	44	1,430	2[3]
6	AL	B-C	66	980	73	235	11	573	Negative	362	3,000	11[3]
8[2]	AL	B	69	92	84	6	26	52	99	3	690	-
9	AS	C	75	595	92	75	69	242	Negative	50	3,810	12[3]
11[2]	AS-AL	C	94	337	99	16	27	343	Negative	145	2,690	1[3]
13	AS	B-C	65	940	90	177	64	470	120	338	1,520	6[3]
16[2]	AS	D	54.8	1,650	82.1	300	80.8	280	43.6	552	10,990	226[4]
17[2]	AS	D	60.0 / 77.3	1,400 / 1,000	81.4 / 90.0	240 / 310	63.4 / 76.8	410 / 360	Negative	1,300 / 732	3,750 / 4,060	24[4] / 22[4]
18	AS	D	22.1	2,680	16.7	650	-	1,025	42.9	1,170	2,050	106[4]
19[2]	AS	D	59.5	5,100	69.8	1,800	55.8	1,700	Negative	2,500	8,360	-
20[2]	AS	C	96.2	317	99.5	19	96.6	114	Negative	100	1,950	19[4]
21	AL	C	62	600	78	27	66	47	89	30	9,800	-
22	AS	B	16.1	1,370	47.5	210	8.3	550	53.4	82	15,400	<.03[4]
23	AS	B	95.4	147	92.6	41	95.4	35	Negative	37	580	21[4]
Average[5]			72		87		58					

[1] Based on 24 hrs composite samples.
[2] Plants considered to be exemplary in performance based on historical data.
[3] Oil and grease are reported as carbon tetrachloride extractables.
[4] Oil and grease are reported as Freon extractables.
[5] Includes exemplary plants as well as Plant 23.

problem during summer periods is algal blooms which, if unchecked, can drastically increase the TSS and COD of the polishing pond effluent. In addition, the acreage requirements of this system limits its potential uniform application.

In contrast, filtration has many of the advantages of polishing ponds and few of the disadvantages. In order to quantify the effectiveness of effluent filtration, samples of biological treatment plant effluents were collected and filtered using filter paper. The results are presented in Table 7-4. Average percent COD, BOD, and TOC removals associated with filtration are 20, 17, and 20, respectively.

Carbon Adsorption

Granular activated carbon technology is continuously being developed and is beiginning to compete actively with biological treatment as a viable treatment alternative or as a biological treatment effluent polishing process for some industrial wastes. As was indicated previously in the Phase 1 study, there exists a limited amenability of many low molecular weight, oxygenated chemicals to adsorption on activated carbon. In addition, experience has indicated that TSS in amounts exceeding 50 mg/l and oils above concentrations of 10 mg/l should not be applied directly to carbon beds.[1] These materials tend to clog and coat the carbon particles, thereby reducing the adsorption effectiveness. This is an obvious consideration in the fatty acid industry. Plants 16, 17, and 18 treat wastewaters from this industry and are characterized by high effluent solids and oils. (See Table 7-3.)

To place carbon adsorption technology in perspective, it must be understood that one of the first full-scale industrial wastewater treatment plants was installed in Pennsylvania in 1969. During the plant survey program, 6 activated carbon plants treating raw wastewaters were surveyed, and the results are presented in Table 7-5. The most interesting fact is that domestic wastewater treatment experience indicates that efficient treatment is provided with contact times between 10 and 50 minutes, while the design contact times in Table 7-5 vary between 22 and 660 minutes (calculated on an empty column basis). These higher contact times are required because of the much higher raw waste loads generated by industry.

The major problems encountered in trying to compare design criteria and present performance of carbon plants are as follows:

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[1] Donald Hager, "A Survey of Industrial Wastewater Treatment by Granular Activated Carbon" Presented at the 4th Joint Chemical Engineering Conference; Vancouver, British Columbia; Sept. 10, 1973.

Table 7-4

Removal by Filtration
(Performed on Biological Treatment Plant Effluent)

Plant	% COD	% BOD	% TOC
3	9	4	3
15	87	56	78
15	85	--	82
14	24	28	14
9	11	--	5
9	10	--	17
13	32	36	8
4	--	--	--
24	8	2	20
12	21	--	7
21	3	--	8
16	84.3	57.8	75.9
25	39.3	--	39.4
20	8.5	17.2	33.0
35	51.4	--	27.7
26	26.2	71.4	41.2
27	--	12.5	25.0
18	86.8	72.1	90.6
17	88.4	55.6	91.6
19	33.3	--	66.0
Average [1]	20	17	20

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[1] Average does not include plants 15, 16, 17, 18, and 26, since these plants have excessively high effluent TSS and would bias the results.

Table 7-5

Activated Carbon Plants Treating Raw Wastewaters

Plant	Pretreatment	Removal Efficiencies-%		Flows-gpd		Hydraulic Loading gpm/sq.ft.		Contact Time-minutes		Carbon Exhaustion Rate	
		Design	Present	Design	Present	Design	Present	Design	Present	Design	Isotherm
28	Solids Removal and Equalization 9-hr detention time	----	Polyol-11	100,000	55,000	5.6	3.0	22	40	0.4 lb. polyol/lb. carbon	----
29	Equalization 150-day detention time	TOC-94	TOC-89	20,000	7,000	0.49	0.17	540	1,550	0.07 lb. TOC/lb. carbon	0.19 lb. TOC/lb. carbon
30	Equalization, Neutralization and solids removal	Phenol-89	Phenol-94	750,000	500,000	4.6	3.1	69	104	.028 lb. phenol/lb. carbon	----
31	Equalization and Neutralization	----	TOC-91	30,000	20,000	----	----	660	912	----	----
32	Equalization and Neutralization	Phenol-99.9	Phenol-95	72,000	22,000	2.0	0.6	215	75	----	----
33	Equalization, Neutralization and solids removal	Color-90	----	800,000	----	7.7	----	27	----	5.4 lbs. color/lb. carbon	----

1. In most cases, design loadings, both organic and hydraulic, have not yet been attained. This means the new plants are sometimes grossly under-loaded.

2. Thermal carbon regeneration is presently an art which is acquired only with actual operating experience. For this reason, start-up problems are often extended, and it is not unusual for the pollutant concentrations of the activated carbon effluent to be higher than the design value. This situation continues until the carbon is regenerated thoroughly.

3. Plants with insufficient spill protection and/or inadequate housekeeping practices may discharge specific low molecular weight hydrocarbons which are not amenable to adsorption. This situation results in an erratic plant performance.

The carbon adsorption isotherm is widely used to screen the applicability of different activated carbons and to calculate theoretical exhaustion rates. The comparison of isotherm and design exhaustion rates for Plant 29 in Table 7-5 further substantiates the fact that isotherm data is preliminary and should not be used for design purposes. However, carbon isotherm data does indicate relative amenability of the particular wastewater to treatment and to fairly typical removal efficiencies.

To investigate the possibility of using activated carbon technology on the effluents from biological treatment plants treating organic chemical waste-waters, a series of carbon isotherms were run at standard conditions using a contact time of 30 minutes. The results of the isotherms are presented in Tables 7-6 through 7-8. Average performance values are presented as follows:

Parameter	Carbon Exhaustion Rate	Soluble Pollutant Removal
	lbs removed/lb carbon	percent
COD	0.41	69
BOD	0.03	20
TOC	0.06	87

Inspection of the specific data in Tables 7-6 through 7-8 indicates that carbon adsorption has varying degrees of amenability with regard to cost-effective wastewater treatment. However, the data does indicate that specific wastewaters are readily treatable using activated carbon.

BPCTCA Treatment Systems

The major purpose for the review of the historic treatment plant data was to be able to quantify BPCTCA reduction factors, which would then

Table 7-6

Summary COD Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

	Carbon Exhaustion Rate			
Plant No.	lbs COD Removed / lb Carbon	lbs Carbon / 1,000 gallons	Max. Soluble COD Removal (%)	Category
14	0.035	232	22	B
15	0.8	8.9	87	
15	0.2	28.6	87 (87)	
3	1.35	1.87	74	D
9	0.30	13.9	84	C
9	0.36	13.3	75 (79)	
13	0.42	10.6		
13	0.36	12.6	70	B-C
4	0.51	2.2	57	B
24	0.34	32.2	69	B
12	4.5	0.27	87	B
21	0.11	21.4	3	C
16	.12	29.5	50.2	D
25	---------------	------------	57.8	
20	4.0	.25	41.6	C
35	---------------	------------	42.4	B-C
26	.45	2.0	72.8	A
18	---------------	------------	83.4	D
23	.069	3.9	63.6	B
27	---------------	------------	20.4	B
17	0.094	44.3	93.9	D
Average[1]	**.41**	**15.7**	**69.0**	

[1] The average does not include Plants No. 12, 14, 20 and 21.

Table 7-7

Summary BOD Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

| Plant | Influent (soluble) mg/L | Effluent (soluble) mg/L | BOD Removal % | Carbon Exhaustion | |
				lbs BOD Removal / lb Carbon	lbs Carbon / 1,000 gal
16	165	82	50.3	–	–
25	12	1	91.6	.021	4.8
20	24	9	62.6	–	–
35	<1				
26	6.3	5.2	17.5	–	–
18	78	0	100	–	–
23	2	<1	>50	–	–
27	7	1	85.7	–	–
17	166	20	88.1	.039	35.5
19					
Averages[1]			**89**	**.03**	**20.1**

[1]Average includes only Plant No. 17 and 25

Table 7-8

Summary TOC Carbon Isotherm Data
(Performed on Biological Treatment Plant Effluent)

Plant	Influent TOC (soluble) mg/L	Effluent TOC (soluble) mg/L	TOC Removal %	Carbon Exhaustion lbs. TOC Removed lb. carbon	lbs. carbon 1,000 gal.
16	87	58	33.4	---	---
25	43	5	88.4	.01	35.9
20	28	12	37.2	---	---
35	34	4	88.3	.13	2.25
26	20	2	90.0	1.35	.12
18	104	19	81.6	.0036	241
23					
27	6	3	50.0	---	---
17	148	20	86.6	.0485	25.4
19	---	---	---		
Average [1]			**87**	**.063**	**21.77**

[1] Average includes Plant Nos. 17, 25, and 35.

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be applied to BPCTCA raw waste load figures for each subcategory in order to generate recommended effluent limitation guidelines. Based on the previous discussions of single-stage biological treatment, it is recommended that the following pollutant reduction factors be consistent with BPCTCA treatment technology:

Parameter	Percent Reduction Factors Applied to Average BPCTCA RWL	Monthly Minimum Average Effluent Concentration mg/L
BOD	92	20
COD	69	--
TSS	65 mg/L	20

---

[1] Controlling Parameter

The BPCTCA effluent discharge recommendations will be made only for BOD. TSS is expressed as a concentration limitation because BPCTCA raw waste loads are minimal as indicated in Chapter VI. The major source of TSS in biological treatment plant effluents are biological solids which, in many cases, are intentionally not wasted for further sludge dewatering but rather are permitted to pass out in the plant effluent. This situation is further compounded in certain plants which have very high TDS, oil, and grease concentrations which tend to hinder settling and thereby contribute to the high effluent TSS.

The major justification for minimum effluent concentration is that a number of the BPCTCA - BOD - RWL data are in the vicinity of 100 mg/L. If BPCTCA reduction factors are applied without due consideration, the resulting effluent concentrations will be below what is achievable with BPCTCA technology. The recommended minimum effluent concentrations were selected based on EPA's preliminary definition of BPCTCA municipal secondary treatment. The minimum TSS concentration is specified for plants attaining the minimum BOD concentration. This insures that adequate solids handling facilities will be provided. The use of these minimum concentration figures is illustrated as follows:

Category	BPCTCA Effluent Limitation		Minimum BOD-BPCTCA concentration mg/L
	kg BOD/kkg	mg/L	
C-5	1.79	12	20

If a particular product is in C-5, the effluent BOD-BPCTCA effluent
limitation is 1.79 kg BOD/kkg product. When using the actual plant
flow RWL, the concentration calculation resulted in a BOD of 12 mg/L.
In this case, the minimum BOD concentration of 20 mg/L would apply
and the BPCTCA effluent limitation would be recomputed using 20 mg/L,
thereby resulting in a BOD effluent limitation of 2.98 kg/kkg.

To evaluate the economic effects of the BPCTCA effluent limitations
on the organic chemicals industry, it was necessary to formulate a
BPCTCA treatment model. The model selected was single stage activated
sludge. (See Figure 7-1.) The BPCTCA design basis and the unit treat-
ment process rationale are discussed at length in the previously de-
scribed Phase I report.

BATEA Treatment Systems

Based on the previous performance data from multiple-stage biological
treatment plants, existing carbon treatment plants and various carbon
isotherms, it has been possible to formulate waste reduction factors
commensurate as BATEA treatment technology:

Parameter	Percent Reduction Factors Applied to BPCTCA Effluent Limitation	Minimum Monthly Average Effluent Concentration
BOD	90	10
COD	69	50
TSS	15 mg/L	10

The BATEA effluent discharge limitations will have two controlling para-
meters, i.e., BOD and COD. The major emphasis, however, should be on
COD removal since the major portion of the carbonaceous oxygen demanding
materials should have been removed with BPCTCA technology.

The BATEA treatment model used for economic evaluation of the proposed
limitations includes the BPCTCA treatment model followed by dual media
filtration and carbon adsorption. A typical flow diagram is shown in
Figure 7-2. The BATEA design basis and the unit sizing criteria are
discussed in the Phase I study. The carbon regeneration facilities
were sized using 0.41 lb COD removed/lb carbon, which is the average re-
sult as determined from the carbon isotherm data.

BADCT Treatment Systems

Based on the previous filtration data, it has been possible to form-
ulate waste reduction factors commensurate as BADCT treatment technology:

Figure 7-1

BPCTCA Waste Treatment Model
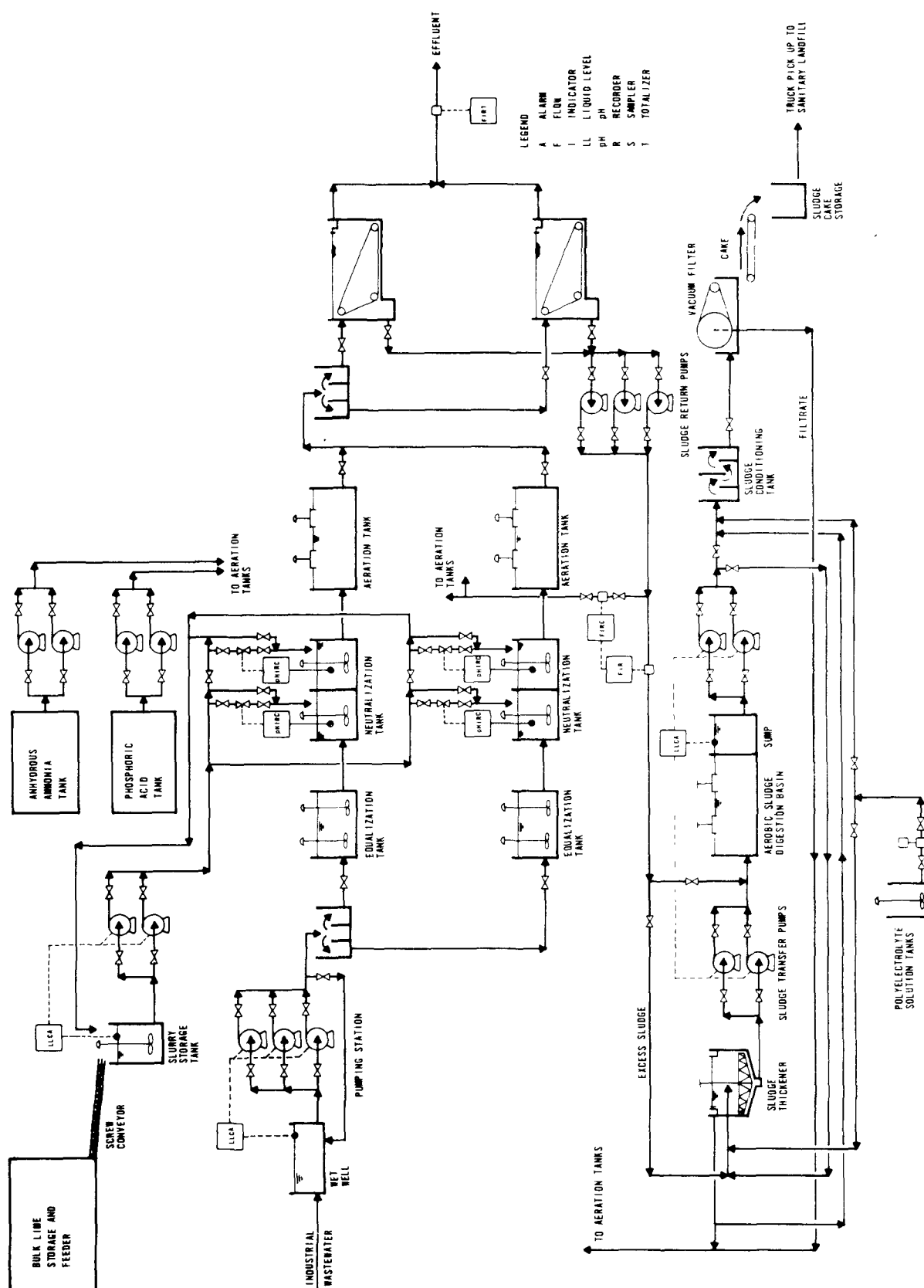
Figure 7-2

BATEA Waste Treatment Model
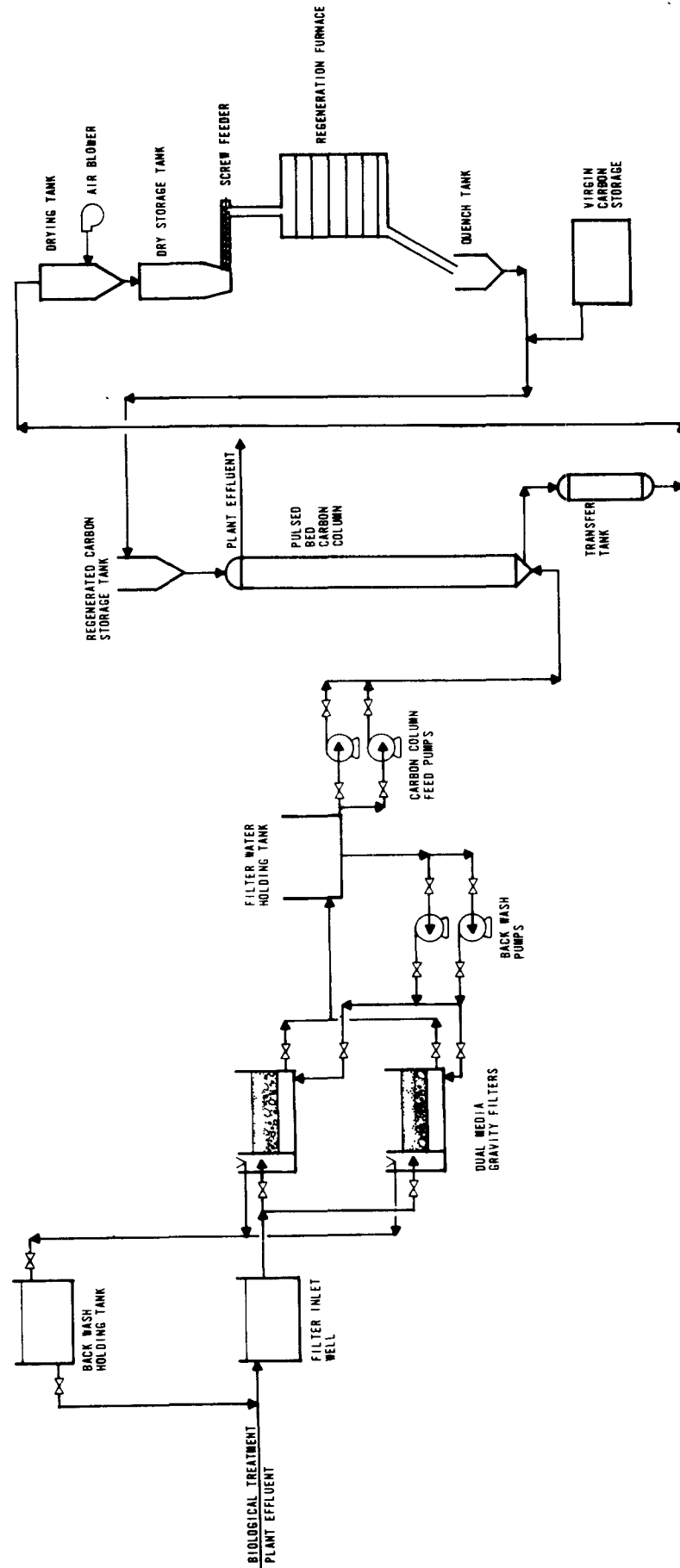
Parameter	Percent Reduction Factors Applied to BPCTCA Effluent Limitation	Minimum Monthly Average Effluent Concentration mg/L
BOD	17	10
COD	20	--
TSS	10 mg/L	10

The BADCT treatment model used for economic evaluation of the proposed limitations includes the BPCTCA treatment model followed by dual media filtration. The design basis and unit sizing criteria are discussed thoroughly in the Phase I study.

SECTION VIII

COST, ENERGY AND NON-WATER QUALITY ASPECTS

Cost

This section provides quantitative cost information relative to assessing the economic impact of the proposed effluent limitations on the organic chemicals industry. A separate economic analysis of treatment cost impact will be prepared by Arthur D. Little, Inc. on a product-by-product basis. In order to evaluate the economic impact on a uniform treatment basis, end-of-pipe treatment models were proposed which will provide the desired level of treatment as follows:

Technology Level	End-of-Pipe Treatment Model
BPCTCA	Single-Stage Activated Sludge.
BADCT	Activated Sludge and Filtration.
BATEA	Activated Sludge, Filtration, and Carbon Adsorption.

The method used to attain the effluent limitations whether through in-plant controls or by end-of-pipe treatment is left up to the individual manufacturer as to which is the most attractive economically.

Extensive annual and capital cost estimates were prepared for numerous end-of-pipe treatment models, which were presented in the Phase 1 study. As an expedient, these cost estimates were linearly extrapolated to include the similiar Phase 2 treatment models.

Of the products which were surveyed during Phase 2, Arthur D. Little, Inc. has selected 35 products for detailed economic evaluation and has provided typical average production figures. The following is a list by subcategory of the products to be evaluated:

Subcategory	Product	Subcategory	Product
A-1	BTX	A-2	Cumene
A-2	Para-Xylene		
B-1	Acetone	B-4	Methyl Chloride
B-2	Vinyl Chloride	B-4	Adiponitrile
B-3	Styrene	B-4	HMDA
B-3	Chlorotoluene	B-4	Benzoic Acid
B-3	Phthalic Anhydride	B-5	MEK
B-3	Chloromethane	B-5	Maleic Anhydride
C-3	Isopropanol	C-5	Calcium Stearate
C-4	Oxalic Acid	C-5	Caprolactam
C-4	Formic Acid	C-5	Isobutylene
C-5	Propylene Oxide	C-6	Hexamethylene Tetramine
C-5	Sec. Butyl Alcohol	C-6	Acrylonitrile
C-5	Hydrazine	C-7	Pentaerythritol
D-3	Fatty Acid	D-4	Sodium Glutamate
D-3	Citronellol-Geraniol	D-4	Tannic Acid
D-3	Ionone	D-4	Citric-Oxalic Acid (fermentation)
D-4	Dye	D-4	Naphthenic Acid

With this information, end-of-pipe treatment models were selected, and appropriate capital and annual costs were provided for each technology level. These costs are presented in Tables 8-1 through 8-31 for each of the product or product groupings listed above. The costs presented on these tables are incremental costs for achieving each technology level. For example in Table 8-10, the total capital cost for single-stage activated sludge treating wastewater from a hexamethylene diamine plant with an average production of 548,000 lbs/day is $1,500,000. Assuming an average COD removal of 69 percent, the expected effluent COD concentration from BPCTCA is 3,280 mg/l which is lower than both BATEA and BADCT recommended effluent COD limitations. This situation is caused by the wide variability in the BPCTCA-RWL data in Subcategory B-4 and the fact that the effluent limitations are based on average values. In this particular case, BOD would be the critical control parameter for each technology level.

The incremental capital costs for this plant to provide filtration to achieve the recommended BADCT - BOD effluent limitation would be $79,000. In contrast, the incremental capital costs for this plant to attain the BATEA effluent limitation is $540,000. For this particular case, multiple-stage biological treatment was provided as BATEA since BOD was the controlling parameter. Table 8-7 indicates the use of the minimum concentration values reported in Section VII. The average BPCTCA effluent

limitation for Subcategory B-3 is reported as 0.0467 kg BOD/kkg of pro-
duction. For the chloromethanes plant examined in Table 8-7, this RWL
would reflect a concentration of 6.5 mg/l. Since the minimum BPCTCA
BOD concentration has been set at 20 mg/l, this value would govern in
this particular case. That is why the BPCTCA - BOD effluent limitation
for the chloromethanes plant described in Table 8-7 was recomputed to
0.056 kg BOD/kkg based on 20 mg/l.

Capital cost estimates were provided for 31 of the 35 products previously
listed. Based on the available information, the treatment costs associated
with the 4 remaining products are minimal as indicated below:

Product	Production 10³ lbs/day	RWL Flow gal/10³ lbs	Wastewater Flow gpd	COD RWL 10³ lbs	COD RWL mg/l	Category
Cumene	822	0.04	33	0.001	300	A-2
Chlorotoluene	30	14,500	435,000	1.82	15	B-3
Oxalic Acid	27.4	52,500	1,440,000	4.36	10	C-4
Ionone	0.6	1,130	678	94	9,970	D-3

The minimal COD-RWL concentrations for chlorotoluene and oxalic acid pre-
clude the necessity for further treatment. The minimal flows in terms of
gpd associated with cumene and ionone production will have minimal impact
on the associated treatment costs. In actuality, these flows would be
treated in conjunction with other wastewaters eminating from other pro-
duction areas or hauled away and disposed of by a licensed hauler.

The preceding cost estimates were prepared for idealized plant sites with
no consideration for treatment site conditions, e.g., high ground water
table, poor soil conditions, etc. In addition, there is the problem of
segregation of process wastewater from non-contact process and stormwater
flows. In particular plants, segregation of wastewater could increase
the previously reported BPCTCA capital cost estimates from 10 to 50 per-
cent depending upon the physical plant layout and localized topography.

Energy

The BPCTCA treatment models were designed assuming sludge dewatering
using vacuum filtration with sludge cake disposal to a sanitary land-
fill. An alternative sludge disposal method is incineration, which
oxidizes the sludge organics and evaporates the water in the sludge.
The remaining inorganic ash is 90 percent of the original volume. The
offsetting factor is the substantial amount of energy required to
realize this volume reduction.

Since the previous cost tables are computed using August 1971 dollars,
the recent energy crisis has not impacted on these figures. The future
availability and pricing of energy will play an ever increasing role
in the selection of wastewater treatment processes and sludge handling
alternatives.

Non-Water Quality Aspects

The major non-water 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 non-water 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.

Table 8-1

BTX

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category A-1

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 1,041 x 10^3 lbs/day	--	--	--	--
Wastewater Flow - gpd	79,000	--	--	--
gals/1000 lbs product	75	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.47	0.015	--	--
mg/l	750	24	--	--
COD Effluent Limitation - lbs COD/1000 lbs product	5.8	--	0.059	0.031
mg/l	9,270	--	94	50^1
Total Capital Costs	--	$900,000	$82,000	$490,000
Annual Costs				
Amortization 8% @ 20 yrs	--	92,000	8,400	50,000
Operating + Maintenance	--	55,800	3,100	132,000
Energy + Power	--	2,200	100	154,000
Total Annual Costs	--	$150,000	$11,600	$336,000

[1] Minimum BATEA concentration of 50 mg/l controlling

Table 8-2

Para-Xylene

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category A-2

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 548 $\times$ 10^3 lbs/day	--	--	--	--
Wastewater Flow - gpd	2,910	--	--	--
gals/1000 lbs product	5.3	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.01	.009	--	--
mg/l	226	20[1]	--	--
COD Effluent Limitation - lbs COD/1000 lbs product	0.025	--	0.006	0.0022
mg/l	565	--	136	50[2]
Total Capital Costs	--	$290,000	$20,000	$20,000
Annual Costs				
Amortization 8% @ 20 yrs	--	30,000	2,000	2,000
Operating + Maintenance	--	29,600	1,000	900
Energy + Power	--	400	100	300
Total Annual Costs	--	$ 60,000	3,100	3,200

[1] Minimum BPCTCA concentration of 20 mg/l controlling
[2] Minimum BATEA concentration of 50 mg/l controlling

Table 8-3

Acetone

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-1

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 301 x 10^3 lbs/day				
Wastewater Flow - gpd	52,800	--	--	--
gals/1000 lbs product	175	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.26	0.035	--	--
mg/l	178	24	--	--
COD Effluent Limitation - lbs COD/1000 lbs product	1.10	--	.24	.073
mg/l	753	--	164	50[1]
Total Capital Costs	--	$610,000	$69,000	$350,000
Annual Costs				
Amortization 8% @ 20 yrs	--	61,000	7,000	36,000
Operating + Maintenance	--	45,700	2,500	6,600
Energy + Power	--	1,300	100	7,100
Total Annual Costs	--	$108,000	$ 9,600	$ 49,700

[1] Minimum BATEA concentration of 50 mg/l controlling

Table 8-4

Vinyl Chloride

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-2

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 1,370 × 10³ lbs/day				
Wastewater Flow – gpd	461,000	---	---	---
gals/1000 lbs product	337	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	7.66	2.38[1]	---	---
mg/l	2,720	846	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	---	---	1.3	0.22
mg/l	---	---	463	78
Total Capital Costs	---	$ 1,850,000	$ 170,000	$1,200,000
Annual Costs				
Amortization 8% @ 20 yrs	---	190,000	17,300	122,000
Operating + Maintenance	---	163,000	7,200	235,000
Energy + Power	---	17,000	300	260,000
Total Annual Costs	---	$ 370,000	$ 24,800	$ 617,000

[1] Possible biological inhibition warrants the use of COD as the controlling parameter.

Table 8-5

Styrene

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-2

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 1,370 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	3,870,000	---	---	---
gals/1000 lbs product	2,820	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	1.62	0.47	---	---
mg/l	69	20[1]	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	5.13	1.18	1.3	1.18
mg/l	218	50	55	50[2]
Total Capital Costs	---	$2,000,000	$ ---	$ ---
Annual Costs				
Amortization 8% @ 20 yrs	---	204,000	---	---
Operating + Maintenance	---	195,000	---	---
Energy + Power	---	21,000	---	---
Total Annual Costs	---	$ 420,000	$ ---	$ ---

[1] Minimum BPCTCA concentration of 20 mg/l controlling.

[2] Minimum BATEA concentration of 50 mg/l controlling.

Table 8-6

Phthalic Anhydride

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-3

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 342 × 10³ lbs/day				
Wastewater Flow - gpd	24,400	---	---	---
gals/1000 lbs product	71	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.128	0.047	0.0233[1]	0.0233[1]
mg/l	216	79	40	40
COD Effluent Limitation - lbs COD/1000 lbs product	0.642	0.92	0.77	0.288
mg/l	1,080	1,600	1,300	486
Effluent COD Based on Expected BPCTCA - mg/l	---	335	---	---
Total Capital Costs	---	$ 480,000	$ 50,000	$50,000
Annual Costs				
Amortization 8% @ 20 yrs	---	49,000	5,000	5,000
Operating + Maintenance	---	25,500	1,700	1,700
Energy + Power	---	5,500	100	100
Total Annual Costs	---	$ 80,000	$ 6,800	$ 6,800

[1]BOD - critical control parameter.

Table 8-7

Chloromethanes

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-3

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 356 × 10³ lbs/day				
Wastewater Flow - gpd	120,000	---	---	---
gals/1000 lbs product	338	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.22	0.056	---	---
mg/l	78	20[1]	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	0.94	0.92	0.77	0.288
mg/l	333	326	273	102
Effluent COD Based on Expected BPCTCA - mg/l	---	101	---	---
Total Capital Costs	---	$ 650,000	$	$
Annual Costs				
Amortization 8% @ 20 yrs	---	66,000	---	---
Operating + Maintenance	---	52,800	---	---
Energy + Power	---	1,200	---	---
Total Annual Costs	---	$ 120,000	$	$

[1]Minimum BPCTCA concentration of 20 mg/l controlling.

Table 8-8

Methyl Chloride

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-4

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 82.2 x 10^3 lbs/day	---	---	---	---
Wastewater Flow - gpd	118,000	---	---	---
gals/1000 lbs product	1,440	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	17.7	1.3	---	---
mg/l	1,470	108	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	62.7	20.2	16.8	6.3
mg/l	5,220	1,680	1,400	522
Total Capital Costs	---	$ 3,300,000	$ 97,000	$ 520,000
Annual Costs				
Amortization 8% @ 20 yrs	---	336,000	9,900	57,500
Operating + Maintenance	---	212,000	3,800	94,000
Energy + Power	---	32,000	100	100,000
Total Annual Costs	---	$ 580,000	$ 13,800	$ 251,500

Table 8-9

Adiponitrile

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-4

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 548 x 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	642,000	---	---	---
gals/1000 lbs product	1,172	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	19.2	1.3	---	---
mg/l	1,960	133	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	135	20.2[1]	16.8	6.3
mg/l	13,800	2,070	1,720	619
Total Capital Costs	---	$ 5,100,000	$ 195,000	$1,600,000
Annual Costs				
Amortization 8% @ 20 yrs	---	520,000	20,000	163,000
Operating + Maintenance	---	480,000	8,400	556,000
Energy + Power	---	50,000	300	669,000
Total Annual Costs	---	$ 1,050,000	$ 28,700	$1,388,000

[1] Possible biological inhibition warrants the use of COD as the controlling parameter.

Table 8-10

Hexamethylenediamine

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-4

(ENR 1580 - August, 1971 Costs)

Average Production - 548×10^3 lbs/day

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Wastewater Flow - gpd	72,000	---	---	---
gals/1000 lbs product	132	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	4.0	1.3	1.10[1]	0.13[1]
mg/l	3,630	1,180	1,000	118
COD Effluent Limitation - lbs COD/1000 lbs product	11.7	20.2	16.8	6.3
mg/l	10,600	18,300	17,300	5,710
Effluent COD Based on Expected BPCTCA - mg/l	---	3,280	---	---
Total Capital Costs	---	$ 1,500,000	$ 79,000	$ 540,000[2]
Annual Costs				
Amortization 8% @ 20 yrs	---	153,000	8,000	55,000
Operating + Maintenance	---	110,000	2,900	32,000
Energy + Power	---	12,000	100	6,000
Total Annual Costs	---	$ 275,000	$ 11,000	$ 93,000

[1] BOD - critical control parameter.

[2] Multiple Stage biological treatment.

Table 8-11

Benzoic Acid

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-4

(ENR 1580 - August, 1971 Costs)

	RWL	Technology Level		
		BPCTCA	BADCT	BATEA
Average Production - 164 x 10^3 lbs/day	---	---	---	---
Wastewater Flow - gpd	55,900	---	---	---
gals/1000 lbs product	341	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	25.6	1.3	1.10[1]	1.13[1]
mg/l	9,000	457	387	46
COD Effluent Limitation - lbs COD/1000 lbs product	50.8	202	16.8	6.3
mg/l	17,900	7,100	5,900	2,220
Effluent COD Based on Expected BPCTCA - mg/l	---	5,600		
Total Capital Costs	---	$ 2,750,000	$ 71,000	$ 516,000[2]
Annual Costs				
Amortization 8% @ 20 yrs	---	280,000	7,200	53,000
Operating + Maintenance	---	173,000	2,600	49,000
Energy + Power	---	37,000	100	4,000
Total Annual Costs	---	$ 490,000	$ 9,900	$ 106,000

[1] BOD - critical control parameter.

[2] Multiple stage biological treatment.

Table 8-12

Methyl Ethyl Ketone

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-5

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 274 × 10³ lbs/day				
Wastewater Flow - gpd	34,500	---	---	---
gals/1000 lbs product	126	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	37.5	9.6	7.95	0.96[1]
mg/l	35,700	9,130	7,550	913
COD Effluent Limitation - lbs COD/1000 lbs product	103	67.9	56.3	21.0
mg/l	98,000	64,600	53,600	20,000
Effluent COD Based on Expected BPCTCA - mg/l	---	30,400	---	---
Total Capital Costs	---	$ 2,450,000	$ 58,000	1,030,000[2]
Annual Costs				
Amortization 8% @ 20 yrs	---	250,000	5,900	105,000
Operating + Maintenance	---	154,000	2,100	91,000
Energy + Power	---	36,000	100	16,000
Total Annual Costs	---	$ 440,000	$ 8,100	$ 212,000

[1]BOD - critical control parameter.

[2]Multiple stage biological treatment.

Table 8-13

Maleic Anhydride

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category B-5

(ENR 1580 - August, 1971 Costs)

	RWL		Technology Level		
			BPCTCA	BADCT	BATEA
Average Production - 137 x 10³ lbs/day	---		---	---	---
Wastewater Flow - gpd	72,800		---	---	---
gals/1000 lbs product	532		---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	263		9.6	7.95	0.96
mg/l	59,300		2,160	1,790	216
COD Effluent Limitation - lbs COD/1000 lbs product	440		67.9	56.3	21.0
mg/l	99,100		15,300	12,700	4,730
Effluent COD Based on Expected BPCTCA - mg/l	---		30,700	---	---
Total Capital Costs	---	$	5,400,000	$ 80,000	$ 760,000
Annual Costs					
Amortization 8% @ 20 yrs	---		551,000	8,200	77,500
Operating + Maintenance	---		369,000	3,000	1,070,000
Energy + Power	---		280,000	100	1,390,000
Total Annual Costs	---	$	1,200,000	$ 11,300	$2,537,500

Table 8-14

Isopropanol

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-3

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 1,370 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	418,000	---	---	---
gals/1000 lbs product	305	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	0.995	0.08	---	---
mg/l	391	31	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	2.99	1.44	1.19	0.44
mg/l	1,180	566	468	173
Effluent COD Based on Expected BPCTCA - mg/l	---	366	---	---
Total Capital Costs	---	$ 1,100,000	$ ---	$1,000,000
Annual Costs				
Amortization 8% @ 20 yrs	---	112,000	---	102,000
Operating + Maintenance	---	112,200	---	77,600
Energy + Power	---	5,800	---	59,400
Total Annual Costs	---	$ 230,000	$ ---	$ 239,000

Table 8-15

Formic Acid

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-4

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 41.1 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	659,000	---	---	---
gals/1000 lbs product	16,000	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	1.05	---	---	---
mg/l	8	20	10	10
COD Effluent Limitation - lbs COD/1000 lbs product	4.5	1.37	1.14	0.43
mg/l	34	10	9	3
Total Capital Costs	---	$ ---	$ ---	$ ---
Annual Costs				
Amortization 8% @ 20 yrs	---	---	---	---
Operating + Maintenance	---	---	---	---
Energy + Power	---	---	---	---
Total Annual Costs	---	$ ---	$ ---	$ ---

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Table 8-16

Propylene Oxide

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

	RWL	BPCTCA	BADCT	BATEA
			Technology Level	
Average Production - 548 x 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	4,180,000	---	---	---
gals/1000 lbs product	7,630	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	31.5	1.79	---	---
mg/l	495	28	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	143	29.7	24.7	9.2
mg/l	2,250	466	388	145
Effluent COD Based on Expected BPCTCA - mg/l	---	700	---	---
Total Capital Costs	---	$ 9,200,000	$ 420,000	$ 5,200,000
Annual Costs				
Amortization 8% @ 20 yrs	---	938,000	43,000	530,000
Operating + Maintenance	---	1,022,000	21,000	1,450,000
Energy + Power	---	140,000	700	1,700,000
Total Annual Costs	---	$ 2,100,000	$ 64,70u	$ 3,680,000

Table 8-17

Sec. Butyl Alcohol

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

		Technology Level			
		RWL	BPCTCA	BADCT	BATEA
Average Production - 219 x 10^3 lbs/day		---	---	---	---
Wastewater Flow -	gpd	862,000	---	---	---
	gals/1000 lbs product	3,940	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product		19.3	1.79	---	---
	mg/l	587	54	---	---
COD Effluent Limitation - lbs COD/1000 lbs product		126	29.7	24.7	9.2
	mg/l	3,830	903	751	280
Total Capital Costs		---	$ 5,600,000	$ 220,000	$1,650,000
Annual Costs					
Amortization 8% @ 20 yrs		---	570,000	22,000	168,000
Operating + Maintenance		---	526,000	9,600	352,000
Energy + Power		---	54,000	300	396,000
Total Annual Costs		---	$ 1,150,000	$ 31,900	$ 916,000

Table 8-18

Hydrazine

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

	RWL	Technology Level		
		BPCTCA	BADCT	BATEA
Average Production - 5.5×10^3 lbs/day	---	---	---	---
Wastewater Flow - gpd	20,000	---	---	---
gals/1000 lbs product	3,640	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	9.09	1.79	---	---
mg/l	300	59	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	115	29.7	24.7	9.2
mg/l	3,790	978	813	303
Total Capital Costs	---	$ 1,900,000	$ 46,500	$ 115,000
Annual Costs				
Amortization 8% @ 20 yrs	---	194,000	4,800	11,700
Operating + Maintenance	---	123,000	1,600	11,300
Energy + Power	---	13,000	100	9,900
Total Annual Costs	---	$ 330,000	$ 6,500	$ 32,900

Table 8-19

Calcium Stearate

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 80 x 10^3 lbs/day	---	---	---	---
Wastewater Flow - gpd	519,000	---	---	---
gals/1000 lbs product	6,490	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	13.8	1.79	---	---
mg/l	255	33	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	32.8	29.7	24.7	9.2
mg/l	606	548	456	170
Effluent COD Based on Expected BPCTCA - mg/l		170		
Total Capital Costs	---	$ 4,700,000	$ ---	$ ---
Annual Costs				
Amortization 8% @ 20 yrs	---	480,000	---	---
Operating + Maintenance	---	418,000	---	---
Energy + Power	---	42,000	---	---
Total Annual Costs	---	$ 940,000	$ ---	$ ---

Table 8-20

Caprolactam

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 685 × 10³ lbs/day				
Wastewater Flow - gpd	2,390,000	--	--	--
gals/1000 lbs product	3,490	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	47.1	1.79	--	--
mg/l	1,620	62	--	--
COD Effluent Limitation - lbs COD/1000 lbs product	93.0	29.7	24.7	9.2
mg/l	3,190	1,020	848	316
Total Capital Costs	--	$8,600,000	$330,000	$3,800,000
Annual Costs				
Amortization 8% @ 20 yrs	--	880,000	34,000	388,000
Operating + Maintenance	--	770,000	16,000	1,050,000
Energy + Power	--	150,000	500	1,230,000
Total Annual Costs	--	$1,800,000	$ 50,500	$2,668,000

Table 8-21

Isobutylene

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-5

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 137 x 10^3 lbs/day	--	--	--	--
Wastewater Flow - gpd	335,000	--	--	--
gals/1000 lbs product	2,450	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	13.6	1.79	--	--
mg/l	665	88	--	--
COD Effluent Limitation - lbs COD/1000 lbs product	64.1	29.7	24.7	9.2
mg/l	3,140	1,450	1,210	450
Total Capital Costs	--	$4,200,000	$150,000	$1,000,000
Annual Costs				
Amortization 8% @ 20 yrs	--	430,000	15,300	102,000
Operating + Maintenance	--	--	6,200	189,000
Energy + Power	--	35,000	200	247,000
Total Annual Costs	--	465,000	21,700	538,000

Table 8-22

Hexamethylene Tetramine

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-6

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 21.9 x 10³ lbs/day	--	--	--	--
Wastewater Flow - gpd	15,900	--	--	--
gals/1000 lbs product	726	--	--	--
BOD Effluent Limitation - lbs BOD/1000 lbs product	83.3	5.74	4.76	0.57
mg/l	13,800	948	784	95
COD Effluent Limitation - lbs COD/1000 lbs product	229	63.2	52.4	19.6
mg/l	37,800	10,400	8,650	3,240
Total Capital Costs	--	$2,400,000	$42,000	$210,000
Annual Costs				
Amortization 8% @ 20 yrs	--	245,000	4,300	21,400
Operating + Maintenance	--	129,000	1,400	69,800
Energy + Power	--	66,000	100	83,900
Total Annual Costs	--	$440,000	5,800	175,100

Table 8-23

Acrylonitrile

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-6

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 658 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	332,000	---	---	---
gals/1000 lbs product	505	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	60	5.74	4.76	0.57
mg/l	14,200	1,360	1,130	136
COD Effluent Limitation - lbs COD/1000 lbs product	179	63.2	52.4	19.6
mg/l	42,500	15,000	12,400	4,650
Total Capital Costs	---	$ 5,200,000	$ 150,000	$2,500,000
Annual Costs				
Amortization 8% @ 20 yrs	---	530,000	15,300	255,000
Operating + Maintenance	---	410,000	6,100	1,970,000
Energy + Power	---	110,000	200	2,520,000
Total Annual Costs	---	$ 1,050,000	$ 21,600	$4,745,000

Table 8-24

Pentaerythritol

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category C-7

(ENR 1580 - August, 1971 Costs)

	RWL	Technology Level BPCTCA	BADCT	BATEA
Average Production - 68.5 x 10³ lbs/day				
Wastewater Flow - gpd	83,800	---	---	---
gals/1000 lbs product	1,220	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	390	36.6	30.4	3.66
mg/l	38,300	3,600	2,990	360
COD Effluent Limitation - lbs COD/1000 lbs product	1,585	365	303	113
mg/l	156,000	35,900	29,800	11,100
Effluent COD Based on Expected BPCTCA - mg/l		48,400		
Total Capital Costs	---	$ 6,300,000	$ 83,000	$1,000,000
Annual Costs				
Amortization 8% @ 20 yrs	---	643,000	8,500	33,000
Operating + Maintenance	---	307,000	3,200	1,750,000
Energy + Power	---	400,000	100	2,290,000
Total Annual Costs	---	$ 1,350,000	$ 11,800	$4,173,000

Table 8-25

Fatty Acid

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-3

(ENR 1580 – August, 1971 Costs)

		Technology Level		
	RwL	BPCTCA	BADCT	BATEA
Average Production – 150 × 10³ lbs/day	---	---	---	---
Wastewater Flow – gpd	504,000	---	---	---
gals/1000 lbs product	3,360	---	---	---
BOD Effluent Limitation – lbs BOD/1000 lbs product	18.1	2.3	1.91^2	0.28
mg/l	646	82	68	10^1
COD Effluent Limitation – lbs COD/1000 lbs product	37.6	21	17.4	6.5
mg/l	1,340	749	621	232
Effluent COD Based on Expected BPCTCA – mg/l	---	415		
Total Capital Costs	---	$ 4,700,000	$ 175,000	$1,000,000
Annual Costs				
Amortization 8% @ 20 yrs	---	479,000	17,900	102,000
Operating + Maintenance	---	436,000	5,500	83,500
Energy + Power	---	45,000	300	67,300
Total Annual Costs	---	$ 960,000	$ 23,700	$ 252,800

[1] Minimum BATEA concentration of 10 mg/l controlling.

[2] BOD – critical control parameter for BADCT.

Table 8-26

Citronellol & Geraniol

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-3

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 1.38×10^3 lbs/day	---	---	---	---
Wastewater Flow - gpd	1,670	---	---	---
gals/1000 lbs product	1,210	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	58.1	2.3	1.91	0.23
mg/l	5,750	228	190	23
COD Effluent Limitation - lbs COD/1000 lbs product	111	21	17.4	6.5
mg/l	11,000	2,080	1,720	644
Effluent COD Based on Expected BPCTCA - mg/l		3,400		
Total Capital Costs	---	$ 1,150,000	$ 16,000	$ 25,000
Annual Costs				
Amortization 8% @ 20 yrs	---	117,000	1,600	2,600
Operating + Maintenance	---	38,000	1,000	3,400
Energy + Power	---	25,000	100	3,400
Total Annual Costs	---	$ 180,000	$ 2,700	$ 9,400

Table 8-27

Dye

Wastewater Treatment Costs for

BPCTCA, BADCT and BATEA Effluent Limitations

Category D-4

(ENR 1580 - August, 1971 Costs)

	RWL	BPCTCA	BADCT	BATEA
		Technology Level		
Average Production - 16.7 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	792,000	---	---	---
gals/1000 lbs product	47,400	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	397	19.8	---	---
mg/l	1,000	50	---	---
COD Effluent Limitation - lbs COD/1000 lbs product	2,060	403	334	125
mg/l	5,210	1,020	844	316
Effluent COD Based on Expected BPCTCA - mg/l	---	1,610		
Total Capital Costs	---	$ 11,500,000	$ 210,000	$ 1,800,000
Annual Costs				
Amortization 8% @ 20 yrs	---	1,170,000	21,400	184,000
Operating + Maintenance	---	730,000	9,800	624,000
Energy + Power	---	800,000	300	752,000
Total Annual Costs	---	$ 2,700,000	$ 31,500	$ 1,560,000

Table 8-28

Sodium Glutamate

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-4

(ENR 1580 - August, 1971 Costs)

	RWL	Technology Level		
		BPCTCA	BADCT	BATEA
Average Production - 32.8 x 10^3 lbs/day				
Wastewater Flow - gpd	264,000	---	---	---
gals/1000 lbs product	8,050	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	84.7	19.8	16.4[1]	1.98[1]
mg/l	1,260	295	244	30
COD Effluent Limitation - lbs COD/1000 lbs product	284	403	334	125
mg/l	4,230	5,990	4,970	1,860
Effluent COD Based on Expected BPCTCA - mg/l	---	1,310	---	---
Total Capital Costs	---	$ 5,100,000	$ 135,000	$1,930,000[2]
Annual Costs				
Amortization 8% @ 20 yrs	---	520,000	13,800	197,000
Operating + Maintenance	---	490,000	5,500	166,000
Energy + Power	---	40,000	200	50,000
Total Annual Costs	---	$ 1,050,000	$ 19,500	$ 413,000

[1]BOD - critical control parameter.

[2]Multiple stage biological treatment.

Table 8-29

Tannic Acid

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-4

(ENR 1580 - August, 1971 Costs)

	RWL	Technology Level BPCTCA	BADCT	BATEA
Average Production - 55 × 10³ lbs/day	---	---	---	---
Wastewater Flow - gpd	60,000	---	---	---
gals/1000 lbs product	1,200	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	153	19.8	16.4[1]	---
mg/l	15,300	1,980	1,640[1]	---
COD Effluent Limitation - lbs COD/1000 lbs product	1,070	403	334	125
mg/l	107,000	40,300	33,400	12,500
Effluent COD Based on Expected BPCTCA - mg/l	---	33,200	---	---
Total Capital Costs	---	$ 4,100,000	$ 76,000	$ 600,000
Annual Costs				
Amortization 8% @ 20 yrs	---	418,000	7,800	61,200
Operating + Maintenance	---	322,000	8,500	770,000
Energy + Power	---	130,000	300	1,000,000
Total Annual Costs	---	$ 870,000	$ 16,600	$ 1,831,200

[1]BOD - critical control parameter.

Table 8-30

Citric Acid

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-4

(ENR 1580 - August, 1971 Costs)

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Average Production - 301 × 10³ lbs/day				
Wastewater Flow - gpd	17,300,000	---	---	---
gals/1000 lbs product	57,500	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	328	19.8	16.4	4.8
mg/l	684	41	34	10[1]
COD Effluent Limitation - lbs COD/1000 lbs product	657	403	334	125[2]
mg/l	1,370	840	696	261
Effluent COD Based on Expected BPCTCA - mg/l	---	425	---	---
Total Capital Costs	---	$ 28,000,000	$ 740,000	$10,000,000
Annual Costs	---			
Amortization 8% @ 20 yrs	---	2,860,000	75,500	1,020,000
Operating + Maintenance	---	2,040,000	42,000	1,900,000
Energy + Power	---	1,300,000	1,300	2,090,000
Total Annual Costs	---	$ 6,200,000	$ 118,800	$ 5,010,000

[1] Minimum BATEA concentration of 10 mg/l controlling.

[2] COD - critical control parameter.

Table 8-31

Naphthenic Acids

Wastewater Treatment Costs for
BPCTCA, BADCT and BATEA Effluent Limitations

Category D-4

(ENR 1580 - August, 1971 Costs)

Average Production - 21.9 x 10^3 lbs/day

		Technology Level		
	RWL	BPCTCA	BADCT	BATEA
Wastewater Flow - gpd	104,000	---	---	---
gals/1000 lbs product	4,750	---	---	---
BOD Effluent Limitation - lbs BOD/1000 lbs product	141	19.8	16.4[1]	1.98[1]
mg/l	3,560	500	414	50
COD Effluent Limitation - lbs COD/1000 lbs product	298	403	334	125
mg/l	7,520	10,100	8,400	3,150
Effluent COD Based on Expected BPCTCA - mg/l	---	2,330	---	---
Total Capital Costs	---	$ 4,300,000	$ 92,000	$1,500,000[2]
Annual Costs				
Amortization 8% @ 20 yrs	---	438,000	9,400	153,000
Operating + Maintenance	---	322,000	3,500	104,000
Energy + Power	---	140,000	100	40,000
Total Annual Costs	---	$ 900,000	$ 13,000	$ 297,000

[1]BOD - critical control parameter.

[2]Multiple stage biological treatment.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY
CURRENTLY AVAILABLE (BPCTCA)

Best practicable control technology currently available (BPCTCA) for the Secondary Organic Products segment of the organic chemicals manufacturing point source category is based upon the utilization of both in-process controls and end-of-process treatment technologies. The goal of these controls and technologies is the reduction and eventual elimination of oxygen-demanding materials from all discharges. These pollutants (as measured by the BOD, COD, and TOC parameters) are responsible for most of the degradation this industry presently inflicts upon the aquatic environment. The following discussions describe the pollution control technologies commensurate with BPCTCA and the procedure used to establish effluent limitations guidelines.

The nature of the specific manufacturing process will determine the combination of process controls and modifications which are best suited for at-source water pollution control. However, some practices are generally applicable to all process plants within this point source category.

The first of these is the implementation of process observation and sampling programs to determine the identity, location, quantity, and composition of all aqueous streams within the plant. Monitoring should include all aqueous process streams as well as storage tank drainage, flare and pump seal waters, storm runoff, and wastewater associated with support activities such as laboratories, materials receiving and shipment, and intake waters treatment. Although not considered as major sources of oxygen-demanding pollutants, utility waters and steam condensate from non-contact cooling and heating should also be included in any such survey. The flows and loadings developed should be allocated to the different processes in the plant in terms of production-based ratios. This provides a clear understanding as to which specific products require high water utilization or generate large amounts of water-borne pollutants. At the present time, this information has been developed by only a very few manufacturers within this industry.

Waste characterization studies of this type logically lead to the selection of various streams for segregation or the application of at-source controls. Exemplary chemical process plants segregate all wastewater which has become contaminated with oxygen-demanding hydrocarbons. These wastewaters include contact wastes which flow continuously from within the process battery limits as well as intermittent wastewaters which have contacted chemicals in other sections of the plant. The segregation and collection of these contaminated wastes from non-contaminated streams such as non-contact cooling waters appreciably reduce the volume of wastewater to be treated in a centralized wastewater treatment plant.

NOTICE: THESE ARE TENTATIVE RECOMMENDATIONS BASED UPON INFORMATION IN THIS REPORT AND ARE SUBJECT TO CHANGE BASED UPON COMMENTS RECEIVED AND FURTHER INTERNAL REVIEW BY EPA.

In most chemical manufacturing processes, the volume of non-contact cooling water required is between 3 and 100 times greater than the water which contacts chemicals within the process. The exact ratio depends upon whether the plant uses once-through cooling water or a recirculating system with cooling towers. However, the quantity of oxygen-demanding hydrocarbons present in these waters is less than one percent of that present in contact waters. The major pollutants associated with non-contact waters are inorganic anions and cations existing as dissolved solids and other chemicals to control slimes, algae, and corrosion. These materials do not normally affect dissolved oxygen levels in receiving waters.

In exemplary plants where contact waters are collected separately from non-contact waters, it is possible to design and operate a treatment system which has been sized to treat the optimum hydraulic and organic pollutant loadings from the manufacturing operations. Fluctuations in influent concentration can be reduced by equalization of the wastes. This practice also serves to smooth out shock loads resulting from process upsets. These may normally cause concentration gradients which could be toxic or inhibitory in a biological treatment system.

One of the most common at-source controls utilized by organic chemical plants is the separation and selective burning of hydrocarbon by-products. These materials are invariably formed because very few chemical reactions are 100 percent selective in the formation of the desired product. In almost every plant surveyed for the production of secondary organic products, some waste organic chemicals are disposed of by burning or hauling to landfill disposal. Although they may not be significant on a flow volume basis, these materials if flammable should not be discharged to the sewer and if not flammable would increase the quantities of hydrocarbons present in wastewaters by an order of magnitude if they were combined with aqueous process wastes.

The devices used for burning may range from simple flares (for materials with high vapor pressures) to complex liquid waste incinerators or pyrolysis furnaces with extensive air pollution control equipment. In many cases, waste organic by-products are suitable as auxiliary boiler fuel. Although the continuation of this practice should be evaluated to insure that adequate air pollution control devices are utilized, it represents a significant contribution to the reduction of hydrocarbons present in the wastewaters from most plants surveyed. For this reason, it is considered as one of the generally applicable in-process control practices for BPCTCA.

A second practice involves the separation of insoluble hydrocarbons from process wastewaters. In many cases, this can be accomplished by simple gravity separation or the use of flotation systems. The fatty acid product/process grouping uses this technique to advantage. Insoluble hydrocarbon skimmings are collected and treated by filtration and sulfuric acid addition to increase product yields.

Process modifications consistent with BPCTCA include the regeneration and reuse of aqueous working fluids in the process. This is normally done by vacuum evaporation. Typical examples include the regeneration of sulfuric acid in processes to produce isobutylene and secondary butyl alcohol.

Other modifications include the direct recycle of a working aqueous fluid such as the absorbent in a gas scrubber or water used in barometric condensers. These techniques are utilized in the processes to manufacture benzoic acid and hexamethylene tetramine. In these cases, the volume of contact water discharged is reduced from once-through operation to the blowdown from a recirculating system. Because of the diverse nature of even the limited number of processes examined in this study, it is not possible to generalize beyond practices such as sewer segregation and non-aqueous disposal of hydrocarbon wastes. For this reason, BPCTCA effluent limitations guidelines were calculated based upon an end-of-process treatment model.

End-of-process treatment technologies commensurate with BPCTCA are based on the utilization of biological systems including the activated sludge process, extended aeration, aerated lagoons, trickling filters, and anaerobic and facultative lagoons. These systems include additional treatment operations such as equalization, neutralization, primary clarification with separation of insoluble hydrocarbons, and nutrient addition. Final removal of suspended solids is accomplished by clarification.

Although the activated sludge process is considered as the single treatment system most generally applicable to the wide variety of wastes generated by this industry, it must be recognized that many specific processes generate wastes which, if directly treated, would be toxic or inhibitory to a biological system accepting only those wastes. However, most of these wastes become non-inhibitory if the influent concentrations are reduced from the extremely high values existing in the raw waste. This has been demonstrated in biological systems treating chlorinated hydrocarbons from the manufacture of ethylene dichloride and vinyl chloride and in systems which treat the combined wastes from a batch chemical plant where the treatability of individual batch wastes may vary widely.

In the case of specific wastes which are biorefractory at any concentration, BPCTCA does not preclude the use of carbon adsorption or other types of physical/chemical treatment to achieve BPCTCA effluent limitations guidelines.

It should also be noted that, at the present time, most manufacturers have elected to dispose of toxic, inhibitory, or difficult wastes by means of deep-well injection or ocean dumping. The geographic location of many plants manufacturing these materials has made this a rather common practice. If deep-well injection or ocean dumping were considered as viable alternatives consistent with BPCTCA, some of the process plants

surveyed would not discharge any process wastes to receiving waters. However, because of the potential danger of underground leakage or con- tamination inherent in the practice of deep-well disposal, effluent limitations guidelines have been developed as if these wastes were to be treated for discharge to surface waters.

The effluent limitations guidelines for BPCTCA were developed using a step-wise approach starting with the process raw waste load (RWL). The process RWL is the production-based ratio relating specific pol- lutants to specific products manufactured by specific manufacturing schemes. During the field sampling program, the process RWL was developed for different manufacturing operations by sampling contact process wastewaters. The RWL is the necessary link between the wide diversity of products and manufacturing operations existing in this industry and the production-based effluent limitations guidelines.

A single set of RWL values was first established for each of the secondary product/process groupings covered in Phase II of this study. This set of values included the following pollution parameters:

Contact Process Wastewater Flow	(liter/kkg of production)
BOD$_5$ Raw Waste Loading	(kg/kkg of production)
COD Raw Waste Loading	(kg/kkg of production)
TOC Raw Waste Loading	(kg/kkg of production)

It was necessary to develop single numerical values for flow as well as values for each of the three waste load parameters despite the fact that field sampling data indicated that significant variation exists between sampling periods for a single process and between different manufacturers operating nominally the same process.

The single set of values assigned to each process was designated as the RWL which can be obtained through the application of in-process pollution control practices which are commensurate with BPCTCA. These practices were discussed previously in this section. The actual RWL values were indicated with each of the separate process descriptions presented in Section IV.

It should be noted that the lowest observed values were not arbitrarily chosen as RWL for BPCTCA. Factors such as process plant age, size, geographic location, and method of discharge (to surface waters or to a municipal treatment plant) were considered when drastically differing RWL were obtained for the same process.

There were many cases where only a single value from one sampling period could be developed for the process, or where the RWL varied drastically between sampling periods or between manufacturers for no apparent reason. In such cases it was necessary to use either the single value or the arithmetic mean as the RWL assigned to the process.

NOTICE: THESE ARE TENTATIVE RECOMMENDATIONS BASED UPON INFORMATION IN THIS REPORT AND ARE SUBJECT TO CHANGE BASED UPON COMMENTS RECEIVED AND FURTHER INTERNAL REVIEW BY EPA.

There were also instances where the data obtainedwere simply not considered as representative of the process. This occurred when aqueous waste streams existing in the vapor phase were vented to the atmosphere, or where the analytical results were unrealistically low for no explicable reason.

In some of the batch or semi-batch manufacturing operations associated with major process Subcategory D, it was not possible to develop individual RWL's for each of the hundreds of specific batch processes in operation. For this reason, commodities such as dyes and dye intermediates, fatty acids, primary derivitives of fatty acids, plasticizers, and pigments were considered as groups of materials whose manufacturing operations must be approached in terms of their aggregate production.

The RWL values assigned to each of the 54 secondary organic product/process groupings were then placed in the major process subcategories described in Section IV (Industry Categorization). Consideration of differences in the feedstocks, unit operations, and chemical conversions is implicit in this method of subcategorization as discussed in Section IV.

Tables 9-1 through 9-4 list the product/process groupings within each major process subcategory along with the RWL values commensurate with BPCTCA for each. The type of treatment and method of ultimate disposal of the process wastes are also indicated for each of the product/process groupings. It should be understood that an end-of-process treatment plant would normally not accept many of the extremely high concentrations shown because of processes existing as part of a multi-process facility. It should be noted that the wastes from 6 of the processes are disposed of by deep-well injection and 23 discharge to municipal treatment systems.

Examination of the RWL data presented in Tables 9-1 through 9-4 indicate large variations in the flows and loadings exhibited by the different product/process groupings within each major process subcategory. The brief tabulation provided in Table 9-5 provides orientation as to the magnitude of these variations.

Although there is a general increasing trend when comparing the major process Subcategories A, B, C, and D, the variation within any one sub-category was considered too large for the practical and equitable application of a single set of values such as the mean for each major sub-category. It should be noted that this variation exists even aften ten of the product/process groups were screened out because of lack of adequate waste characterization data. These products are listed as follows:

TABLE 9-1

Major Process Subcategory A (Non-Aqueous Processes)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Description	Disposition of Process Wastes	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD₅	COD	TOC
			L/kkg	kg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
Cumene	Alkylation of Benzene by Propylene	Part of Large Plant	0.334	<0.0001(<300)	<0.0001(<300)	<0.0001(<300)
p-Xylene	Isomerization, Crystalliza-tion and Filtration of Mixed Xylenes	Part of Large Plant	44.3	0.01(226)	0.025(564)	0.007(158)

TABLE 9-2

Major Process Subcategory B (Vapor-Phase Processes)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Description	Disposition of Process Wastes	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD$_5$	COD	TOC
			L/kkg	kg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
Adiponitrile	Chlorination of Butadine	Deep Well Injection	9,770.	19.2(1,970)	135.(13,800)	44.(4,500)
Benzoic Acid Bezaldehyde	Catalytic Oxidation of Toluene with Air	Municipal Treatment	2,840.	25.6(9,010)	50.8(17,900)	19.6(6,900)
Chlorinated Methanes	Chlorination of Methyl Chloride & Methane Mixture	Discharge to Surface Waters	2,820.	0.22(78)	0.94(333)	0.37(131)
* Chlorobenzene	Chlorination of Benzene	Part of Large Plant	-	-	-	-
Chlorotoluene	Chlorination of Toluene	Municipal Treatment	121,000.	0.24(2)	1.82(15)	0.24(2)
Diphenylamine	Deamination of Aniline	Discharge to Surface Waters	526.	0 087(165)	0.313(595)	0 228(433)
Hexamethylene-diamine	Hydrogenation of Adiponitrile	Deep Well Injection	1,700.	60.8(35,800)	114.(67,100)	41 7(24,500)
Hexamethylene-diamine	Ammonolysis of 1,6-Hexanediol	Deep Well Injection	1,100.	4.0(3,640)	11.7(10,600)	2.5(2,270)
Maleic Anhydride	Oxidation of Benzene	Act.Sldg. Trt (Part of Large Plant)	4,430	263 (59,400)	440 (99,300)	138.(31,200)
Methyl Chloride	Esterification of Methanol with Hydrochloric Acid	Deep Well Injection or Municipal Treatment	12,000	17.7(1480)	62.7(5230)	12.8(1,070)
Methyl Ethyl Ketone	Dehydrogenation of Sec.-Butyl Alchol	Part of Large Plant	1,050	37.5(35,700)	103.(98,100)	40.2(38,300)

TABLE 9-2 (Continued)

Major Process Subcategory B (Vapor-Phase Processes)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Description	Disposition of Process Wastes	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD₅	COD	TOC
			L/kkg	Lg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
Perchloro-ethylene	Chlorination of Chlorina-ted Hydrocarbons	Deep Well Injection	5,400.	0.44(81)	2.83(524)	0.17(31)
*Phthalic Anhydride	Oxidation of Naphthalene	Incineration	All Waste Incinerated			
Phthalic Anhydride	Oxidation of o-Xylene	Part of Large Plant	594	0.128(215)	0.642(1,080)	0.02(34)
Tricresyl Phosphate	Condensation of Cresol and Phosphorus Oxychloride	Municipal Treatment	28,000.	1.12(40)	11.4(407)	1.96(70)

* - Effluent Limitation Guidelines are not Developed for these Product/Process Groupings because of Inadequate RWL Data to Characterize the Operation.

TABLE 9-3

Major Process Subcategory C (Aqueous Reaction Systems)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Description	Disposition of Process Wastes	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD_5	COD	TOC
			L/kkg	kg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
*Acetic Esters Ethyl Acetate	Esterification of Ethyl Alchol with Acetic Acid	Part of Large Plant	1,294	0.049(38)	0.102(79)	0.034(26)
Propyl Acetate	Esterification of Propyl Alchol with Acetic Acid	Part of Large Plant	1,186.	0.009(8)	0.012(10)	0.005(4)
Acrylonitrile	Ammoxidation of Propylene	Deep Well Injection	4,210.	60.(14,300)	179.(42,500)	78(18,500)
p-Aminophenol	Catalytic Reduction of Nitrobenzene	Evaporation	15,000.	888(59,200)	1620.(108,000)	456(30,400)
Calcium Stearate	Neutralization of Stearic Acid	Municipal Treatment	54,100	13.8(255)	32.8(606)	23.1(427)
Caprolactam	DSM Caprolactam Process	Discharge to Surface Waters	29,100.	47.1(1,620)	93.0(3,200)	-
Cyclohexanone Oxime	Hydroxylamine Process	Discharge to Surface Waters	1,910.	-	6.29(3,290)	-
Cresol, Synthetic	Methylation of Phenol	Municipal Treatment	2,090.	297.(142,000)	632.(302,000)	217.(104,000)
Formic Acid	Hydrolysis of Formamide	Discharge to Surface Waters	134,000.	1.05(7.8)	4.5(34)	1.4(10)
Hexamethylene Tetramine	Synthesis with Ammonia	Municipal Treatment	6,040	83.3(13,800)	229(37,900)	71.0(11,800)
Hydrazine Solutions	The Raschig Process	Discharge to Surface Waters	30,300.	9.09(300)	115(3,800)	0.182(6)

TABLE 9-3 (Continued)

Major Process Subcategory C (Aqueous Reaction Systems)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Descripiton	Disposition of Process Wastes	Flow	Process Raw Waste Loads (BPCTCA) BOD_5	COD	TOC
			L/kkg	kg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
Isobutylene	Extraction from a Mixture of C_4 Hydrocarbons	Part of Large Plant	20,400.	13.6(668)	64.1(3,140)	12.9(632)
Isopropanol	Hydrolysis of Propylene	Municipal Treatment	2,540.	0.995(392)	2.99(1,180)	1.32(520)
*Organic Solvent Complex	Numerous Oxidation Processes	Activated Sludge Treatment	3,640.	-	-	23.3(6,400)
Oxalic Acid	Nitric Acid Oxidation of Carbohydrates	Municipal Treatment	437,000.	-	4.36(10)	1.31(3)
Pentaery-thritol	Aldehyde Condensation	Act. Sldg. Trt (Part of Large Plant)	10,200.	390.(38,200)	1,590.(156,000)	830.(81,400)
*Propylene Glycol	Hydrolyses of Pro-pylene Oxide	Discharge to Surface Waters	5,500.	0.016(3)	0.055(10)	0.006(11)
Propylene Oxide	Chlorohydrin Process	Discharge to Surface Waters	63,500.	31.5(496)	143.(2,250)	22.7(357)
Saccharin	Synthesis from Phthalic Anhydride Derivatives	Municipal Treatment	269,000.	253.(9,400)	879.(3,270)	384.(1430)
Sec. Butyl Alcohol	Sulfonation and Hydroly-sis of Mixed Butylenes	Part of Large Plant	32,800.	19.3(588)	126.(3,840)	33.1(1,010)

*Effluent Limitation Guidelines are not Developed for these Product/Process Groupings because of Inadequate RWL Data to characterize the Operation.

TABLE 9-4

Major Process Subcategory D (Batch Processes)

RWL for Each Product/Process Grouping Considered as BPCTCA

Product	Process Description	Disposition of Process Waters	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD$_5$	COD	TOC
			L/kkg	kkg/kkg(mg/L)	kg/kkg(mg/L)	kg/kkg(mg/L)
Citric Acid	Fermentation of Molasses	Discharge to Surface Waters	477,000.	328.(688)	657.(1,380)	242.(507)
Citronellol & Geraniol	Citronella Oil Distillation	Municipal Treatment	10,100.	58.1(5,750)	111.(11,000)	37.7(3,730)
Dyes and Dye Intermediate	Batch Manufacture	Most Disch. to Mun. Trt.	395,000.	397.(1,010)	2,060.(5,220)	775.(1,960)
Fatty Acids	Hydrolysis of Natural Fats	Most Disch. to Mun. Trt.	28,000.	18.1(646)	37.6(1,340)	9.8(350)
Fatty Acid Derivatives	Esterification, Ammination, Etc.	Most Disch. to Mun Trt.	6,400.	18.(2,810)	27.9(4,360)	8.47(1,320)
Ionone and Methylionone	Condensation and Cyclization of Citral	Municipal Treatment	9,370	23.0(2,450)	94.0(10,000)	33.0(3,520)
*Methyl Salicylate	Esterification of Salicylic Acid with Methanol	Municipal Treatment	-----	------	-----	------
*Miscellaneous Batch Chemicals	Numerous Batch Processes	Most Disch to Surf Wat.	-----	------	-----	------
Monosodium Glutamate	Fermentation of Beet Sugar Molasses	Municipal Treatment	67,000	84.7(1,260)	284.(4,240)	91.(1,360)
Naphthenic Acid	Extraction & Acidification of Caustic Sludge from Petroleum Refinery	Part of Large Plant	39,700.	141.(3,550)	298.(7,510)	104.(2,620)

TABLE 9-4 (Continued)

Major Process Subcategory D (Batch Processes)

RwL for Each Product/Process Grouping Considered As BPCTCA

Product	Process Description	Disposition of Process Waters	Process Raw Waste Loads (BPCTCA)			
			Flow	BOD$_5$	COD	TOC
o-Nitroaniline	Ammonolysis of o-nitrochlorobenzene	Municipal Treatment	269,000.	16.9(63)	105(390)	30.9(115)
p-Nitroaniline	Ammonolysis of p-nitrochlorobenzene	Municipal Treatment	39.100	2.55 (65)	79.1(2,020)	**22.2**(568)
*Pentachlorophenol	Chlorination of Phenol	Municipal Treatment	2.960.	0.941(318)	17.5(5,910)	2.29(774)
Pigments	Diazotization and coupling of amine, sulfuric acid, etc.	Municipal Treatment	658,000.	385 (585)	3,420(5,200)	513 (780)
Plasticizers	Condensation of Phthalic Anhydride	Municipal Treatment	650	53.9(82,900)	82.6(127,000)	33.4(51,400)
Tannic Acid	Extraction of Natural Vegetable Matter	Municipal Treatment	10,000	153(15,300)	1,070(107,000)	173(17,300)
*Vanillin	Alkaline Oxylation of Spent Sulfite Liquor	Ocean Disposal	134,000.	2,310 (17,300)	14,400(111,300)	266(29,600)

* Effluent Limitation Guidelines Are Not Developed For These Product/Process Groupings Because of Inadequate Data to Characterize the Operation

TABLE 9-5

Range of RWL Variation Within Major Process Sub-Categories

Major Process Sub-Category Product/Process Groupings*	A 2	B 13	C 16	D 13
Flow (lit./kkg.)				
Minimum	0.334	526.	1910.	650.
Mean	44.3	14,700.	70,000.	165,000.
Maximum	44.3	121,000.	437,000.	658,000.
BOD (kg./kkg.)				
Minimum	< 0.0001	0.087	0.995	16.9
Mean	0.01	33.1	132.	129.
Maximum	0.01	263.	888.	397.
COD (kg./kkg.)				
Minimum	< 0.0001	0.313	2.99	27.9
Mean	0.025	71.9	357.	640.
Maximum	0.025	440.	1620.	3420.
TOC (kg./kkg.)				
Minimum	< 0.0001	0.020	1.31	8.47
Mean	0.007	23.2	152.	185.
Maximum	0 007	138.	830.	775.

* Those product/process groupings for which effluent limitations guidelines will be developed.

Product	Process
Chlorobenzene	Chlorination of Benzene
Phthalic Anhydride	Oxidation of Naphthalene
Ethyl Acetate	Esterification of Ethanol
Propyl Acetate	Esterification of Isopropanol
Propylene Glycol	Hydrolysis of Propylene Oxide
Solvent Complex	Numerous Oxidation Processes
Methyl Salicylate	Synthesis with Salicylic Acid
Batch Chemicals Complex	Numerous Batch Processes
Vanillin	Synthesis from Sulfite Liquor
Pentachlorophenol	Chlorination of Phenol

Effluent limitations guidelines for these operations should be developed on an individual basis after more data has been obtained.

The development of separate effluent limitations guidelines based on the RWL for each of the remaining 44 processes was considered impractical because of the 44 separate sets of guidelines this would entail.

Therefore, each major subcategory was divided into additional subcategories. Product/process groups were assigned to each of these new subcategories based upon the magnitude of their RWL. Tables 9-6 through 9-9 show the division of the major process categories and list each of the product/process groups within the new subcategories. It should be noted that this technique is an extension of that utilized in Phase 1 of this study dealing with the Major Organic Products (EPA 440/1-73/009). Because of this, the new subcategories relating to the Secondary Organic Products have been numbered sequentially to follow those developed previously.

The mean RWL for each of the new subcategories was used as the baseline in the subsequent development of effluent limitation guidelines for that subcategory. These mean values are summarized in Table 9-10. Separate effluent limitation guidelines were developed for each of the 13 subcategories through the application of waste reduction to the mean values shown in Table 9-10.

It should be noted that, even with the use of these 13 subcategories, there is still some spread above and below the mean for each. Obviously those product/process groupings which have RWL's above the mean for their subcategory must reduce process waste discharges to a greater extent than required by the application of reduction factors to the mean. However, the lowest observed RWL values for many of these processes are significantly below the mean for their subcategories. Examination of the process descriptions provided in Section IV indicates that the lowest observed RWL value for 36 of the 44 product/process groupings are less than or equal to the BPCTCA mean RWL for their respective subcategories. Some of these reduced RWL values are directly related to specific in-process controls or modifications. Others represent the lowest value obtained during several sampling periods.

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TABLE 9-6

Division of Major Process Sub-Categories

Sub-Category A-2	Flow L/kkg	BOD_5 kg/kkg	COD kg/kkg	TOC kg/kkg
Cumene	0.334	<0.0001	<0.0001	<0.0001
p-Xylene	44.3	0.01	0.025	0.007
MEAN	44.3	0.01	0.025	0.007

TABLE 9-7

Division of Major Process Sub-Categories

	Flow L/kkg	BOD5 kg/kkg	COD kg/kkg	TOC kg/kkg
Sub-Category B-3				
Chloromethanes	2,820.	0.220	0.940	0.370
Chlorotoluene	121,000.	0.24	1.82	0.24
Diphenylamine	526.	0.087	0.313	0.228
Perchloroethylene	5,400.	0.44	2.83	0.170
Phthalic Anhydride (o-Xylene)	594.	0.128	0.642	0.02
Tricresyl Phosphate	28,000.	1.12	11.4	1.96
MEAN	2,340.	0.373	2.99	0.498
Sub-Category B-4				
Adipontrile	9,770.	19.2	135.	44.
Benzoic Acid & Benzaldehyde	2,840.	25.6	50.8	19.6
HMDA (Hexanediol)	1,100.	4.0	11.7	2.50
Methyl Chloride	12,000.	17.7	62.7	12.8
MEAN	6,430.	16.6	65.1	19.7
Sub-Category B-5				
HMDA (Adiponitrile)	1,700.	60.8	114.	41.7
Maleic Anhydride	4,430.	263.	440.	138.
Methyl Ethyl Ketone	1,050.	37.5	103.	40.2
MEAN	2,390.	120.	219.	73.3

TABLE 9-8

Division of Major Process Sub-Categories

	FLOW L/kkg	BOD$_5$ kg/kkg	COD kg/kkg	TOC kg/kkg
Sub-Category C-3				
Cyclohexane Oxime	1,910.	----	6.29	----
Isopropanol	2,540.	0.995	2.99	1.32
MEAN	2,230.	0.995	4.64	1.32
Sub-Category C-4				
Formic Acid	134,000.	1.05	4.5	1.4
Oxalic Acid	437,000.	1.31	4.36	1.31
MEAN	285,000.	1.18	4.43	1.36
Sub-Category C-5				
Calcium Stearate	54,100.	13.8	32.8	23.1
Caprolactam (DSM)	29,100.	47.1	93.	---
Hydrazine Solutions	30,300.	9.09	115.	----
Isobutylene	20,400.	13.6	64.1	12.9
Propylene Oxide	63,500.	31.5	143.	22.7
Sec. Butyl Alcohol	32,800.	19.3	126.	33.1
MEAN	38,400.	22.4	95.7	23.0
Sub-Category C-6				
Acrylonitrile	4,210.	60.	179.	78.
Hexamethylene Tetramine	6,040.	83.3	229.	71.
MEAN	5,130	71.7	204.	74.5
Sub-Category C-7				
p-Aminophenol	15,000.	888.	1,620.	456.
Cresol, Synthetic	2,090	297.	632.	217.
Pentaerythritol	10,200.	390.	1,590	830.
Saccharin	26,900.	253.	879.	384.
MEAN	13,500	457.	1,180	472

TABLE 9-9

Division of Major Process Sub-Categories

	FLOW	BOD$_5$	COD	TOC
	L/kkg	kg/kkg	kg/kkg	kg/kkg
Sub-Category D-1				
o-Nitroaniline	269,000	16.9	105.	30.9
p-Nitroaniline	39,100	2.55	79.1	22.2
MEAN	154,000	9.73	92.	26.5
Sub-Category D-2				
Citronellol and Geraniol	10,100.	58.1	111.	37.7
Fatty Acids	28,000.	18.1	37.6	9.8
Fatty Acid Derivatives	6,400.	18.	27.9	8.47
Ionone and Methyl Ionone	9,370.	23.	94.	33.
MEAN	13,500.	29.3	67.6	22.2
Sub-Category D-3				
Plasticizers	650.	53.9	82.6	33.4
MEAN	650.	53.9	82.6	33.4
Sub-Category D-4				
Citric Acid	477,000.	328.	657.	242.
Dyes and Intermediates	395,000.	397.	2,060.	775.
Naphthenic Acid	39,700	141.	298.	104.
Pigments	658,000.	385.	3,422.	513.
Sodium Glutamate	67,000.	84.7	284.	91.
Tannic Acid	10,000.	153.	1,070.	173.
MEAN	274,000.	248	1,300.	316.

Table 9-10

Summary of Mean RWL for Each Secondary
Organic Product Sub-Category

Sub-Category	Flow (lit./kkg)	BOD (kg/kkg)	COD (kg/kkg)	TOC (kg/kkg)
A-2	44.3	0.010	0.025	0.007
B-3	2335.	0.373	2.99	0.498
B-4	6430.	16.6	65.1	19.7
B-5	2390.	120.	219.	73.3
C-3	2225.	0.995	4.64	1.32
C-4	285,000.	1.18	4.43	1.36
C-5	38,400.	22.4	95.7	23.0
C-6	5,130.	71.7	204.	74.5
C-7	13,500.	457.	1180.	472.
D-1	154,000.	9.72	92.0	26.5
D-2	13,500.	29.3	67.6	22.2
D-3	650.	53.9	82.6	33.4
D-4	274,000.	248.	1300.	316.

Although the effluent limitations guidelines for BPCTCA may be obtained by whatever combination of in-process and end-of-process means is best. suited to the individual manufacturers, the numerical values for the guidelines were calculated through the application of waste reduction factors based upon the use of a biological treatment system. The waste reduction factors used for calculating the BPCTCA effluent limitations guidelines for the BOD and COD parameters are listed as follows:

BOD   92 percent reduction (Effluent is 8 percent of RWL.)

COD   69 percent reduction (Effluent is 31 percent of RWL.)

These factors are based upon the performance of biological treatment systems described in Section VII - Control and Treatment Technologies. The performance data used to develop these factors, in many cases, were obtained over a full year's operation and are indicative of treatment systems which accept a wide variety of wastes. For this reason, these same reduction factors were applied to the BPCTCA mean RWL for each subcategory.

It should be noted that BOD should be used as the controlling parameter for BPCTCA effluent limitation guidelines. The values specified for COD should only be used where it can be demonstrated through the use of biological treatability studies that the waste (even after dilution with other wastes from the plant) can not be effectively reduced in a biological system. In such cases it is anticipated that some combination of in-process controls, coupled with end-of-process systems such as activated carbon adsorption applied to any of the 49 product/process groupings, can provide the required 69 percent reduction of COD. In addition, the 69 percent represents an overall efficiency and therefore can be related to the end-of-process treatment facilities in which some product/process will be treated greater or less than this volume. It should also be noted that compliance with both the BOD and COD effluent limitations is not required. Reduction of the BOD to levels developed through the application of the 92 percent reductions are considered adequate for BPCTCA effluent limitations guidelines.

There are some cases where the strict application of 92-percent BOD reduction would result in specific reduced effluent concentrations which are beyond the capabilities of the biological treatment systems considered as BPCTCA. Examination of Tables 9-1 through 9-4 indicate that the application of a 92-percent BOD reduction factor to the BPCTCA mean RWL for Subcategories A-2, B-3, C-4, and D-1 would result in effluent concentrations which are unrealistically low. Because of this, an effluent concentration of 20 mg/L BOD is specified as the BPCTCA effluent limitations guideline for three of these subcategories. The RWL concentrations were used for Subcategory C-4 since these are already below 10 mg/L.

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The remaining two parameters for which BPCTCA effluent limitations guidelines are specified are total suspended solids (TSS) and pH. It is not possible to specify production-based limitations for these parameters. Concentration guidelines have been established as follows:

TSS   65 mg/L

pH   6-9

The basic effluent limitation guidelines for BPCTCA are presented in Table 9-11. BPCTCA effluent values for the BOD and COD parameters were obtained in the manner indicated previously. It should be noted and clearly understood that these values shown as the BPCTCA effluent should not be directly applied as effluent limitations guidelines. They must be first multiplied by adjustment factors based on treatment plant performance developed in Section XIII. The last two columns in Table 9-11 indicate the actual effluent limitations guidelines for BPCTCA which have been adjusted for:

1. The maximum average of daily values for any period of 30 consecutive days.

2. The maximum value for any one day.

The total effluent limitation for a multi-process plant would be the summation of these values relating to individual processes. Concentration guidelines for TSS and pH relate to the entire facility and should be applied in the manner shown in Table 9-11.

TABLE 9-11

Effluent Limitations Guidelines for the Secondary Organic Segment of the Organic Chemicals Point Source Category Commensurate with Best Practicable Control Technology Currently Available (BPCTCA)

Sub-Category[1]	Average BPCTCA RWL (kg/kkg)	Reduction Factor	Average BPCTCA Effluent (kg/kkg)	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days (kg/kkg)	Maximum Value For Any One Day (kg/kkg)
A-2					
BOD	0.010	N.S.	0.000892[2]	0.00178	0.00401
COD	0.025	69%	0.00388	0.00776	0.0132
B-3					
BOD	0.373	N.S.	0.0467[3]	0.0934	0.210
COD	2.99	69%	0.927	1.94	3.15
B-4					
BOD	16.6	92%	1.33	2.66	5.99
COD	65.1	69%	20.2	40.4	68.7
B-5					
BOD	120.	92%	9.60	19.2	43.2
COD	219.	69%	67.9	135.8	231.
C-3					
BOD	0.995	92%	0.0796	0.159	0.358
COD	4.64	69%	1.44	2.88	4.90
C-4					
BOD	1.18	N.S.	1.18[4]	2.36	5.31
COD	4.43	N.S.	4.43[5]	8.86	15.1
C-5					
BOD	22.4	92%	1.79	3.58	8.06
COD	95.7	69%	29.7	59.4	101.
C-6					
BOD	71.7	92%	5.74	11.5	25.8
COD	204.	69%	63.2	126.	215.
C-7					
BOD	457.	92%	36.6	73.2	165.
COD	1180.	69%	365	730.	1240.
D-1					
BOD	9.72	N.S.	3.08[6]	6.16	13.9
COD	92.0	69%	28.5	57.0	96.9
D-2					
BOD	29.3	92%	2.30	4.60	10.4
COD	67.6	69%	21.0	42.0	71.4
D-3					
BOD	53.9	92%	4.30	8.60	19.4
COD	82.6	69%	25.6	51.2	87.0
D-4					
BOD	248	92%	19.8	39.6	89.1
COD	1300.	69%	403.	806.	1370.

BPCTCA Average Monthly Effluent Limitations Guidelines for TSS — 65mg/L
BPCTCA Maximum Daily Effluent Limitations Guidelines for pH — 6.0-9.0

N.S. indicates Value Not Specified

Notes:
[1] Individual Product/Process Groupings assigned to each sub-category are indicated in Tables 9-6,7,8,9
[2] Value obtained by multiplying 20 mg/ℓBOD by mean flow of 44.3 L/kkg for Sub-category A-2
[3] Value obtained by multiplying 20 mg/ℓBOD by mean flow of 2335 L/kkg for Sub-category B-3
[4] Value obtained by taking mean RWL for Sub-category C-4
[5] Value obtained by taking mean RWL for Sub-category C-4
[6] Value obtained by multiplying 20 mg/'BOD by mean flow of 154,000 L/kkg for Sub-category D-1

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY
ACHIEVABLE (BATEA)

Best available technology economically achievable (BATEA) for the Secondary Products segment of the organic chemicals point source category is based upon the most exemplary combination of in-process and end-of-process treatment and control technologies.

In-process practices include those mentioned previously for BPCTCA as well as the following:

1. The reuse of aqueous waste streams from one process in another so that the discharge is eliminated.

2. The recycle of waste streams from one unit operation within a process to another with the subsequent recovery of a product or co-product.

3. The concentration and disposal of wastewaters by means which eliminate the discharge entirely.

Process modifications for BATEA go beyond those described for BPCTCA in that they would require changes to major unit operations or chemical conversions within the process. Modifications for segregation of the sewer and drainage system for a process consistent with BPCTCA might be expected to amount to 1 to 4 percent of the battery limits capital cost. Recycle of aqueous waste streams for product recovery might involve replacement of existing distillation columns or reactors which could amount to more than 10 percent of the battery limits capital cost.

Specific examples of practices consistent with BATEA include: the reuse of aqueous hydrochloric acid streams in the manufacture of different chlorinated methanes; the recycle of aqueous waste streams for product recovery in the manufacture of hexamethylene diamine, maleic anhydride, and methyl ethyl ketone; and the use of evaporators or incinerators to completely eliminate discharges in the manufacture of phthalic anhydride and p-amino phenol.

Unfortunately, the wide diversity of the organic chemicals industry prevents prescribing a concise list of process modifications which are applicable to the industry as a whole (or even to the small fraction of its products covered in both phases of this study). This problem is aggravated by the fact that the industry as a whole zealously guards information relating to the nature of a specific manufacturing process. This secrecy may or may not be warranted in order to maintain a competitive

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position. However, it makes the development of effluent limitation guide-
lines based solely upon the application of in-process technologies im-
possible. Therefore, although the use of in-process techniques may repre-
sent a viable alternative for specific manufacturers, general effluent
limitations guidelines for BATEA have been developed based upon the appli-
cation of additional end-of-process treatment technologies.

Treatment commensurate with BATEA requires the application of activated
carbon adsorption or the use of additional biological systems in series
with the treatment previously described for BPCTCA. The specific choice
of which system should be utilized depends upon the specific process or
group of processes in operation at any given facility.

The performance of these treatment systems has been discussed in Section
VII - Control and Treatment Technologies. The incremental waste reduc-
tions associated with these technologies is indicated as follows for the
BOD and COD parameters:

BOD   90 percent reduction (BATEA effluent is 10 percent of BPCTCA
       effluent)

COD   69 percent reduction (BATEA effluent is 31 percent of BPCTCA
       effluent)

Effluent limitations guidelines for BATEA were calculated by applying
these reduction factors to average effluent for BPCTCA shown in Table 9-11.

There are specific subcategories where the direct use of these reduction
factors will still result in effluent concentrations which are below
the capabilities of the control systems considered as BATEA. In the case
of Subcategories A-2, B-3, and D-1, effluent limitations guidelines for
BATEA were obtained by applying minimum concentrations of 10 mg/L BOD
and 50 mg/L COD to the mean wastewater flow for the subcategory. The
mean RWL was again used for Subcategory C-4 since concentrations in the
raw waste are below 10 mg/L.

It should also be noted that the BATEA requires suspended solids removal
to an average concentration of 15 mg/L through the use of filtration.
This concentration limitation should again be applied to the total effluent
from any multi-process facility.

The effluent limitation guidelines for BATEA are presented in Table 10-1.
Again it must be understood that the BOD and COD values specified as the
average effluent for BATEA should not be directly applied before adjust-
ment for variations in treatment plant performance. The factors used here
are the same as for BPCTCA and are discussed in Section XIII - Variation
in Treatment Plant Performance.

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IN THIS REPORT AND ARE SUBJECT TO CHANGE BASED UPON COMMENTS RECEIVED
AND FURTHER INTERNAL REVIEW BY EPA.

TABLE 10-1

Effluent Limitations Guidelines for the Secondary Products of the Organic

Chemicals Point Source Category Commensurate with Best Available Technology Economically Achievable (BATEA)

Sub-Category[1]		Average BPCTCA Effluent (kg/kkg)	Reduction Factor	Average BATEA Effluent (kg/kkg)	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days (kg/kkg)	Maximum Value For Any One Day (kg/kkg)
A-2						
	BOD	000892	N.S.	000443[2]	000886	.00199
	COD	00388	69/	00120	00240	.00408
B-3						
	BOD	0467	N.S.	0234[3]	0468	105
	COD	927	69/	287	574	976
B-4						
	BOD	1 33	90/	133	266	599
	COD	20.2	69/	6 26	12.5	21.3
B-5						
	BOD	9 60	90%	960	1 92	4 32
	COD	67.9	69/	21 1	42 2	71.7
C-3						
	BOD	0796	90/	.00796	0159	0358
	COD	1.44	69/	446	892	1 52
C-4						
	BOD	1 18	N.S.	1.18[4]	2 36	5 31
	COD	4 43	N.S.	4.43[5]	8 86	15 1
C-5						
	BOD	1.79	90/	179	358	.806
	COD	29.7	69/	9 21	18 4	31 3
C-6						
	BOD	5 74	90/	574	1.15	2.58
	COD	63.2	69/	19 6	39 2	66.6
C-7						
	BOD	36.6	90%	3 66	7.32	16.5
	COD	365.	69%	113.	226	384.
D-1						
	BOD	3 08	N.S.	1 54	3 08	6.93
	COD	28 5	69/	8 84	17 68	30.1
D-2						
	BOD	2.30	90%	230	460	1.04
	COD	21.0	69/	6.51	13.0	22.1
D-3						
	BOD	4 30	90%	430	860	1.94
	COD	25 6	69/	7 94	15.9	27 0
D-4						
	BOD	19 8	90%	1 98	3.96	8.91
	COD	403	69/	125	250	425

BATEA Average Monthly Effluent Limitations Guidelines for TSS   15 mg/L

BATEA Maximum Daily Effluent Limitations Guidelines for pH   6 0-9.0

Notes: N.S. Indicates Value Not Specified

[1] Individual Product/Process Groupings assigned to each sub-category are indicated in Tables 9-6,7,8,9

[2] Value obtained by multiplying 10 mg/<BOD by mean flow of 44 3 L/kkg for Sub-category A-2

[3] Value obtained by multiplying 10 mg/<BOD by mean flow of 2335 L/kkg for Sub-category B-3

[4] Value obtained by taking mean RWL for Sub-category C-4

[5] Value obtained by taking mean RWL for Sub-category C-4

[6] Value obtained by multiplying 10 mg/<BOD by mean flow of 154,000 L/kkg for Sub-category D-1

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

Determination of the best available demonstrated control technology (BADCT) for new process plants involves the evaluation of the most exemplary water pollution control measures. As was the case with BPCTCA and BATEA, it is not possible to prescribe effluent limitation guidelines based upon the direct application of a uniform set of in-process modifications. Instead, an end-of-process treatment model utilizing a biological system followed by additional removal of BOD, COD and TSS by filtration was utilized.

Reductions in the BOD and COD parameters were obtained through laboratory tests of the effluents from activated sludge treatment systems sampled during the study. The results of these tests are described in Section VII, Control and Treatment Technologies. These reductions were applied to the effluent obtained from BPCTCA and are listed as follows:

    BOD   17% reduction   (BADCT eff. is 83% of BPCTCA eff.)
    COD   20% reduction   (BADCT eff. is 80% of BPCTCA eff.)

As with BATEA, the suspended solids limitation is indicated as a concentration value of 10 mg/L to be applied to the effluent from an entire facility.

Table 11-1 indicates the BADCT effluent limitation guidelines for the 44 product/process groupings according to the 13 subcategories established for secondary organic products. As with BPCTCA and BATEA, the values shown for average BADCT effluent should not be directly applied until they are adjusted for variation in treatment plant performance.

TABLE 11-1

Effluent Limitations Guidelines for the Secondary Organic Products Segment of the

Organic Chemicals Point Source Category Commensurate with Best Available Demonstrated Control Technology (BADCT)

Sub-Category[1]		Average BPCTCA Effluent (kg/kkg)	Reduction Factor	Average BADCT Effluent (kg/kkg)	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days (kg/kkg)	Maximum Value For Any One Day (kg/kkg)
A-2	BOD	.000892	N.S.	.000443[2]	.000886	.00199
	COD	.00388	20%	.00310	.00620	.0140
B-3	BOD	.0467	N.S.	.0234[3]	.0468	.105
	COD	.927	20%	.742	1.484	2.52
B-4	BOD	1.33	17%	1.11	2.22	5.00
	COD	20.2	20%	16.2	32.4	55.1
B-5	BOD	9.60	17%	7.97	15.9	35.9
	COD	67.9	20%	54.3	108.6	185.
C-3	BOD	.0796	17%	.0661	.132	.297
	COD	1.44	20%	1.15	2.30	3.91
C-4	BOD	1.18	N.S.	1.18[4]	2.36	5.31
	COD	4.43	N.S.	4.435	8.86	15.1
C-5	BOD	1.79	17%	1.49	2.98	6.71
	COD	29.7	20%	23.8	47.6	80.9
C-6	BOD	5.74	17%	4.76	9.52	21.4
	COD	63.2	20%	50.6	101.2	172.

TABLE 11-1

Effluent Limitations Guidelines for the Secondary Organic Products Segment of the
Organic Chemicals Point Source Category Commensurate with Best Available Demonstrated Control Technology (BADCT)

Sub-Category		Average BPCTCA Effluent (kg/kkg)	Reduction Factor	Average BADCT Effluent (kg/kkg)	Maximum Average of Daily Values for Any Period of Thirty Consecutive Days (kg/kkg)	Maximum Value For Any One Day (kg/kkg)
C-7	BOD	36.6	17%	30.4	60.8	137.
	COD	365.	20%	292.	584.	993.
D-1	BOD	3.08	N.S.	1.54[6]	3.08	6.93
	COD	28.5	20%	22.8	45.6	77.5
D-2	BOD	2.30	17%	1.91	3.82	8.60
	COD	21.0	20%	16.8	33.6	57.1
D-3	BOD	4.30	17%	3.57	7.14	16.1
	COD	25.6	20%	20.5	41.	69.7
D-4	BOD	19.8	17%	16.4	32.8	73.8
	COD	403.	20%	322.	644.	1095.

BADCT Average Monthly Effluent Limitations Guidelines for TSS   15 mg/L
BADCT Maximum Daily Effluent Limitations Guidelines for pH   6.0-9.0

Notes:

    N.S. indicates Value Not Specified

[1] Individual Product/Process Groupings Assigned to Each Sub-Category Are Indicated In Tables 9-6,7,8,9.

[2] Value Obtained By Multiplying 10 mg/L≤BOD By Mean Flow Of 44.3   L/kkg For Sub-Category A-2

[3] Value Obtained By Multiplying 10 mg/L≤BOD By Mean Flow of 2335   L/kkg For Sub-Category B-3

[4] Value Obtained By Taking Mean RWL For Sub-Category C-4

[5] Value Obtained By Taking Mean RWL For Sub-Category C-4

[6] Value Obtained by Multiplying 10 mg/L≤BOD By Mean Flow of 154,000   L/kkg For Sub-Category D-1

SECTION XII

PRETREATMENT GUIDELINES

Pollutants from specific processes within the organic chemicals industry may interfere with, pass through inadequately treated, or otherwise be incompatible with a publically-owned treatment works. The following section examines the general wastewater characteristics of the industry and the pretreatment unit operations which may be applicable.

A review of the wastewater 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:

Sub-Group 1	Sub-Group 2
Subcategory A	Subcategory C
Subcategory B	Subcategory D

The principal difference in the general characteristics of the process wastewaters from the manufacture of chemicals in these two Sub-Groups is that the wastewaters of Sub-Group 1 are more likely to include significant amounts of free and emulsified oils (petroleum origin), whereas the wastewaters of Sub-Group 2 are more likely to include significant amounts of heavy metals. Detailed analyses for specific products in the industry are presented in Section IV.

The types and amounts of heavy metals in the wastewater depend primarily on the manufacturing process and on the amounts and types of catalysts lost from the process. Most catalysts are expensive, and therefore, are recovered for reuse. Only recoverable catalysts (heavy metals), generally in small concentrations, appear in the wastewater. The products and processes in Sub-Group 2 are most likely to have heavy metals in their wastewater, and wastewaters associated with dye/pigment production (Subcategory D) also may have high heavy metal concentrations due to the production of metallic dyes. Fatty acid wastewaters (Subcategory D) contain free and emulsified oil (animal and vegetable origin) of significance.

The manufacture of acrylonitrile (Subcategory D) produces a highly toxic wastewater which is difficult to treat biologically. The toxicity characteristics have been attributed to the presence of hydrogen cyanide in excessive quantities (200 mg/L). In addition, the wastewater is generally acidic (pH 4 to 6) and contains high concentrations of organic carbon (TOC = 18500 mg/L). These wastewaters are generally segregated from other process wastes and are disposed of by other means (e.g., incineration);

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 wastewaters from the manufacture of acrylonitrile.

Table 12-1 shows the pretreatment unit operations which may be necessary to protect joint wastewater treatment processes.

Oil separation may be required when the oil (petroleum origin) content of the wastewater exceeds 50 mg/L. Animal and vegetable oils in the fatty acid wastewaters will have to be segregated in order to minimize solids separation problems in the wastewater treatment facility.

The heavy metals present in organic chemical wastes are in many cases so low in concentration that heavy metals removal is not required from the standpoint of treatability characteristics. However, the effluent limitations for toxic 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 concentrations) and spill protection for spent acids and spent caustics may be required in some cases.

Biological Treatment Inhibition

The scope of this study did not allow for a specific toxicity evaluation of individual product wastewaters. However, the completeness of the RWL analytical data did provide a wastewater profile which could be used to evaluate possible biological inhibition. The list and concentrations of inhibitory pollutants in EPA's Federal Guidelines - Pretreatment of Discharge to Publicly Owned Treatment Works were examined, and specific comments are presented in Section VI. This previous list was amended in the Phase I report to include phenol and iron:

Parameter	Inhibition to Biological Treatment	Inhibition to Anaerobic Sludge Digestion
Phenol	50 mg/L	---
Iron	---	5 mg/L

Table 12-1

Pretreatment Unit Operations For the
Organic Chemicals Industry

Pretreatment Sub-Group	Suspended Growth Biological System	Fixed Growth Biological System	Independent Physical - Chemical System
1	Oil Separation + Equalization + Neutralization + Spill Protection + Chemical Precipitation[1]	Oil Separation + Equalization + Neutralization + Spill Protection + Chemical Precipitation[1]	Oil Separation + Equalization + Neutralization + Chemical Precipitation[1]
2[2]	Equalization + Neutralization + Spill Protection + Chemical Precipitation[1]	Equalization + Neutralization	Equalization + Neutralization

[1]Need for chemical precipitation depends on extent of catalyst recovery.

[2]Oil separation may be required for the fatty acid industry.

SECTION XIII

ALLOWANCE FOR VARIABILITY IN TREATMENT PLANT PERFORMANCE

Biological treatment, as well as activated carbon wastewater treatment, will produce an effluent of variable quality. In order to enforce the recommended average effluent limitations, it is necessary for EPA to set maximum allowable limitations so as to provide a procedure for evaluating plant performance compiled from a limited data base.

Biological Wastewater Treatment

Historically, biological treatment plants have been designed to remove some particular percent removal, e.g., 90 percent BOD, which was defined as a yearly average. Very little emphasis was placed on the effluent variability during winter periods. As long as plants met their required removal efficiencies during the summer months when stream quality was critical, the plant performance was considered adequate. Increased under-standing of biological kinetics and advanced instrumentation have provided design engineers with the knowledge required to substantially minimize effluent variability.

During the survey program, daily historic performance data were provided for only four treatment facilities, namely Plant Nos. 2, 11, 13, and 14. (See Table 7-2.) Plants 2 and 11 are multiple-stage biological plants treating Subcategory C wastewaters. Both of these treatment plants utilize activated sludge and were designed based on the criteria presented in Table 13-1. Plants 11 and 2 have primary settling and nutrient addition. In Plant 11, 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 2 has two parallel trains of 3 aeration basins each for a total of 6 basins. Clarification and air flotation are provided in order to re-duce the aeration basin mixed liquor (MLSS) which average about 7,000 to 8,000 mg/L. A polishing lagoon with an atypical detention time provides additional organic and solids removal. Plant 2 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. Plant 11 is located in the southern United States and is not subject to extreme seasonal tem-perature fluctuations. However, Plant 11 also has provision for steam addition to maintain basin temperature.

Plant 13 provided only effluent data so that it was not possible to effectively evaluate the plant's performance. Lastly, the performance data from Plant No. 14 indicated it was not considered exemplary in per-formance because the plant's annual BOD removal was only 73 percent, and the plant had not been designed to adequately perform during colder winter periods.

Table 13-1

Summary of Plant Design Criteria

Description	Plant No.11	Plant No.2
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/MG	450	540
Final Clarifier		
Overflow Rate - 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/MG	10	1.5

Twelve months of daily historic data from Plants 2 and 11 were statistically analyzed graphically and the normalized results are summarized in Table 13-2. Only COD data was available from Plant 2, while BOD and TOC data were available from Plant 11.

The significance of the data is that the biological treatment plant on the average (50 percent of the time) is producing an effluent with a BOD_5 concentration of 20 mg/L, but will also produce an effluent with 90 mg/L of BOD_5 5 percent of the time.

Variations in the performance of a treatment plant are attributable to one or more of the following:

1. Seasonal variations in the wastewater 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 could be reflected in performance.

5. In-plant process bottle necking 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.

6. The effluent COD variability is also a function of the changing ratios between refractory and readily degradable organics in the plant's influent wastewater. This would be more of a concern in Subcategory D wastes than in the existing data from Subcategory C wastewaters.

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 13-2 were examined to compare various ratios of probability of occurrence to the 50 percent probability of occurrence. This data is as follows:

Table 13-2

Effluent Variation of Biological
Treatment Plant Effluent

Probability of Occurrence % less than or equal to	Plant No. 11 BOD₅ Daily mg/L	Plant No. 11 BOD₅ Weekly mg/L	Plant No. 11 BOD₅ Monthly mg/L	Plant No. 2 COD Daily mg/L	Plant No. 2 COD Weekly mg/L	Plant No. 2 COD Monthly mg/L	Plant No. 11 TOC Daily mg/L	Plant No. 11 TOC Weekly mg/L	Plant No. 11 TOC 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	1,000	150	130	122
90	60	40	35	1,200	1,130	1,230	180	150	140
95	90	50	40	1,600	1,400	1,430	220	170	150
99	160	70	55	2,500	2,000	1,940	300	210	185

Ratio of Probability	Daily	BOD5	Weekly	Monthly
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 95/50 BOD ratio is 4.5, while the corresponding monthly ratio
is 2.0. 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 monthly average be used
as the time basis for the effluent guidelines. In addition, a 95-percent
confidence limit should be used, since the 95/50 values should be within
a range typically observed in the past as being reasonable when treatment
plant data were analyzed statistically.

Use of a 95-percent confidence limit suggests that the plant could be in
violation no more than one month per year. Therefore, review of the in-
dustrial self-reporting questionnaire would indicate if the plant were
permanently in violation. If the stipulated effluent limit was 20 mg/L
and a plant reported 40 mg/l on two successive months, then the plant
would be in violation.

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

Parameter	Monthly Effluent Adjustment Factor[1]	Weekly Effluent Adjustment Factor[1]	Daily Effluent Adjustment Factor[1]
BOD	2.0	2.5	4.5
COD	2.0	2.5	3.4

[1] 95/50 ratio of confidence limits.

Activated Carbon Wastewater Treatment

Of the six activated carbon wastewater plants surveyed, only one had sufficient data that could be analyzed statistically. Five months of effluent data (May through September) were obtained from Plant No. 30. (See Table 7-5.) The results of the statistical analyses are shown below:

Ratio of Probability	Daily Basis		
	BOD	COD	Phenol
99/50	2.0	2.1	14
95/50	1.6	1.5	11
90/50	1.4	1.3	6.3

The limited data does not justify the recommendation of a specific daily adjustment factor.

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SECTION XIV

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SECTION XV

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