United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

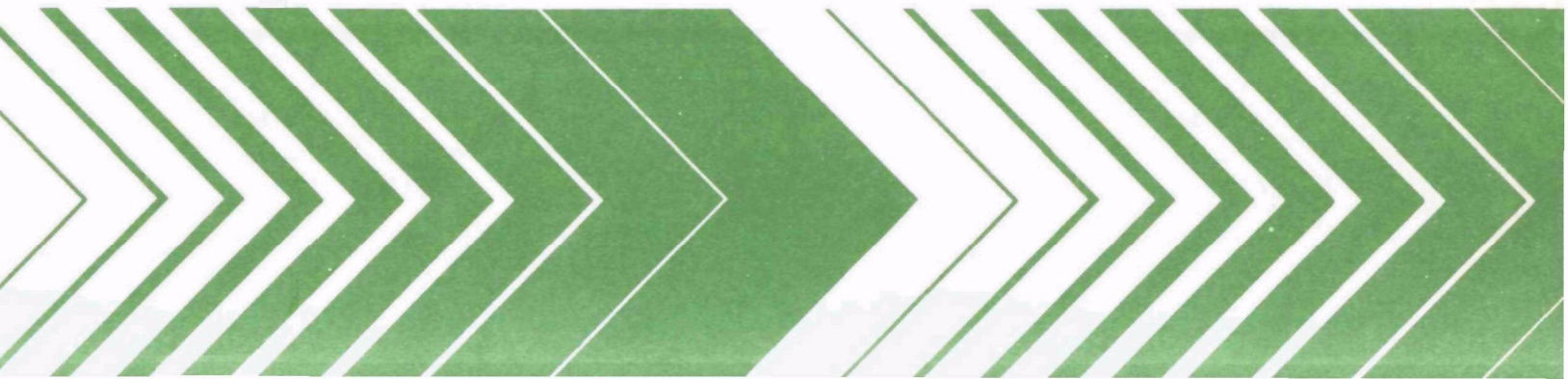
EPA-600/2-79-210d
December 1979

Research and Development

EPA

Status Assessment of Toxic Chemicals

Benzene



RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-79-210d
December 1979

STATUS ASSESSMENT OF TOXIC CHEMICALS:

BENZENE

by

J. C. Ochsner
T. R. Blackwood
Monsanto Research Corporation
Dayton, Ohio 45407

and

L. D. Zeagler
Radian Corporation
Austin, Texas 78766

Contract No. 68-03-2550

Project Officer

David L. Becker
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory - Cincinnati, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of vinylidene chloride. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Benzene, one of the most significant commercial organic chemicals in the United States, is a component of gasoline and a major intermediate in the organic chemicals industry. Because of its health hazards, it is also very important from an environmental standpoint. Produced in quantity second only to ethylene, the estimated 1977 capacity is 6.8×10^6 m^3 divided among more than 50 manufacturing plants. Increasing demand is expected to continue, possibly by 7.5%/yr until at least 1980.

Benzene is primarily used in the synthesis of other organic chemicals. Ethylbenzene, cumene, and cyclohexane production account for more than 80% of benzene used in the United States. Although production and process consumption is concentrated in the Texas Gulf and Northeast areas, its presence in gasoline gives it nationwide distribution. In fact, the largest total mass of emission is a result of motor vehicle operations (456×10^6 kg/yr). Major industrial sources of benzene emission include degreasing (73.1×10^6 kg/yr), ethylbenzene/styrene (9.5×10^6 kg/yr), and cyclohexane manufacture (7.8×10^6 kg/yr).

Benzene clearly produces adverse health effects. It has long been recognized as a poison if ingested in large quantities, and at nonlethal concentrations, a variety of human central nervous system disorders are observed. Federal standards for occupational exposure to benzene have been set, but further reduction in allowable concentrations has been proposed. Regulatory action under the Clean Air Act is awaiting results of an air monitoring program. Water quality criteria are anticipated under the Federal Water Pollution Control Act (FWPCA) by July 1978. The Consumer Products Safety Commission is considering action contingent on results of an Academy of Sciences study.

The following recommended areas for further study are: 1) ambient levels of benzene and the population exposed, 2) environmental reactivity, 3) benzene loss due to spills, accidents, or leaks, 4) benzene emissions from fugitive sources, 5) effects from nonlethal doses of benzene, 6) benzene's connection with leukemia, and 7) effect of modern motor vehicle emission controls on benzene emissions.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

CONTENTS

Foreword iii
Abstract iv
Tables viii
Abbreviations ix
Conversion Factors and Metric Prefixes x
Acknowledgement xi

1. Introduction 1
2. Summary 2
3. Source Description 5
    Physical and chemical properties 5
    Production 6
    Process description 6
    Uses 12
    Transportation 13
4. Environmental Significance and Health Effects 18
    Environmental significance 18
    Health effects 18
5. Control Technologies 26
    Emission source control methods 26
    Control efficiencies 26
6. Regulatory Action 32

References 33
Glossary 36

TABLES

Number		Page
1	Benzene.	3
2	Producing Companies, Plant Locations, and Capacity of the Benzene Industry.	7
3	Estimated Benzene Production (1976).	11
4	Benzene Consumption (1976)	13
5	Benzene Emission Sources	19
6	Evaporative Emission Factors for Benzene Storage Tanks Without Controls	21
7	Ambient Monitoring Data for Benzene.	22
8	Toxicity Data for Benzene.	25
9	Control Devices and Reported Control Efficiencies for the Maleic Anhydride Industry.	30

ABBREVIATIONS

FWPCA	--Federal Water Pollution Control Act
LC_{Lo}	--lowest reported concentration to have caused death
LC_{50}	--calculated concentration expected to kill 50% of an exposed population
LD_{Lo}	--lowest reported dose to have caused death
LD_{50}	--dose expected to kill 50% of a population
MRC	--Monsanto Research Corporation, Dayton, Ohio
NIOSH	--National Institute of Occupational Safety and Health
OSHA	--Occupational Safety and Health Administration
OTS	--Office of Toxic Substances
ppb	--parts per billion
ppm	--parts per million
TC_{Lo}	--lowest concentration reported to produce toxic effects
TD_{Lo}	--lowest dose reported to produce toxic effects

CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Gram/second (g/s)	Pound/hr	7.937
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Meter (m)	Foot	3.281
Meter^3 (m^3)	Barrels	6.293
Meter^3 (m^3)	Foot^3	3.531×10^1
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^2
Metric ton	Kilogram	1.000×10^3
Metric ton	Pound-mass	2.205×10^3
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kPa = 1×10^3 pascals
Milli	m	10^{-3}	1 mg = 1×10^{-3} gram

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\epsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

ACKNOWLEDGEMENT

This report was assembled for EPA by Radian Corporation, Austin, TX, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

SECTION 1

INTRODUCTION

Benzene is one of the most significant commercial organic chemicals in the United States. It is a component of gasoline and a major intermediate in the organic chemicals industry. Large quantities of benzene enter the environment and have become the subject of increasing concern and widespread investigation. Benzene clearly produces adverse health effects. Its commercial significance and pervasiveness mean that regulatory action must be considered. Devising a management strategy will be a complex and difficult problem.

Much of the information needed to define regulatory action is currently being generated by agencies outside the U.S. Office of Toxic Substance (OTS). The purpose of this report is to summarize available information on health effects, ambient concentrations, and sources of benzene. Production methods and quantities are described along with control techniques and regulatory action under consideration.

SECTION 2

SUMMARY

Benzene is a volatile, colorless, flammable liquid that is one of the most important industrial organic chemicals produced in the United States. Because of its potential health hazards, it is also very important from an environmental standpoint. However, a general lack of data prevents any accurate prediction of its environmental reactivity.

Benzene is produced in over 50 locations in quantities second only to ethylene. The estimated capacity for 1977 is 6.8 million m^3. Increasing demand is expected to continue, possibly by 7.5%/yr until at least 1980.

The two major sources of benzene are petroleum and coal, with petroleum being the largest source. Six processes are used to manufacture benzene; four operate on petroleum derivatives and two operate on coal.

Benzene is primarily used in the synthesis of other organic chemicals. Ethylbenzene, cumene, and cyclohexane production account for more than 80% of benzene used in the United States. Barring any unexpected events, benzene will remain as one of the most important chemicals to industry.

Benzene is shipped in drums and tank cars domestically by water (79.6%), rail (14.8%), and truck (5.6%). Most pipeline shipment is restricted to that which is captively used by the plant in which it is produced.

There are several sources of benzene emissions. The largest total mass of emission is from motor vehicles (exhaust fumes), 450 million kg/yr. Major industrial sources of benzene include degreasing and ethyl benzene/styrene manufacture, 73.1 million kg/yr and 9.5 million kg/yr, respectively. About 576,000 metric tons of benzene are released to the atmosphere from the production and use of benzene and products which contain it.

Information on levels of benzene in the atmosphere is sparse. However, one study indicated high values for metropolitan areas (Los Angeles and Toronto) which may be primarily due to exhausts from motor vehicles. Benzene has been identified in the drinking

water of three U.S. locations at levels of 2.0 ppb. It has also been identified in subsurface water at levels of 10 ppm in brine from one area, and 24 ppm in another geographic area having extensive oil and gas deposits.

Benzene has long been recognized as a poison if ingested in large quantities. The effects of nonlethal doses, including long-term illnesses, are not fully understood. Many researchers have concluded that more study is definitely needed, especially to determine if benzene can cause cancer.

Control of benzene emissions can be achieved by preventing release of the pollutant or by treating the waste streams. Various techniques of implementing these ideas have been developed and are summarized in Table 1. Also presented are emissions sources and rates, population exposed, and regulatory action.

TABLE 1. BENZENE

Emission source	Extent of problem: Emission rate, 10^6 kg/yr	Extent of problem: Population exposed	Control method	Regulatory agency or action
Production:				
Catalytic reforming	2.6	Production of benzene is generally localized in the Texas Gulf and Northeast areas.	Incineration or vapor recovery systems. Wet scrubbing in an absorber or a combination of the above. (>95% efficiency). Water treatment generally involves primary separation (70% to 90% efficiency) followed by secondary and possibly tertiary treatment.	OSHA has proposed a reduction of the 10 ppm standard to 1 ppm 8-hr weighted average with a ceiling of 5 ppm over a 15-min period.
Toluene dealkylation	1.4			
Toluene disproportionation	0.04			
Pyrolysis gasoline	0.6			
Coke-oven light oil	0.2			
Coke-oven operations	0.2			
Transport and storage:				
Bulk terminal loading/storage	0.04		Modified loading procedures (submerged or bottom loading) in conjunction with vapor recovery devices. Improved storage tank designs.	
Industrial use:				
Ethyl benzene/styrene	9.5	Process consumption of benzene is generally localized in the Texas Gulf and Northeast areas.	Incineration or vapor recovery systems. Wet scrubbing in an absorber or a combination of the above. (>95% efficiency.) Water treatment generally involves primary separation (70% to 90% efficiency) followed by secondary and possibly tertiary treatment.	OSHA has proposed a reduction of the 10 ppm standard to 1 ppm 8-hr weighted average with a ceiling of 5 ppm over a 15-min period.
Cumene/phenol	2.4			
Cyclohexane	7.8			
Aniline	0.1			
Chlorobenzenes	2.6			
Maleic anhydride	2.0			
Detergent alkylate	0.01			
Surface coatings (paints)	3.2			
Degreasing	73.1			
Nitrobenzene	3.4			
Fumaric acid	0.3			
Acrylonitrile	0.2			
Use of products containing benzene:				
Automobile tank loading	5.9	The presence of benzene in gasoline gives it nationwide distribution. Scarce data indicate that most Americans are probably exposed continuously to very low levels of benzene.	Vapor recovery and modified loading procedures. Catalytic converter. Proper procedure after benzene-containing spill.	EPA has initiated an air monitoring program which will determine benzene levels in selected areas. Benzene has been designated a priority pollutant under the Federal Water Pollution Control Act.
Service station tanks	0.2			
Motor vehicles	450			
Oil spills	10			

Based upon the information in this report the following areas for further study are recommended:

- More data is needed on ambient levels of benzene and the population exposed.
- More information is needed on benzene's environmental reactivity, for instance, its environmental residence time.
- Information is lacking on the amount of benzene lost due to spills, accidents, or leaks.
- The extent of benzene emissions from fugitive sources is unknown.
- The effects from nonlethal doses of benzene are not fully understood.
- More studies are needed to determine if there is a connection between benzene and leukemia.
- The effect that modern emission controls will have on benzene emissions from motor vehicles is an area for study.

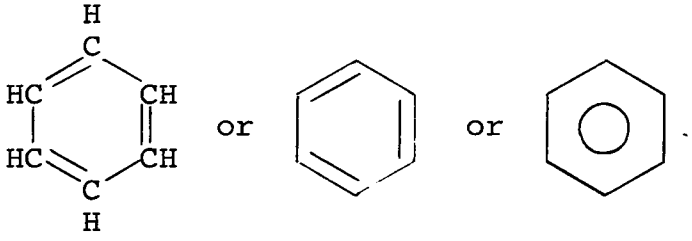
SECTION 3

SOURCE DESCRIPTION

PHYSICAL AND CHEMICAL PROPERTIES

Benzene is one of the most important industrial organic chemicals produced in the United States. Because of its potential health hazards, it is also very important from an environmental standpoint. The behavior of benzene after it has been emitted to the air or to a body of water is dependent to a large extent upon its physical properties. These will control its stability, chemical reactions, and long-term ambient concentrations in the environment.

Benzene is a volatile, colorless, flammable liquid. Its chemical formula is C_6H_6, and it has a structure represented as



Its important chemical properties are listed below:

Molecular weight	78.11
Vapor pressure	13 kPa at 25°C
Boiling point	80.1°C at 101 kPa
Specific gravity	0.8787 at 20°C/4°C
Octanol/water partition coefficient	2.28
Physical state	Liquid
Vapor specific gravity (air = 1)	2.77
Melting point	5.5°C
Solubility	Slightly (1.79×10^3 g/m^3 H_2O)

Little is known about benzene's environmental reactivity. In the atmosphere, it slowly reacts with oxidizing materials. Benzene is not photochemically reactive, but it is biodegradable (1). It is quite persistant, and due to its high vapor pressure, it is highly mobile in the atmosphere.

Benzene has been detected in both inland and marine waters. Because of its biodegradability, some benzene is oxidized by microorganisms in both air and water environments. A general lack of data prevents any accurate prediction of the environmental residence time of benzene (2).

PRODUCTION

Benzene is one of the most significant petrochemicals in the United States. It is produced in quantity second only to ethylene. In 1973, over 5.170×10^6 m^3 of benzene were produced in the United States. The estimated capacity for 1977 is 6.805×10^6 m^3 divided among more than 50 manufacturing plants. A list of benzene manufacturers is presented in Table 2 (3). The flexibility of most aromatics operations enables the reporting of only approximate capacities.

PROCESS DESCRIPTION

The two major sources of benzene are petroleum and coal, with petroleum supplying the largest percentage. Six processes are used to manufacture benzene; four of them operate on petroleum derivatives and two operate on coal. These processes are listed in Table 3 by estimated 1976 production and number of sites.

Petroleum-derived benzene is isolated from catalytic reformate and pyrolysis gasoline and produced directly by the dealkylation and disproportionation of toluene. Coal-derived benzene is isolated from coke-oven light oil, a byproduct of coke manufacture. Each of these processes is subsequently described.

---

(1) Dorigan, J. Scoring of Organic Air Pollutants: Chemistry Production and Toxicity of Selected Synthetic Organic Chemicals. Mitre Corporation, September 1976.

(2) Ocean Affairs Board, National Research Council. Assessing Potential Ocean Pollutants. Report No. 0-309-02325-4, U.S. Environmental Protection Agency and National Science Foundation, Washington, D. C., January 1975. 456 pp.

(3) Directory of Chemical Producers--U.S.A. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 1059 pp.

TABLE 2. PRODUCING COMPANIES, PLANT LOCATIONS, AND CAPACITY OF THE BENZENE INDUSTRY (3)

Company	Location	Annual capacity, 10^3 m^3	Raw material
Amerada Hess Corp.			
Hess Oil Virgin Islands Corp., subsidiary	St. Croix, VI	95	Petroleum
American Petrofina, Inc.			
American Petrofina Co. of Texas, subsidiary	Port Arthur, TX	57	Petroleum, captive
Cosden Oil & Chemical Co., subsidiary	Big Spring, TX	170	Petroleum, partly captive
Armco Steel Corp.	Middletown, OH	11	Coal
Ashland Oil, Inc.			
Ashland Chemical Co., division	Ashland, KY	238	Petroleum, partly captive
Petrochemicals division	North Tonawanda, NY	57	Petroleum
Atlantic Richfield Co.	Carson, CA	45	Petroleum
ARCO Chemical Co., division	Channelview, TX	132	Petroleum
	Houston, TX	159	Petroleum
Bethlehem Steel Corp.	Bethlehem, PA	19	Coal
	Sparrows Point, MD	57	Coal
CF&I Steel Corp.	Pueblo, CO	11	Coal
The Charter Co.			
Charter Oil Co., subsidiary			
Charter International Oil Co., subsidiary	Houston, TX	19	Petroleum
Cities Service Co.			
Chemicals Group			
Columbian Chemicals division	Lake Charles, LA	95	Petroleum
Coastal States Gas Corp.			
Coastal States Marketing, Inc., subsidiary	Corpus Christi, TX	265	Petroleum, partly captive

(continued)

TABLE 2 (continued)

Company	Location	Annual capacity, 10^3 m^3	Raw material
Commonwealth Oil Refining Co., Inc.			
Commonwealth Petrochemicals, Inc., subsidiary	Ponce, PR	700	Petroleum
Crown Central Petroleum Corp.			
Chemicals division	Pasadena, TX	87	Petroleum
Dow Chemicals U.S.A.	Bay City, MI	114	Petroleum, captive
	Freeport, TX	189	Petroleum, captive
Exxon Corp.			
Exxon Chemicals Co., division			
Exxon Chemicals Co. U.S.A.	Baton Rouge, LA	83	Petroleum
	Baytown, TX	227	Petroleum, partly captive
Getty Oil Co.			
Getty Refining and Marketing Co. subsidiary	El Dorado, KS	49	Petroleum, captive
Gulf Oil Corp.			
Gulf Oil Chemicals Co., division			
Petrochemicals, division	Alliance, PA	265	Petroleum
	Philadelphia, PA	125	Petroleum, captive
	Port Arthur, TX	144	Petroleum, captive
Independent Refining Corp.	Winnie, TX	11	Petroleum
Interlake, Inc.	Toledo, OH	4	Coal
Jones and Laughlin Industries, Inc.			
Jones & Laughlin Steel Corp., subsidiary	Aliquippa, PA	38	Coal
Kerr-McGee Corp.			
Southwestern Refining Co., Inc. subsidiary	Corpus Christi, TX	61	Petroleum

(continued)

TABLE 2 (continued)

Company	Location	Annual capacity, 10^3 m^3	Raw material
Marathon Oil Co.	Texas City, TX	23	Petroleum, captive
Mobil Corp. Mobil Oil Corp. Mobil Chemicals Co., division Petrochemicals division	Beaumont, TX	38	Petroleum
Monsanto Co. Monsanto Chemicals Intermediates Co.	Chocolate Bayou, TX	284	Petroleum, captive
Northwest Industries, Inc. Lone Star Steel Co., subsidiary	Lone Star, TX	4	Coal
Pennzoil Co. Atlas Processing Co., subsidiary	Shreveport, LA	57	Petroleum
Phillips Petroleum Co. Phillips Chemicals Co.	Sweeney, TX	84	Petroleum, captive
Phillips Puerto Rico Core, Inc., subsidiary	Guayama, PR	416	Petroleum, partly captive
Quintana-Howell	Corpus Christi, TX	27	Petroleum
Shell Chemicals Co.	Deer Park, TX	379	Petroleum
	Odessa Park, TX	45	Petroleum
	Wood River, IL	170	Petroleum
Standard Oil Co. of California Chevron Chemical Co., subsidiary Petrochemicals division Industries Chemicals	El Segundo, CA	87	Petroleum, captive
Standard Oil Co. (Indiana) Amoco Oil Co., subsidiary	Texas City, TX	322	Petroleum, captive
The Standard Oil Co. (Ohio) BP Oil Inc., subsidiary	Marcus Hook, PA	30	Petroleum

(continued)

TABLE 2 (continued)

Company	Location	Annual capacity, 10^3 m^3	Raw material
Sun Oil Co., Inc.			
Sun Oil Co. of Pennsylvania, subsidiary	Marcus Hook, PA	57	Petroleum
	Toledo, OH	132	Petroleum
	Tulsa, OK	91	Petroleum
Suntide Refining Co., subsidiary	Corpus Christi, TX	132	Petroleum, captive
Tenneco Inc.,			
Tenneco Oil Co., division	Chalmette, LA	38	Petroleum
Texaco, Inc.	Port Arthur, TX	170	Petroleum, partly captive
	Westville, NJ	132	Petroleum, partly captive
Union Carbide Corp.			
Chemicals and Plastics division	Taft, LA	189	Petroleum, captive
Union Oil Co. of California	Beaumont, TX[a]	84	Petroleum
	Lemont, IL	64	Petroleum
Union Pacific Corp.			
Champlin Petroleum Co., subsidiary	Corpus Christi, TX	38	Petroleum, captive
United States Steel Corp.			
USS Chemicals division	Clairton, PA	170	Coal
	Geneva, UT	15	Coal
TOTAL		6,805	

[a]Joint venture with American Petrofina of Texas, subsidiary of American Petrofina Incorporated.

NOTE: Some petroleum operators also isolate benzene from purchased coal-derived light oil.

Sources: Compiled in association with the World Hydrocarbons Program and communication with industry.

TABLE 3. ESTIMATED BENZENE PRODUCTION (1976)

Process	Capacity, 10^6 m^3	Number of sites[a]
Catalytic reforming	2.8	39
Toluene dealkylation	1.5	16
Toluene disproportionation	0.04	2
Pyrolysis gasoline	0.68	10
Purchased coke-oven light oil	0.21	5
Coke-oven operations	0.25	6
TOTAL	5.28	

[a]More than one process per site may be performed.

Catalytic Reforming

Catalytic reforming converts the paraffins and naphthalenes in naphtha to a higher octane reformate; the reformate contains a high percentage of aromatics. Reactions include cyclization of paraffins and dehydration and dealkylation of naphthalenes. Reformers are dedicated to production of either gasoline-blending components or petrochemical feedstocks. Feed to the latter produces a reformate containing 40% to 60% aromatics. The aromatic fraction is separated from the reformate via solvent extraction. The aromatic-rich extract can then be further separated into benzene, toluene, and xylenes by distillation. Benzene purities of 99.9% can be obtained (4).

Olefin Production--Pyrolysis Gasoline

Ethylene and propylene (and other olefins) are produced by cracking lower paraffins (propane or butane) or heavier stocks (naphtha or gas oils). A byproduct is pyrolysis gasoline, which can contain up to 80% aromatics (4). Purification of the gasoline requires hydrogenation for olefin saturation followed by solvent extraction. Processing details can be found in the literature (4-6).

(4) Parsons, T. B., et al. Industrial Process Profiles for Industrial Use: Basic Petrochemicals Industry, Chapter 5. Contract 68-02-1319, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977.

(5) Refining Handbook. Hydrocarbon Processing, 53(9):192, 1974.

(6) Petroleum Processing Handbook, Chapter 3. W. F. Bland and R. L. Davidson, eds. McGraw-Hill Book Co., New York, New York, 1967. pp. 1-152.

Toluene Dealkylation/Disproportionation

Toluene is used as the feedstock for two different benzene-producing reactions. In the presence of hydrogen, it can be dealkylated to yield benzene and methane. Higher alkyl aromatics are sometimes dealkylated to yield naphthalenes, with appreciable quantities of benzene formed as a byproduct. If 2 mol of toluene are catalytically reacted, 1 mol of benzene and 1 mol of xylene are produced (disproportionation). Products of all reactions must undergo distillation for separation. The toluene feed to these reactions generally comes from solvent extraction of catalytic reformate and can contain mixed xylenes as well as toluene (4).

Coke-Oven Light Oil

Coke manufacturing, which involves high-temperature coal carbonization, produces a light byproduct containing benzene. Further processing of the light oil sometimes includes hydrogenation for sulfur removal. Standard separations techniques are employed for benzene purification. There is a large potential for producing benzene from coal liquefaction processes, but these are several years from commercialization.

USES

The primary end use for benzene is in the synthesis of other organic chemicals. Ethylbenzene, cumene, and cyclohexane production account for more than 80% of the benzene used in the United States. A detailed breakdown is presented in Table 4 (7) and detailed discussions of these uses of benzene are found in Reference 8. A chemical tree is presented in Figure 1 (7).

Historically, demand has increased significantly because of the market for styrene monomer, phenol, cyclohexane, nitrobenzene, and maleic anhydride. Increasing demand is expected to continue, possibly by 7.5%/yr until at least 1980 (9). Barring some

---

(7) Chemical Origins and Markets, Fifth Edition, G. M. Lawler, ed. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

(8) Wilkins, G. E. End Use Patterns for Significant Organic Chemicals. Contract 68-02-1319, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1976.

(9) Ponder, T. C. Benzene: Outlook Through 1980. Hydrocarbon Processing, 55(11):217-218, 1976.

TABLE 4. BENZENE CONSUMPTION (1976) (7)

Product use	Percent
Ethylbenzene	50.0
Cumene	16.6
Cyclohexane	14.9
Aniline	4.3
Chlorobenzenes	3.5
Maleic anhydride	2.7
Detergent alkylate	2.6
Miscellaneous applications	3.0
Exports	2.4

catastrophe or emergence of a less expensive raw material, benzene will remain as one of the most important chemicals to industry.

TRANSPORTATION

Drums and tank cars are standard containers for benzene. According to one study (10), 79.6% of domestically shipped benzene goes by water, 14.8% by rail, and 5.6% by truck. Most pipeline shipment is restricted to benzene that is used captively by the plant in which it is produced.

(10) Dawson, G. W., A. J. Shuckrow, and W. H. Swift. Control of Spillage of Hazardous Polluting Substances. Contract 14-12-866 (PB 197 596), U.S. Department of the Interior, Federal Water Quality Administration, Washington, D.C., November 1970. 96 pp.

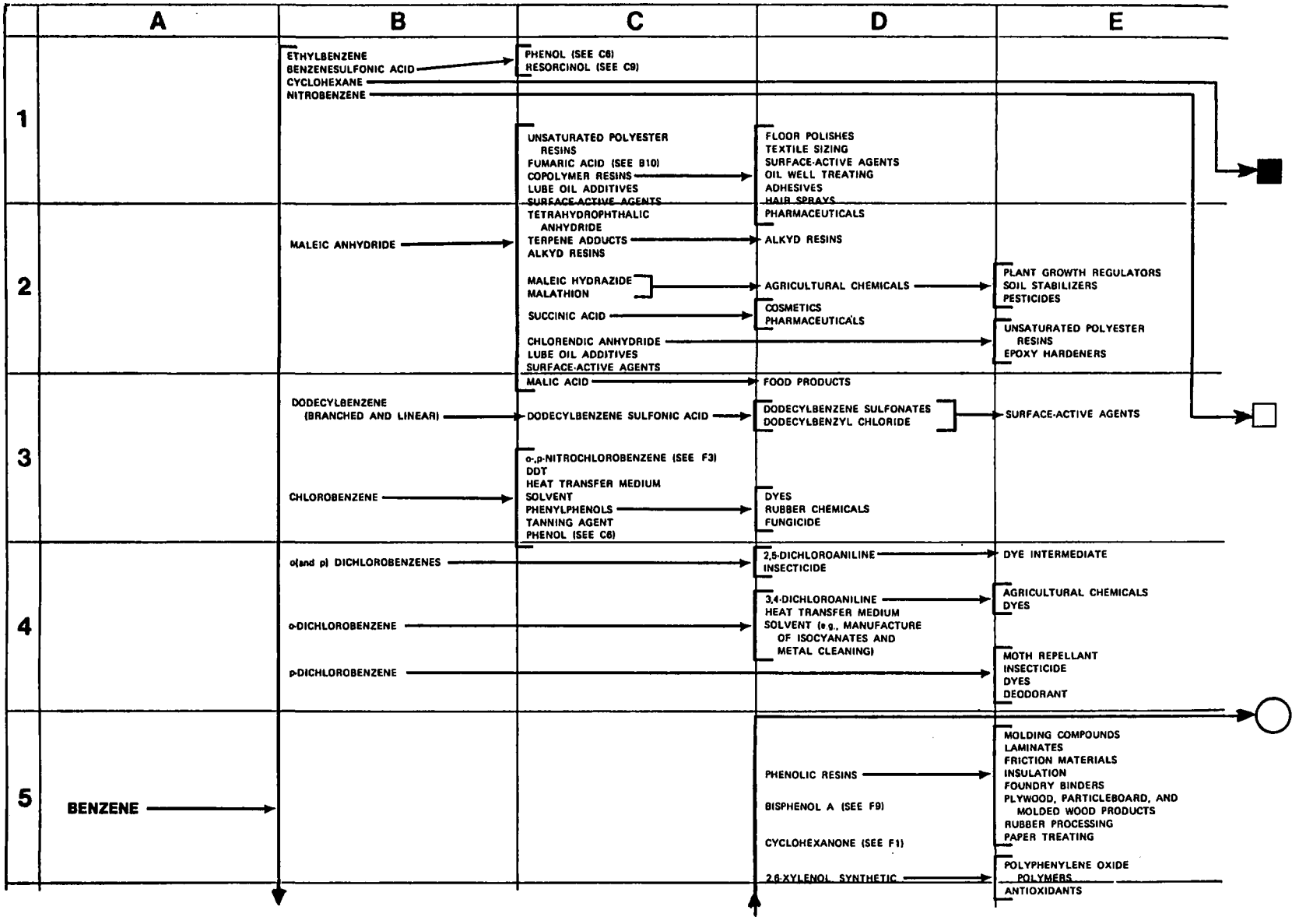


Figure 1. Benzene product flow diagram (7).

Reproduced by permission of SRI International, Menlo Park, CA.

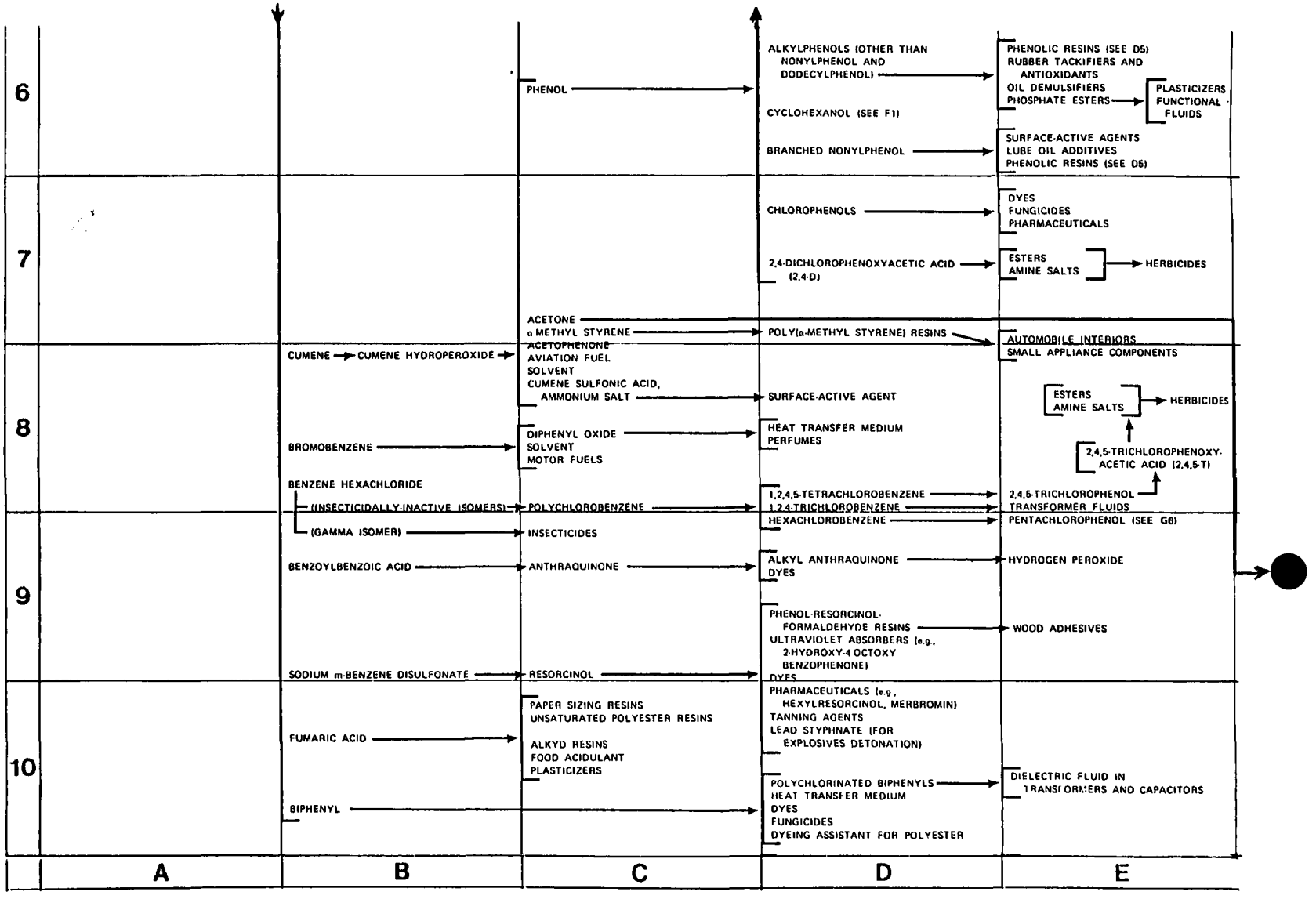


Figure 1 (continued)

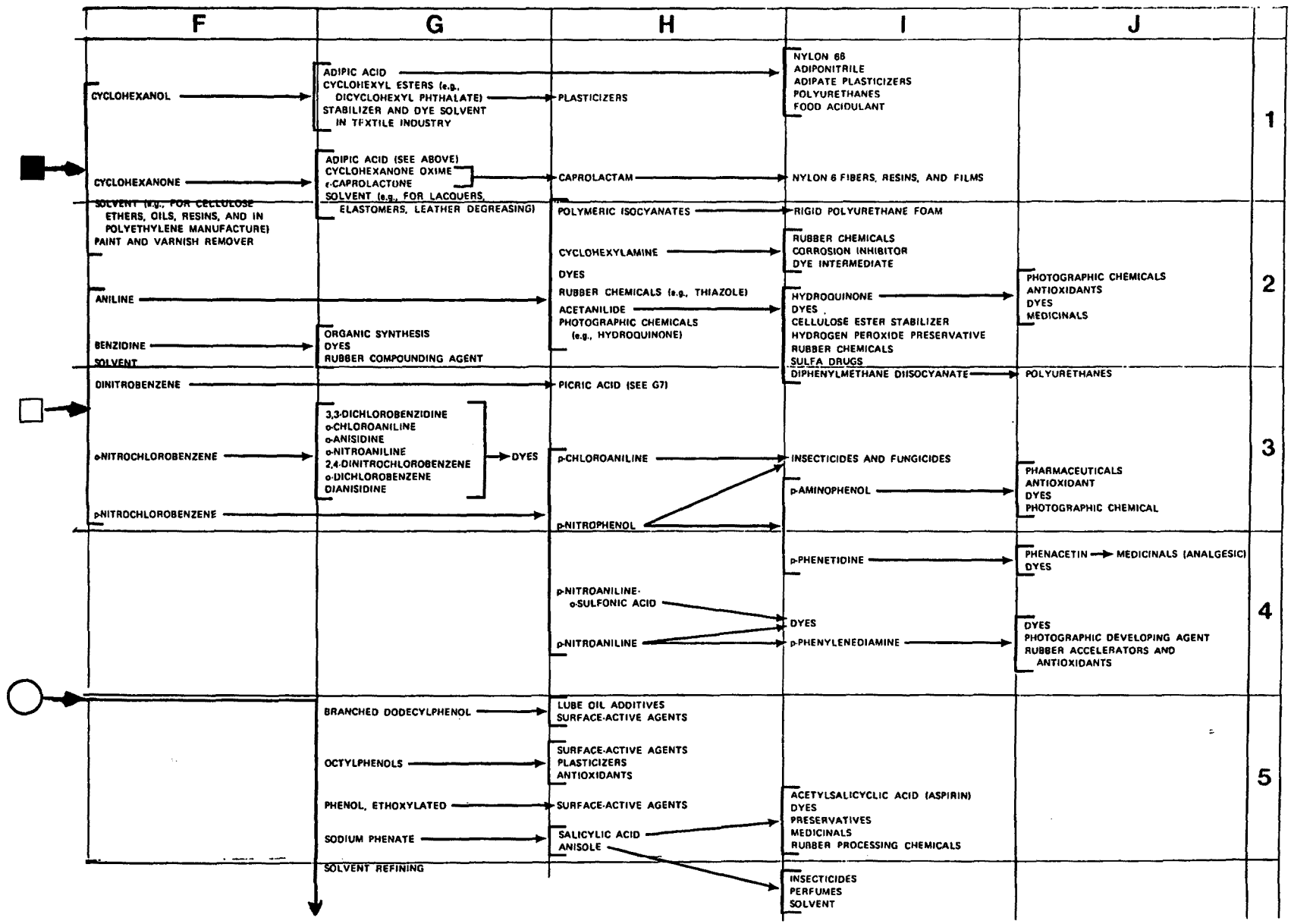


Figure 1 (continued)

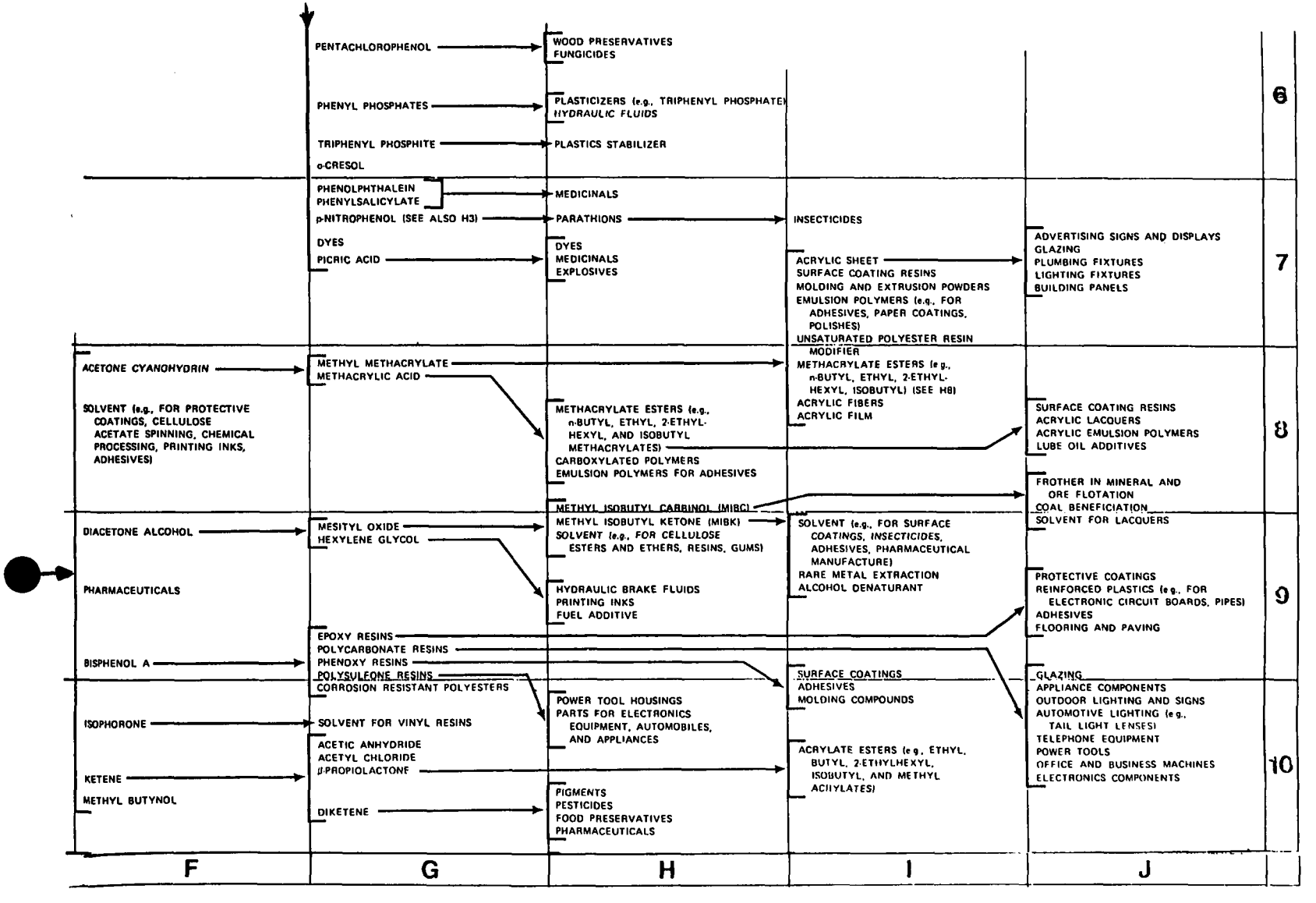


Figure 1 (continued)

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

Benzene is one of the major petrochemical intermediates produced and used in the United States. It has also been identified as a potential hazard. This section will examine sources of benzene emissions, ambient levels of benzene that result, secondary emissions formed, and the population at risk.

Sources of Emissions

There are several sources of benzene emissions. The largest emission source of benzene is motor vehicles (exhaust fumes). The largest individual sources of benzene are estimated to be from cyclohexanes, nitrobenzene and chlorobenzenes manufacture. Table 5 shows that in 1976, an estimated 576×10^6 kg of benzene were emitted to the atmosphere from 132×10^6 stationary and mobile sources. This includes an estimated 110 million kg/yr from production, transportation, storage, and use of benzene, 456 million kg/yr from refueling and operation of motor vehicles, and 10 million kg/yr from oil spills (private communication, T. W. Hughes, Monsanto Research Corporation; Reference 11; and engineering estimates as described in this section).

Production and Subsequent Processing Into Other Products--
The processes employed for benzene production are catalytic reforming/aromatics extraction, olefin manufacture/pyrolysis gas processing, toluene hydrodealkylation and disproportionation, and coking of coal. Hydrocarbons can be emitted from each of these processes in the form of fugitive leaks; e.g. from valves or flanges. Although emission factors exist for fugitive hydrocarbon emissions from oil refineries (12), no data specifically

---

(11) Eimutis, E. C., and R. P. Quill. Source Assessment: Noncriteria Pollutant Emissions. EPA-600/2-77-107e, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1977. 113 pp.

(12) Compilation of Air Pollutant Emission Factors, Second Edition (with Supplements 1-7). Publication No. AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1973.

TABLE 5. BENZENE EMISSION SOURCES

Emission source	1976 Estimated benzene emission rate, 10^6 kg/yr (11)	Number of sources	Mass emissions per source, kg/yr
Benzene production:			
Catalytic reforming	2.6[a]	39	67,000
Toluene dealkylation	1.4[a]	16	88,000
Toluene disproportionation	0.04[a]	2	20,000
Pyrolysis gasoline	0.6[a]	10	60,000
Coke-oven light oil	0.2[a]	5	40,000
Coke-oven operations	0.2[a]	6	33,000
Benzene consumption:			
Ethylbenzene/styrene	9.5[a]	12	190,000
Cumene/phenol	2.4[a]	9	270,000
Cyclohexane	7.8[a]	8	975,000
Aniline	0.1[a]	7	14,000
Chlorobenzenes	2.6	7	370,000
Maleic anhydride	2.0[a]	9	220,000
Detergent alkylate	0.01	5	2,700
Surface coatings (paints)	3.2[a]	8,745	370
Degreasing	73.1	1,300,000	56
Nitrobenzene	3.4	9	380,000
Fumaric acid	0.3[a]	6	50,000
Acrylonitrile	0.2[a]	6	33,000
Other sources:			
Automobile tank loading	5.9	226,500	26
Service station tanks	0.2	226,500	80
Bulk terminal loading/storage	0.04	30,900	1
Motor vehicles	450[b]	130,000,000	3
Oil spills	10[b]	787	12,000
TOTALS	576	131,800,000	

[a]Private communication, T. W. Hughes, Monsanto Research Corporation, Dayton, Ohio.

[b]See text, 1971 emissions estimates.

address benzene. Processes that use catalysts undergo periodic catalyst regeneration to burn off hydrocarbons adhering to the catalyst surface. Existing data on emissions from these sources encompass only hydrocarbons in general. There are potential aqueous emissions from olefins/pyrolysis gasoline manufacture, pyrolysis gas hydrotreating, coal coking, and aromatics extraction. A sludge is produced in the extraction processes as well. All of these streams have the potential of containing benzene.

Benzene is a feedstock for several organic chemical production processes as well as a gasoline blending component. Fugitive hydrocarbon (includes benzene) emission potential is as common as the lack of emission data. Almost all of the processes are catalytic, and benzene could be released during solid catalyst regeneration. [Process units maintained at atmospheric pressure by open vents can be sources of benzene emissions. [In nitrobenzene manufacture, 8.2 kg benzene/metric ton[a] nitrobenzene can be emitted from absorber vents (13).] Scrubber air from the recovery section in maleic anhydride production can contain as much as 107 kg benzene/metric ton of product (13).

Benzene is released to aqueous streams in different ways, depending on the process. The liquid-phase ethylbenzene process discharges a scrubber effluent water containing 11 kg of benzene/metric ton water (13). The vapor process has spent caustic and wash streams that contain significant amounts of benzene. Cumene recovery produces a wastewater stream contaminated with benzene. Solvent extraction is employed in cyclohexane production, and this produces a benzene-contaminated wash water. Water washing of the nitrobenzene product stream produces an aqueous waste containing benzene. Scrubbing and stripping operations in the bromobenzene and biphenyl processes also generate aqueous benzene mixtures.

Storage--
Benzene, a fluid of intermediate volatility, is stored in floating roof tanks (internal or external) or fixed-roof tanks having vapor recovery systems. Emissions from these tanks result from poor floating roof seals, evaporation from wetted walls during emptying of floating roof tanks, venting of vapor recovery units, and exceeding the vapor space capacity in variable vapor space tanks (internal roof). Methods for calculating losses are well

---

[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented in the prefatory material.

- - - - - - - - - - -

(13) Industrial Process Profiles for Environmental Use: Chapter 6, The Organic Chemicals Industry, Part I (Draft). Contract 68-02-1320, Task 17, and Contract 68-02-1325, Task 70, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

documented (14). Storage losses account for significant fractions of all hydrocarbon emissions. Table 6 presents evaporative emission factors for benzene storage tanks without controls (12).

TABLE 6. EVAPORATIVE EMISSION FACTORS FOR BENZENE STORAGE TANKS WITHOUT CONTROLS (12)

Fixed roof tanks			Floating roof tanks		
Breathing loss, kg/day-m^3			Standing storage loss, kg/day-m^3		Variable vapor space tanks
New tank conditions	Old tank conditions	Throughput loss, kg/m^3	New tank conditions	Old tank conditions	Throughput loss, kg/m^3
0.0094	0.011	0.27	0.0013	0.0031	0.25

Transportation--
Benzene is transported in railroad tank cars or carried on ships or trucks in 0.21-m^3 drums. Emissions can result from spills, leaks, loading, and accidents. Detailed studies of hydrocarbon losses have been performed, but little information on benzene losses exists (15, 16). In a study of hazardous material spillage into water streams, benzene was ranked as sixth among chemicals likely to cause significant water pollution due to spillage during transport (10).

Motor Vehicles--
Motor vehicles are sources of benzene emissions during both fueling and operation. Gasoline evaporation from vehicle refueling results in 1.4 kg of hydrocarbons/m^3 pumped (12). Loading and unloading of trucks and underground tanks at service stations have been estimated to transfer about 1.5 kg/m^3. The large quantities of gasoline consumed annually result in an emission of 24 million kg/yr of benzene (17); however, this estimate is based on an assumption that 1% benzene exists in the vapor. The vapor contains only 0.01% (11). Emissions of unburned hydrocarbons from engine exhausts also present a hazard. Approximately

(14) Burklin, C. E., and R. L. Honerkamp. Revision of Evaporative Hydrocarbon Emission Factors. Radian Project 100-086-01, Radian Corporation, Austin, Texas, June 1976.

(15) Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

(16) Burklin, C. E., E. C. Cavanaugh, J. C. Dickerman, S. R. Fernandes, and G. C. Wilkins. Control of Hydrocarbon Emissions from Petroleum Liquids. EPA-600/2-75-042, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1975. 245 pp.

(17) Benzene from Gasoline Evaporation is "Significant Health Hazard," EDF says. Environmental Report 1977, 1363.

450 million kg of benzene were released in hydrocarbon emissions from motor vehicles in 1971.

Oil Spills--

The OTS has reported a possible release of from 10 to 11 million kg/yr of benzene due to oil spills; however, no data have yet been found to support this figure The maximum content of benzene in crude oil is approximately 3.0% (18). If all crude oil contained 3% benzene and if it all evaporated when the oil spilled, approximately 0.3 billion kg/yr of oil would have to be lost to produce 10 million kg of benzene. Since one source reports annual oil spillage to be about 1.8 billion kg/yr (2), the OTS estimate is reasonable.

Environmental Levels

Information on levels of benzene in the atmosphere is deficient. Table 7 summarizes ambient monitoring data for benzene in selected areas of the United States and shows that the observed ambient levels of benzene are 1 ppb to 100 ppb (volume basis). The high values for metropolitan areas (Los Angeles and Toronto) may be primarily due to exhausts from motor vehicles (19).

TABLE 7. AMBIENT MONITORING DATA FOR BENZENE (19)

Geographical location	Sampling/analysis technique	Concentrations, ppb		
		Lowest	Average	Highest
Vancouver, Canada	Cold trap/GC-FID[a]	1		10
Near solvent reclamation plants	Grap sample/GC-MS, IR[b]			23
Los Angeles Basin	Cold trap/GC-FID	5		22
Downtown Los Angeles	Grab sample/GC-FID	15		60
Los Angeles Basin	Cold trap/GC-FID		15	57
Zurich, Switzerland	Charcoal trap/GC-MS,GC-FID			54
Riverside, California	Cold trap/GC-FID	7		8
Toronto, Canada	Cold trap/GC-FID		13	98

[a]GC-FID is gas chromatograph-flame ionization detector.

[b]GC-MS, IR is gas chromatograph-mass spectroscopy and infrared analysis, respectively.

NOTE: Blanks indicate no reported data.

Levels of benzene in bodies of water are also presented in a report on potential ocean pollutants (2). Benzene has been identified in drinking water in three United States locations (from the Mississippi and Potomac Rivers). Levels were approximately 2.0 ppb. In one EPA study of organic compounds in drinking water of 10 cities, benzene was detected in water from four cities

(18) Smith, H. M. Qualitative and Quantitative Aspects of Crude Oil Composition. Bulletin 642, U.S. Department of the Interior, Bureau of Mines, Washington, D.C., 1968.

(19) Howard, P. H., and P. R. Durkin. Sources of Contamination, Ambient Levels, and Fate of Benzene in the Environment. EPA-560/5-75-005, U.S. Environmental Protection Agency, Washington, D.C., December 1974. 73 pp.

at concentration levels of 1.0 mg/m^3 to 3.0 mg/m^3. Benzene has also been identified as a component of subsurface water, reaching concentrations of 10.4 ppm in one subsurface brine and up to 24 ppm in another area having extensive oil and gas deposits. Levels of light aromatics in marine waters near oil production platforms have been reported to be in the 0.1 ppb to 0.7 ppb range, with average levels being less than 1 ppb. No data have been found on levels of benzene in soil, wildlife, and fish (2).

Population at Risk

Production and process consumption of benzene are generally localized in the Texas Gulf area and in the Northeast; however, the presence of benzene in gasoline gives it nationwide distribution. The scarce data that currently exist indicate that most Americans are probably exposed continuously to very low levels of benzene. Persons that live and work in areas of major benzene production and consumption obviously are exposed to larger concentrations. Until definitive studies are made concerning true ambient levels and the actual risks involved with such exposure, no estimate should be made of the number of people currently at risk from exposure to benzene emissions.

HEALTH EFFECTS

Benzene has long been recognized as a poison if ingested in large quantities. The effects of nonlethal doses, including long-term illnesses, are not as fully understood; however, information on benzene's effects on both humans and animals is available.

Effects on Humans

Numerous fatalities from occupational benzene poisoning have been reported since the early 1900's. After inhalation or ingestion, benzene is absorbed rapidly by the blood. At nonlethal concentrations, a variety of human central nervous system disorders are observed, depending upon the extent of exposure. These maladies include euphoria followed by giddiness, headache, nausea and staggering gait, as well as fatigue, insomnia, dizziness, and unconsciousness. Observed damage to the human blood-forming system includes anemia, reduction in platelet numbers, and depression of the white blood cell count.

Oral ingestion can cause local irritation of the mucous membranes, bronchitis, pneumonia, signs and symptoms of systemic intoxication, and collapse (20). Skin exposure may cause blisters. A scaly dermititis results from prolonged exposure.

---

(20) Criteria for a Recommended Standard: Occupational Exposure to Benzene. U.S. Department of Health, Education and Welfare, Public Health Service Center for Disease Control, Washington, D.C., 1974.

Results of several tests on humans are reported in the literature (20). The current lowest lethal concentration (LC_{LO}) is 20,000 ppm for 5 min (21). The lowest toxic concentration (TC_{LO}) reported for humans is 210 ppm.

Chronic benzene exposure also has resulted in chromosome aberrations in human lymphocytes. As early as the 1930's, benzene was suspected in cases of leukemia. Available epidemiological data indicate that the compound does induce leukemia although the data cannot be considered to constitute unequivocal evidence that benzene acting alone is leukemogenic. There currently seems to be no typical response in the blood to chronic exposure at low levels (22). In one study, no correlation between the extent of exposure and the severity of the benzene poisoning was reported to exist (20). Results of similar studies are also reported in this work. Most recently, National Institute of Occupational Safety and Health (NIOSH) studies in two Ohio rubber plants revealed incidences of leukemia five times higher than normal (23). This report prompted current Occupational Safety and Health Administration (OSHA) emergency standards. Although benzene is suspected to cause leukemia, no fully convincing experimental proof exists.

There are other chronic effects of exposure to benzene. Mutations in the pulmonary system and in bone marrow have been observed, along with liver, kidney, and lung damage, hormone alteration, and bone marrow hyperplasia (1).

Effects on Animals

Acute effects on animals are similar to those on humans. Acute toxicity data currently available is summarized in Table 8 (1, 21). Much of the work done on animals is summarized in Reference 20.

Most testing in the studies of chronic effects of benzene has been performed on animals. The results of carcinogenity tests on mouse skin indicate the lowest toxic dose is 1,232 mg/kg for a 52-wk exposure (1). Studies of both long- and short-term

(21) Markle, R. A., et al. Potentially Toxic and Hazardous Substances in the Industrial Organic Chemicals and Organic Dyes and Pigments Industry. Contract 68-02-1323, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1976.

(22) Industrial Hygiene and Toxicology, Volume II. F. A. Patty, ed. John Wiley & Sons, Inc., New York, New York, 1962. 2305 pp.

(23) Benzene Emerging Standard Set by OSHA. Chemical & Engineering News, 55(19):4, 1977.

TABLE 8. TOXICITY DATA FOR BENZENE (1, 21)

Acute toxicity	Dosage	Animal	Route
LD_{50}[a]	468 mg/kg	Mouse	Intraperitoneal
	1,150 mg/kg	Rat	Intraperitoneal
	3,800 mg/kg	Rat	Oral
	4,700 mg/kg	Mouse	Oral
LD_{Lo}[b]	530 mg/kg	Guinea pig	Intraperitoneal
	1,400 mg/kg	Frog	Subcutaneous
	2,000 mg/kg	Dog	Oral
LC_{50}[c]	10,000 ppm/7 hr	Rat	Inhalation

[a]Calculated dose expected to kill 50% of the exposed population.

[b]Lowest reported dose to cause death.

[c]Calculated concentration expected to kill 50% of the exposed population.

inhalation of benzene vapors by dogs show that benzene concentrates in fat, bone marrow, urine, and red blood cells following a rapid distribution through the body (20).

Attempts by the National Cancer Institute and others to induce leukemia in animals with benzene have not been successful. However, results of inhalation experiments with mice, the species most susceptible to leukemia, are not yet available. Many researchers have concluded that more study is definitely needed (20).

SECTION 5

CONTROL TECHNOLOGIES

Benzene emissions can be controlled by preventing the release of the pollutant or by treating the waste streams. Various techniques of implementing these ideas have been developed. Applicable control methods, their efficiencies, and the economics of their use are briefly described.

EMISSION SOURCE CONTROL METHODS

Different control methods have been developed for different sources of emissions. The following are generally applicable to any process containing emissions of benzene.

Fugitive Emissions

Most fugitive hydrocarbon emissions can be controlled only by regular inspection, maintenance, and good housekeeping. For sources such as pump and compressor seals, wastewater systems, and storage tanks, specific devices have been designed to help control emissions. Other sources require major equipment additions such as installing an integrated vapor recovery/flare system for all vents and relief valves (24, 25).

Catalyst Regeneration

Several of the processes for producing or using benzene employ solid catalysts, which require periodic regeneration. Any unburned benzene (or other hydrocarbon) in the flue gas could be removed by incineration in a heater firebox or smoke plume burner. These devices are not usually used due to the infrequency of catalyst regenerations.

---

(24) Rosebrook, D. D., et al. Sampling Plan for Fugitive Emissions from Petroleum Refineries. Radian Contract 200-144, Task 6, Radian Corporation, Austin, Texas, January 1977.

(25) Control Techniques for Volatile Organic Emissions from Stationary Sources. Publication No. AP-68, Project 220-187-12, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Draft report submitted to the EPA by Radian Corporation, July 1977.)

Vents

Benzene can be continuously emitted through vents. Emissions can be eliminated by routing them to an integrated vapor recovery or incineration system, wet scrubbing in an absorber, a combination scrubbing-incineration system, or an adsorption system.

Aqueous Discharge Prevention

Aqueous emissions are often generated by water wash of products, water quenches, steam stripping, and vacuum production using steam ejectors and barometric condensers. In some cases, the initial production of such benzene-contaminated streams can be prevented. For example, a stripping column can replace water wash. Vacuum pumps, surface condensers, and oily water incinerators can eliminate the contaminated effluent from ejectors and barometric condensers (26).

Aqueous Discharges Treatment

Aqueous effluents from benzene processes can be treated in standard wastewater treatment units. If benzene was the only pollutant, a covered hydrocarbon/water separator would be sufficient (26). Most benzene processes are part of a large refinery or chemical plant, which generally has primary, secondary, and, often, tertiary treatment systems. These systems are more complex than can be described in this document (24, 25, 26).

Organic Sludges

A benzene-contaminated sludge is often a byproduct of solvent extraction processes for aromatics purification. Standard practice is to dry it and use it as landfill; however, incineration is an alternative (25, 27) When the sludge is dried an unknown amount of benzene could be released to the air.

Control of Storage Losses

Although not generally applied, there are several methods of controlling emissions from benzene storage. Replacement of old

---

(26) Sittig, M. Pollution Control in the Organic Chemical Industry. Noyes Data Corporation, Park Ridge, New Jersey, 1974. 304 pp.

(27) Cavanaugh, E. C., J. D. Colley, P. S. Dzierlenga, J. M. Felix, D. C. Jones, and T. P. Nelson. Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquefied Natural Gas Plants. EPA-600/2-75-068, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1975. 476 pp.

floating roof seals with newer double seals will reduce emissions by 50% to 75% (28). Use of pressure tankage for new construction is also possible as a control method since emissions from pressure tanks are virtually negligible. Storage emissions control is discussed in Reference 25.

Transportation of Benzene

Losses resulting from benzene transportation are very similar to losses resulting from gasoline transportation. Controls can be applied at marine terminals, tank truck terminals, and rail car terminals. Modified loading procedures (submerged or bottom loading) in conjunction with vapor recovery devices are the principal technologies available. Detailed descriptions of such methods are found in Reference 25.

Motor Vehicles

Benzene emissions due to gasoline evaporation at service stations can be controlled in ways similar to those used in other loading and unloading operations. Both vapor recovery systems and modified loading methods can be applied to bulk handling of gasoline. Vapor recovery units on gasoline pumps can significantly reduce emissions (25, 29).

Exhaust emissions of benzene are controlled primarily by carburetion adjustment. This will allow more complete combustion of the hydrocarbons found in gasoline.

The emergence of the catalytic converter is expected to have an impact on benzene emissions from motor vehicle exhaust. For example, in exhaust sample testing the converter was able to reduce benzo(a)pyrene emissions (a difficult to control polycyclic organic), by an order of magnitude from 1968 emission-controlled vehicles. Actual figures were from 2 to 6 mg/m^3 down to 0.5 mg/m^3 of fuel consumed (30). If such a high degree of control is achieved with polycyclic organics, reduction in benzene emissions would also be expected from catalytic converters.

---

(28) American Petroleum Institute, Evaporative Loss Committee. Evaporative Loss from Floating Roof Tanks. Bulletin 2517, Washington, D.C., 1972.

(29) Burklin, C. E., E. C. Cavanaugh, J. C. Dickerman, and S. R. Fernandes. A Study of Vapor Control Methods for Gasoline Marketing Operations, Volume I. EPA-450/3-75-046-9, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1975. 215 pp.

(30) Preferred Standards Path Report for Polycyclic Organic Matter. Draft report, U.S. Environmental Protection Agency, Durham, North Carolina, October 1974. 107 pp.

Oil Spills

Accidental spills of oil (or benzene) are virtually unavoidable. Several steps can be taken whenever a benzene-containing hydrocarbon is spilled into a body of water (10). These include notifying the nearest users of the water; removing the source of the spill from the water; skimming of hydrocarbon liquids from the surface; treating the water with activated carbon, a coagulant, and a polyelectrolyte (where feasible); and removing the resultant floc. These techniques are generally more applicable to inland waterways than to oceans.

CONTROL EFFICIENCIES

The efficiency of any method of controlling benzene emissions depends on such factors as operating conditions, quality and quantity of the waste stream, and state of repair of the system. Table 9 lists present producers of maleic anhydride (a benzene consumer industry), their control technology, and reported control efficiencies (31).

Incineration

Incineration is an acceptable form of controlling benzene emissions from sludges and concentrated hydrocarbon liquids. Incineration can be accomplished in afterburners (direct flame and catalytic) and boilers. Properly designed and operated incinerators usually achieve organic vapor removal efficiencies in excess of 95%.

Adsorption

Benzene can by physically adsorbed from a gas stream by activated carbon. Such adsorption is usually more efficient than incineration for removing organics in concentrations lower than 200 ppm. Efficiencies are usually around 100% (25).

Absorption (Scrubbing)

Absorption or scrubbing involves the dissolution of certain vapor-phase components into a liquid solvent. Benzene is removed from gas streams in such a unit operation. When the concentration of benzene in the gas is low, large quantities of absorbent and long contact times are required for adequate removal. For this reason, scrubbers are often used in series with incinerators.

---

(31) Lewis, W. A. Jr., G. M. Rinaldi, and T. W. Hughes. Source Assessment: Maleic Anhydride. Contract 68-02-1874, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio. 118 pp.

TABLE 9. CONTROL DEVICES AND REPORTED CONTROL EFFICIENCIES FOR THE MALEIC ANHYDRIDE INDUSTRY (31)

Company	Emission points		
	Flaking pelletizing, and packaging	Product recovery scrubber	Storage tank vents
Amoco Chemicals Corp.	NR[a]	NR	NR
Ashland Oil, Inc.	-[b]	Scrubber[c]	Floating roof tanks[c]
Denka Chemical Corp.	Scrubber[c]	Thermal incinerator 93%, 95%	Floating roof tanks[c]
Koppers Co.	Scrubber[c]	Thermal incinerator 97%[e]	Return vents[c]
Monsanto Co.	Scrubber[c]	-[f]	Scrubber[c]
Reichold Chemicals, Inc.	-[b]	Carbon absorber 84%[d]	Scrubber, conservation vents[c]
Tenneco, Inc.	-[f]	-[f]	Scrubber, conservation vents[c]
U.S. Steel Corp.	Scrubber[c]	Catalytic incinerator 85%[d]	Floating roof tanks[c]

[a]Not reported.
[b]Plant does not have the emission point.
[c]Control efficiency not reported.
[d]Hydrocarbon control efficiency.
[e]Carbon monoxide control efficiency.
[f]No control.

Vapor Recovery

Benzene loss due to fugitive emissions from pressure relief devices, loading and unloading operations, and gasoline marketing operations can be minimized by vapor recovery systems. These allow the vapors to be collected and routed to knockout drums, condensers, refrigeration units, absorbers, or simply the tank from which they came. Control efficiencies are between 85% and 100%, depending upon the source of the emissions; gasoline marketing emissions are the most difficult to control (25).

Alternate Loading Methods

Bulk handling of benzene-containing hydrocarbons is subject to losses due to loading and unloading. Procedure changes in loading practices can reduce emissions by the amounts shown below.

Emission source	Percent reduction
Marine terminals	60 to 80
Rail and tank truck terminals	40 to 60
Gasoline service stations	∿60

The preferred methods include vapor-freeing ballasted and empty-ship cargo tanks at sea, slower tank loading, submerged filling, and bottom loading.

Wastewater Treatment

Treatment of benzene-contaminated water generally involves primary separation followed by secondary and possibly tertiary treatment. Hydrocarbon removal efficiency for the primary separations step is generally between 70% and 90% (24). No data are known for benzene removal efficiencies in any treatment step. Standard texts on wastewater treatment plant design are readily available, such as Metcalf and Eddy (32).

Storage Vessels

Installation of double seals on floating roof tanks can reduce emissions by 50% to 75% (28). Construction of pressure storage vessels would virtually eliminate emissions.

(32) Metcalf, L., and H. P. Eddy. Wastewater Engineering Collection, Treatment, Disposal. McGraw-Hill Book Company, New York, New York, 1972. 734 pp.

SECTION 6

REGULATORY ACTION

In 1974 NIOSH (National Institute of Occupational Safety and Health) published a criteria document for occupational exposure to benzene which recommended adherence to the existing Federal standard of 10 ppm as a time-weighted average with a ceiling of 25 ppm. OSHA has proposed a reduction of the standard to a 1 ppm 8-hr time-weighted average with a ceiling of 5 ppm over a 15-min period. An OSHA (Occupational Safety and Health Administration) Emergency Temporary Standard has been stayed pending a hearing on a request for injunction. NIOSH is conducting retrospective studies of benzene mortality and airborne benzene levels in service stations; however, the OSHA regulations would apply to sources with only 5 or more employees; thus service stations remain unregulated.

EPA has initiated an air-monitoring program which will determine benzene levels in selected areas. Qualitative results obtained to date indicate widespread low-level benzene contamination. Studies are in progress to document the extent of hazard and the best regulatory approach under the Clean Air Act. EPA has conducted a limited survey of drinking water supplies in which benzene was identified in some samples and has begun a more extensive survey which will seek out benzene as well as a number of other pollutants. Benzene has been designated a priority pollutant under the FWPCA (Federal Water Pollution Control Act), and ocean dumping is already strictly regulated. Additional water quality criteria for benzene are anticipated from EPA under the FWPCA Consent Decree by July 1978. The Consumer Products Safety Commission is awaiting results of the National Academy of Sciences study on the health effects of benzene to determine if the results warrant further action.

REFERENCES

1. Dorigan, J. Scoring of Organic Air Pollutants: Chemistry Production and Toxicity of Selected Synthetic Organic Chemicals. Mitre Corporation, September 1976.

2. Ocean Affairs Board, National Research Council. Assessing Potential Ocean Pollutants. Report No. 0-309-02325-4, U.S. Environmental Protection Agency and National Science Foundation, Washington, D.C., January 1975. 456 pp.

3. Directory of Chemical Producers--U.S.A. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 1059 pp.

4. Parsons, T. B., et al. Industrial Process Profiles for Industrial Use: Basic Petrochemicals Industry, Chapter 5. Contract 68-02-1319, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977.

5. Refining Handbook. Hydrocarbon Processing, 53(9):192, 1974.

6. Petroleum Processing Handbook, Chapter 3. W. F. Bland and R. L. Davidson, eds. McGraw-Hill Book Co., New York, New York, 1967. pp. 1-152.

7. Chemical Origins and Markets, Fifth Edition, G. M. Lawler, ed. Chemical Information Services, Stanford Research Institute, Menlo Park, California, 1977. 118 pp.

8. Wilkins, G. E. End Use Patterns for Significant Organic Chemicals. Contract 68-02-1319, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1976.

9. Ponder, T. C. Benzene: Outlook Through 1980. Hydrocarbon Processing, 55(11):217-218, 1976.

10. Dawson, G. W., A. J. Shuckrow, and W. H. Swift. Control of Spillage of Hazardous Polluting Substances. Contract 14-12-866 (PB 197 596), U.S. Department of the Interior, Federal Water Quality Administration, Washington, D.C., November 1970. 96 pp.

11. Eimutis, E. C., and R. P. Quill. Source Assessment: Non-criteria Pollutant Emissions. EPA-600/2-77-107e, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1977. 113 pp.

12. Compilation of Air Pollutant Emission Factors, Second Edition (with Supplements 1-7). Publication No. AP-42, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1973.

13. Industrial Process Profiles for Environmental Use: Chapter 6, The Organic Chemicals Industry, Part I. (Draft). Contract 68-02-1320, Task 17 and Contract 68-02-1325, Task 70, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

14. Burklin, C. E., and R. L. Honerkamp. Revision of Evaporative Hydrocarbon Emission Factors. Radian Project 100-086-01, Radian Corporation, Austin, Texas, June 1976.

15. Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

16. Burklin, C. E., E. C. Cavanaugh, J. C. Dickerman, S. R. Fernandes, and G. C. Wilkins. Control of Hydrocarbon Emissions from Petroleum Liquids. EPA-600/2-75-042, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, September 1975. 245 pp.

17. Benzene from Gasoline Evaporation is "Significant Health Hazard", EDF says. Environmental Report 1977, 1363.

18. Smith, H. M. Qualitative and Quantitative Aspects of Crude Oil Composition. Bulletin 642, U.S. Department of the Interior, Bureau of Mines, Washington, D.C., 1968.

19. Howard, P. H., and P. R. Durkin. Sources of Contamination, Ambient Levels, and Fate of Benzene in the Environment. EPA-560/5-75-005, U.S. Environmental Protection Agency, Washington, D.C., December 1974. 73 pp.

20. Criteria for a Recommended Standard: Occupational Exposure to Benzene. U.S. Department of Health, Education and Welfare, Public Health Service Center for Disease Control, Washington, D.C., 1974.

21. Markle, R. A., et al. Potentially Toxic and Hazardous Substances in the Industrial Organic Chemicals and Organic Dyes and Pigments Industry. Contract 68-02-1323, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1976.

22. Industrial Hygiene and Toxicology, Volume II. F. A. Patty, ed. John Wiley & Sons, Inc., New York, New York, 1962. 2305 pp.

23. Benzene Emerging Standard Set by OSHA. Chemical & Engineering News, 55(19):4, 1977.

24. Rosebrook, D. D., et al. Sampling Plan for Fugitive Emissions from Petroleum Refineries. Radian Contract 200-144, Task 6, Radian Corporation, Austin, Texas, January 1977.

25. Control Techniques for Volatile Organic Emissions from Stationary Sources. Publication No. AP-68, Project 220-187-12, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Draft report submitted to the EPA by Radian Corporation, July 1977.)

26. Sittig, M. Pollution Control in the Organic Chemical Industry. Noyes Data Corporation, Park Ridge, New Jersey, 1974. 304 pp.

27. Cavanaugh, E. C., J. D. Colley, P. S. Dzierlenga, J. M. Felix, D. C. Jones, and T. P. Nelson. Environmental Problem Definition for Petroleum Refineries, Synthetic Natural Gas Plants, and Liquified Natural Gas Plants. EPA-600/2-75-068, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1975. 476 pp.

28. American Petroleum Institute, Evaporative Loss Committee. Evaporative Loss from Floating Roof Tanks. Bulletin 2517, Washington, D.C., 1972.

29. Burklin, C. E., E. C. Cavanaugh, J. C. Dickerman, and S. R. Fernandes. A Study of Vapor Control Methods for Gasoline Marketing Operations, Volume I. EPA-450/3-75-046-9, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1975. 215 pp.

30. Preferred Standards Path Report for Polycyclic Organic Matter. Draft report, U.S. Environmental Protection Agency, Durham, North Carolina, October 1974. 107 pp.

31. Lewis, W. A. Jr., G. M. Rinaldi, and T. W. Hughes. Source Assessment: Maleic Anhydride. Contract 68-02-1874, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Cincinnati, Ohio. 118 pp.

32. Metcalf, L., and H. P. Eddy. Wastewater Engineering Collection, Treatment, Disposal. McGraw-Hill Book Company, New York, New York, 1972. 734 pp.

GLOSSARY

aromatic: Designating any of a series of benzene ring compounds.

fugitive emission: Gaseous or particulate emissions from industry-related operations that escape to the atmosphere without passing through a primary exhaust system.

miticide: Material used primarily in the control of plant-feeding mites, especially spider mites.

olefin: Any series of unsaturated open-chain hydrocarbons containing one double bond.

pyrolysis: Decomposition of a compound by the action of heat alone.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-79-210d		

4. TITLE AND SUBTITLE
Status Assessment of Toxic Chemicals: Benzene

5. REPORT DATE
December 1979 issuing date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
T.R. Blackwood, J.C. Ochsner
L.D. Zeagler

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Monsanto Research Corp
1515 Nichols Road
Dayton, Ohio 45407

Radian Corp
8500 Shoal Creek Blvd
P.O. Box 9948
Austin, Texas 78766

10. PROGRAM ELEMENT NO.
1AB604

11. CONTRACT/GRANT NO.
68-03-2550

12. SPONSORING AGENCY NAME AND ADDRESS
Industrial Environmental Research Lab. - Cinn, OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Task Final 11/77 - 12/77

14. SPONSORING AGENCY CODE
EPA/600/12

15. SUPPLEMENTARY NOTES
IERL-Ci project leader for this report is Dr. Charles Frank, 513-684-4481.

16. ABSTRACT

Benzene is one of the most ubiquitous organic chemicals, widely employed as a solvent, as a fuel component, and for the synthesis of other organic chemicals. This report details the emission of benzene from industrial sources and from the largest source of all, the operation of motor vehicles. Descriptions of the health hazards of benzene exposure are included, and both current and anticipated regulations are listed. The report is concluded with recommendations of areas for further study.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Aromatic Hydrocarbons, Aromatic Monocyclic Hydrocarbons, Hydrocarbons, Unsaturated Hydrocarbons, Chlorobenzenes	Organics, Organic Chemical Synthesis	68A 68D 68G

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	49
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

☆ U.S. GOVERNMENT PRINTING OFFICE 1980-657-146/5510