256
1/23/81
T.S.

①

Dr. 2222

ANL/CNSV-9

MASTER

R-1339

Energy and Materials Flows in the Production of Olefins and Their Derivatives

L. L. Gaines and S. Y. Shen

ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

prepared for
U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

DISCLAIMER

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
The University of Iowa
Iowa State University
The University of Kansas
Kansas State University
Loyola University of Chicago
Marquette University
The University of Michigan
Michigan State University
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A09
Microfiche copy: A01

Dr. 2222

Distribution Category:
Energy Conservation—
Industry (UC-95f)

Master

ANL/CNSV-9

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ENERGY AND MATERIALS FLOWS IN THE PRODUCTION OF OLEFINS AND THEIR DERIVATIVES

by

L.L. Gaines and S.Y. Shen
Energy and Environmental Systems Division
Special Projects Group

August 1980

Work Sponsored by

U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Conservation and Solar Energy
Office of Industrial Programs

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

CONTENTS (Cont'd)

TABLES

TABLES (Cont'd)

TABLES (Cont'd)

FIGURES

FIGURES (Cont'd)

FIGURES (Cont'd)

PREFACE

This report is one of a series being prepared for the U.S. Department of Energy, Office of Industrial Programs, on energy and materials flows in energy-intensive industries. Each report gives an overview of the particular industry, including its products, corporate structure, and present and emerging technologies. Analysts in the private sector should gain a better understanding of the effects of changes in the cost and availability of energy. In cases where firms can substitute one material input for another, the reports will help these firms consider the impact of energy considerations on possible alternatives. Government analysts responsible for expediting industrial energy conservation should profit from having a compact and ready source of background information to help place proposed projects in perspective and to serve as a point of departure for specific evaluations. The industries studied to date and the current status of the corresponding reports are listed below.

The information presented in the report series is derived from previous reports, government and industry statistics, trade and technical publications, patents, textbooks, industry interviews, and plant visits. Some of these sources provide incomplete, out-of-date, or conflicting data; therefore, ANL staff perform additional research to supplement, update, and reconcile the sources.

Energy and Materials Reports

Industry	Status (as of Nov. 1980)	
Fabrication of aluminum products	Published 1979 (ANL/CNSV-3)	
Fabrication of iron and steel semifinished products	Published 1979 (ANL/CNSV-8)	
Olefins and their derivatives	Published 1980 (ANL/CNSV-9)	
Petroleum refining	In press (ANL/CNSV-10)	
Primary copper	In press (ANL/CNSV-11)	
Air products	Approved for publication	to be published in 1981
Pulp and paper	Approved for publication	
Cement	Approved for publication	
Primary aluminum	Draft	
Primary iron and steel	Draft	

ABBREVIATIONS

ABS	Acrylonitrile butadiene-styrene
ACR	Advanced cracking reactor
AGO	Atmospheric gas oil
BFW	Boiler feed water
bis-HET	Bishydroxyethyl terephthalate
BTX	Benzene, toluene, xylene fraction
CH_2Cl-CH_2Cl	1,2-Dichloroethane
CH_3	Methyl
CO_2	Carbon dioxide
DMT	Dimethyl terephthalate
EDC	Ethylene dichloride
E_{in}	Energy input
FRP	Fiber-reinforced plastics
HC	Hydrocarbons
HCl	Hydrochloric acid
HCN	Hydrogen cyanide
HDPE	High-density polyethylene
HGO	Heavy gas oil
HHV	Higher heating value
H_2S	Hydrogen sulfide
LDPE	Low-density polyethylene
LGO	Light gas oil
LiC_4H_9	Lithium butyl
LLDPE	Linear low-density polyethylene
MEA	Monoethanolamine
NaOH	Sodium hydroxide
-OH	Hydroxyl
PAN	Polyacrylonitrile
PE	Polyethylene
PET	Polyethylene terephthalic (polyester)
PO	Propylene oxide
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride

ABBREVIATIONS (Cont'd)

Q	Quad (1 x 10^{15} Btu)
SAN	Styrene-acrylonitrile
SBR	Styrene-butadiene rubber
TPA	Terephthalic acid
TRC	Thermal regenerative cracking
VCM	Vinyl chloride monomer
VGO	Vacuum gas oil

ENERGY AND MATERIALS FLOWS IN THE PRODUCTION OF OLEFINS AND THEIR DERIVATIVES

by

L.L. Gaines and S.Y. Shen

ABSTRACT

Production of olefins and their derivatives uses almost 3.5% of the oil and gas consumed annually in the United States. It is estimated that their production requires an input energy of 2 Q, which is 50% of the energy used in the production of all petrochemicals. Substantial amounts of this energy could be recovered through recycling. For example, recycling of a single plastic product, polyester soft drink bottles, could have recovered about 0.014 Q in 1979. (About 1.4 Q is used to produce plastic derivatives of olefins.) Petrochemical processes use fuels as feedstocks, as well as for process energy, and a portion of this energy is not foregone and can be recovered through combustion of the products. The energy foregone in the production of ethylene is estimated to be 7800 Btu/lb. The energy foregone in plastics production ranges from 12,100 Btu/lb for the new linear low-density polyethylene to 77,200 Btu/lb for nylon 66, which is about 60% of the total energy input for that product. Further investigation of the following areas could yield both material and energy savings in the olefins industry: (1) recycling of petrochemical products to recover energy in addition to that recoverable through combustion, (2) impact of feedstock substitution on utilization of available national resources, and (3) effective use of the heat embodied in process steam. This steam accounts for a major fraction of the industry's energy input.

EXECUTIVE SUMMARY

Ethylene, propylene, and butadiene are the principal olefin compounds; their derivatives are plastics, synthetic fibers, and rubbers, all of which are used in industrial and consumer products. Olefins and their derivatives account for approximately 50% of the energy consumed in the production of all petrochemicals. Large amounts of fuels are required, both as feedstocks (the materials from which the products are made) and as energy inputs to the processes themselves. Total annual energy input for the production of these materials in the United States is about 2 Quads (Q) (2 x 10^{15} Btu or 2 x 10^{18} J). This energy is almost exclusively in the form of oil and gas, and accounts for 3.5% of total U.S. consumption of these fuels.

Using fuels as feedstocks is a major difference between manufacturing petrochemicals and metals. Much of the energy contained in the feedstock remains in the final petrochemical product, which can be burned to recover its heat of combustion. However, petrochemical products as fuels differ from oil and gas in that energy recovery through recycling is possible after the products have served their initial purpose.

ENERGY-ACCOUNTING METHODOLOGY

Although the basic principles of the energy-accounting methodology used in this report are quite simple, the actual computations are rather complicated. Certain terms need to be defined precisely or the results can be confusing. The terms used in this report that require careful definition are:

- Heat of combustion of feed is the sum of the heats of combustion of all feedstocks entering into a process sequence, starting with oil and gas.
- Net process energy is the total fuel required to complete all steps of a manufacturing process minus the heat of combustion of any by-product fuels not burned within that process sequence.
- Total energy input is the sum of the heat of combustion of the feed and the net process energy. It is the total energy embodied in the final product.
- Product heat of combustion is defined as the sum of the heats of combustion of all process products and nonfuel by-products. It is the energy that would be recovered if the final products were burned.
- Energy foregone is the difference between the total energy input and the product heat of combustion. It is that quantity of energy embodied in the final product that cannot be recovered by combustion. However, all or part of it can be recovered by those recycling options that reuse the product as a material. Energy foregone is independent of the accounting methodology chosen.

Table ES.1 gives the total energy inputs and outputs per pound of product for olefins, polymeric derivatives, and oxygenated derivatives. Also shown are the total energy input and energy foregone for 1979 U.S. production of each product. The energies in the table are derived from flowcharts of energy and materials flows for the manufacture of olefins, intermediate products, and final products, and represent lower bounds on actual energy use. These flowcharts, which appear with the process descriptions in Sec. 4, contain estimates derived from published and private literature, personal communications, and the authors' own engineering judgments of energy and material use in best current industrial practice. Note that published estimates for energy use for a given process often do not specify whether they are for best practice or not and may differ from one another by as much as a factor of two. Much of this variation can be explained by plant-to-plant

Table ES-1. Energy Requirements for Production of Olefins and Derivatives from Oil and Gas[a]

Material	Figure Number	Net Heat of Feed Combustion[b] (Btu/lb)	Net Processing Energy[c] (Btu/lb)	Total Energy Input (Btu/lb)	Product Heat of Combustion[b] (Btu/lb)	Energy Foregone (Btu/lb)	U.S. Totals (1979)		
							Production (10^6 lb)	Total Energy Input (10^{12} Btu)	Total Energy Foregone (10^{12} Btu)
Olefins									
Ethylene	4.6	26,800	2,600	29,400	21,600	7,800	29,200	858	228
Propylene	4.6	26,800	900	27,700	21,000	6,700	14,300	396	96
Mixed C_4 Stream from Cracking	4.6	26,200	800	27,000	20,300	6,700	4,500	122	30
1,3-butadiene (coproduct)	4.11	26,700	4,800	31,500	20,000	11,500	2,200	69	25
1,3-butadiene (oxidative dehydrogenation)	4.11	21,500	14,500	36,000	20,000	16,000	360[d]	13	6
1,3-butadiene (avg. 1980)	4.11	29,400	4,800	34,200	20,000	14,200	3,600	122	51
Polymers									
Low-density polyethylene	4.28	28,100	10,400	38,500	20,000	18,500	7,800	300	144
Linear low-density polyethylene	4.34	27,600	4,500	32,100	20,000	12,100	1,000[d]	32	12
High-density polyethylene	4.31	27,300	9,200	36,500	20,050	16,500	5,000	183	83
Polypropylene	4.32	28,000	6,200	34,200	20,000	14,200	3,800	130	54
Polystyrene	4.36	23,600	10,700	34,300	17,800	16,500	4,000	137	66
Polyvinyl chloride	4.40	12,600	13,000	25,600	7,700	17,900	6,100	156	109
Styrene-butadiene rubber	4.26	27,400	10,900	38,300	19,100	19,200	1,400	54	27
Polybutadiene	4.17	30,900	16,100	47,000	19,400	27,600	400	19	11
Polyacrylonitrile	4.44	29,400	28,200	57,600	13,900	43,700	760	44	33
Polyester	4.48	24,700	24,000	48,700	11,400[d]	37,300	4,200	205	157
Nylon 66	4.52	27,700	62,700	90,400	13,200[d]	77,200	1,900	172	147
Oxygenated Derivatives									
Ethylene oxide	4.54	24,100	3,000	27,100	12,400	14,700	5,300	144	78
Ethylene glycol	4.60	18,200	5,600	23,800	8,200	15,600	4,600	109	72
Propylene oxide	4.58	25,200	38,500	63,700	13,900[d]	49,800	2,200	140	110
Propylene glycol	4.61	18,900	29,600	48,500	10,200	38,300	620	30	24
Ethanol	4.64	15,700	9,600	25,300	12,800	12,500	1,300	33	16
Isopropanol	4.65	20,000	5,200	25,200	14,400	10,800	2,000	50	22

[a] Additional inputs include air (for O_2 processes) and brine (Cl_2 processes); [b] Higher heating value (HHV); [c] All steps from raw feed; [d] Estimate.

differences in age, maintenance, other equipment in place, other products made at the site, etc. The total energy input numbers in Table ES.1 are estimated to be accurate to -10% and +60%; that is, a given plant may use as much as 60% more energy but probably will not use more than 10% less energy. See Sec. 4.1 for further details of the energy accounting calculations.

SUMMARY OF RESULTS

Several types of general results and a few specific targets for further investigation have emerged from this study. Some of the results relate to energy use per pound of product, and the remainder deal with national totals (see Table ES.1).

The heat of combustion of feed per pound of hydrocarbon product varies very little from product to product and is typically about 25 x 10^3 Btu/lb (58 kJ/g). The product heat of combustion is about 20 x 10^3 Btu/lb (46.5 kJ/g). (The heats of combustion of feed and products is less for products containing nitrogen and/or oxygen in addition to hydrogen and carbon.) Although the heat of combustion of feed does not vary much, its percentage of total energy input varies widely. For olefins production, the feedstock represents most of the energy input, and about 65% by weight of the feedstock is in the form of naphtha and gas oil. (These are refinery fractions for which olefins production must compete with gasoline and heating oil production.) The remainder of the feedstock is liquefied gases, comprising ethane from natural gas processing plants (18% by weight of feed) and propane and butane from natural gas processing plants and refineries (16% by weight). About 25% of the energy input to olefins production is foregone, because it is converted to by-product fuels that drive the production process. For plastics, about 75% of the approximately 35 x 10^3 Btu/lb (81 kJ/g) energy input is from feedstock and 33-50% of this feedstock energy input is foregone.

In general, the percentage of energy input from feedstock drops as more process steps are required to make the product. Feedstock represents only about 30% of the energy embodied in nylon 66, which requires a complicated series of process steps. Also, as process energy to make a product increases, so does the energy foregone. For a product like nylon or polyester, as much as 80% of the energy input is foregone and cannot be recovered by product combustion. These materials must be recycled into new products if significant amounts of energy are to be recovered.

The 1979 U.S. total energy input to the manufacture of olefins and their derivatives (summed only over final products to avoid double counting) was about 2 Q (2 x 10^{15} Btu or 2 x 10^{18} J) and used almost 3.5% of the 57 Q (57 x 10^{15} Btu or 60 x 10^{18} J) of oil and gas consumed in the United States.* This energy is lost if the products are discarded. If they were burned for energy recovery, about 0.9 Q (0.9 x 10^{15} Btu or 0.9 x 10^{18} J) could be recovered. This energy could replace other fuels for steam generation. For example, olefin products could be co-fired with coal in electric generating stations. However, recycling the products would recover more energy and replace oil and gas inputs to olefins production.

---

*Monthly Energy Review, U.S. Dept. of Energy (July 1980).

The largest total energy inputs are for consumer plastics -- polyethylene, polypropylene, polystyrene, and polyvinyl chloride -- because of their large production volumes. One-half to two-thirds of the energy consumed in the manufacture of these materials could be recovered by burning solid waste. In addition, there are several other olefin-derived products that consume substantial energy in processing, most of which is foregone. Propylene oxide requires a large amount of process energy (over 60 x 10^3 Btu/lb or 139 kJ/g) in a short chain of processes. Therefore, it is appropriate to investigate propylene oxide production processes that are less energy intensive. Of course, more efficient processes for all of the products examined are possible.

Polyester production processes have the largest total energy foregone of the final products examined. However, the energy is consumed in a long series of processes, none of which stands out as particularly energy intensive. Therefore, improvement in one of the process steps would not substantially reduce overall energy consumption. A different route requiring fewer steps would be needed to reduce process energy significantly. Alternatively (and the two paths could be pursued simultaneously), the product could be recycled. Polyester has been recycled successfully; most of the energy embodied in the products can be recovered. Commercial market tests of polyester bottle recycling are being carried out by Celanese Corporation. Recycling the approximately 300 million lb (136 million kg) of polyester bottles produced in the United States in 1979 would have recovered 0.014 Q (14 x 10^{12} Btu or 15 x 10^{15} J). This is only one example of how substantial quantities of oil and gas could be saved annually by a serious commitment to recycling olefins and their derivatives. Total energy savings could reach approximately 1 Q (10^{15} Btu or 10^{18}J).

1 INTRODUCTION

The purpose of this report is to give the reader an understanding of the energy and materials flows in the largest and most important segment of the petrochemical industry -- olefins and their derivatives. This segment is quite complex, with a wide variety of possible input materials producing an even broader spectrum of outputs. All of the commercially important compounds within this segment are discussed, as the production of one is often linked both physically and economically with the production of others.

In addition to the abstract and executive summary, this report has six major sections:

- Section 1. Introduces the report and gives a general description of the subjects to be discussed.
- Section 2. Describes the properties and uses of olefins and their derivatives and discusses possible substitutes for these chemicals.
- Section 3. Discusses the geographical and company structure of the industry and gives production, employment, and overall industry energy consumption statistics.
- Section 4. Analyzes both conventional and new production processes for each of the subject compounds, with energy and materials use summarized in flowcharts for each product.
- Section 5. Discusses opportunities for energy conservation through recycling.
- Section 6. Presents the conclusions and recommends areas for further investigation.

The report is for readers with a variety of interests and levels of expertise. Therefore, technical language is kept to a minimum and, where necessary, explained for nonexpert readers. Process details are included for those who are or who wish to become more familiar with the industry. Readers who are interested in particular products can consult the appropriate subsections. Table 1.1 is provided to assist the reader in converting to SI units of measurement.

A petrochemical is any product derived from petroleum or natural gas. Petroleum is a complex mixture of hydrocarbons from which it is theoretically possible to synthesize almost any organic (carbon-containing) compound. In fact, more than 3000 compounds,[1] representing about 98% of U.S. production of industrial organic chemicals,[2] are derived from petroleum or natural gas, with the remainder derived from coal or biomass. Petrochemicals are generally produced in high purity (90-99.99%), because they are often intermediate products in a several-step process. Figure 1.1 illustrates the routes, via petrochemical intermediates, to some of the industry's major end products.

Although about 80 billion lb (36.3 million t) of petrochemicals (excluding fertilizers) are produced annually, their manufacture accounts for less than 8% of the petroleum and natural gas consumed in the United States.[2]

Table 1.1. Conversion Table

Multiply	By	To Obtain
Btu	1055.0	J
Btu/lb	0.0023	kJ/g
°C	1.8, then add 32	°F
°F - 32	0.55	°C
psi	0.068	atm
in.	2.54	cm
in.^{3}/lb	7.43	cm^3/kg
lb	0.4536	kg
cal/cm-sec-°C	418.6	W/m-K
lb/gal	1.71	kg/L
gal	3.78	L

The value of petrochemicals per unit weight is considerably higher than that of most oil products, indicating that petrochemical manufacture should be a high-priority use for petroleum. This is not a new idea, having been stated in 1872 by the Russian chemist, Mendeleev: "This material [oil] is too precious to be burnt. When burning oil, we burn money; it should be used as a chemical base material."[3]

There are three primary classifications of petrochemicals: olefins, aromatics, and paraffins. Olefins (also called alkenes) are unsaturated organic chains that contain one or more double bonds. Olefins are particularly important as chemical intermediates because of the reactivity of the double bond. Ethylene (C_2H_4, proper name ethene, see Fig. 1.2a) alone accounts for more than 25% of the petrochemical industry's production. The value of the 29 billion lb (13.2 million t) of ethylene produced in 1979 was $4.5 billion, and the additional value of the approximately 18 billion lb (8.2 million t) of its major coproducts propylene (C_3H_6, proper name propene, see Fig. 1.2b) and butadiene (C_4H_6, see Fig. 1.2c) was $2.9 billion. A second, less important group of petrochemicals is the aromatics (compounds containing a benzene ring, see Figs. 1.2d, 1.2e, and 1.2f). The major aromatic intermediates are benzene, xylene, and toluene, with a combined production of about 31 billion lb (14.1 million t) in 1979.[4] A third class of organic compounds is the paraffins (or alkanes), which are saturated (no double bonds) chain compounds (see Figs. 1.2g and 1.2h). Paraffins are less reactive than olefins and generally are burned as fuels or cracked to olefins (see Sec. 4.2). Because of their dominance in the petrochemical industry, olefins and their derivatives are the only class of petrochemicals discussed in the rest of this report.

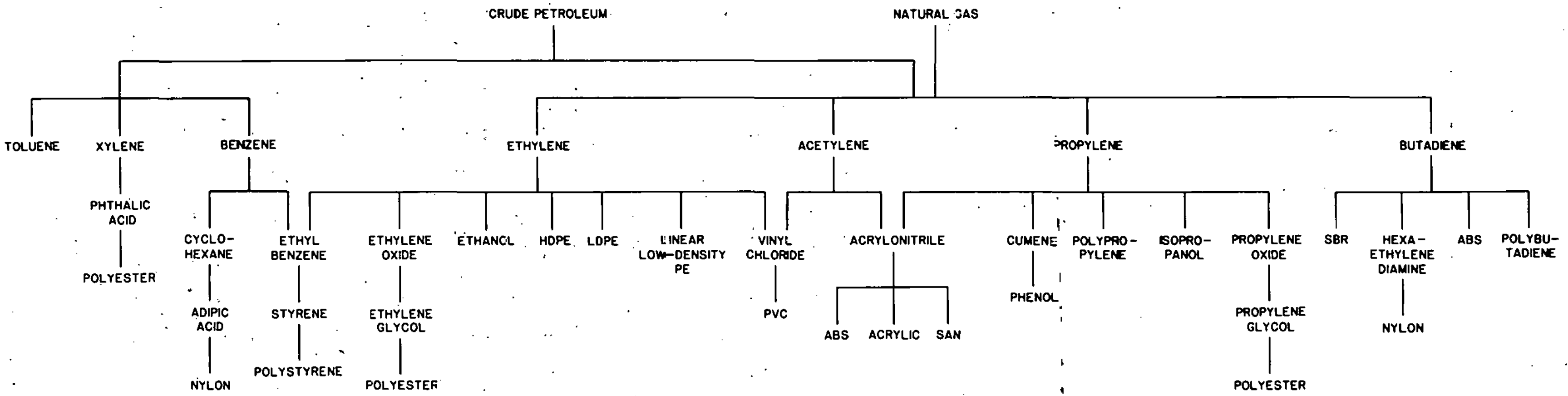
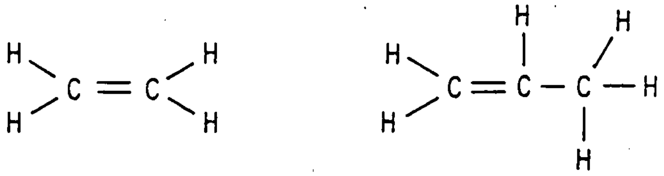
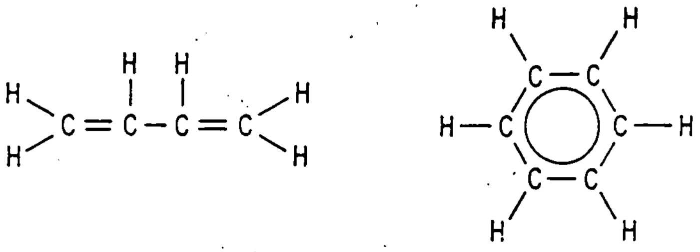


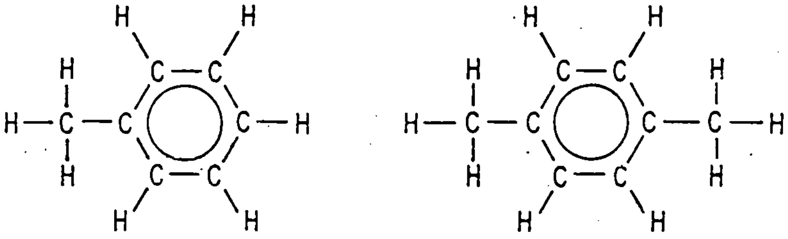
Fig. 1.1. Routes to Major Olefin End Products



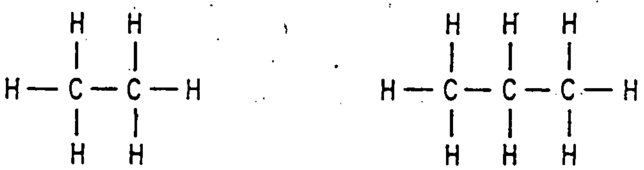
a. Ethylene b. Propylene



c. 1, 3 Butadiene d. Benzene



e. Toluene f. p-xylene



g. Ethane h. Propane

Fig. 1.2. Molecular Structures of Important Petrochemicals

2 PROPERTIES AND USES OF OLEFINS AND THEIR DERIVATIVES

There are three olefins of major commercial importance: ethylene, propylene, and butadiene. Polymers (plastics, rubbers, and fibers) are the most important group of olefin derivatives. Also of interest are the oxygen-containing derivatives, which include oxides, glycols, and alcohols. Physical properties of olefins and derivative compounds are shown in Table 2.1. Properties of rubbers and plastics derived from olefins are given in Tables 2.2 and 2.3, while those of fibers are given in Table 2.4. The uses for these materials are summarized in Tables 2.5 and 2.6.

2.1 OLEFINS

Ethylene is a gas at 32°F (0°C) and atmospheric pressure and has a specific gravity 0.00126. Since the liquid density at the same temperature is 0.610, ethylene is usually liquefied to reduce the volume of material to be handled. Its critical temperature and pressure* are 49°F (9.5°C) and 734 psia (49.98 atm), respectively.

Although ethylene can be used as an anesthetic and as a fruit-ripening agent,[19] virtually all of the material produced is used as an intermediate compound for the major derivatives shown in Fig. 2.1. The largest and most rapidly growing use for ethylene is in the production of polyethylene (PE), which now accounts for almost 45%.[11] Manufacture of ethylene oxide, which is used mostly as an intermediate in the production of automobile antifreeze and polyester fibers, consumes another 20%. Ethylene dichloride and ethyl benzene manufacture account for 15% and 10%, respectively;[11] these compounds are used primarily for plastics manufacture (polyvinyl chloride [PVC] and polystyrene [PS]). Ethanol consumes another 6%, with the remainder divided among smaller users. End uses for ethylene derivatives are discussed in Secs. 2.2 and 2.3.

Virtually all the propylene produced is used in the manufacture of derivatives, about 70% of it for polymers. The major derivatives are shown in Fig. 2.2. Polypropylene (PP) manufacture consumes 26%, while acrylonitrile, used mostly for fiber manufacture, accounts for 16%. Isopropanol and propylene oxide account for 11% and 14%, respectively, with another 11% going to cumene manufacture for the production of acetone and phenol.[13]

There are several C_4 olefins, but only one -- 1,3-butadiene -- is of major commercial importance. It is especially reactive because of the conjugated double bond structure. Almost all 1,3-butadiene produced is used for polymers (see Fig. 2.3): styrene-butadiene rubber (SBR) accounts for 50% and polybutadiene 20%. Other rubbers account for 10%, while hexamethylene diamine for nylon production uses another 10%.[11] The remaining 10% goes to the production of plastics (acrylonitrile butadiene-styrene [ABS]).

The C_5 and higher olefins have no major chemical uses and are either used in gasoline manufacture or cracked to produce lower olefins.

---

*Critical temperature is the temperature above which a gas cannot be liquefied by pressure alone. Critical pressure is the pressure below which a gas can exist in equilibrium with its liquid at its critical temperature.

Table 2.1. Properties of Major Olefin Derivatives

Common Name	Proper Name	Formula	Mol. Wt.	Color, Normal State	Odor, Taste	mp (°C)	bp (°C)	Explosive Range (%)	Specific Gravity[a]	Toxicity
Acrylonitrile	Vinyl Cyanide	CH_2CHCN	53	Colorless Liquid	Mild Odor	-83	77.3	3-17	0.81	
Butadiene	1,3-Butadiene	$CH_2(CH)_2CH_2$	54	Colorless Gas	-	-108.7	-4.7	2-12	0.62 (4 atm)	
Ethyl Alcohol	Ethanol	C_2H_5OH	46	Clear Colorless Liquid	Fragrant	-114.1	78.32	-	0.79	Moderate Ingestion
Ethyl Benzene	Ethyl Benzene	$C_6H_5CH_2CH_3$	106	Colorless Liquid	Aromatic	-95	136.2	-	0.87 (20 atm)	Moderate
Ethylene	Ethene	CH_2CH_2	28	Colorless Gas	Faint Pleasant Odor	-169.4	-103.8	-	0.00126 (0°C)	
Ethylene Dichloride	1,2-Dichloroethane	$ClCH_2CH_2Cl$	99	Colorless Oily Liquid	Pleasant Odor, Sweet Taste	-35.4	83.5	6-17	1.25 (4 atm)	High
Ethylene Glycol	1,2-Ethanediol	CH_2OHCH_2OH	62	Colorless Liquid	Sweet Taste	-13	197.5	3.2	1.11 (4 atm)	High
Ethylene Oxide	Oxirane	$(CH_2)_2O$	44	Colorless Gas	-	-111.3	10.7	3-100	0.90 (0°C, 4 atm)	Moderate
Isopropyl Alcohol	Isopropanol	$CH_3CHOHCH_3$	60	Clear Colorless Liquid	-	-89.5	82.3	2.5-5.2	0.79	Moderate Ingestion
Propylene	Propene	CH_3CHCH_2	42	Colorless Gas	Slightly Sweet Aroma	-185	-47.7	-	0.51	
Propylene Glycol	1,2-Propanediol	$CH_2OHCHOHCH_3$	76	Colorless Liquid	Practically Odorless	-	188.2	2.6-12.6	1.04 (20 atm)	
Propylene Oxide	Methyl Oxirane	OCH_2CHCH_3	58	Colorless Liquid	Ethereal Odor	-104.4	58.1	2.1-21.5	0.83 (25°C, 25 atm)	Moderate
Styrene	Vinyl Benzene	$C_6H_5CHCH_2$	104	Yellowish Oily Liquid	Aromatic Odor	-30.6	145.2	1-6	0.91 (20 atm)	Moderate
Vinyl Chloride	Chloroethene	CH_2CHCl	62.5	Colorless Gas	Ethereal Odor	-15.8	-13.4	3.6-2.6	0.91 (4 atm)	Moderate

[a] Specific gravity measured at 20°C and 1 atmosphere, unless otherwise noted.

Sources: Refs. 5, 6, and 7.

Table 2.2. Typical Properties of Thermoset Elastomers[a]

	Natural Rubber	Polyisoprene	Styrene Butadiene	Butadiene	Isobutene Isoprene	Ethylene Propylene Co- or Terpolymer
ASTM D1418 Designation	NR	IR	SBR	BR	IIR	EPM or EPDM
Specific Gravity	0.92	0.91	0.94	0.91	0.92	0.86
Tensile Strength (psi)	4000	4000	3500	3000	3000	3000
Elongation (%)	700	700	600	600	800	600
Hardness (Shore A)	30-90	30-90	40-90	40-80	40-80	30-90
Brittle Point (°F)	-80	-80	-80	-100	-80	-90
Resilience (at 73°F)	A	A	B	A	D	B
Compression Set	A	A	A	B	C-B	B-A
Electrical Properties	A	A	A	A	A	A
Adhesion to Metal	A	A	A	A	C-A	C-B
Resistance to:						
Tearing	A	A	C	C	B	C
Abrasion	A	A-B	A	A	C	B
Flame	D	D	D	D	D	D
Ozone	NR	NR	NR	NR	A	A
Weather	D	D	D	D	A	A
Oxidation	B	B	C	C	A	A
Water	A	A	B-A	B	C-A	A
Steam	C	C	C	C	C-A	B-A
Acids (dilute/conc)	A/C-B	A/C-B	C-B/C-B	C-B/C-B	A/A	A/A
Alkalies (dilute/conc)	A/C-B	A/C-B	C-B/C-B	C-B/C-B	A/A	A/A
Synthetic Lubricants	NR	NR	NR	NR	NR	NR
Lubricating Oils (high aniline/low aniline)	NR/NR	NR/NR	NR/NR	NR/NR	NR/NR	NR/NR
Animal, Vegetable Oils	D-B	D-B	D-B	D-B	B-A	B-A
Aliphatic Hydrocarbons	NR	NR	NR	NR	NR	NR
Aromatic Hydrocarbons	NR	NR	NR	NR	NR	NR
Gas Permeability	C	C	C	C	A	C

[a] A = excellent; B = good; C = fair; D = use with caution; NR = not recommended.

Source: Ref. 8.

Table 2.3. Typical Properties of Plastics

Property	LDPE	HDPE	PP		PS	PVC		Nylon		Polyester	
			Unmodified Resin	Glass Reinforced	General Purpose Grades	Rigid	Flexible	66	6	Unreinforced Resin	20-30% Glass Reinforced
Physical											
Specific Gravity	0.910-0.925	0.941-0.965	0.905	1.05-1.24	1.04-1.09	1.03-1.58	1.20-1.70	1.13-1.15	1.13	1.31-1.41	1.45-1.67
Specific Volume (in.^{3}/lb)	30.4-29.9	29.4-28.7	30.8-30.4	24.5	26.0-25.6	20.5-19.1	-	24.2	24.5	21.1-20.2	18.2-17
Water Absorption, 24 hr (%)	<0.01	<0.01	0.01-0.03	0.01-0.05	0.03-0.10	0.04-0.4	0.15-0.75	1.5	1.6	0.08-0.09	0.06-0.07
Mechanical											
Tensile Strength (psi)	600-2,300	3,100-5,500	5,000	6,000-14,500	5,000-12,000	6,000-7,500	1,500-3,500	11,800	11,800	8,000-8,900	14,400-17,600
Elongation (%)	90-800	20-1,000	10-20	2.0-3.6	0.5-2.0	40-80	200-450	60	200	50-300	1-5
Tensile Modulus (10^5 psi)	0.14-0.38	0.6-1.8	1.6	4.5-9.0	4.0-6.0	3.5-6.0	-	4.2	3.8	2.8	13-16
Flexible Modulus (10^5 psi)	0.80-0.60	1.0-2.0	1.7-2.5	3.8-8.5	4.0-4.7	3-5	-	4.1	2.45	2.8-3.8	8.5-16
Flexural Strength (psi)					8,000-17,000					12,000-14,700	22,000-27,500
Impact Strength, izod (ft-lb/in. of Notch)	No break	0.5-20	0.5-2.2	1.0-5.0	0.2-0.45	0.4-20.0	-	0.9	1.0	0.9-1.2	1.0-2.2
Thermal											
Thermal Conductivity (10^{-4} cal-cm/sec-cm^2-°C)	8.0	11.0-12.4	2.8	-	2.4-3.3	3.5-5.0	3.0-4.0	1.7	1.7	1.1-1.2	1.3-2.6
Coef. of Thermal Expansion (10^{-5} in./in.-°C)	10-22	11-13	5.8-10.2	2.9-5.2	6.0-8.0	5-10	7-25	8.1	8.3	4.3-8.9	3.3-3.5
Deflection Temperature (°F)											
At 264 psi	90-105	110-130	125-140	230-300	190-220	140-170	-	150	152	122-160	380-416
At 66 psi	100-121	140-190	200-250	310	180-230			360	365	302-325	420-442
Continuous, No-Load Service Temp (°F)	180-212	250	225-260	270-290	150-170	140-220	150-175	225	225	250	300
Electrical											
Dielectric Constant, 73°F											
At 60 Hz			2.2-2.6	2.37	2.45-2.65	3.2-4.0	5.0-9.0	4.0	3.8	3.3	3.8
At 10^3 Hz	2.25-2.35	2.30-2.35	2.2-2.6	2.36	2.40-2.65	3.0-3.3	4.0-8.0	3.9	3.7	3.2-3.4	3.6-4.0
Volume Resistivity (ohm-cm)	10^{15}	10^{15}	10^{17}	2×10^{16}	10^{17}-10^{19}	$>10^{16}$	10^{11}-10^{15}	10^{14}-10^{15}	3×10^{15}	10^{15}	10^{16}
Arc Resistance (sec)	135-160	-	160	100	60-135	60-80	-	130-140	-	63-190	80-146
Optical											
Refractive Index	1.51	1.54	-	-	1.60	-	-	-	-	-	-
Transmittance (%)	4.50	10-50	-	-	87-92	-	-	-	-	-	-

Source: Ref. 8.

Table 2.4. Summary of Characteristics of Common Natural and Synthetic Fibers

Fiber	Chemical Composition	Sp gr	Moisture Regain,[a] %	Tensile Strength,[a] 10^3 psi	Thermal Effects	Resistance to Chemicals		
						Acids	Alkalis	Organic Solvents
Acetate	Cellulose acetate	1.32	6	20-28	Loss of strength at 195-225°F (91-107°C); sticking point is 350°F (177°C); softens at 395-405°F (202-207°C); melts at 500°F (260°C); burns fairly slowly	Strong acids decompose material; dissolves in acetic acid	Resistant to weak alkalis; strong alkalis saponify the material	Dissolves in acetone and is softened by alcohol; affected by most solvents
Acrylic	85% or more acrylonitrile	1.17-1.19	1.0-2.5	30-62	Sticking point is 410-490°F (210-254°C); loses strength at 350°F (177°C)	Resistant to most acids	Boiling, strong alkalis destroy the material; resistant to weak alkalis	Unaffected by common solvents
Cotton	Cellulose	1.54	7.0-8.5	60-120	Quite resistant to degradation by heat; after about 5 hr at a 250°F (121°C), material yellows; decomposes above 300°F (149°C)	Disintegrates in cold concentrated acids and hot dlute acids.	Mercerizes, but without damage	Quite resistant to most solvents
Modacrylic	35-84% acrylonitrile	1.30-1.37	0.3-4.0	44-50	Stiffens and shrinks above 250°F (121°C); excess heat causes discoloration; does not support combustion	Resistant to most acids	Resistant	Generally unaffected, but warm acetone dissolves the material
Nylon 6	Polyamide based on caprolactam	1.14	4.5	60-85[d] 111-122[c]	Slight discoloration above 300°F (149°C); melts at 415-430°F (213-221°C)	Similar to nylon 66	Very little effect	Similar to nylon 66
Nylon 66	Polyamide based on hexamethylene diamine and adipic acid	1.14	4.0-4.5	65-85[d] 111-122[c]	Sticking point is 445°F (230°C); melts at about 480°F (249°C); loss of 10% of strength in less than 1 hr of exposure at 350°F (177°C)	Resistant to weak acids; decomposed by strong mineral acids	Very little effect	Resistant but soluble in some phenolic materials and in 90% formic acid
Olefin	Polypropylene	0.90	<0.1	35-80	Softens at 305-315°F (152-157°C) and melts at 325-340°F (163-171°C); tends to shrink above 265°F (130°C)	Quite resistant	Quite resistant	Dissolves in chlorinated hydrocarbons at elevated temperatures
Polyester	Ester of a dihydric alcohol and terephthalic acid	1.38	0.40-0.8	81-88[d] 105-160[c]	Sticking point is 455°F (235°C); melts at 480-550°F (249-288°C); up to 10% loss of strength after 18 hr at 350°F (177°C)	Disintegrates in concentrated H_2SO_4; otherwise resistant	Resistant, disintegrates slowly in boiling strong alkalis	Generally unaffected except by some phenolic materials
Rayon	Regenerated cellulose	1.46-1.54	11-16.6	28-47[b] 58-83[c]	Loss of strength at 300°F (149°C); decomposes at 350-400°F (177-204°C); burns readily, but does not melt	Acts like cotton	Loss of strength and swelling in strong alkalis	Resistant to most solvents
Wool	Keratin	1.32	11-17	17-29	Marked effects above 212°F (100°C); scorches at 400°F (204°C); chars at 570°F (299°C)	Destroyed by hot H_2SO_4; otherwise resistant to acids	Strong alkalis destroy the material; attacked by weak alkalis	Quite resistant to most solvents

[a] At 70°F (21.1°C) and 65% relative humidity; [b] Regular to medium tenacity; [c] High tenacity; [d] Regular filament. Source: Ref 9.

Table 2.5. Organic Chemical Usage

Chemical	Usage	Reference
Acrylonitrile	Acrylic Fibers 42% Acrylonitrile-Butadiene-Styrene and Styrene-Acrylonitrile Resins 19.0% Nitrile Elastomers 4% Other 17.5% Exports 17.5%	10
Butadiene	Styrene-Butadiene Rubber 50% Polybutadiene Rubber 20% Other Rubbers 10% Other (including Hexamethylenediamine) 20%	11
Ethyl Benzene	Styrene 97.5% Solvent Applications 1.0% Exports 1.5%	10
Ethylene	Polyethylenes 45% Ethylene Oxide/Glycol 20% Vinyl Chloride 15% Styrene 10% Other 10%	11
Ethylene Dichloride	Vinyl Chloride 81% 1,1,1-Trichloroethane 3% Trichloroethylene 3% Perchloroethylene 3% Ethylene Amines 3% Lead-Saving Agent in Gasoline 2% Vinylidene Chloride 2% Exports 3%	10
Ethylene Glycol	Antifreeze 49% Polyester 45% Industrial Grade E.C. 6%	12
Ethylene Oxide	Ethylene Glycol 69% Surfactants 13% Glycol Esters 7% Ethanolamines 6% Other 5%	12
Isopropyl Alcohol	Acetone 49% Solvent Uses other than Drugs & Cosmetic Products 35% Solvent Uses in Drug & Cosmetic Products 5% Other (e.g., Synthesis of Isopropyl Acetate, Isopropylamine, Herbicidal Esters) 7% Exports 4%	10
Propylene	Polypropylene 26% Acrylontrile 16% Isopropyl Alcohol 11% Propylene Oxide 10% Cumene 11% Other 22%	13
Propylene Glycol	Polyester Resins 46% Pet Food 10% Cellophane 9.5% Tobacco Humectant 9.0% Synthesis of Polymeric Plasticizers 6% Component of Brake and Other Fluids 4% Other 6% Exports 9.5%	10
Propylene Oxide	Urethane Polyols 60% Flexible Foam 80% Rigid Foam 10% Non-Foam 10% Propylene Glycols 25% Other 15%	12
Styrene	Styrenic Resins 80% Styrene Butadiene Rubber 10% Other 10%	14
Vinyl Chloride Monomer	Vinyl Polymers 100%	14

Table 2.6. Polymer Usage

Polymer Type and Name	Markets	Plastic Processing Methods	Reference
Plastics			
Acrylonitrile-Butadiene-Styrene	Appliances 21% Automotive 16% Business Machines 6% Consumer Electronics 3% Furniture 1% Luggage & Cases 2% Modifiers 2% Pipe & Fittings 27% Recreational 7% Other 16%	Injection Molding 42% Extrusion 54% Other 40%	15
Nylon	Transportation 36% Building/Construction 1% Packaging 9% Industrial/Machinery 7% Electrical/Electronic 20% Consumer/Institutional 6% Exports 8% All Others 13%	Injection Molding 70% Extrusion 22% Other 8%	15
Polyester Film	Photographic Films 41.5% Magnetic Tape 13.6% Electrical Applications 8.5% Packaging 6.2% Stationery & Drafting 4.6% Tapes and Labels 4.3% Metallized Film Miscellaneous Applications 4.6% Exports 12.8%		10
High-Density Polyethylene	Packaging 45% Exports 12% Consumer/Institutional 12% Building/Construction 10% Electrical/Electronics Transportation 2% Industrial/Machinery 1% Other 14%	Blow Molding 37.8% Injection Molding 21.8% Extrusion 21.1%	15,16
Low-Density Polyethylene	Packaging 62% Exports 11% Consumer/Institutional 10% Electrical/Electronic 7% Building/Construction 3% Transportation 1% Others 6%	Film 65% Injection Molding 10% Coatings 10% Extrusions 5%	15,17
Polypropylene	Consumer/Institutional 19% Furniture/Finishings 19% Packaging 16% Exports 12% Transportation 11% Electrical/Electronic 7% All others 16%	Injection Molding 40% Fibers 30% Film 10%	15,17

Table 2.6. (Cont'd)

Polymer Type and Name	Markets	Plastic Processing Methods	Reference
Polyvinyl Chloride	Building/Construction 54% Electrical/Electronic 11% Consumer/Institutional 7% Packaging 7% Transportation 5% Furniture/Finishing 5% Exports 4% All Others 7%	Extrusions (mostly pipe) 60% Calendered Sheet and Film 10% Coatings 10% Molding 10%	15,17
Polystyrene	Packaging 36% Consumer/Institutional 23% Electrical/Electronic 10% Building/Construction 8% Exports 4% Furniture/Finishings 3% Industrial/Machinery 1% All Others 15%	Injection Molding 50% Extrusions 30% Foam Beads 10%	15,17
Fibers			
Acrylic	Apparel 58% Home Furnishings 30% Industrial Applications 10% Other 1% Exports 1%		10
Modacrylic	Apparel 46% Home Furnishings 17% Industrial 2% Other 1% Exports 34%		10
Polyester	Apparel 62% Home Furnishings 15% Industrial 9% Other 11% Exports 3%		10
Elastomers			
Styrene-Butadiene	Tires & Tread Rubber 62% Automotive & Mechanical Goods 5% Latex 10% Nonautomotive Mechanical Goods 14% Other 5% Exports 4%		18
Polybutadiene	Tires & Tire Products 87% Other 9% Exports 4%		18

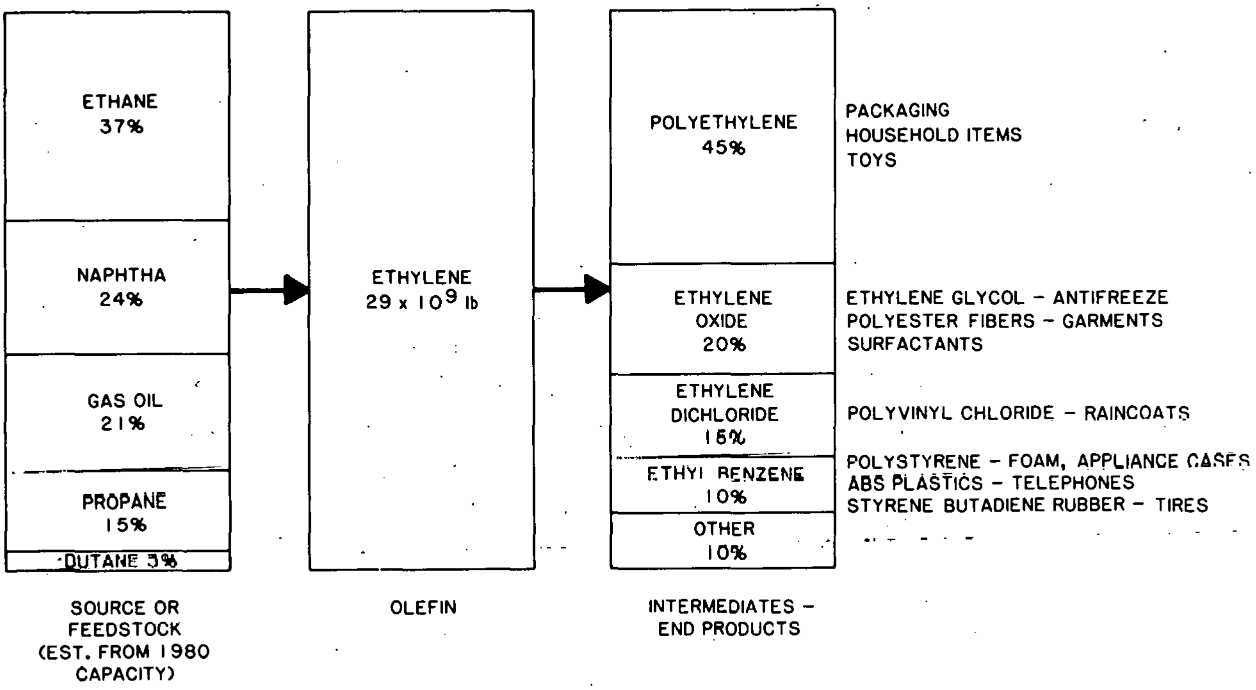


Fig. 2.1. Sources and Derivatives of Ethylene
(Sources: Refs. 4, 11, and 20)

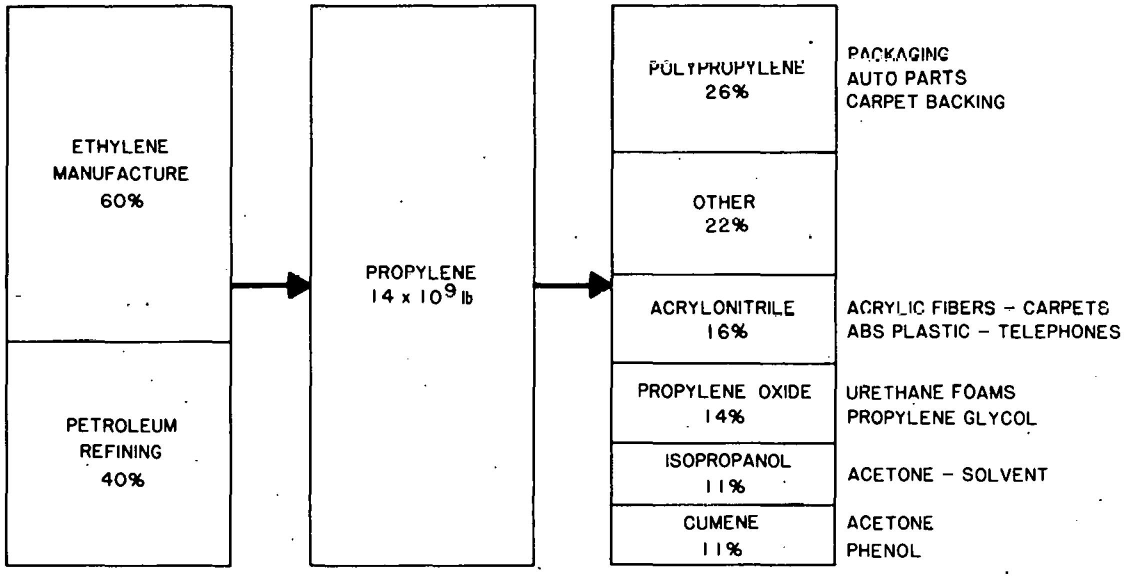


Fig. 2.2. Sources and Derivatives of Propylene
(Sources: Refs. 4 and 13)

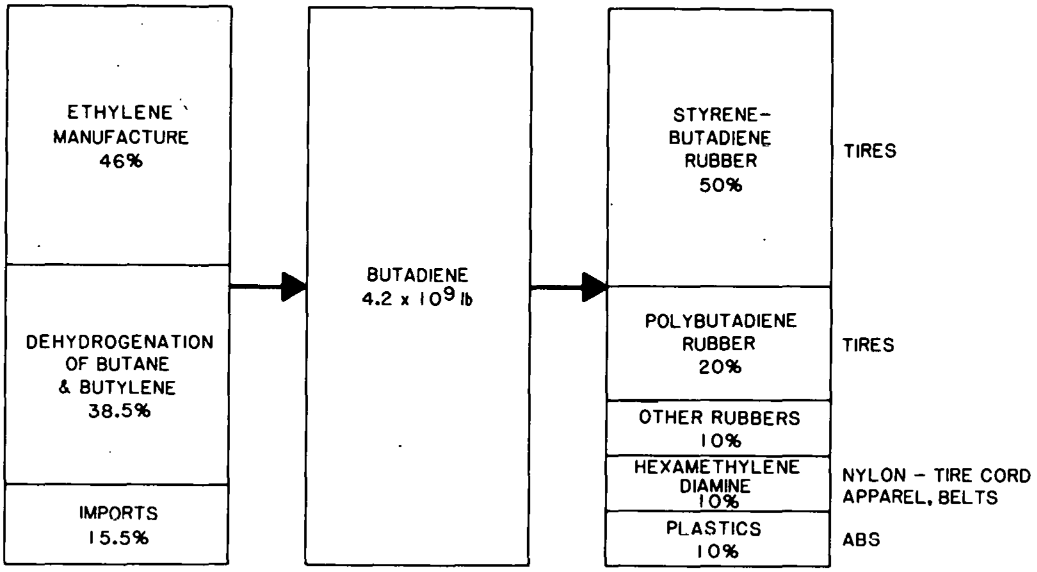


Fig. 2.3. Sources and Derivatives of 1,3-Butadiene (Sources: Refs. 11 and 21)

2.2 POLYMER DERIVATIVES

Polymers have molecules composed of large numbers of smaller units or monomers. These macromolecules can contain many thousands of monomers in chains or cross-linked networks. At least 500 units are necessary for maximum chain strength.[22] Polymers do not form regular crystals easily and tend to be amorphous glasses. They melt over a range of temperatures and often decompose instead of vaporizing, because it is easier to break molecular bonds than to disentangle a molecule from its neighbors.

Polymers are generally divided into three classes -- elastomers, plastics, and fibers -- depending on their properties. Those with flexible chains, weak intermolecular forces, and/or bulky molecular units that cannot fit easily into a crystalline structure are elastomers or rubbers. Polymers with strong intermolecular forces and small monomer units tend to crystallize and show typical fiber properties. Plastics are materials intermediate between elastomers and fibers. Some materials are available in more than one form. The properties of elastomers, plastics, and fibers are compared in Table 2.7.

2.2.1 Elastomers

An elastomer is a material capable of recovery from large deformations (e.g., stretching to twice its length) when the deforming force is removed. It is or can be made to be insoluble in boiling solvents. Synthetic rubbers made largely from butadiene meet about 75% of industrial and commercial needs for elastomers in the United States, with natural rubber meeting the rest.[9] Table 2.8 gives the percentages of total demand satisfied by various

Table 2.7. Mechanical Properties of Polymers

	Elastomers	Plastics	Fibers
Initial Modulus of Elasticity (psi)	15-150	1,500-15,000	150,000-1,500,000
Upper Limit of Extensibility (%)	100-1,000	20-100	Less than 10
Crystallization Tendency	Low when unstressed	Moderate to high	Very high
Molecular Cohesion, (J/mole)	4,200-8,400	8,400-21,000	21,000-42,000
Examples	Natural rubber, styrene butadiene rubber, polybutadiene	Polyvinyl chloride, polystyrene, polyethylene	Polyamides, silk, polyester, polyacrylonitrile

Source: Ref. 22.

elastomers. All of the large-volume rubbers are suitable for use in automotive products, footwear, belting, flooring, and numerous domestic items. As can be seen from the stuctures shown in Fig. 2.4, each type of rubber has residual double bonds and is, therefore, capable of chemical reaction at these reactive sites. Vulcanization (or cross-linking) via an agent like sulfur can thus be accomplished to improve resistance to solvents and to increase rigidity.

Table 2.8. Synthetic Rubber Production, 1979

Type of Rubber	% of Total
Styrene-butadiene	54.9
Polybutadiene	15.7
Butyl	7.7
Nitrile	3.0
Polychloroprene	7.2
Ethylene-propylene	6.9
Others	4.6

Source: Ref. 23.

There are differences in the properties of elastomers that make some of them more suitable for certain uses than others. Styrene-butadiene rubber is a copolymer of styrene and butadiene generally containing about 75% by weight butadiene.^{25,26} Although its properties are, in general, slightly inferior to those of natural rubber, SBR finds broad usage because it is cheaper and more uniform, and withstands aging. Because it is strong and abrasion-resistant, 65% of all SBR is used in passenger car tires.^{18} It is less suitable than natural rubber for heavy-duty truck tires because of greater heat buildup caused by continual flexing. Styrene-butadiene rubber is also used for a large portion of rubber footwear, molded products, and rubber hose. The market for SBR is expected to be stagnant.

Polybutadiene (butadiene rubber) has lower tensile strength and tear resistance than natural rubber but has better abrasion, aging, and oxidation

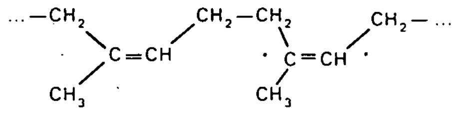
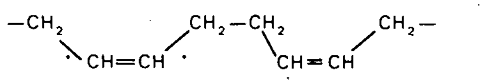
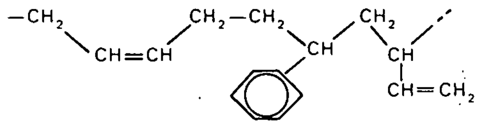
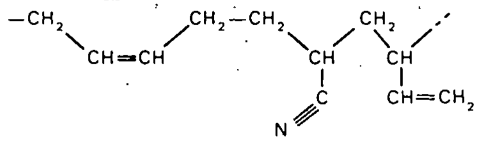
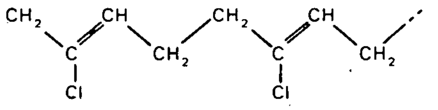
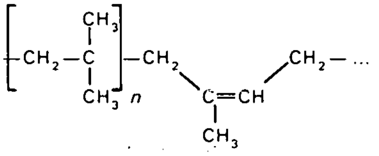
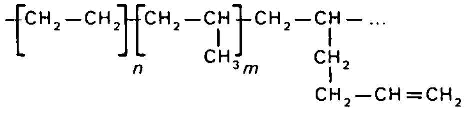
Type	Chain unit structure (typical)	Remarks
Natural Rubber Polyisoprene (PI)		Regular hydrocarbon chains, flexible due to easy rotation about bonds indicated (*) Can crystallise at high extension, or on prolonged storage at low temperatures.
Polybutadiene (PB)		
Styrene-Butadiene (SBR)		Irregular chains less flexible; does not crystallise
Nitrile-Butadiene (NBR) (Hycar)		Irregular chains resistant to hydrocarbon solvents, due to effect of nitrile (CN) group.
Polychloroprene (PCP) (Neoprene)		Regular chain, with Cl atoms attached. Can crystallise. Resists oxidation, moderate solvent resistance.
Butyl Rubber		Regular hydrocarbon chains. Can crystallise.
Ethylene-propylene terpolymers (EPT or EPDM)		Irregular hydrocarbon chains.

Fig. 2.4. Molecular Structures of Elastomers (Source: Ref. 24)

resistance and superior low-temperature properties.[27,28] Its major use is as a blend with natural rubber for heavy-duty tires or with SBR for better-wearing auto tires. Numerous other synthetic rubbers have been developed with properties appropriate for specific end uses, but none of them has captured more than 5% of the total market.

2.2.2 Plastics

A plastic is a material that can be shaped while soft and then hardened to a more rigid state. If the process can be repeated indefinitely by heating and cooling, the material is called a thermoplastic; if the hardening is irreversible due to chemical reaction, the material is called a thermoset. Most of the major commercial plastics are thermoplastics. Because of the wide variations in materials (see Table 2.3), it is very difficult to define the properties of plastics in a concise manner. The matter is rendered even more complicated because of the increased variety of properties available through the action of colorants, plasticizers, fillers, and reinforcing agents. In general, plastics are electrical insulators; are resistant to fats, oils, and inorganic salts; and will soften on heating. Most commercial plastics are transparent or light in color before the addition of colorants.

Because plastics have a wide range of properties, they are used for an increasing variety of end uses. Figure 2.5 shows the steps from monomer to final demand. Figure 2.6 shows the distribution of plastics use in the United States. The largest sectors are packaging and construction, with 26% and 20% of the market, respectively.[15] Figure 2.7 shows the predominance of olefin derivatives in plastics manufacture. Specific properties and uses of the major-volume, olefin-derived thermoplastics (polyethylene, polypropylene, polyvinyl chloride, and polystyrene) are discussed below. Molecular structures of these materials are shown in Fig. 2.8. Major plastics producers and trade names of their products are shown in Table 2.9.

2.2.2.1 The Polyethylenes

The molecular weight of polyethylene ranges from 1000 to over one million. It is moisture resistant and chemically inert, resisting attack by strong acids (except concentrated nitric acid) and bases. However, it is not impermeable to certain organic compounds, such as ethers, gasoline, aromatics, or essential oils, especially above 140°F (60°C). Polyethylene surfaces must be coated if they are to come in contact with these materials. Clear polyethylene is subject to oxidation when exposed to sunlight in the presence of oxygen; hence, it must be colored or otherwise stabilized if it is to be used outdoors. It is flammable and burns slowly if unmodified. The softening temperature is 220-260°F (105-125°C). Polyethylene is intermediate in stiffness between polystyrene and polyvinyl chloride.

Even without copolymers or additives, a wide range of properties is available from polyethylene. These properties are correlated with density, which depends on the polymerization process used (see Sec. 4.3.1). Low-density polyethylene (LDPE) (also called high-pressure, regular, ASTM Type 1, and conventional) has a specific gravity less than 0.925.[9] The molecular chains are branched every 15 to 40 carbons, and the structure is about 65% crystalline. Medium- or intermediate-density polyethylene is classified as ASTM Type II and has specific gravities between 0.925 and 0.94. High-density polyethylene (HDPE) (density greater than 0.94) is also called low-pressure, linear, and Type III. It is about 85% crystalline, with branches only about once per thousand atoms. (See Fig. 2.9a and b for comparison of low- and high-density polyethylene structures.) As density increases, so do tensile strength, hardness, softening temperature, chemical resistance, coefficient of friction, and production cost; however, flexibility and transparency decrease, as does resistance to environmental stress cracking.

By far the largest single use for LDPE is in plastic films, which now account for 65% of the total.[17] These films are used mostly in packaging such diverse items as food, clothing, fertilizers, and wet, dusty, or adhesive industrial materials, where the plastic serves as a liner in metal or fiber

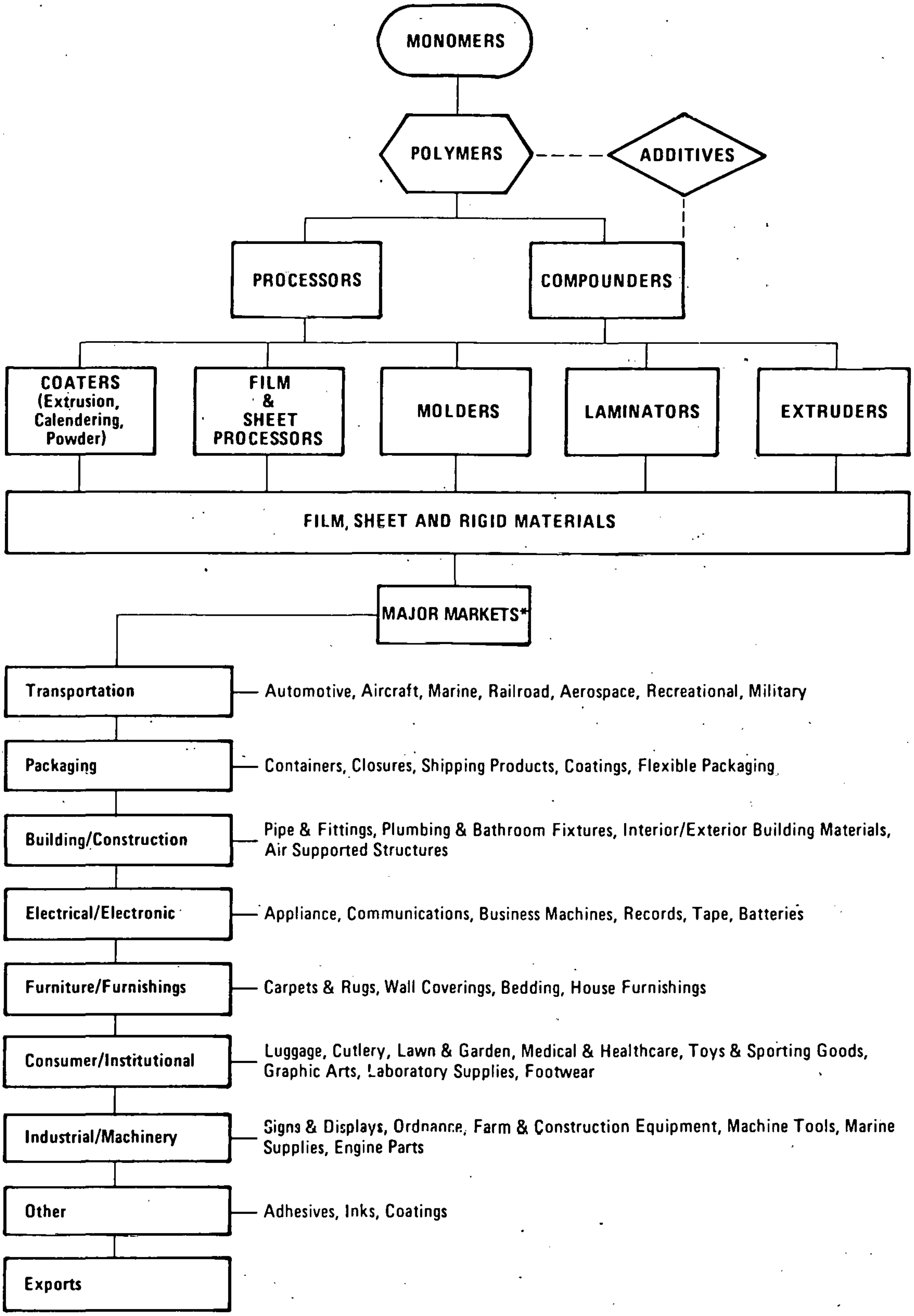


Fig. 2.5. Plastics Flow Chart (Source: Ref. 15)

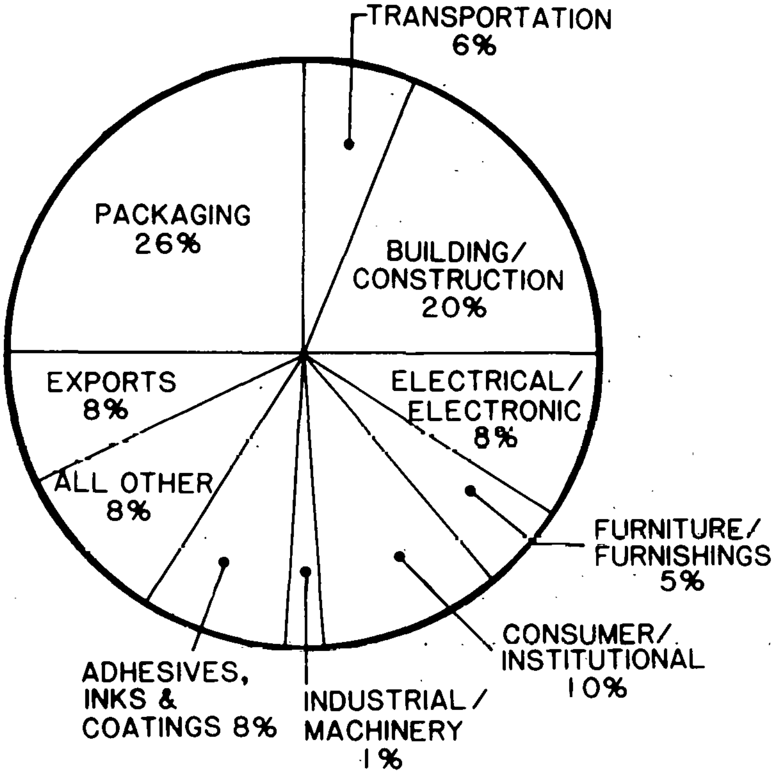


Fig. 2.6. Major Plastics Markets, 1978 (Source: Ref. 15)

drums. Disposable polyethylene liners with capacities to 4600 gal (17,000 L) can be used in trucks or railway cars to haul milk, fruit juices, or vegetable oils, all of which must be kept free of contamination.[29] Film is also used for shower curtains, diaper liners, garment bags, and surgical replacement of membranes and blood vessels.

Moldings are the largest outlet for HDPE (45% blow molding, 20% injection molding) and the second largest for LDPE (about 10% injection molding).[17] Items produced in this way include toys, chairs, automotive parts, carboys, pails, bowls, beakers, and bottles for bleaches, oils, detergents, and foods. Only HDPE is used for containing liquids because of its higher impermeability. Other uses for polyethylene are wire and cable insulation (especially for the residential market), pipes for drainage and irrigation, chemical machinery, and coatings for items like cardboard milk containers.

Within the space of five weeks in 1979, Union Carbide and Dow Chemical announced U.S. polyethylene capacity expansions that could total nearly a million tons by 1982. These expansions are based on new low-pressure polymerization processes that produce linear low-density polyethylenes (LLDPE) and will represent about 20% of total estimated LDPE capacity. At specific gravities of 0.917 to 0.945, LLDPE falls below the density range of HDPE. The new polymer, made by a process related to the HDPE method, has a straight (linear) backbone, though with more and longer branches than HDPE.

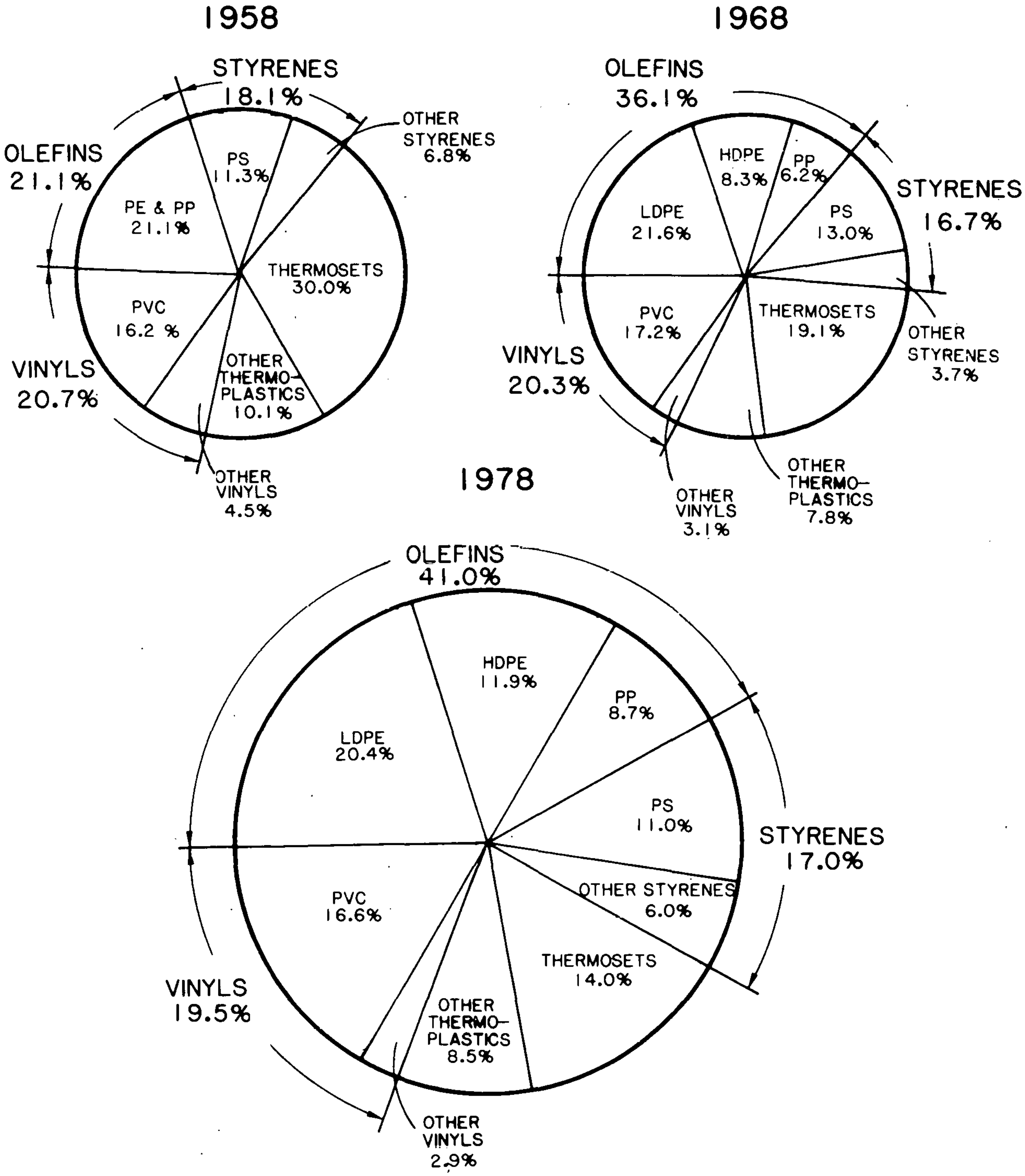


Fig. 2.7. Percentage Distribution of Plastics Sales and Captive Use by Material (Source: Ref. 15)

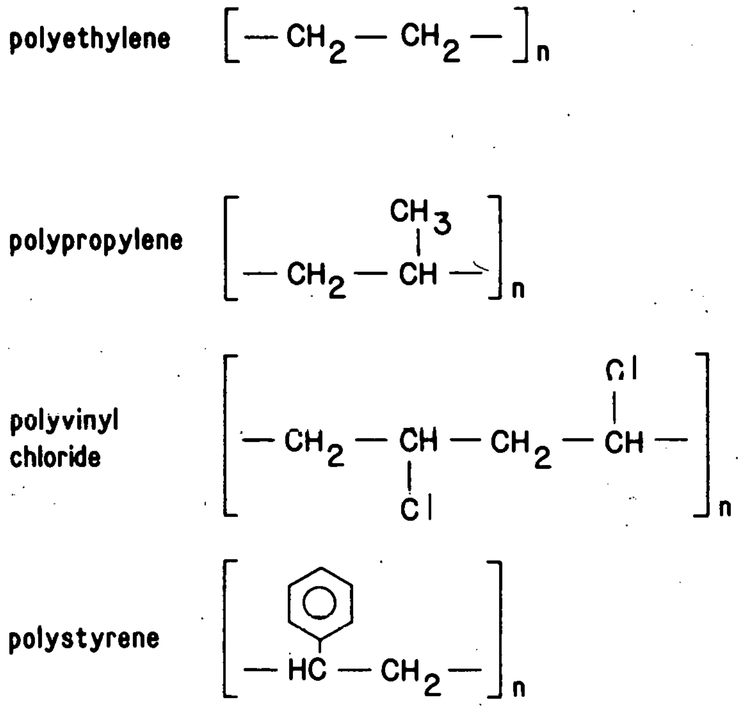


Fig. 2.8. Molecular Structures of Plastics

Desirable properties reported for LLDPE are as follows:

- Film resins have higher impact, tear, and tensile strength than conventional LDPE of the same melt index and density. Chief target markets of extruded films are in heavy-duty shipping sacks, stretch wrap, and ice bags.
- Injection-molding grades exhibit low warpage, environmental stress-crack resistance, low-temperature impact, and better tear and heat resistance as compared with LDPE. The Dow resin is used in large Rubbermaid trash cans and selected Tupperware items.

LLDPE does not always offer the best property package. Some examples where conventional LDPE seems preferable are: blown clarity film (better optical properties), shrink film (lower hot-melt strength), and extension coatings (rheological properties more appropriate for high-speed operations). Also, LLDPE cannot be substituted directly for conventional LDPE in terms of processability. It is on the average a stiffer, more crystalline material, requiring higher melt temperatures and pressure. Exxon estimates that in unmodified, conventional blown film equipment, LLDPE extrusion throughput may be 10-25% less.

Processors in at least three market areas have made significant commercial use of LLDPE: wires and cables, premium housewares, and blown films.

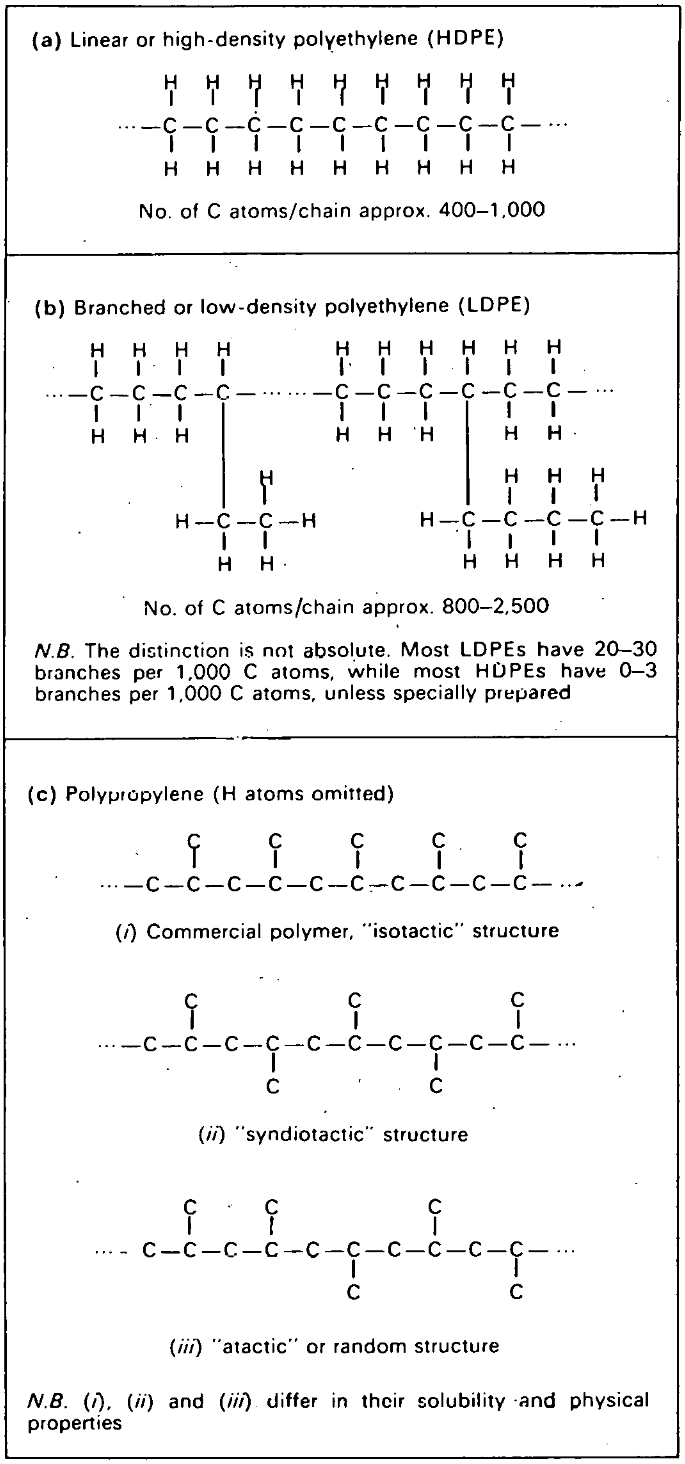
Table 2.9. Plastic Producers and Product Trade Names

Plastic	Producer	Trade Name
Acrylonitrile-Butadiene-Styrene	Abtec Chemical	Abson
	ARCO Polymers	Dylel
	BASF Wyandotte	Luran
	Borg Warner Chemicals	Blendex, Cycolac, Cycoloy, Cycopac, Cycovin, Decoloy, Marbon
	Dow Chemical	Tybrene
	Monsanto	Lustran
	USS Chemicals	Arylon T, Kralastic
Styrene Acrylonitrile	Dart Industries	Acrylafil
	Dow Chemical	Tyril
	Monsanto	Lustran
Nylon	Allied Chemical	Capron
	American Hoechst	Fosta
	BASF Wyandotte	Ultramid
	Belding	Moleculoy
	Chemplast	Ertalon
	Custom Resins	X-tal
	Dart Industries	Xylon
	DuPont	Dymetrol, Elvamide, Felor, Herox, Tynex, Vylor, Zytel
	Henkel	Milvex, Vesalon
	Monsanto	Vydyne, Vydyne R
	Rilsan	Platamid
	Texapol	Texalon
	Wellman	Wellamid, Well-Blend
Polyethylene	Allied Chemical	Paxon
	American Hoechst	Hostalen
	ARCO Polymers	Super Dylan
	BASF Wyandotte	Lupolen
	Dart Industries	ElRey
	Dow Chemical	Ethron, Tyrin
	DuPont	Alathon
	Gulf Oil Chemicals	Hex One, Poly-Eth, Poly-The
	Hercules	Hi-fax, 1900
	Northern Petrochemical	Norchem, Pow'r-pak
	Phillips Chemical	Marlex
	Soltex Polymer	Eltex, Fortiflex
	Union Carbide	Bakelite
	U.S. Industrial Chemicals	Microthene, Petrothene

Table 2.9. (Cont'd)

Plastic	Producer	Trade Name
Polypropylene	American Hoechst	Alprodur, Hostalen
	Amoco Chemical	Avi-sun, Olane, Olefil, Oleflo, Oleflow, Oleform, Olemer, Oletemp, Olex
	ARCO/Polymers	Dypro
	BASF Wyandotte	Luparen
	Dart Industries	El Rex, Le Rexene, Procon, Profil
	Gulf Oil Chemicals	Poly-pro
	Hercules	A-fax, Hercocel, Pro-fax
	Northern Petrochemical	Pow'r-pak
	Novamont	Moplen
	Phillips Chemical	Plasti-Glas
	Soltex Polymer	Fortilene
Polystyrene	A & E Plastik Pak	Bipak
	American Hoechst	Fostafoam, Fostalite, Fostarene, Fosta Tuf-Flex
	Amoco Chemicals	Forar
	ARCO/Polymers	Dylene, Evenglo
	BASF Wyandotte	Styropor
	Dow Chemical	Pelaspan, Pelaspen-pac, Polyfibre, Styron, Styrospan, Styrotherm
	Carl Gordon Industries	Polytone, Superdense, Superflex, Superflow
	Monsanto	Cerex, Lustrex, Verelite
	Northern Petrochemical	Pow'r-pak
	Polysar Resin	E-Z Flow, Jet Flow
Polyvinyl Chloride	Abtec Chemical	Abson
	American Hoechst	Hostaphan
	BASF Wyandotte	Luvitherm, Vinuron
	Diamond Shamrock	Dacovin, Intamix
	Firestone Plastics	Exon
	General Tire & Rubber	Vxgen, Vygen
	B.F. Goodrich Chemical	IGeon, Hi-Temp Geon
	Goodyear Tire & Rubber	Pliovic
	Great American Chemical	Irvinil
	Hooker Chemicals & Plastics	Rucon
	ICI Americas	Genclor
	Mobay Chemical	Vestolit
	Pantasote	Kohinoor
	Tenneco Chemicals	Polytrend
	Union Carbide	Bakelite

Source: Ref. 15.



(a) Linear or high-density polyethylene (HDPE)

No. of C atoms/chain approx. 400–1,000

(b) Branched or low-density polyethylene (LDPE)

No. of C atoms/chain approx. 800–2,500

N.B. The distinction is not absolute. Most LDPEs have 20–30 branches per 1,000 C atoms, while most HDPEs have 0–3 branches per 1,000 C atoms, unless specially prepared

(c) Polypropylene (H atoms omitted)

(*i*) Commercial polymer, "isotactic" structure

(*ii*) "syndiotactic" structure

(*iii*) "atactic" or random structure

N.B. (*i*), (*ii*) and (*iii*) differ in their solubility and physical properties

Fig. 2.9. Molecular Structures of Polyolefins (Source: Ref. 24)

Much industry discussion centers on blown films because of their huge tonnages in conventional LDPE and because of resin savings that LLDPE may make possible.

2.2.2.2 Polypropylene

Polypropylene has a molecular weight on the order of 40,000.[30] The structure is similar to that of polyethylene, but with a methyl (CH_3) group attached to every other carbon in the chain. These can be arranged randomly (atactic), all on the same side of the carbon chain (isotactic), or alternately (syndiotactic). These steroisomers are shown in Fig. 2.9. Polymers containing a high percentage of isotactic chains are more crystalline than those with many atactic chains; commercial products are 60-70% crystalline, which is about the same percentage as for LDPE. The isotactic form melts about 340°F (170°C), which is considerably above the polyethylene melting range.[30] In addition, polypropylene has excellent chemical resistance at temperatures up to approximately 250°F (120°C). These high-temperature properties, coupled with good surface hardness and high compression, flexural, and tensile strengths, make polypropylene the choice for a variety of uses in spite of its higher price. Although it burns the fastest of all the polyolefins, polypropylene can be made nonflammable. It can also be made resistant to ultraviolet light. It is the lightest of all the major plastics (specific gravity = 0.91) and is colorless (translucent) and odorless. It has good dielectric properties and low creep, as does polyethylene.

Polypropylene has numerous uses, the largest of which (fibers and filaments) accounts for only 30% of the total produced.[17] Knitted goods, ropes, and nets can be made from polypropylene, as well as outdoor and auto carpets.[30] A new use of nonwoven polypropylene fiber is Phillips Petroleum's Petromat, which is laid under new road surfaces to prevent cracking. Transportation uses another 11% of polypropylene for various vehicle parts, such as steering wheels, accelerator pedals, fender liners, and trim.[15] It is especially suitable for automotive uses because of low weight and high strength. For uses such as inner fender liners, every pound of plastic can replace two pounds of metal.[31] Polypropylene use averaged 44 lb (19.9 kg) per car in 1979 and is expected to reach an average of 54 lb (24.5 kg) by 1985.[15] Some of these uses are made feasible by the relatively high use temperatures of the polymer. Also made feasible are laboratory ware and medical equipment products where sterilization is required, as well as some major household applications like washing machine tubs and dishwasher parts.

Other household and domestic uses include wastepaper baskets, toilet seat hinges, key cases, lunch boxes with integral hinges, and toys. Polypropylene is used in packaging (blow-molded bleach and detergent bottles and as thin films around cigarette packs).[1] It is also used for tubing and pipe, since it can be welded and imparts no odor, taste, or toxic materials.[29] In addition, polypropylene tubing is inexpensive and is flexible enough to be threaded through old walls as replacement plumbing.

2.2.2.3 Polyvinyl Chloride

The polyvinyl chloride structure resembles polyethylene, but every fourth hydrogen is replaced by chlorine. It is available as a rigid material or with plasticizers added to make it flexible. Unplasticized PVC is hard and tough, with a specific gravity of 1.4. Although PVC is flame resistant and extinguishes itself when flame is removed, it is not very stable in the presence of heat or light. Unless treated with stabilizers, it will soften above 158°F (70°C) and then decompose to give off toxic hydrochloric acid (HCl). Polyvinyl chloride is chemically inert to acids, salts, and petroleum products but not to aromatic hydrocarbons, chlorinated compounds, or ketones.* It is more impermeable to atmospheric gases than polyethylene; foods packaged in PVC retain their flavor better. Fungi will not grow on PVC. Polyvinyl chloride has excellent strength and clarity, and can be produced in a variety of colors.[32]

Because it is inexpensive, easy to process, and can be compounded with other resins and additives to obtain a variety of properties, PVC is extensively used in diverse areas. The largest use category for PVC is construction, which accounts for more than 54% of production.[14] Residential water pipes are often made from PVC, as are electrical conduit and some industrial pipe (e.g., those that carry sour crude oil, salt water, acids, alkalies, salts, and alcohols).[29] Other rapidly growing uses of PVC in construction include wire and cable coating, wall panels, siding, doors, flooring, gutters and downspouts, weather-stripping, and insulation. Household items that can be made from PVC are shower curtains, raincoats, tablecloths (film); toothbrush handles, ice cube trays, wastepaper baskets, flashlight lenses, phonograph records, credit cards (rigid PVC); and garden hose, dolls, inflatable toys, bottles for toiletries, cosmetics, household chemicals and food, and imitation leather for shoes, bags, wallets, belts, luggage, and automobile upholstery (flexible or plasticized PVC).

2.2.2.4 Polystyrene

Styrene monomer is made by dehydrogenation of ethyl benzene, which is made by reacting ethylene with benzene (see Sec. 4.3.1.1). Polystyrene is a clear, colorless material that can be dyed to a variety of transparent and opaque colors. Its high light transmittance leads to such uses as lenses, light fixtures, and sign covers. Polystyrene is flammable and does not self-extinguish. It distorts at about 176°F (80°C) and softens at about 212°F (100°C). The melting point can be raised with additives, as can the impact strength, which is low for this rigid, brittle material. Tensile strength is high, but polystyrene stress-cracks easily. It is resistant to water, acids, and other water-soluble compounds but is attacked by oils and organic solvents. It is an excellent electrical insulator. If the polymer is expanded into foam through the use of steam (see Sec. 4.3.1.2), the properties are changed considerably. Strength decreases with density, as does thermal conductivity. Very low thermal conductivity is maintained down to -94°F (-70°C). The foam softens and burns at a lower temperature than does the solid material, but it can be made self-extinguishing.

---

*A ketone is an organic compound with an oxygen double-bonded to a carbon that is not at the end of a chain.

Packaging represents the largest category of uses, with rapid growth in foam beads and blocks for packing fragile items. Numerous appliance parts are made of polystyrene, ranging from electrical insulators and capacitor dielectrics to knobs, clock cases, radio cabinets, and flashlight lenses. Household uses include light fixtures, toys, bottles, glasses, place mats, wall tile, flower pots, knobs, and circular slide holders. Polystyrene is also used for pipes, auto instrument panels, photographic film, medical syringes, and woodwind instrument reeds. The expanded material is used for ice buckets and beverage cups, picnic coolers, thermal building insulation, and buoyant lifesaving equipment. Glass-reinforced polystyrene is extremely strong and can be used in automobile assemblies. High-impact polystyrene is modified with rubber for use in refrigerator inner doors, hot drink cups, and toys. Telephones are made from ABS resin, which is a copolymer of acrylonitrile, butadiene, and styrene.

2.2.2.5 Reinforced Plastics

Use of reinforced plastics has been rapidly increasing in recent years. Although these materials have been employed in limited applications since the early 1900s, their widespread use grew out of military applications of fiber-reinforced plastics (FRP) during World War II. The rapid growth of reinforced plastics shipments is shown in Table 2.10 for major market sectors between 1974 and 1979. Total shipments grew by 60% during this five-year interval, for an average annual compound growth rate of 9.8%. Land transportation applications grew most rapidly (doubling in five years), which can be attributed to vehicle manufacturers seeking to achieve improved fuel economies by reducing vehicle weight. Fiber-reinforced plastics can perform most structural functions at a lighter weight than equivalent steel components. The energy implications of the materials competition between FRP, steel, and aluminum in automotive applications have been analyzed.[33]

2.2.3 Fibers

A fiber has been defined as: "a slender and greatly elongated natural or synthetic filament (as of wool, cotton, asbestos, gold, glass, or rayon) typically capable of being spun into yarn."[34] Fibers are largely crystalline, high-molecular-weight polymers. Properties include high strength, moderate elasticity, flexibility, and ability to be interlocked or bonded with other fibers in order to amplify these characteristics.[9] The structures of the various fibers are compared in Fig. 2.10. The greatest differences between natural and synthetic fibers are the greater strength, the lower wrinkling, and lower moisture capacity of the synthetics. This latter characteristic explains why cotton apparel is more comfortable in hot weather. Fibers can be formed into rigid or semirigid structures similar to wood or paper or into nonrigid structures suitable for textiles. In addition, fibers have been used for filling (upholstery, packing). Synthetic fibers have made their biggest impact in the textile uses of fibers (spinning or matting), which include apparel, hosiery, tire cord, and carpeting.

The most widely used fibers are natural fibers (wool, cotton, linen), cellulosics or wood-derived fibers (rayon, acetate), and synthetics (acrylics,

Table 2.10. Reinforced Plastics Shipments by Market (both thermoset and thermoplastic)

Market	Shipments (10^6 lb) 1974	1975	1976	1977	1978 Estimate	1979 Estimate
Aircraft & aerospace	30	24	22	23	22	23
Appliances & equipment	82	64	98	112	123	130
Construction	198	175	248	276	323	342
Consumer goods	75	64	102	116	116	125
Corrosion-resistant products	174	163	157	189	216	233
Electrical rods, tubes, and parts	94	82	123	154	170	180
Marine & marine accessories	320	285	365	400	430	451
Land transportation	293	265	398	460	532	580
Miscellaneous	75	58	66	72	74	77
Total	1,341	1,180	1,579	1,802	2,006	2,141

Source: Ref. 15.

polyester, and nylons). Acrylics, polyester, and nylon, all of which are derived from petroleum, will be discussed in the following subsections.

2.2.3.1 Acrylics

Acrylic fibers are polymers of acrylonitrile, a highly reactive compound produced from propylene. Major uses of acrylonitrile are fibers (42%) and plastic copolymers (19%). The latter consist of ABS and styrene-acrylonitrile (SAN) resins.[10]

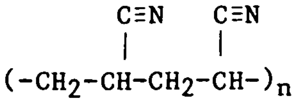
Polyacrylonitrile fibers are classified as acrylic if they contain 85% or more acrylonitrile. They are classified as modacrylic if they contain less than 85% and more than 35% acrylonitrile. Both types are very resistant to light, insects, and microbiological attack.[9] They are generally resistant to chemicals; however, acrylics are destroyed by strong alkali and modacrylics are dissolved by warm acetone. Both are stronger than wool. Acrylic fibers have superior high-temperature properties, but modacrylics are easier to dye. Although acrylic fibers are similar in feel to wool, they are 30-50% cheaper and have had a considerable impact on the wool market. They can be blended with wool or with other synthetics. Fabrics made from acrylics are warm, have excellent dimensional stability, and can be dyed to a variety of hues. Major producers of acrylic fibers tend to specialize in particular end uses. Acrilan (Chemstrand) is used mostly for carpets and blankets, while Orlon (DuPont) is used for apparel such as sweaters and coats. Pile fiber and filter cloth can be made from acrylics or modacrylics. The best known of the modacrylics is Dynel, which is 40% acrylonitrile and 60% vinyl chloride. It is used for apparel, blankets, draperies, water-softener bags, and wigs.

$(C_6H_{10}O_5)_n$

cotton

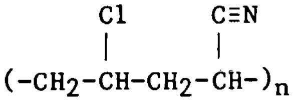
$(C_{42}H_{157}O_{15}N_5S)_n$

wool



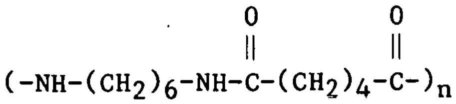
$$(-CH_2-\overset{C\equiv N}{\overset{|}{CH}}-CH_2-\overset{C\equiv N}{\overset{|}{CH}}-)_n$$

acrylic



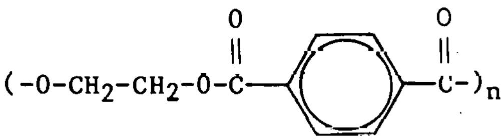
$$(-CH_2-\overset{Cl}{\overset{|}{CH}}-CH_2-\overset{C\equiv N}{\overset{|}{CH}}-)_n$$

modacrylic



$$(-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-)_n$$

nylon 66



polyester

Fig. 2.10. Molecular Structures of Fibers (Source: Ref. 9)

2.2.3.2 Polyester

The name polyester refers to any polymer having an ester group* in the chain. There is only one polyester of commercial importance, polyethylene terephthalate (PET), which is trademarked Dacron by DuPont. Polyester is made from terephthalic acid and ethylene glycol. Since the acid is made from p-xylene, polyester could be classified as an aromatic derivative, but it is included here because its production consumes about one billion pounds of ethylene per year.

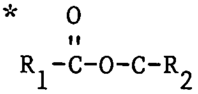
Polyester fibers are strong and are resistant to bacteria, insects, mildew, most organic solvents, weak acids, and bases.[35] They are degraded by strong alkalies and by strong acids at high temperatures. Polyester fabrics, which are generally lightweight and not very warm, become saturated at a moisture content below 1%, making polyester garments uncomfortable in hot weather.[35] They also pass moisture through from one side to the other, making them unsuitable for rainwear. They attract oily soil. However, polyester has the distinctive property of being compatible with natural fibers.[30] Polyester is blended with cotton to improve moisture absorption and opacity over pure polyester and wrinkle-resistance over cotton. Garments account for more than half of polyester use, and include blouses, dresses, shirts, and suits. Polyester fiberfill is used as stuffing and insulation in quilted apparel, pillows, and sleeping bags. The strength, heat resistance, and chemical resistance of polyester have led to its use in tire cords and belts, sailcloths, filter cloths, webbings, and work clothing. About 7% of 1979 PET consumption went to the manufacture of plastic soft drink bottles.[36] This market is growing rapidly.

2.2.3.3 Nylon

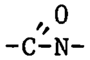
Nylon has been defined as: "any long chain synthetic polymeric amide** which has recurring amide groups as an integral part of the main polymer chain and which is capable of being formed into a filament in which the structural elements are oriented in the direction of the axis."[29] These polymers are named according to the number of carbon atoms in the intermediates that react to yield the fiber.[22] Two are commercially important -- nylon 66 (polyhexamethylene adipamide), which made up about 70% of the 2.15 billion lb (1 million t) produced in the United States in 1979, and nylon 6 (polycaprolactam), which made up most of the remaining 30%. Both nylon 6 and nylon 66 are made in several steps from benzene feedstocks. Nylon 66 also uses butadiene for manufacture of hexamethylene diamine.

Commercial nylon fibers have molecular weights in the range of 12,000-20,000.[35] They are durable, elastic, flexible, strong (wet as well as dry), and resistant to abrasion. Nylon is resistant to alkalies, dilute acids, and most organic solvents, but it is degraded by light. It will not support

---

* 

$R_1-\overset{O}{\overset{\|}{C}}-O-C-R_2$

**An amide is a compound with a  $-\overset{O}{\overset{\|}{C}}-N-$ group.

fungal or bacterial growth. It is a good electrical insulator and is, therefore, subject to static charge.[35] Nylon 66 melts at about 507°F (264°C), but turns yellow and loses strength when heated to over 302°F (150°C) for several hours.

The largest use for nylon is in tire cord, with home furnishings, apparel, and industrial applications not far behind. Carpeting and carpet backing are the major home furnishing uses. Hosiery and other stretch garments, along with lingerie, make up the largest apparel demand for nylon. Industrial applications include those for textile nylon (e.g., filter media, conveyors, and ropes) and those for nylon in plastic form (e.g., bearings, gears, and electrical parts). Because nylon has a low coefficient of friction, some bearings and gears can be operated with no lubrication. Special applications of nylon include parachutes (which must be light and strong) and fishing nets and sails (which must be light, strong, and resistant to salt).

2.3 OXYGENATED DERIVATIVES

All of the remaining large-volume (greater than one billion pounds per year) derivatives of olefins contain one or more oxygen atoms and can be classified as oxides, glycols, or alcohols. All are soluble in water, ethanol, and ether. No oxygenated derivative of butadiene is produced in large volume.

2.3.1 Oxides

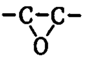
These compounds are extremely reactive (unstable) because of the strained epoxy (oxirane) group* and, therefore, are used almost entirely as intermediates. However, ethylene oxide can be used directly as a sterilant and fumigant that leaves no residues, as an anti-acid when alkali cannot be used, and as a rocket fuel.[19] The most important derivative of ethylene oxide is ethylene glycol (discussed in Sec. 2.3.2), which accounts for about 69% of demand. Surface active agents constitute 13%. Glycol ethers (7%) are used as solvents and jet-fuel additives, while ethanolamines (6%) are used in detergent and soap production.[12] Polyethylene glycols (8%) are used as solvents, plasticizers, and lubricants. One particular application as a lubricant is to reduce friction between the water and walls of fire hoses, thereby doubling the range.[9]

Propylene oxide is used primarily in the production of rigid (10%) and flexible (80%) urethane foams[12] and in propylene glycol production.

2.3.2 Glycols

A glycol is a difunctional alcohol -- a compound with two hydroxyl (-OH) groups. Because it has a high boiling point, is miscible with water,

---

*
$-\underset{O}{C-C}-$

and is noncorrosive, ethylene glycol has been used extensively as antifreeze in automotive cooling systems and in aircraft deicing fluids. Until recently, this use accounted for more than 60% of production -- it now accounts for only 49%. Production of polyester fiber (polyethylene terephthalate) has grown rapidly and now uses 45% of ethylene glycol produced.[12] Small amounts of the material are used in the manufacture of glycol ethers and low-freezing-point explosives.

Propylene glycol is used mostly in the production of unsaturated polyester for reinforced plastics. Because it is nontoxic, it is used instead of ethylene glycol as a plasticizer for cellophane and vinyl polymers; as a solvent for essences, flavorings, and pharmaceuticals; and as a tobacco additive.

2.3.3 Alcohols

An alcohol is an organic compound containing an hydroxyl group. The two important alcohols derived from olefins are ethyl alcohol (ethanol) and isopropyl alcohol or isopropanol (2-propanol).

The largest industrial use for ethanol (41%) is as a solvent for cellulose and other resins, hair and scalp preparations, other cosmetics and external pharmaceuticals, detergents, disinfectants, and flavorings.[30] Acetaldehyde manufacture (for acetic acid and then, in turn, for acetate production) consumes 29%; other chemical syntheses use 28%.[30] This latter category includes compounds such as glycol ethers, ethyl chloride, amines, and ethyl acetate. Since it must be made by fermentation, beverage alcohol is not included here.

Isopropyl alcohol is used mainly for the production of acetone (49%), an important solvent in the organic chemical industry. An additional 40% is used as a solvent for oils, gums, shellac, synthetic resins, drugs, and cosmetics. Isopropanol is a chemical intermediate (7%) for the production of isopropyl acetate, herbicidal esters, and xanthates.[10] Rubbing alcohol is the familiar household application for isopropanol.

2.4 MATERIALS COMPETITION

It is possible to consider substitution of one material for another on three levels: (1) feedstock substitution in production of a given material, (2) material substitution in the production of a given end product, and (3) substitution of an entirely new product for a given end use. The impacts of such substitutions on the whole economy can be studied by the use of input-output analysis. Many organic chemicals, including olefins, can be produced from coal or biomass rather than from petroleum and natural gas. Substitution among light organics in end products, solvents, or intermediates is also possible (e.g., methanol can be used instead of ethylene glycol for antifreeze), but there are no substitutes for them as a class.

Synthetic polymers have substituted for natural materials in the production of a wide range of end products. This substitution has taken place because of the superior properties of the polymers. In addition, an abundance of cheap petroleum and natural gas as well as innovative research and technology advances have made these materials inexpensive. Synthetic fibers are strong, wrinkle-resistant, and come in a variety of weights, textures, and colors. Nylon has taken most of the lingerie and hosiery market from cotton and silk. Polyester has replaced cotton and linen in much of the shirt, suit, and dress market, and acrylics are replacing wool for many knitwear and outerwear uses. In nonapparel uses, polypropylene competes with jute and sisal for carpet-backing and twine, and several synthetics are used in household and industrial textiles. Automobile tire cord used to be made of cotton, then rayon, and now, nylon.

Synthetic rubber has largely replaced natural rubber for tires, not so much because of superior properties but because of lower price, availability, and uniformity. However, more natural rubber may be used in the future as synthetics become more expensive and radial tires find wider use.[31] Radial tires use more natural rubber and less SBR and get about double the mileage of bias tires.

Plastics have partially or entirely replaced natural materials for a broad range of uses because of their versatility, light weight, ease of fabrication, and superior properties (electrical resistivity, nonpermeability, colorability, etc.). Plastics are being substituted for metal in several markets. In the automotive area, plastics have largely replaced metals in dashboards and interior trim, and are replacing miscellaneous gears, parts under the hood, and some exterior parts like front end panels. The increasing penetration of plastics in automobiles can be seen from Table 2.11, which shows the materials used in cars versus time. Table 2.12 shows major parts, their weights, and the plastics from which they are made. There are,

Table 2.11. Estimated Automotive Materials Composition for Selected Car Model Years

	1965		1968		1971		1974		1980	
Material	lb per Unit	% of Total	lb per Unit	% of Total	lb per Unit	% of Total	lb per Unit	% of Total	lb per Unit	% of Total
Cast Iron	414	12.0	440	12.1	488	12.2	467	12.2	378	11.8
Malleable Iron	55	1.6	60	1.8	84	2.1	123	3.2	96	3.0
Carbon Steel	1,901	55.1	1,977	54.3	2,152	53.8	2,030	53.0	1,644	51.3
Galvanized Steel	62	1.8	66	1.0	72	1.8	77	2.0	74	2.3
Aluminized Steel	28	0.8	29	0.8	32	0.8	35	0.9	38	1.2
Alloy Steel	131	3.8	127	3.5	132	3.3	96	2.5	61	1.9
Stainless Steel	11	0.3	11	0.3	12	0.3	12	0.3	13	0.4
Aluminum	62	1.8	66	1.8	76	1.9	83	2.2	115	3.6
Zinc	59	1.7	58	1.6	60	1.5	34	0.9	16	0.5
Copper	35	1.0	36	1.0	32	0.8	23	0.6	19	0.6
Lead	35	1.0	36	1.0	40	1.0	36	0.9	26	0.8
Glass	97	2.8	98	2.7	104	2.6	96	2.5	80	2.5
Rubber	166	4.8	182	5.0	204	5.1	199	5.2	160	5.0
Plastics	35	1.0	73	2.0	104	2.6	152	4.0	190	5.9
Miscellaneous[a]	359	10.5	375	10.3	408	10.2	378	9.6	295	9.2
Average Weight	3,450	100.0	3,640	100.0	4,000	100.0	3,841	100.0	3,205	100.0

[a] Includes sealers, lubricants, solder, cotton, and other materials.

Source: Ref. 15.

Table 2.12. Major Plastics Applications in 1979 Automobiles[a]

Area	Application	Material	Pounds per Car
Interior	Crash pad	Urethane, ABS, PVC	5
	Headrest pad	Urethane, PVC	4
	Trim, glove box	PP, PVC, ABS	18
	Seating foam	Urethane	24
	Seat belts	Nylon	3
	Upholstery	PVC, nylon, polyester	18
	Instrument panels	ABS, SAN, urethane	8
	Headliners	Styrene, PVC	6
	Carpeting	Nylon	9
	Package shelf	ABS	3
Exterior	"Soft" bumpers	Urethane	20
	Fascia panels	Urethane	22
	Fascia retainers	Glass-reinforced PP	7
	Fender liners	PP	12
	Front end panels	Glass-reinforced polyester, glass-reinforced polycarbonate	14
	Wheel covers	Polyphenylene oxide	8
	Fender extension	Glass-reinforced polyester, nylon	3
	Grille	ABS	4
	Lamp housing (rear)	PP, ABS	4
	Styled roof	PVC	6
	Bumper sight shield	Ethylene-propylene-terpolymer-rubber, urethane	12
	Window louvers	Polybutylene terephthalate	2
Under the Hood	Ducts	PP	4
	Battery case	PP	2
	Fan shroud	PP	3
	Heater and air conditioning	Polyester, PP	9
	Electrical housing and wiring	Phenolic, PVC, silicone	11
	Electronic ignition components	Polybutylene terephthalate, phenolic	1
	Master brake reservoir	Nylon, HDPE	1
	Battery trays	Glass-reinforced PP	1
Total			244

[a] Other than soft interior components, many applications are not on every car; weights given are averages for fully formulated, filled plastic parts.

Source: Ref. 15.

of course, important classes of automotive uses, such as engine parts, for which plastics are not suitable. The desire for decreasing auto weight is leading to a number of novel uses for plastics. A fiber-reinforced plastic wheel weighs 11 lb (5 kg) less than a steel wheel. The Ford Motor Company is developing a new plastic hood "sandwich" design with triangular reinforcements between the layers for increased strength with low weight.[37] The amount of plastic in new cars (and, thus, the overall weight saving) is increasing rapidly, as is shown by contrasting the 1977 Ford Comet (105 lb or 48 kg) and the 1978 Mercury Zephyr (150 lb or 68 kg). The total is expected to approach 300 lb (149.5 kg) per car by 1985.[15]

Plastics are also replacing metals in construction applications, such as siding, roofing, and pipe. About 9% of construction material is now plastic, which is distributed among several applications and resins as shown in Table 2.13. These uses have been restricted, however, by building code restrictions on plastic pipe and by labor union pressure against plastic roofing and siding.[30] (Although polyethylene pipe is more expensive than steel, it can be laid continuously from a coil and, therefore, requires less labor.) Plastics also compete with wood, glass, bricks, tile, and cement in the construction market.

Table 2.13. Plastics Consumption in Building Construction

	Year (10^6 lb)			Annual Growth (%)	
Item	1963-65	1978	1990	Historic	Projected
By Application					
Pipe and fittings	107	2,475	4,710	25.2	5.5
Interior products	528	2,264	4,680	11.0	6.2
Exterior products	131	733	1,675	13.1	7.1
Electrical products	228	685	1,380	8.2	6.0
Plumbing fixtures	30	435	880	21.0	6.0
Total	1,024	6,592	13,325	14.2	6.0
By Resin					
Vinyl	471	3,228	6,017	14.7	5.3
Polyethylene	127	492	1,045	10.2	6.5
Polyester	55	274	643	12.2	7.4
Phenolic	114	377	454	8.9	1.5
Acrylonitrile-butadiene-styrene	9	331	525	29.4	3.9
Acrylic	19	241	545	19.9	7.0
Urethane	17	711	1,710	30.6	7.6
Polystyrene	54	218	1,012	10.5	13.6
Polycarbonate	-	90	185	-	6.2
Other	158	630	1,189	10.4	5.4
Total	1,024	6,592	13,325	14.2	6.0

Source: Ref. 15.

Use of plastics has increased greatly in the packaging market, where they compete with paper bags, glass bottles, wax-coated containers, cardboard, fiberboard, wood boxes, and metal drums. Because of light weight, strength, inertness, transparency, and flexibility, plastic is superior as well as less expensive for most of these uses. Plastics compete with leather for shoes, belts, luggage, handbags, and outerwear, and with wood for low-cost furniture. Materials such as copper, zinc, tin, and lead are targets for future substitutions.[38]

Polymers also compete among themselves, and minor cost changes can displace a product from a specific application in as little as three years.[30] Polyvinyl chloride and polystyrene compete for appliance parts, and polyvinyl chloride and polyethylene for pipes and plumbing. The packaging market is very competitive, with polyvinyl chloride, polystyrene, and HDPE suitable for rigid containers, and polyvinyl chloride, LDPE, and cellophane competing with wax paper and aluminum foil for film. A comparison of major plastics is summarized in Table 2.14. Plastics Design Forum has published a number of articles on the design considerations and performance capabilities of specific resins.[39-55]

In all of the foregoing applications, natural materials could again be used in the event of extremely high synthetic polymer prices. However, there are a number of new products for which the synthetic is vastly superior to its possible natural substitute. Magnetic tape made from cellophane would not have the strength, flexibility, or compactness of the Mylar (polyester film) product. Disc storage is a substitute for tape but is more costly at present. A small-volume use for which synthetic polymers have no substitute is the replacement of human body parts. The crucial properties here are inertness and strength for applications such as nylon hip joints and polyethylene blood vessels. A list of biomedical uses for plastics is shown in Table 2.15. Applications for petroleum products for which there are no substitutes should have top priority for access to raw materials.

Table 2.14. Advantages and Disadvantages of Various Plastics

Type of Plastic	Advantages	Disadvantages
Polyethylene	Flexible; easily processed; electrically insulating; water barrier; nearly chemically inert	Soft; low-temperature service; easily scratched
Polyvinyl Chloride	Easily processed; can be plasticized to allow rigid-to-soft flexibility; good weathering	Some properties such as inertness reduced by plasticizers; will sunfade; attacked by hydrocarbons
Polystyrene	Clear; easily processed; easily compounded to improve impact resistance; good stain, abrasion resistance	Not outdoor material; fades; brittle unless compounded; loses some resistance to staining; attacked by hydrocarbons
Polypropylene	Very flexible; very low density; does not stress-crack; excellent electrical resistance; can be electroplated; superior weathering	Cannot be heat-sealed; difficult to dye; somewhat soft in unmodified state
Acetals	Low coefficient of friction; easily processed; High abrasion resistance; solvent resistant	Must be copolymer for dimensional stability; some loss in properties during reprocessing of scrap; not suitable for outdoor applications
Polycarbonates	High heat resistance; excellent clarity; self-lubricating	Difficult to process owing to water absorption; difficult to color
Cellulosics	Excellent films; transparent; propionate films very tough	High water absorption; UV sensitive; easily scorched
Acrylics	Optical clarity; excellent outdoor material	Crazes; attached by solvents; easily scratched; brittle
Nylons	Low coeffficient of friction; nearly chemically inert; easily processed; good impact; fatigue characteristics	Absorbs water; retains set; statically charged
Polysulfones	High-temperature applications; high strength; self-extinguishing; easily colored	Attacked by hydrocarbons

Table 2.14. (Cont'd)

Type of Plastic	Advantages	Disadvantages
Teflon	Chemically inert; low friction coefficient; high-temperature application	Cannot be extruded or injection-molded; soft
Polyimides	600°F applications; very high dielectric strength	Cannot be molded using conventional equipment; expensive
Polybenzimidazoles	900°F applications; excellent adhesives; can be glass-reinforced for added strength	In experimental quantities only; cannot be molded on conventional machines
Polymethylpentene	Good strength at 400°F; good optical quality; lightweight; excellent electrical properties	Available in powder form only; colors must be dry-blended; sun-fades; flammable
Acrylonitrile-Butadiene-Styrene	Easily tailored properties; excellent impact strength; high gloss retention; can be plated	Fades in outdoor applications; not easily colored
Amino Resins	Excellent surface characteristics; excellent strength; solvent resistance; chip resistance	Usually filled with α-cellulose; unfilled not easily colored; not easily injection molded
Unsaturated Polyesters	Usually used with glass for reinforcing; easily colored; resin available in variety of forms	Flammable; some attack by ultraviolet light
Urethanes	Easily foamed; good bearing surfaces	Difficult to reinforce
Epoxies	Low heat curing; high strength; excellent adhesive; good chemical resistance; easily filled	Viscous liquid; entrains air bubbles; requires separate catalyst
Diallylphthalate	High water resistance; good high-temperature properties; excellent strength	Not easily colored; material not easily processed
Phenolics	Good surface finish; low water absorption; excellent flame resistance	Cannot be colored

Table 2.15. Sample Plastic Materials Used in Biomedical Applications

Material	Application
Acrylics	Denture bases, artificial teeth, contact lenses
Cellulosics	Membranes for kidney dialysis
Fluoropolymers	Catheters, tubing
Polycarbonate	Blood oxygenators, cardiotomy reservoirs, dental crowns
Polyester	Artificial limbs and sockets, sutures, implants, catheters
Polyethylene	Blood oxygenators, tubing, catheters, sutures
Polypropylene	Blood oxyenators, sutures, dialysis boards, intravenous catheters
Polyurethane	Splints, artificial limbs, catheters
Polyvinyl Chloride	Tubing, catheters, dental products

Source: Ref. 15.

3 DESCRIPTION OF THE U.S. OLEFINS INDUSTRY

3.1 PRODUCTION STATISTICS

Petrochemicals production has grown very rapidly from 1935, when it represented only 0.5% by weight of total chemicals, to 1970, when it represented 41% (see Table 3.1). Aliphatic organics (chain compounds that are generally olefins or their derivatives) have been a relatively constant 55-60% of petrochemicals production, with the exception of a period around 1950 when the percentage reached 72.9%.[56] This probably reflected war needs for synthetic rubber. Ethylene has been the largest volume organic chemical since 1953 and has had more or less typical growth, i.e., from 1 billion lb (455,000 t) produced in 1948, to 5 billion lb (2.3 million t) in 1960, to 15 billion lb (6.8 million t) in 1971,[9] and to 29.2 billion lb (13.3 million t) in 1979.[4] Ethylene production is compared with the production of other major organic feedstocks in Fig. 3.1. The United States is the largest producer of ethylene[24] and is self-sufficient, producing about one-third of the world total and exporting 5-10% of its production.

The changing distribution of ethylene usage is shown in Fig. 3.2. Ethanol was the largest volume derivative until 1950, when production reached 440 million lb (968,000 t).[58] In 1979, 1.3 billion lb (595,000 t) was produced,[23] but ethanol now ranks behind polyethylene, ethylene oxide, ethylene dichloride (a precursor of polyvinyl chloride), and ethyl benzene (styrene), and is expected to be the slowest-growing of that group. The growth of the polyethylene industry has been spectacular: polyethylene was commercially introduced in the late 1940s, and in 1979 over 12 billion lb (5.5 million t)

Table 3.1. Total Chemical Production in the United States

Year	Total Chemicals Produced (10^6 t)	Total Petroleum Chemicals Produced (10^6 t)	Petroleum Chemicals (%)
1935	8.9	0.5	5
1940	11.2	1.1	10
1945	29.0	4.5	15
1950	33.5	7.2	21
1955	60.2	14.4	24
1960	82.3	24.7	30
1965	129.3	42.3	33
1966	139.3	48.9	35
1968	154.8	59.5	38
1969	164.3	66.2	40
1970	170.1	69.9	41
1979[a]	238.1	78.0	33

[a] Based on the top 50 chemicals only.

Sources: Refs. 56 (1935-1970) and 57 (1979).

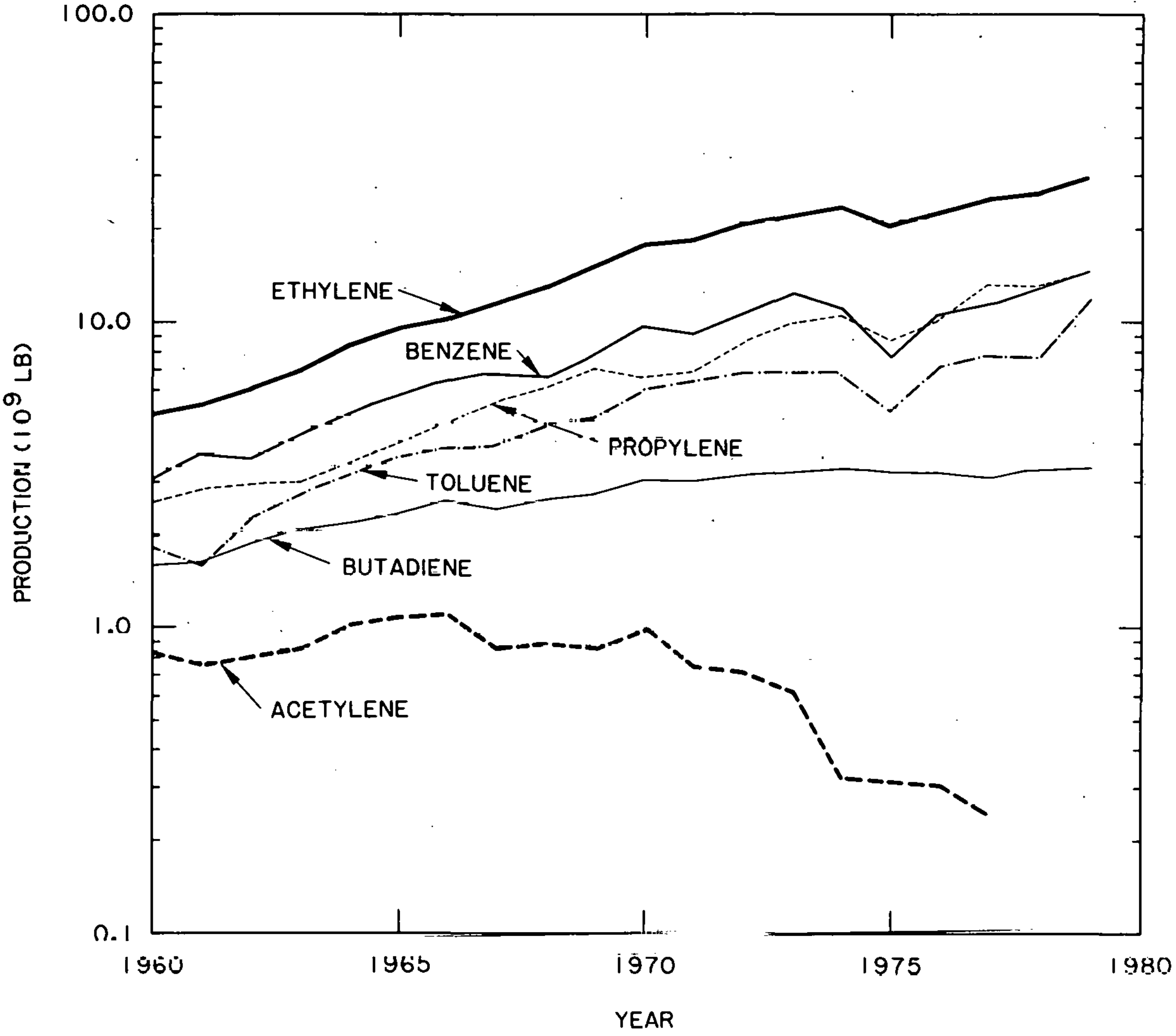


Fig. 3.1. U.S. Production of Major Petrochemicals, 1960-1979 (Sources: Refs. 4, 22, and 57-60)

was produced.[23] Projected demand for the most important ethylene derivatives is shown in Table 3.2, along with total ethylene demand, which is expected to grow at about 8% per year until 1985. Production figures for 1969-1979 for all major petrochemicals are shown in Table 3.3.* (Note the large volumes of olefins and their derivatives.) May, 1980, prices for the compounds considered in this report are shown in Table 3.4. Past ethylene prices are shown in Fig. 3.3. The May, 1980, price of $0.24/lb is about four times the 1974 price, which is due in large part to the increased cost of feedstocks. The economics of production is discussed in Sec. 4.

---

*In order to convert from derivative production to precursor consumption (e.g., from propylene oxide production to propylene usage to produce that product), multiply by the numbers in Tables 3.5 and 3.6.

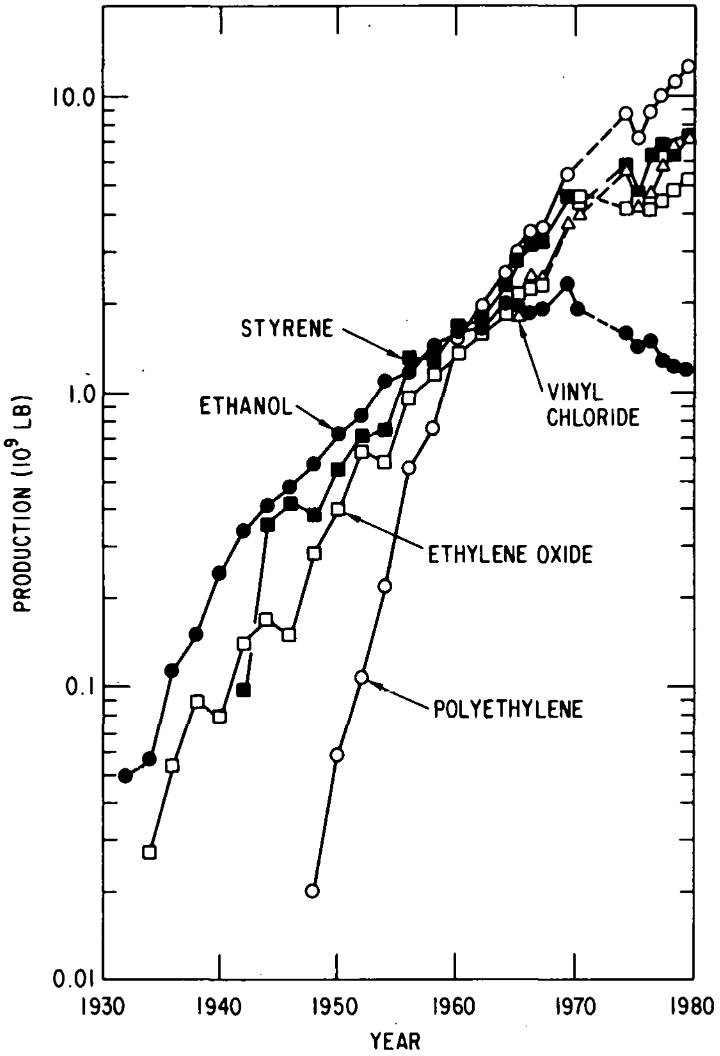


Fig. 3.2. Production of Ethylene Derivatives, 1930–1980 (Sources: Refs. 4, 19, 23, and 57–60)

Production capacity for ethylene and coproducts propylene and butadiene has grown more rapidly than demand. Nameplate plant capacities for 1977–1990 are given in Table 3.7. Effective capacity is usually about 90% of nameplate capacity due to maintenance and turnaround time, but production has only been approximately 80%. (Effective capacity may be somewhat less for new large plants using heavy feedstocks.) Comparison of planned capacities with projected demand shows that overcapacity will continue until about 1984. Part of the apparent excess capacity is old plants that have been shut down but not removed from the capacity figures.

The entire chemical industry (SIC 28) is the largest energy consumer of all the two-digit SIC codes. Its 1977 consumption of purchased fuels and electricity is reported by the Bureau of the Census to be 2.9 Q (2.9 x 10^{15} Btu or 3.1 x 10^{18} J).[70] This figure is consistent with the 3.3 Q (3.3 x 10^{15} Btu or 3.5 x 10^{18} J) figure of the Manufacturing Chemists Association,

Table 3.2. Projected Ethylene Demand (10^6 lb)

Derivative		1974	1976	1979	1980	1984	1985	Annual Growth (%)
Low-density polyethylene	a	-	6,580	-	10,270	-	13,650	8.5
	b	6,325	-	-	10,030	14,765	-	8.0
	c	6,360	-	9,350	-	13,200	-	8.5
High-density polyethylene	a	-	3,090	-	5,260	-	8,530	12.0
	b	3,020	-	-	4,540	6,390	-	7.0
	c	3,110	-	5,180	-	7,990		
Styrene	a	-	1,780	-	2,490	-	3,600	8.5
	b	1,895	-	-	2,845	3,970	-	7.0
	c	2,110	-	2,820	-	3,780		
Ethylene oxide	a	-	4,930	-	6,300	-	8,400	6.0
	b	4,385	-	-	6,215	8,320	-	6.0
	c	4,180	-	5,260	-	6,840		
Vinyl chloride	a	-	2,800	-	3,850	-	5,400	7.5
	b	2,070	-	-	3,110	4,410	-	7.0
	c	2,780	-	3,670	-	5,720		
Ethanol	a	-	860	-	920	-	990	1.5
	b	1,985	-	-	2,225	2,425	-	2.0
	c	990	-	1,120	-	1,250		
Totals (including other uses)	a	-	23,160	-	33,250	-	46,590	8.0
	b	23,515	-	-	37,255	54,660	-	8.0
	c	23,200	-	32,300	-	45,700	-	7.0

Sources: a = Ref. 61 (1977); b = Ref. 1 (1976); c = Ref. 59 (1975).

an association whose members represent more than 80% of the basic industrial chemicals industry.[71] Both of these references assume 100% efficiency for the production of electricity in converting electricity to its fuel equivalent. If 33% efficiency is assumed, total energy purchased by the chemical industry in 1977 is 4 Q (4×10^{15} Btu or 4.2×10^{18} J), of which 40% is in the form of electricity. An additional 2.3 Q (2.3×10^{15} Btu or 2.4×10^{18} J) are consumed as feedstocks. Feedstocks consume 5.5% of the nation's oil (defined as natural gas liquids plus crude oil), compared to 55% for transportation.[38] Energy sources and their uses (fuel or feedstock) for the entire chemical industry are shown in Table 3.8. (Note that 40% of the energy is in the form of feedstock and that 50% of the fuel is natural gas.)

The total quantities of fuels and electricity purchased in 1977 by the 16 largest energy-consuming industries at the four-digit SIC level are given in Table 3.9. Three of the four industries that manufacture primarily olefins and their derivatives are included, as is the largest

Table 3.3. Production Statistics for Major Petrochemicals

MAN-MADE FIBERS

Millions of lb	Production 1979	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969	Annual change 1978–79	1969–79
CELLULOSIC FIBERS													
Acetate[a]	324	308	290	298	313	382	462	429	476	498	498	5%	−4%
Rayon	606	597	598	543	436	817	895	965	915	875	1078	2	−6
NONCELLULOSIC FIBERS													
Acrylic[b]	761	726	709	621	525	631	742	626	545	492	533	5	4
Nylon[c]	2,720	2550	2326	2075	1857	2124	2175	1974	1595	1355	1411	7	7
Olefins[d]	759	692	635	577	497	531	492	416	322	262	269	10	11
Polyester	4,178	3800	3642	3340	2995	2926	2888	2328	1142[e]	1022[e]	939[e]	10	na
Textile glass	1,012	923	787	676	546	683	688	572	468	467	501	10	7
Other	18[f]	16[f]	16[f]	14[f]	12[f]	12[f]	13[f]	11[f]	688[g]	455[g]	376[g]	12	na
TOTAL	**10,378**	**9611**	**9002**	**8144**	**7181**	**8105**	**8354**	**7322**	**6152**	**5427**	**5606**	**8%**	**6%**

a Includes diacetate and triacetate; excludes production for cigarette filtration. b Includes modacrylic. c Includes aramid. d Includes olefin yarn and monofilaments, and olefin and vinyon staple and tow. e Does not include yarn and monofilaments. f Includes only yarn and monofilaments; yarn is chiefly saran and spandex. g Includes only yarn and monofilaments; yarn includes polyester, anidex, saran, spandex, vinyon, and TFE fluorocarbon. na = not available. **Source:** Textile Economics Bureau

PLASTICS

Millions of lb[a]	Production 1979	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969	Annual change 1978–79	1969–79[b]
THERMOSETTING RESINS													
Epoxy[c]	361	299	261	244	198	249	223	184	165	165	166	21%	8%
Polyester[d]	1,147	1,209	1,061	1,042	834	911	1,051	933	730	569	688	−5	5
Urea	1,367	1,122	963	821	690	835	867	739	636	746	817	22	7
Melamine	200	202	200	186	115	164	170	171	168			−1	
Phenolic[e]	1,781	1,617	1,458	1,340	1,051	1,335	1,387	1,453	1,194	1,186	1,181	10	4
TOTAL	**4,857**	**4,448**	**3,943**	**3,631**	**2,888**	**3,494**	**3,698**	**3,481**	**2,893**	**2,666**	**2,852**	**9%**	**5%**
THERMOPLASTIC RESINS													
Polyethylene													
Low density[f]	7,793	7,111	6,471	5,813	4,743	5,973	5,803	5,274	4,458	4,240	3,880	10	7
High density[g]	5,010	4,201	3,652	3,125	2,468	2,837	2,637	2,325	1,924	1,604	1,610	19	12
Polypropylene	3,840	3,074	2,747	2,632	1,902	2,249	2,162	1,726	1,288	1,031	1,090	25	13
Polystyrene													
Acrylonitrile-butadiene-styrene	1,191	1,134	1,069	988	642	857	877	810	686[h]	568	584	5	8
Styrene-acrylonitrile	124	120	115	113	109	109	121	99	77[h]			3	
Solid (straight and rubber modified)	4,005	3,823	3,446	3,195	2,662	3,364	3,322	3,139	2,553	2,371	2,205	5	6
Styrene-butadiene copolymers and other styrene resins	916	878	813	756	585	679	703	624	433	611	555	4	5
Polyamide, nylon type	327	275	254	247	135	204	205	157	110[h]	91	92	19	14
Polyvinyl alcohol	148	127	119	123	118	142	96	62	58[h]	49	57	17	10
Polyvinyl chloride and copolymers[i]	6,119	5,723	5,253	4,716	3,648	4,850	4,562	4,259	3,471	3,115	3,032	7	7
Other vinyl resins[j]	220	197	197	225	187	209	199	194	167[h]	170	171	12	3
TOTAL	**29,693**	**26,663**	**24,136**	**21,933**	**17,199**	**21,473**	**20,687**	**18,669**	**15,225**	**13,850**	**13,276**	**11%**	**8%**

a Dry weight basis. b Annual change calculated for 1969–79 is approximate, because figures from Society of the Plastics Industry for 1979 and International Trade Commission for 1969 are not completely comparable. c Unmodified. d Unsaturated. e Includes other tar acid resins. f 0.940 density and below. g Density above 0.940. h Figure from International Trade Commission. i Dry resin content. j Includes polyvinyl butyral, polyvinyl formal, and polyvinylidene chloride. **Sources:** Society of the Plastics Industry, for years 1971 to 1979, and International Trade Commission for previous years

SYNTHETIC RUBBER

Thousands of metric tons	Production 1979	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969	Annual change 1978–79	1969–79
Styrene-butadiene rubber[a]	1378	1395	1395	1333	1179	1465	1536	1500	1440	1352	1425	−1%	0%
Polybutadiene	397	378	361	352	290	310	337	300	258	284	267	5	4
Butyl	194	154	149	125	80	165	160	131	108	120	132	26	4
Nitrile	75	73	70	73	55	88	84	74	66	68	70	3	1
Polychloroprene	183	161	165	165	144	163	na	na	na	na	na	14	na
Ethylene-propylene	175	174	158	130	84	126	120	91	61	64	76	1	9
Polyisoprene	125[b]	138[b]	62	74	61	92	119	134	119	122	111	−9	0[e]
Other[c]			56	51	47	88	270[d]	227[d]	226[d]	221[d]	204[d]		
TOTAL	**2528**	**2475**	**2418**	**2304**	**1941**	**2498**	**2626**	**2457**	**2277**	**2232**	**2286**	**2%**	**1%**

a Excludes high-styrene latex (more than 45% styrene). b Separate polyisoprene production figure unavailable; only one producer in 1978 and 1979, and figures withheld to avoid disclosing company data. c Excludes polyurethane rubber. d Includes polychloroprene (neoprene). e Annual change for 1969–79 calculated by comparing polychloroprene plus polyisoprene and other in 1979 with polyisoprene and other (including polychloroprene) in 1969. na = not available. **Sources:** Rubber Manufacturers Association, Department of Commerce

Table 3.3. (Cont'd)

ORGANIC CHEMICALS

Millions of lb unless otherwise noted	Production											Annual change	
	1979[a]	1978	1977	1976	1975	1974	1973	1972	1971	1970	1969	1978–79	1969–79
Acetic acid, synthetic	3,329	2,776	2,570	2,463	2,197	2,584	2,429	2,235	1,956	1,932	1,770	20%	7%
Acetone	2,502	2,519	2,219	1,869	1,640	1,980	1,989	1,818	1,538	1,615	1,518	−1	5
Acrylonitrile	2,019	1,752	1,646	1,518	1,215	1,412	1,354	1,115	979	1,039	1,157	15	6
Aniline	681	606	584	544	407	551	458	410	366	398	334	12	7
Benzene, mg[b,c]	1,730	1,488	1,457	1,425	1,024	1,488	1,453	1,252	1,076	1,134	1,185	16	4
Bisphenol A	576	471	455	449	293	370	320	255	187	202	182	22	12
1,3-Butadiene[d]	3,552	3,515	3,259	3,507	2,597	3,682	3,644	3,527	3,340	3,101	3,123	1	1
***n*-Butanol**	732	756	660	625	490	558	519	590	466	468	405	−3	6
Caprolactam	945	919	867	780	713	668	656	640	575	na	na	3	na
Carbon disulfide	447	476	505	508	479	782	777	768	753	721	799	−6	−6
Carbon tetrachloride	704	737	809	857	906	1,163	1,047	997	1,009	1,011	883	−4	−2
Cumene	3,995	3,380	2,644	2,716	2,003	2,906	2,665	2,293	2,144	1,983	1,687	18	9
Cyclohexane	2,412	2,332	2,265	2,187	1,734	2,352	2,123	2,298	1,748	1,841	2,232	3	1
Diisodecyl phthalate	177	171	161	143	106	147	171	153	136	123	137	4	3
Dodecylbenzene[e]	627	526	526	629	495	533	498	524	550	553	529	19	2
Ethanol, synthetic	1,308	1,267	1,339	1,496	1,429	1,618	1,962	1,851	1,630	1,957	2,361	3	−6
Ethanolamines[f]	421	362	308	286	250	307	293	284	259	264	255	16	5
Ethyl chloride	572	540	612	669	575	662	660	576	620	678	679	6	−2
Ethylbenzene[g]	8,530	8,385	8,312	5,770	4,822	6,048	5,688	5,676	4,984	4,827	4,907	2	6
Ethylene	29,187	25,955	25,172	22,475	20,499	23,891	22,329	20,852	18,450	18,089	16,436	12	6
Ethylene dichloride	11,821	11,001	10,997	8,042	7,977	9,165[h]	9,293[h]	7,809	7,558	7,460	6,037	7	7
Ethylene glycol	4,597	3,904	3,675	3,335	3,809	3,341	3,278	3,761	3,070	3,038	2,571	18	6
Ethylene oxide	5,277	5,012	4,364	4,184	4,467	4,200[i]	4,167	3,962	3,598	3,865	3,408	5	4
2-Ethylhexanol	318[j]	420	493	450	387	395	402	526	287	457	405	−24	−2
Formaldehyde, 37%	6,446	6,381	6,046	5,449	4,558	5,764	6,424	5,652	4,522	4,427	4,398	1	4
Isopropyl alcohol	1,968	1,730	1,888	1,936	1,521	1,939	1,835	1,790	1,674	1,919	2,014	14	0
Maleic anhydride	354	341	294	264	216	290	282	274	229	216	201	4	6
Methanol, synthetic	7,411	6,443	6,453	6,242	5,176	6,878	7,064	6,472	4,950	4,932	4,206	15	6
Methyl chloride	449	454	476	378	366	493[h]	544[h]	454	437	423	403	−1	1
Methyl ethyl ketone	649	661	512	428	425	506	541	509	484	480	484	−2	3
Methyl chloroform	710	644	635	631	459	592	548	441	376	300	324	10	8
Methylene chloride	635	570	478	538	497	600	520	471	401	402	366	11	6
Perchloroethylene	770	725	614	669	679	734	706	734	705	707	635	6	2
Phenol, synthetic[k]	2,946	2,682	2,338	2,121	1,746	2,298	2,241	2,052	1,744	1,708	1,636	10	6
Phthalic anhydride	1,039	978	926	902	702	977	1,023	933	794	734	760	6	3
Propylene[c]	14,298[l]	13,014[l]	13,328[l]	10,030[l]	8,709[l]	10,475	9,884[m]	8,472[m]	6,891[m]	6,641[m]	7,235[m]	10	7
Propylene glycol	617	547	489	517	391	510	502	563	421	428	461	13	3
Propylene oxide	2,249	2,047	1,866	1,823	1,524	1,756	1,753	1,520	1,194	1,179	1,177	10	7
Styrene, monomer	7,484	7,186	6,867	6,301	4,673	5,956	5,975	5,941	4,682	4,336	4,640	4	5
Terephthalic acid, dimethyl ester[n]	4,264	5,954	5,410	5,051	4,614	4,262	2,564[o]	4,405[p]	3,574	2,989	2,750	22	10
Toluene, mg[b,c]	1,637	1,054	1,018	999	705	922	958	916	876	830	759	55	8
Vinyl acetate	1,983	1,692	1,586	1,481	1,290	1,403	1,503	1,211	931	803	729	17	11
Vinyl chloride	7,544	6,941	5,986	5,677	4,196	5,621	5,351	5,089	4,336	4,040	3,736	9	7
***o*-Xylene**	1,075	1,013	985	854	703	1,056	1,068	832	785	799	850	6	2
***p*-Xylene**	4,175	3,516	3,172	2,911	2,484	2,707	2,326	2,208	1,662	1,590	1,628	19	10

a Preliminary figures. b Tar distillers not included to avoid disclosing individual company data; includes material for use in blending motor fuels. c All grades. d Rubber grade. e Includes straight-chain dodecylbenzene, tridecylbenzene, and other straight-chain alkylbenzenes. f Mono-, di-, and triethanolamines. g Does not include ethylbenzene produced and consumed in continuous-process styrene manufacture. h Production figure may be too low, because some methyl chloride and ethylene dichloride were produced but not separated or accurately measured by some producers. i Approximate figure. j By weight. k Does not include data for coke ovens and gas retort ovens. l Includes refinery propylene. m Includes data for propane-propylene mixture. n Includes both the acid and its dimethyl ester (DMT), without double counting; acid figures multiplied by 1.16 to convert to equivalent DMT. o Includes only dimethyl ester and not acid. p Figure may be too high because of possible double counting of some acid and ester. na = not available. **Source:** International Trade Commission

Source: Ref. 23.

Table 3.4. Typical Bulk Chemical Prices, May, 1980

Compound	Price (cents)	Unit
Butadiene	33	lb
Ethylene	24	lb
Ethyl alcohol	188	gal
Ethyl chloride	20	lb
Ethylene glycol	35	lb
Ethylene oxide	40	lb
Polyethylene resin[a]	43-65	lb
Polypropylene	50	lb
Polystyrene	49	lb
Polyvinyl chloride[a]	39-59	lb
Propylene	21	lb
Propylene glycol	42	lb
Propylene oxide	35	lb
Styrene	39	lb

[a] Variation due to grade.

Source: Ref. 62.

plastics fabrication industry. SIC 2869,* which includes olefins and non-polymer derivatives, ranks third behind steel mills (SIC 3312) and petroleum refining (SIC 2911). Plastics materials and resins (SIC 2821) ranks 10th, and noncellulosic organic fibers (SIC 2824) ranks 12th. Synthetic rubber (SIC 2822 is not included in Table 3.8, because its energy purchases are only 33% as great as the smallest energy consumer of the top 16 companies. Miscellaneous plastic products (SIC 3079) ranks 16th. Energy purchases by the industries producing olefins and derivatives (SIC 2869, 2821, 2822, and 2824) totaled 1.43 Q (1.43×10^{15} Btu or 1.50×10^{18} J) in 1977,[70] or half of all fuels and electrical energy purchased by the entire chemical industry that year. If this total is corrected to reflect a 33% electrical generating efficiency, it is 1.7 Q (1.7×10^{15} Btu or 1.8×10^{18} J). Twenty-three percent is in the form of electricity, 54% is gas, 9% is petroleum products (mostly residual fuel oil), 9% is coal, and 9% is other fuels. An estimated additional 1.7 Q (1.7×10^{15} Btu or 1.8×10^{18} J) were consumed in 1977, in approximately equal portions of oil and gas, as feedstock for the production of olefins and their derivatives. Note that these energy numbers are somewhat higher than those for the production of olefins and their derivatives, as SIC 2869 produces other products in addition to olefins and nonpolymer derivatives.

---

*SIC 2869 (industrial organic chemicals, not elsewhere classified) was SIC 2818 before 1972 and used to include urea. It comprises a wide variety of miscellaneous organic chemicals; olefins and nonpolymer derivatives account for about 75% of the value of product shipments.

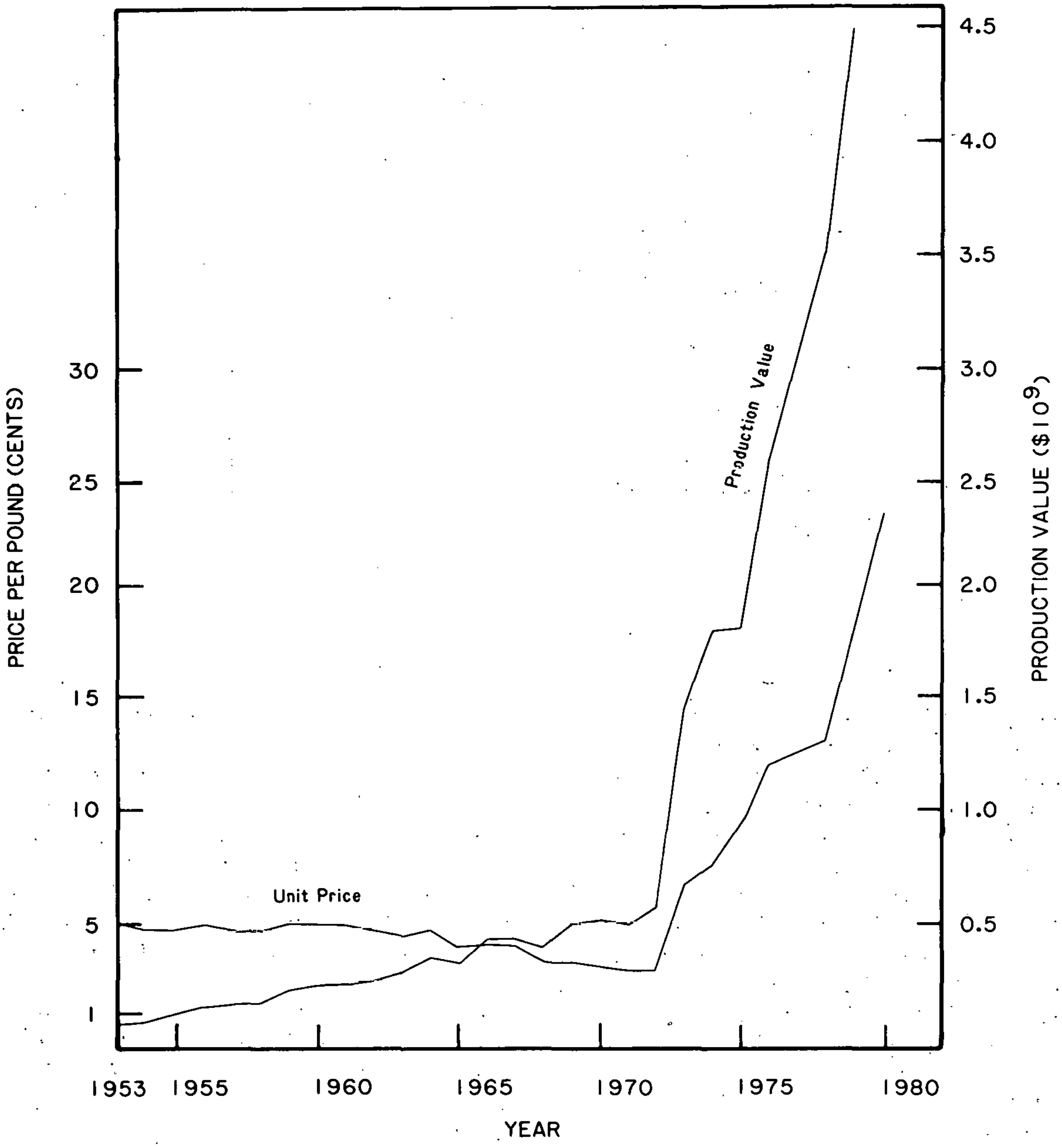


Fig. 3.3. U.S. Trends in Ethylene Prices and Revenues, 1953-1979 (Sources: Refs. 11 and 63-66)

Table 3.5. Unit Consumption of Ethylene

Chemical	lb of Ethylene Consumed per lb Chemical Made from Ethylene
Ethanol	0.60-0.65[a]
Ethylene dichloride	0.31-0.33
Ethylene glycol (via oxide)	0.68
High-density polyethylene	1.02-1.06
Linear low-density polyethylene	0.99
Low-density polyethylene	1.01-1.05
Styrene monomer	0.30
Vinyl chloride monomer	0.46

[a] 4.0-4.3 lb/gal.

Sources: Refs. 67-69.

3.2 INDUSTRY STRUCTURE

Table 3.6. Unit Consumption of Propylene

Chemical	lb of Propylene Consumed per lb of Chemical Made from Propylene
Acrylonitrile	1.15-1.38
Cumene	0.41
Dodecene	1.27
Isopropanol	0.90-0.93
Nonene	1.21
Polypropylene	1.05-1.1
Propylene oxide	0.94

Source: Ref. 67.

Large firms (more than \$5 billion in yearly sales) dominate the petrochemical industry. The major ethylene producers and their mid-1978 and planned 1982 capacities are shown in Table 3.10. Table 3.11 lists the major U.S. chemical producers; note that the oil companies are ranked, even though chemicals make up a maximum of only 17% of their sales. About a dozen firms account for 70% of 1974 capacity and for over 75% of mid-1978 capacity. Because of economies of scale and equipment improvements, the most economical size of ethylene plant to build has a capacity of at least 1 billion lb/yr (455,000 t/yr) and costs roughly \$200 million (1978\$) for the equipment inside battery limits.[72] Thus, the trend towards domination by giant companies is expected to continue, as only large firms can afford the capital and risks involved in expansion.

Most of the recently completed or planned expansion in ethylene production is by oil companies, which have expanded their share of capacity from about 42% in 1974 to over 57% in 1978.[73] Oil companies also produce substantial quantities of other organic chemicals and plastics (see Table 3.12). As light feedstocks become unavailable or too expensive for new olefins plants, ethylene produced from heavier petroleum fractions (naphtha and gas oil) becomes competitive, and refiners have the distinct advantages of producing the feedstock and of having experience in handling the large quantities of coproducts produced (see Sec. 4). In addition to forward integration

Table 3.7. Projected U.S. Ethylene Production (10^{12} lb)

	1977	1980	1985	1990
Demand	25.4	31.0	41.0	54.0
Capacity based on:				
Ethane	13.7	15.1	16.5	16.5
Propane	6.3	6.0	5.0	4.0
Butane	1.0	1.0	1.0	0.8
Refinery gas	0.4	0.4	0.4	0.4
Naphtha	6.1	9.8	13.2	16.0
Atmospheric gas oil	3.9	6.4	8.9	15.0
Vacuum gas oil	1.1	2.4	4.3	11.0
Total	32.5	41.1	49.3	63.7
Imports	-	0.3	0.5	0.5

Source: Ref. 20.

Table 3.8. U.S. Feedstock and Fuels for the Chemical Industry, 1974

Material	Total Chemical Feed (%)	Total Fuel to Chemical Industry (%)	Total (10^{12} Btu)	Total Energy to Chemical Industry (%)	Chemical Industry Share of U.S. Totals (%)		
					Feed	Fuel	Total
Natural gas	31	49	1.05	41	3	7	10
Natural gas liquids	32	-	0.36	14	21	0	21
Crude oil	0.41	8	0.53	21	3	1	4
Coal	-	26	0.37	14	-	6	6
Electricity	-	17	0.25	10	-	8	8
Total	1.11	100	2.56	100	3	4	7

Source: Ref. 38.

by oil companies in order to diversify, there is an increasing tendency toward backward integration, i.e., the control of feedstocks as protection against soaring prices and uncertainties of supply. Dow has recently brought on-line a new 180,000 bbl/day refinery.[36,73]

Vertical integration in the chemical industry is not limited to feedstock and olefins production. Most olefins and many intermediates are used by the manufacturing company or its subsidiaries in further processes, since unit profits are higher at the finished-product end of the chain. Some products, such as ethylene oxide or propylene oxide are very difficult to transport and are, therefore, immediately converted to derivatives. Only 45% of the petrochemicals produced in 1977 were sold on the open market[65] -- the rest were transferred within companies. Widespread vertical integration can be seen by examining company production capacities in Tables 3.13-3.15. Integration would probably proceed even further were limits not imposed by antitrust laws.

Table 3.9. Consumption of Purchased Fuels and Electrical Energy by the Sixteen Largest Energy-Consuming Industries, 1977

Rank	SIC Code	Description	Consumption (10^{12} Btu)
1	3312	Blast furnaces and steel mills	1,389.7
2	2911	Petroleum refining	1,185.5
3	2869	Industrial organic chemicals, n.e.c.[a]	1,062.8
4	2621	Papermills, excluding building paper	564.8
		Largest 4	4,202.8
5	2631	Paperboard mills	474.5
6	3241	Cement, hydraulic	449.4
7	2819	Industrial inorganic chemicals, n.e.c.	422.0
8	3334	Primary aluminum	322.8
		Largest 8	1,668.7
9	2873	Nitrogenous fertilizers	245.5
10	2821	Plastics materials and resins	181.8
11	2865	Cyclic crudes and intermediates	148.3
12	2824	Organic fibers, noncellulosic	147.3
13	3221	Glass containers	145.4
14	3714	Motor vehicle parts and accessories	136.9
15	2812	Alkalies and chlorine	132.8
16	3079	Miscellaneous plastic products	125.8
		Largest 16	7,135.3
		All others	5,602.5
		Total	12,737.9

[a] Not elsewhere classified.

Source: Ref. 70.

There is also a considerable degree of horizontal integration in the petrochemicals industry. A typical producer will make several products from a single intermediate in order to provide a hedge against changes in demand or to produce a complete line of products.[30] Large companies are integrated both horizontally and vertically. Dow Chemical Co., for example, produces over one hundred grades of polyethylene, a dozen different ethylene oxide derivatives, more than a dozen ethylene chloride derivatives, and many other product lines from ethylene. These products are made primarily from purchased petroleum fractions and natural gas liquids.

The ethylene industry is concentrated on the U.S. Gulf Coast, with the majority of plants located in Texas and Louisiana; the rest are spread through the Midwest and California (see Fig. 3.4). Plastics fabricators are more widespread (see Table 3.16). Some ethylene is used at the point of production, and some is shipped to consumers. Although ethylene can be shipped by tanker or truck at -148°F (-100°C),[9] the most economical method is to pipe the vapor through a pipeline network connecting several major producers and consumers. A schematic map of such a pipeline (called the "spaghetti bowl") is shown in Fig. 3.5. Note that the network also connects

Table 3.10. Capacities of U.S. Ethylene Suppliers (10^6 lb/yr)

Supplier	Mid-1978	Planned for 1982
Allied/BASF/Borg-Warner	750	750
Amoco	2,000	2,000
Atlantic Richfield[a]	2,725	2,725
Chemplex	540	740
Cities Service	940	940
Conoco	650	650
Conoco/Monsanto	630	1,500
Corpus Christi Petrochemicals	-	1,200
Dow[b]	3,740	4,740
DuPont	825	825
Eastman	1,250	1,250
El Paso/Dart	575	575
Exxon	1,880	3,180
Goodrich	350	350
Gulf	2,750	2,750
Mobil	930	930
Monsanto	100	100
Northern Petrochemical	950	950
Olin	120	120
Phillips	1,140	2,140
Puerto Rico Olefins[c]	900	900
Shell	2,900	5,700
Sun Olin	225	225
Texaco	550	1,550
Union Carbide[d]	4,120	4,800
USI Chemicals	400	400
Total	31,940	41,990

[a] Excludes 500 million lb/yr ARCO/Polymers unit now on standby.

[b] After permanent shutdown of Bay City, Mich., unit.

[c] Actual capacity may be as low as 750 million lb/yr.

[d] Includes Gulf Coast Olefins unit.

Source: Ref. 16.

to storage areas (salt domes), which are used to store 99.9% pure ethylene in a dense phase under 100 atm pressure during times of low price or consumption. As of January, 1979, the inventory was 2 billion lb (910,000 t), or about one month's production. When ethylene is removed from the domes, the pressure is maintained by pumping in brine.

Liquid intermediates can be shipped by tanker over long distances; however, the most economical production of petrochemicals is achieved when intermediate transport is minimized. Therefore, several process steps

Table 3.11. The Top Fifty Chemical Producers

Rank 1979	Rank 1978[a]	Company	Chemical sales 1979 ($ millions)	Change from 1978	Total sales 1979 ($ millions)	Chemical sales as % of total sales	Industry classification	TOTAL COMPANY Net income ($ millions)	Profit margin[b] Per cent 1979	Profit margin[b] Rank 1979	Profit margin[b] Rank 1978	Return on stockholders' equity[c] Per cent 1979	Return on stockholders' equity[c] Rank 1979	Return on stockholders' equity[c] Rank 1978
1	1	**Du Pont**	$9700	20%	$12,572	77%	Basic chemicals	$ 938.9	7.5%	13	10	18.0%	14	9
2	2	**Dow Chemical**	6634	33	9,255	72	Basic chemicals	783.9	8.5	7	8	20.1	7	6
3	5	**Exxon**	5807	44	79,106	7	Petroleum	4295.2	5.4	29	32	19.0	11	19
4	3	**Union Carbide**	5300[d]	14	9,177	58	Basic chemicals	556.2	6.1	22	23	13.8	34	35
5	4	**Monsanto**	5215	21	6,193	84	Basic chemicals	331.0	5.3	30	16	11.9	40	32
6	7	**Celanese**	3010	23	3,146	96	Basic chemicals	141	4.5	37	35	13.6	36	31
7	6	**W. R. Grace**	2619[d]	2	5,267	50	Specialty chemicals	222.6	4.2	38	37	14.2	33	29
8	8	**Shell Oil**	2599	37	14,431	18	Petroleum	1125.6	7.8	11	11	16.1	23	23
9	11	**Gulf Oil**	2437[d]	43	23,910	10	Petroleum	1322	5.5	28	34	15.2	28	39
10	9	**Allied Chemical**	2150	16	4,332	50	Basic chemicals	175.6	4.1	39	22	14.3	32	30
11	10	**Hercules**	2039	19	2,345	87	Basic chemicals	172.5	7.4	14	20	18.2	13	26
12	12	**Occidental Petroleum**	1994[d]	20	9,555	21	Petroleum	561.6	5.9	26	49	33.0	1	48
13	15	**Standard Oil (Ind.)**	1958	50	18,610	11	Petroleum	1506.6	8.1	9	13	18.0	15	14
14	20	**Phillips Petroleum**	1693	52	9,503	20	Petroleum	891.1	9.4	5	5	20.9	6	4
15	13	**American Cyanamid**	1685[d]	18	3,187	53	Basic chemicals	168.5	5.3	31	19	12.5	39	28
16	21	**Atlantic Richfield**	1662	52	16,234	10	Petroleum	1165.9	7.2	15	14	19.1	10	12
17	14	**Eastman Kodak**	1576	17	8,028	20	Photographic equipment	1000.8	12.5	2	2	18.6	12	5
18	16	**Stauffer Chemical**	1496	15	1,526	98	Basic chemicals	136.0	8.9	6	6	16.0	25	8
19	19	**Rohm & Haas**	1479	30	1,590	93	Basic chemicals	95.5	6.0	23	31	15.0	29	38
20	31	**Tenneco**	1470[d]	82	11,209	13	Petroleum	571	5.1	32	21	15.4	26	17
21	17	**Borden**	1454[d]	16	4,313	34	Dairy products	134.0	3.1	42	38	11.3	41	25
22	18	**Ethyl Corp.**	1440[d]	17	1,657	87	Specialty chemicals	97.5	5.9	25	17	16.1	24	13
23	23	**Mobil**	1325	32	44,721	3	Petroleum	2007.2	4.5	36	39	19.1	9	27
24	22	**Diamond Shamrock**	1234	23	2,357	52	Basic chemicals	178.1	7.6	12	9	17.5	17	11
25	33	**U.S. Steel**	1207	58	12,929	9	Steel	(293.0)[e]	—	—	—	—	—	—
26	24	**FMC**	1135	14	3,307	34	Farm and construction machinery	151.6	4.6	35	26	13.1	38	21
27	25	**Air Products**[f]	1062	16	1,230	86	Basic chemicals	97.5	7.9	10	12	17.2	18	10
28	37	**Texaco**	1047	53	38,350	3	Petroleum	1759.1	4.6	34	41	16.5	21	42
29	30	**BASF Wyandotte**	1045	28	1,103	95	Basic chemicals	9.7	0.9	48	40	3.7	47	36
30	29	**Standard Oil of Calif.**	1043	26	29,948	3	Petroleum	1784.7	6.0	24	28	19.2	8	20
31	28	**B. F. Goodrich**	1041	21	2,988	35	Rubber products	82.6	2.8	44	42	9.2	44	43
32	26	**Ashland Oil**	1017	15	6,474	16	Petroleum	186.4	2.9	43	45	17.5	16	40
33	27	**PPG Industries**	972	10	3,092	31	Glass products	218.9	7.1	16	27	16.4	22	34
34	38	**American Hoechst**	968	42	1,174	82	Basic chemicals	30	2.6	45	45	na	—	—
35	32	**Mobay Chemical**	955	23	955	100	Basic chemicals	58.1	6.1	21	30	16.8	20	24
36	39	**Union Oil of Calif.**	865	28	7,568	11	Petroleum	500.6	6.6	17	15	16.9	19	15
37	41	**Ciba-Geigy**	844	27	1,320	64	Specialty chemicals	na	na	—	—	na	—	—
38	42	**Williams Cos.**	840	27	1,850	49	Agricultural chemicals	69.5	3.8	41	48	9.3	43	47
39	34	**Olin**	823	15	1,778	46	Basic chemicals	71.2	4.0	40	36	9.6	42	41
40	35	**Reichhold Chemicals**	794	14	875	91	Basic chemicals	12.2	1.4	47	47	6.2	46	45
41	42	**Conoco**	792	32	12,648	6	Petroleum	815.4	6.3	19	29	21.6	5	16
42	36	**International Minerals**[g]	780	12	1,475	53	Agricultural chemicals	120.8	8.2	8	7	15.3	27	7
43	40	**National Distillers**	773	16	2,115	37	Alcoholic beverages	135.8	6.4	18	24	13.3	37	37
44	44	**Lubrizol**	725	24	725	100	Specialty chemicals	90.8	12.5	1	1	24.2	2	2
45	48	**Dow Corning**	610	27	610	100	Specialty chemicals	71.5	11.7	3	3	21.8	4	3
46	50	**Borg-Warner**	595	26	2,717	22	Automobile equipment	155.6	5.7	27	18	14.4	31	18
47	49	**Nalco Chemical**	579	22	579	100	Specialty chemicals	63.3	10.9	4	4	24.2	3	1
48	46	**Akzona**	576	11	1,012	57	Basic chemicals	25.6	2.5	46	43	7.9	45	44
49	47	**Pennwalt**	562	17	1,079	52	Basic chemicals	50.0	4.6	33	25	13.7	35	22
50	45	**NL Industries**	537	1	1,810	30	Basic chemicals	114.6	6.3	20	33	14.7	30	33

a Revised. **b** Net income as a percentage of net sales. **c** Net income as a percentage of net worth. **d** Chemical sales include significant amounts of nonchemical products, such as fabricated plastics, coatings, metals, minerals, and the like. **e** Deficit. **f** For the year ended Sept. 30. **g** For the year ended June 30. **na** = not available. **Note:** Industry classifications are based largely, but not entirely, on the federal Enterprise Standard Industrial Classification system.

Source: Ref. 23.

Table 3.12. Oil Companies' Share of Chemical Production Capacities[a]

	1974			1978			1982		
	Number of producers	Number of oil companies	Oil companies' % share of industry capacity	Number of producers	Number of oil companies	Oil companies' % share of industry capacity	Number of producers	Number of oil companies	Oil companies' % share of industry capacity
PLASTICS									
High-density polyethylene	12	4.50	32.8%	12	5.50	39.3%	13	5.50	43.0%
Low-density polyethylene	12	4.50	27.7	13	5.50	32.8	13	5.50	34.4
Polypropylene	9	4.00	51.6	12	6.00	55.6	12	6.00	53.1
Polystyrene	19	3.00	22.2	16	5.00	30.9	16	5.00	29.4
Polyvinyl chloride	23	2.00	10.6	22	2.00	10.3	22	2.00	9.6
ORGANIC CHEMICALS									
Acetone	13	5.50	35.2	13	5.50	43.4	14	5.50	38.7
Acrylonitrile	4	1.00	24.5	4	1.00	18.3	4	1.00	18.3
Alkylbenzene, linear	4	1.00	31.9	4	1.00	36.9	4	1.00	36.9
Benzene	32	24.00	79.8	33	26.50	85.0	34	26.90	80.9
Cumene	12	10.00	63.5	14	11.00	60.5	15	12.00	63.2
Cyclohexane	9	8.00	97.4	9	8.00	97.7	9	8.00	97.8
Ethylene	23	10.50	42.5	25	12.00	57.3	27	12.38	58.1
Ethylene glycol	11	2.50	10.7	11	2.50	11.7	13	3.10	13.3
Isopropanol	4	3.00	63.6	4	3.00	74.6	4	3.00	74.6
Orthoxylene	12	9.00	86.3	12	9.00	86.9	12	9.00	86.9
Paraxylene	11	9.50	86.5	11	9.00	87.4	11	9.00	86.9
Phenol	11	3.00	9.0	12	4.00	21.3	12	4.00	18.7
Phthalic anhydride	9	3.00	21.5	9	3.00	18.2	9	3.00	17.3
Propylene	35	23.50	68.4	35	24.00	78.0	38	24.38	75.2
Propylene glycol	5	1.50	23.9	5	1.50	23.6	5	1.50	23.6
Propylene oxide	5	1.50	29.1	5	1.50	28.8	5	1.50	26.5
Styrene	11	4.50	27.4	10	4.50	27.2	11	4.50	23.9
DMT	5	1.00	10.2	3	–	–	3	–	–
TPA	2	1.00	80.4	2	1.00	93.2	2	1.00	93.2
Total terephthalates	5	1.00	29.5	4	1.00	45.6	4	1.00	45.6
Vinyl chloride	10	2.00	31.7	11	2.00	25.3	12	2.00	21.6

[a] Includes share of joint ventures.

Source: Ref. 73 (reprinted from the October 17, 1979 issue of CHEMICAL WEEK by special permission. Copyright 1979 by McGraw-Hill, Inc., New York, New York)

generally are carried out at the same location. For instance, most polystyrene manufacturers start with ethylene or ethyl benzene, which they convert to styrene and then polymerize in the same plant complex.

Sales and income for specific companies are shown in Table 3.11. Values of shipments for petrochemical industries are compared with other sectors of the chemical industry in Table 3.17. This table also shows that these sectors are highly concentrated (>90%) in large firms. Organic chemical exports for 1979 were $5.06 billion, while imports were $2.16 billion. Exports and imports of plastics were $3.24 billion and $0.63 billion, respectively.[73] General statistics, including establishments and number of employees, are shown in Table 3.18 for SIC 2869 (which includes

---

*Styrene is in SIC 2865 and accounts for only a small fraction of the value of shipments of that SIC.

Table 3.13. Annual Thermoplastic Monomer Capacities by Company in 1978 and Planned Expansions (10^3 t)

Company	Ethylene	Polymer Grade Propylene	Styrene	Terephthalic Acid	Ethylene Oxide	Vinyl Chloride
Allied Chemical	110[a]				23	
Amerada Hess		59				
American Hoechst			399			
Amoco Chemicals	910	83	381	910+455(79)		
Arco Polymers	1,213	240	200			
BASF Wyandotte	110[a]				143	
Borden Chemical						136
Borg-Warner	110[a]					
Celanese					181	
Chemplex	227					
Cities Service	400	240				
Conoco	295+(80)[b]					317
Dart[b]		80[c]				
Diamond Shamrock						454
Dow	1,781+454(79)		839		290	771+181(81)
duPont	375			700		
Eastman Kodak	580	91		420	88	
El Paso	235		68			
Ethyl Corp.						136
Exxon Chemicals	825+590(80)	395				
Fina (Cosden Oil)			435[c]			
Georgia Pacific						454(80)
Goodrich	136					454
Gulf	1,277	400	272			
Hercules Inc.				525		
I.C.I.	445[a](80)					136
Mobil	410	55				
Monsanto	330+(80)		680			
Northern Petrochemical	400	182			100	
Oxirane (50% Arco)			590		261	
Phillips	515+454(78)	145				
PPG					70+136(down)	408+227(80)
Shell Chemical	1,380+590(79)	163			136+300(79)	699
Solvay	d					
Stauffer Chemicals						77
Sun	109		36		50	
Texaco	240+454(79)				227	
Union Carbide	1,356+308(78)		136		1,150	
U.S.I.	182					
U.S.S. Chemicals	227[e]		54[e]			
Other			49	150	150	136
1978 Totals	13,733	2,133	4,157	2,705	2,869	3,724

[a] Joint venture.

[b] Number in parentheses is the year that the added capacity is expected to come on line.

[c] Cosmar is a Cosden/Borg Warner joint venture.

[d] Joint venture of ICI, Solvay, and Champlain in Corpus Christi Petrochemical.

[e] Purchased during 1978 by U.S.S. from Arco Chemical.

Source: Ref. 69.

Table 3.14. Annual Thermoplastic Resin Capacities by Company in 1978 and Planned Expansions (10^3 t)

Company	PET Film or Bottle	PP	HDPE	LDPE	Solid PS	PVC	Number of Resins Produced
Air Products & Chemicals						125+40(78)[a]	1
Allied Chemical			275				1
American Hoechst	Yes		+100(80)		280		2
Amoco Chemicals		250+110(79)	135		180		3
Arco Polymers		180	150	180+115(80)	215		4
BASF Wyandotte					55		1
BF Goodrich					500		1
Borden Chemical					240		1
Borg-Warner	Yes						1
Certain Teed						100+20(79)	1
Chemplex			85+45(79)	140+50(79)			2
Cities Service				160			1
Conoco						180+75(78)	1
Diamond Shamrock						260+15(79)	1
Dow			275	465+100(81)	455		3
duPont	45		205	320			3
Eastman Kodak	120 film	65		150			3
Ethyl Corp.						80	1
Exxon Chemicals		250		295+135(81)			2
Fina (Cosden Oil)						275	1
Firestone						180+90(79)	1
Georgia Pacific						260+180(79)	1
Goodrich Tire & Rubber	Yes					120+25(78)	1 1
Gulf		180	200	390	100		4
Hammond Plastics					75		1
Hercules Inc.		520+55(79)	10				1
Hooker-Ruco						80	1
I.C.I.	Yes						1
3M	55						1
Mobil				135	60		2
Monsanto Plastics		80		370			2
Northern Petrochemical		90		295+90(80)			2
Novamont		80+120(79)					1
Phillips		85		405			2
Polysar					135		1
Rexene (Dart)		130		180+70(78)			2
Robintech						100	1
Shell Chemical		275			135		2
Shintech						100+50(78)	1
Soltex Polymers		90(79)	275				2
Stauffer Chemicals						190	1
Tenneco Chemicals						240+80(78)	1
Union Carbide			205	660+435(1)		140+7(78)	3
U.S.I.			230	225+105(78)			2
U.S.S. Chemicals					100		1
Other	33				50	285	
1978 Totals	193	2,105	2,530	4,580	2,480	3,080	

[a] Number in parentheses is the year that the added capacity is expected to come on line.

Source: Ref. 69.

Table 3.15. Miscellaneous Material Capacities

Material	Company	Capacity (10^6 lb/yr)
Nylon 66	DuPont	1100
	Monsanto	450
	Allied	230
	Dow-Badische	150
Propylene oxide (Propylene glycol)	Dow	1400 (450)
	BASF	175 (0)
	Oxirane	1320 (250)
	Olin	130 (70)
	Union Carbide	0 (100)
Ethanol	Union Carbide	820
	Publiker	410
	USI	400
Isopropanol	Union Carbide	85
	Celanese	60
	Eastman	40

Source: Ref. 36.

olefins and major chemical intermediates),* SIC 2821 (plastics), SIC 2822 (synthetic rubber), and SIC 2824 (synthetic fibers). Similar statistics for SIC 3079 (plastics fabricators) by geographical location are included in Table 3.11.

Numerous trade associations represent the petrochemicals industry. The Manufacturing Chemists Association has 108 member companies that produce more than 80% of domestic output of industrial chemicals.[75] There are also societies that represent specific parts of the industry, such as the Synthetic Organic Chemical Manufacturers Association and the Society of the Plastics Industry, as well as more general groups like the American Institute of Chemical Engineers. Names and addresses for major trade associations are listed in Table 3.19. Numerous U.S. and foreign periodicals and other sources that publish product uses, market distribution, process descriptions and economics, and plant capacities are listed in Table 3.20. Special issues of these publications that are of particular use in obtaining the latest statistics are listed in Table 3.21.

There are also a number of previous reports from which information can be obtained about various topics concerning olefins and their derivatives. These reports are described briefly in Table 3.22. Much of the data in the publicly available reports are now out of date. The private consultant reports contain the latest information and in extensive detail. They are extremely lengthy and are available only to subscribers to the whole series.

Fig. 3.4. Distribution of Ethylene Plants in the United States (Source: Ref. 63)

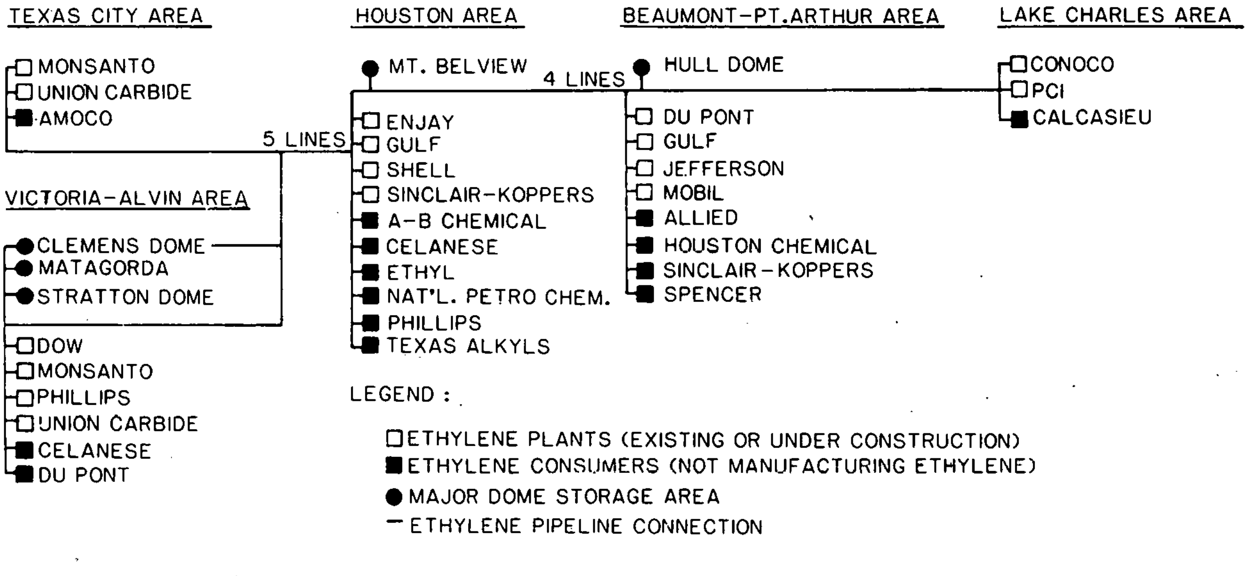


Fig. 3.5. Simplified Version of Ethylene Network, Greater Houston Area (Source: Ref. 67)

Table 3.16. Geographic Location and General Statistics of SIC 3079, Miscellaneous Plastics Products, 1973[a]

Region	Number of Employees	Payroll ($ 10^6)	Number Prod. Workers	Wages Prod. Workers ($ 10^6)	Value Added by Manuf. ($ 10^6)	Value of Industry Shipments ($ 10^6)
New England						
Massachusetts	19,100	144.6	15,300	96.8	323.9	581.6
Rhode Island	4,700	35.5	3,800	22.4	99.0	165.3
Connecticut	6,600	49.5	5,200	33.4	94.9	175.1
Middle Atlantic						
New York	32,300	247.1	25,400	162.2	523.0	960.0
New Jersey	27,500	219.5	20,200	148.8	551.9	1,029.1
Pennsylvania	22,800	187.3	18,100	131.3	382.6	732.1
East North Central						
Ohio	40,900	353.4	33,500	255.4	790.7	1,438.5
Indiana	18,000	141.6	14,700	102.1	307.9	557.5
Illinois	30,400	247.9	24,400	164.0	519.9	918.2
Michigan	19,500	157.7	15,400	102.2	330.9	641.2
Wisconsin	9,000	73.6	7,300	50.4	172.2	312.1
West North Central						
Minnesota	7,200	58.5	5,800	40.9	132.8	239.7
Iowa	4,500	39.1	3,600	27.5	100.6	166.1
Missouri	9,000	60.7	7,800	44.4	153.8	267.4
South Atlantic						
Maryland	3,700	27.2	2,900	18.1	61.8	112.6
Virginia	6,800	59.3	5,300	42.1	136.3	252.3
North Carolina	9,400	67.0	7,600	44.8	178.8	364.2
Georgia	4,100	28.4	3,400	19.6	80.4	153.3
Florida	6,100	44.7	5,000	30.9	108.1	175.2
East South Central						
Tennessee	8,400	62.2	7,000	45.6	208.3	342.5
Mississippi	3,400	22.7	2,800	16.0	58.9	113.8
West South Central						
Texas	13,500	98.4	11,000	68.3	268.6	483.5
Mountain	-	-	-	-	-	-
Pacific						
California	40,500	321.1	31,800	213.1	745.1	1,322.8
Total	347,400	2,747.0	277,300	1,880.3	6,330.4	11,504.1

[a] Includes information by state where available. The government has grouped the data in larger two- or three-digit categories for the remaining states.

Source: Ref. 15.

Table 3.17. Chemical Industry Profile, 1978

SIC	Industry	Total Plants	Large Plants	Shipments ($\$ 10^6$)	% in Large Plants
SIC 28	Chemicals				
2812	Alkalies and chlorine	69	36	2,293.8	91
2813	Industrial gases	307	33	1,871.9	42
2816	Inorganic pigments	90	37	1,277.6	83
2819	Industrial inorganic chemicals n.e.c.[a]	514	190	9,288.6	83
2821	Plastics materials and synthetic resins	443	197	16,117.2	88
2822	Synthetic rubber	61	39	3,994.6	97
2823	Cellulosic man-made fibers	20	13	1,191.4	98
2824	Noncellulosic synthetic organic fibers	68	55	5,218.9	99
2831	Biological products	80	32	623.3	83
2833	Medicinals and botanicals	93	29	2,245.7	87
2834	Pharmaceutical preparations	470	215	13,315.1	92
2841	Soap and other detergents	252	76	6,729.6	84
2842	Polishes and sanitation goods	490	113	4,215.0	66
2843	Surface-active agents	64	14	683.8	61
2844	Toilet preparations	237	120	6,455.9	91
2851	Paints and allied products	797	195	6,410.0	64
2861	Gum and wood chemicals	87	26	913.8	61
2865	Cyclic crudes and intermediates	183	78	4,781.7	86
2869	Industrial organic chemicals n.e.c.	431	186	22,018.0	89
2873	Nitrogenous fertilizers	221	53	2,625.5	65
2874	Phosphatic fertilizers	91	38	2,318.0	63
2875	Fertilizers - mixing only	242	21	1,458.9	32
2879	Agricultural chemicals n.e.c.	196	42	2,777.7	65
2891	Adhesives and sealants	259	66	1,601.4	63
2892	Explosives	63	30	683.2	93
2893	Printing ink	192	26	894.2	46
2895	Carbon black	35	11	363.2	53
2899	Chemical preparations n.e.c.	531	119	4,649.1	64
SIC 30	Rubber and miscellaneous plastics products				
3011	Tires and inner tubes	132	96	6,755.3	98
3021	Rubber and plastic footwear	42	37	293.6	99
3031	Reclaimed rubber	11	2	74.2	39
3041	Rubber and plastic hose and belting	130	77	1,241.5	91
3069	Fabricated rubber products n.e.c.	788	297	5,321.9	81
3079	Miscellaneous plastics products	3,748	1,104	26,835.9	67

[a] Not elsewhere classified.

Source: Ref. 15.

Table 3.18. Industry Statistics by Geographical Areas, 1977 and 1972

		1977											1972	
		All Establishments		All Employees		Production Workers								
SIC Code	Geographic Area	Total	With 20 Employees of More	Number (10^3)	Payroll ($ 10^6)	Number (10^3)	Hours (10^6)	Wages ($ 10^6)	Value added by Manufacture ($ 10^6)	Cost of Materials ($ 10^6)	Value of Shipments ($ 10^6)	New Capital Expenditures ($ 10^6)	All Employees (10^3)	Value added by manufacture ($$10^6$)
2869: Industrial Organic Chemicals, N.E.C.	United States	561	341	112.0	2,096.8	70.3	145.3	1,215.4	10,416.9	13,446.6	23,842.2	3,126.4	102.4	4,988.0
	New England Div.:													
	Massachusetts	10	5	1.2	21.5	0.7	1.5	12.4	48.4	75.9	122.4	3.3	AA	(D)
	Middle-Atlantic Div.:													
	New York	37	21	3.8	65.0	2.0	4.5	28.2	188.7	191.7	376.6	(D)	6.1	158.6
	New Jersey	71	44	7.8	139.7	5.4	10.9	84.6	524.4	805.4	1,323.9	(D)	13.1	446.9
	Pennsylvania	24	14	4.4	72.9	2.7	5.3	41.6	173.0	374.6	559.8	23.2	2.2	36.7
	East North Ctrl Div.:													
	Ohio	31	17	3.1	56.0	1.9	4.1	33.7	282.5	373.4	638.8	51.3	3.1	99.6
	Illinois	27	10	2.0	31.8	1.2	2.3	19.5	175.0	181.8	350.4	30.4	CC	(D)
	Michigan	21	13	8.4	158.1	5.2	10.0	87.5	365.8	408.7	758.7	88.5	FF	(D)
	South Atlantic Div.:													
	West Virginia	13	13	8.7	150.5	6.3	12.7	104.7	650.5	773.2	1,409.8	121.6	9.4	549.6
	North Carolina	14	8	0.7	10.7	0.4	0.9	5.2	60.5	62.4	115.6	(D)	CC	(D)
	South Carolina	12	9	1.1	15.6	0.7	1.4	8.7	101.7	97.8	193.1	21.6	0.6	26.8
	Florida	7	5	1.2	19.5	0.7	1.8	11.9	79.6	79.8	154.7	20.7	CC	(D)
	East South Ctrl Div.:													
	Tennessee	12	8	6.2	104.2	3.8	7.7	56.2	196.6	517.0	712.4	(D)	FF	(D)
	West South Ctrl Div.:													
	Arkansas	6	4	0.8	12.5	0.6	1.3	7.6	87.3	95.7	177.1	(D)	(NA)	(NA)
	Louisiana	30	26	14.9	305.2	9.6	21.3	185.6	1,703.7	2,482.4	4,143.9	(D)	FF	(D)
	Texas	71	49	28.6	605.5	17.0	35.0	332.1	4,233.7	5,174.2	9,350.7	1,416.6	23.9	1,843.4
	Pacific Div.:													
	California	42	19	3.6	69.3	1.9	3.5	28.5	213.3	340.3	553.0	29.6	EE	(D)
	All other States	113	76	15.5	258.8	10.2	21.1	167.4	1,332.2	1,412.5	2,901.3	(D)	(NA)	(NA)
2821: Plastics Mat'ls & Resins	United States	424	337	57.4	973.9	36.9	77.2	566.2	4,015.3	6,735.3	10,662.1	862.1	54.8	2,160.5
2822: Synthetic Rubber	United States	62	31	10.1	185.3	7.2	14.2	125.6	570.1	1,296.9	1,866.8	53.2	11.8	491.7
2824: Organic Fibers, Non-cellulosic	United States	65	57	73.0	1,075.8	54.0	103.6	697.3	2,789.4	3,599.0	6,345.6	338.1	78.2	2,039.8
3079: Misc. Plastics Products	United States	10,043	4,363	453.8	4,922.8	357.4	704.3	3,290.7	11,816.1	12,120.3	23,742.0	1,144.8	346.9	6,004.7

Note: For 1972, the following employee size ranges substitute for actual figures withheld to avoid disclosure: AA, 150 to 249 employees; BB, 250 to 499 employees; CC, 500 to 999 employees; EE, 1,000 to 2,499 employees; FF, 2,500 employees or more; (D), withheld to avoid disclosing operations of individual companies; (NA), Not available; and N.E.C., Not elsewhere classified.

Table 3.19. Trade Associations and Professional Organizations

Name	Address/Phone
American Institute of Chemical Engineers	345 E. 47th St., N.Y. 10017 212/644-8025
American Chemical Society	1155 16th St., NW, Washington, D.C. 20036 202/872-4600
Chemical Coaters Assn.	Hitchcock Bldg., Wheaton, Ill. 60187 312/446-7840
Chemical Fabrics & Film Assn.	453 Route 211 East, Middletown, N.Y. 10940 914/342-5895
Chemical Manufacturer's Assn.	1825 Connecticut Ave., NW, Washington, D.C. 20009 202/328-4200
Chemical Marketing Research Assn.	139 Chestnut Ave., Staten Island, N.Y. 10305 212/727-0550
Chemical Specialties Manufacturers Assn.	1001 Connecticut Ave., NW, Washington, D.C. 20036 202/872-8110
Composite Can & Tube Institute	1800 M St., NW, Washington, D.C. 20036 202/223-4840
Drug, Chemical & Allied Trades Assn.	350 Fifth Ave., Suite 3014, New York, N.Y. 10001 212/736-8884
Dry Color Manufacturers Assn.	561 Franklin Ave., Nutley, N.J. 07110 201/667-3011
INDA	10 East 40th St., New York, N.Y. 10016 212/686-9170
International Institute of Synthetic Rubber Products	45 Rockefeller Plaza, New York, N.Y. 10020 212/541-7373
National Flexible Packaging Assn.	12025 Shaker Blvd., Cleveland, Ohio 44120 216/229-6373
National Paint and Coatings Assn.	500 Rhode Island Ave., NW, Washington, D.C. 20005 202/462-6272
Polyurethane Manufacturers Assn.	600 S. Michigan Ave., Chicago, Ill. 60505 312/427-2487
Rubber Manufacturers Assn.	1901 Pennsylvania Ave., NW, Washington, D.C. 20006 202/785-2602
Single Service Institute	250 Park Ave., New York, N.Y. 10017 212/697-4545
Society of Plastics Engineers	656 W. Putnam Ave., Greenwich, Conn. 06830 203/661-4770
Society of the Plastics Industry	355 Lexington Ave., New York, N.Y. 10017 212/573-9400
Society of the Plastics Industry - Canada	1262 Don Mills Road, Don Mills, Ontario 416/449-3444
Synthetic Organic Chemical Manufacturers Assn.	1075 Central Park Ave., Scarsdale, N.Y. 10583 914/725-1492

Source: Ref. 15.

Table 3.20. Publications Pertaining to Chemical Industry

Name	Address/Phone
Trade Publications	
Canadian Plastics	1450 Don Mills Road, Don Mills, Ontario, Canada 416/445-6641
Chemical & Engineering News	405 Lexington Ave., New York, N.Y. 10017 212/697-3223
Chemical Engineering	1221 Ave. of the Americas, New York, N.Y. 10020 212/997-2464
Chemical Engineering Progress	345 E. 47th St., N.Y. 10017 212/644-8022
Chemical Processing	430 N. Michigan Ave., Chicago, Ill. 60611 312/644-2020
Chemical Week	1221 Ave. of the Americas, New York, N.Y. 10020 212/997-2922
European Chemical News	33/39 Bowling Green Lane, London EC1R One, England
Materials Engineering	600 Summer Ave., Stamford, Conn. 06904 203/348-7531
Modern Packaging	205 East 42nd St., New York, N.Y. 10017 212/573-8107
Modern Plastics	1221 Ave. of the Americas, New York, N.Y. 10020 212/997-1221
Plastics Design Forum	1129 East 17th Ave., Denver, Colo. 80218 303/832-1022
Plastics Design & Processing	700 Peterson Rd., Libertyville, Ill. 60448 312/362-8711
Plastics Engineering	656 W. Putnam Ave., Greenwich, Conn. 06830 203/661-4770
Plastics Focus	505 Fifth Ave., New York, N.Y. 10017 212/724-4039
Plastics Industry News - Institute of Polymer Industry Central	P.O. Box 1176, Tokyo, Japan
Plastics Machinery & Equipment	1129 East 17th Ave., Denver, Colo. 80218 303/832-1022
Plastics Technology	633 Third Ave., New York, N.Y. 10017 212/986-4800
Plastics World	221 Columbus Ave., Boston, Mass. 02116 617/536-7780
Business Consulting Groups and Publishers	
Business Communications Co., Inc.	471 Glenbrook Rd., Stamford, Conn. 06906 203/323-5623
Chem Systems Inc.	747 Third Ave., New York, N.Y. 10016 212/421-9460
The Conference Board	845 Third Ave., New York, N.Y. 10022 212/759-0900
Springborn Labs	P.O. Box J, Hazardville Station, Enfield, Conn. 06082 203/749-8371
Frost & Sullivan, Inc.	106 Fulton St., New York, N.Y. 10038 212/233-1080
Hull & Co.	77 Pondfield Road, Bronxville, N.Y. 10708 914/779-8300
Charles H. Kline & Co.	330 Passaic Ave., Fairfield, N.J. 07006 201/227-6262
Arthur D. Little, Inc.	35 Acorn Park, Cambridge, Mass. 02140 617/864-5770
Morton Research Corporation	1745 Merrick Ave., Merick, N.Y. 11566 516/378-1066
Noyes Data Corp.	Mill Road at Grand Ave., Park Ridge, N.J. 07656 201/391-8484

Table 3.20. (Cont'd)

Name	Address/Phone
Business Consulting Groups and Publishers (Cont'd)	
Predicasts, Inc.	200 University Circle Research Center, 11001 Cedar Ave., Cleveland, Ohio 44106 216/795-3000
Peter Sherwood Associates, Inc.	60 East 42nd St., New York, N.Y. 10017 212/687-3653
Stanford Research Institute	Menlo Park, Calif. 94025 415/326-6200
Technomic Publishing Co.	265 W. State St., Westport, Conn. 06880 203/226-6356
Technomic Research Associates, Inc.	1 North Wacker Drive, Chicago, Ill. 60606 312/346-5901
Roger Williams Technical & Economic Services, Inc.	34 Washington Rd., P.O. Box 426, Princeton, N.J. 08540 609/799-1200
Government Publications	
Annual Survey of Manufactures	Bureau of the Census
Census of Manufactures	Bureau of the Census
Current Industrial Reports	Bureau of the Census
Foreign Trade Reports: FT 135 (imports), FT 410 (exports)	Bureau of the Census
Guide to Census Bureau Data Files and Special Tabulations	Bureau of the Census
Guide to Foreign Trade Statistics	Bureau of the Census
Mineral Industry Surveys	Bureau of Mines
Standard Industrial Classification Manual	Office of Management and Budget
Statistical Abstract of the U.S.	Department of Commerce
Statistical Services of the U.S. Government	Office of Management and Budget
Synthetic Organic Chemicals	International Trade Commission
U.S. Industrial Outlook	Department of Commerce
Wholesale Price Index	Bureau of Labor Statistics
Newspapers	
Chemical Marketing Reporter	100 Church St., New York, N.Y. 10007 212/732-9820
Journal of Commerce	99 Wall St., New York, N.Y. 10005 212/425-1616
Rubber & Plastics News	1 Cascade Plaza, Suite 1302, Akron, Ohio 44308 216/253-2183

Source: Ref. 15.

Table 3.21. Special Issues of Periodicals

Publishing Organization	Title of Publication	Frequency of Publication	Special Items of Interest
The Society of the Plastics Industry, Inc.	Facts & Figures of the Plastics Industry	Annual (Sept)	Facts and figures on different plastics, i.e., production by process for different plastics, areas of use for plastics, etc.
American Chemical Society	Chemical & Engineering News	Weekly	Annual issue (early June) on facts and figures for the chemical industry contains production and financial data on chemicals and the chemical industry. Key Chemical Review and Key Polymer Review give production data, prices, forecasts, uses, etc., for selected polymers and chemicals (repeated approximately once a year for each chemical or polymer).
Schnell Publishing Company, Inc.	Chemical Marketing Reporter	Weekly	Prices of chemicals.
United States International Trade Commission	Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals (including synthetic plastics and resin materials)	Monthly	Monthly production figures. December issue has cumulative totals for the year.

Table 3.22. Other Reports on Olefins and Derivatives

Author/Date	Title	Products Treated	Source of Energy Data	Comments
Public Literature				
Drexel University for DOE/1979	Energy Analysis of 108 Industrial Processes	Olefins and polymers	Not given	Process flow charts and unclear energy balances with no totals. Terms not defined. No text. No references.
Radian Corp. for EPA/1977	Industrial Process Profiles for Environmental Use: Chapter 5 - Basic Petrochemicals Industry	Olefins and aromatics	Trade journals, textbooks	Describes unit processes and waste streams. Includes overview. Energy use included for some unit processes.
A.D. Little, Inc. for EPA/1976	Environmental Considerations of Selected Energy Conserving Manufacturing Options: Vol. VI - Olefins Industry Report	Ethylene	ADL estimates	Good overview and commercial and developmental process description; lots of information on effluents. Biggest fault is treatment of ethylene only. Discusses energy allocation to coproducts. Some tables unclear; materials flows do not all balance.
Dow Chemical for EPA/1975	Energy Consumption: Fuel Utilization and Conservation in Industry	Ethylene/ propylene	Industry data	Includes quantity and type of heat rejected and fuel utilization by operation.
Battelle Columbus Lab. for FEA/1975	Evaluation of the Theoretical Potential for Energy Conservation in Seven Basic Industries	LDPE, HDPE, PS, PVC, SBR	Trade journals	Calculations of first and second law process efficiencies. However, feedstock energy included, so all processes look good. No description of feedstock production. Tables unclear. Data old at publication.
Gordian Associates for FEA/1974	The Potential for Energy Conservation in Nine Selected Industries, Vol. I - Plastics and Vol. IX - Synthetic Rubber	LDPE, HDPE, PS, PVC, SBR	Census of Manufactures, trade journals	Consistent energy and materials accounting for final products, split by type of fuel. Derivation of some of their numbers unclear when compared with their original sources. Includes brief process description.
IR&T Corp. for FEA/1974	Data Base for the Industrial Energy Study of the Industrial Chemicals Group	Monomers and oxygenated derivatives	Trade journals, confidential reports, government statistics	Clear tables of energy use for each product, broken down by fuel. Includes regional data. No text.
Larry N. Teasley, Washington Univ., Masters Thesis/ 1974	Energy Implications of Polymer Production and Use	Olefins and derivatives except propylene oxide and glycol	Government statistics, previous reports, texts, trade publications	Describes careful energy accounting from raw material in ground to final product. Tables unclear as to starting material. Numbers incompatible with other sources.
Confidential Reports				
Chem Systems/ ongoing series for subscribers	Process Evaluation/Research Planning (PERP) Reports	Olefins, aromatics, plastics, SBR, oxygenated derivatives	Confidential industry data, trade journals, in-house engineering estimates	Judged most accurate of all sources because of industrial contacts and clients. Include detailed process flows and total utility consumptions as part of economic analysis for both commercial and developmental processes. Most recent reports not available to the public.
Stanford Research Institute/ongoing series for subscribers	Process Economics Program Reports			
Springborn Lab. for clients/1979	The Impact of Energy Costs, Technological Change, and Capital Equipment Costs Upon Raw Materials Competition 1978-1983-1988	Olefins, LDPE, HDPE, PS, PVC, polyester		Interesting discussion of competition among materials for markets. Projects market shares.

4 ENERGY AND MATERIALS ANALYSIS

4.1 ENERGY AND MATERIALS ACCOUNTING

The analysis is performed with one unit of a given output in mind, i.e., process A requires α_1, α_2, ..., α_N units of input materials I_1, I_2, ..., I_N to produce one unit of a given product P, with β_1, β_2, ..., β_n units of coproducts B_1, B_2, ..., B_n. The term coproduct is used for products of process A (other than the main product P) that are salable at considerably more than their fuel value. There is, in theory, a continuum between fuels and salables. But, in practice, when a product is consumed as a fuel in the process, it is not included in the B_i's. If a product is used mainly as a fuel but is not totally consumed in process A, its fuel value generally is subtracted from gross process fuel to give net fuel into the process.

In the analysis of olefins and their derivatives, the inputs and outputs of most production processes also have value as fuels. This is a major difference in energy accounting between olefins and their derivatives and metals. Thus, when considering the energy that is consumed in the production of an output material by process A, changes in the total available heat of combustion between the input and the output materials need to be taken into account, in addition to the process energy involved in process A and the production of inputs I_1, I_2, ..., I_N.

If the heats of combustion of I_1, I_2, ..., I_N are $H_I{}^1$, $H_I{}^2$, ..., $H_I{}^N$, respectively, the total available heat of combustion of the inputs is:

$$H_{in} = \sum_{i=1}^{N} \alpha_i H_I^i \tag{4.1}$$

If the heat of combustion of P is H_P and that of coproducts B_1, B_2, ..., B_n is $H_B{}^1$, $H_B{}^2$, ... $H_B{}^n$, respectively, then the total heat of combustion that can be recovered from products is:

$$H_{out} = H_P + \sum_{i=1}^{n} \beta_i H_B^i \tag{4.2}$$

The change in fuel value in process A is thus $\Delta H = H_{in} - H_{out}$.

The net process energy, E_p, is estimated from industrial utility summaries. It includes all purchased fuels, the largest categories of which are electricity and steam, and does not include process by-products that are consumed as fuels (by-product fuels). (By-product fuels are accounted for in feedstock.) The energy requirements for specific unit processes within the production process generally are less available because of the proprietary nature of the information. A 33% efficiency in the generation of electricity is assumed in all cases. The available energy in steam is estimated by computing "exergy" numbers for given pressures by using T-S diagrams of steam.[76]

In the process analysis, the energy input through the use of steam can cause uncertainty. Current industrial flow sheets and utility summaries tend to give minimal information on the outlet pressure of steam and the use of waste heat. Therefore, the net energy foregone that is due solely to the production of a particular product is overestimated if information regarding only the inlet steam is used. Whenever possible, the portion of the process energy resulting from the use of steam has been adjusted based on available information on the practical use of outlet steam in large-scale production processes.

If the process energy in the production of one unit of each of the inputs I_1, I_2, ..., I_N is E_1, E_2, ..., E_N, respectively, then the total sum of net process energies is:

$$E = E_p + \sum_{i=1}^{N} \alpha_i E_i \qquad (4.3)$$

The total energy into the process is $E_{in} = E + H_{in}$.

The total energy foregone in process A to produce one unit of P, β_1 unit of B_1, β_2 unit of B_2, ..., and β_n unit of B_n is:

$$E_{in} - H_{out} = E + \Delta H \qquad (4.4)$$

In this analysis, the total energy foregone is divided among the coproducts by weight. The total energy foregone in producing one unit of each of the coproducts by process A is estimated to be:

$$E_f = \frac{E + \Delta H}{1 + \sum_{i=1}^{n} \beta_i} \qquad (4.5)$$

This accounting procedure is very suitable for computer application.

In general, products are produced by more than one process. Final estimates of the total energy foregone in producing product P are based, where possible, on a weighted average of the E_f's by current capacity of each process idealized to best industrial practice or, when one process dominates, on the most popular process.

In our energy and materials flowcharts, which generally represent the most modern commercial technology, a circle is used to denote a material input (I) or output (P or B) for a process, which is represented as a box. A triangle denotes an energy input or output. If an input (I) has energy embodied in it, a "feedstock box" (a semicircle over a triangle) is used, in which the total energy consumed in making that quantity of the material is inscribed. For an unprocessed fuel, this is the heat of combustion. The "feedstock box" is a shorthand notation to avoid listing process steps back to initial feedstocks in each flowchart. A complete flowchart can be reconstructed by replacing the "feedstock box" with the flowchart it summarizes, scaled to the appropriate weight of output.

4.2 PRODUCTION OF OLEFINS

Virtually all of the olefins produced in the United States today are derived from petroleum and natural gas feedstocks. Some ethylene (and more propylene and butadiene) is produced from refinery by-product streams, but the percentage has been declining (from 40% in 1956 to less than 10% in 1979). This is largely because of the great quantities of ethylene produced. It is estimated that the off-gases from a 100,000 bbl/day refinery would supply 300,000 lb/day (136 t) of ethylene,[36] which is only 10% of the production from a single new ethylene plant. Most ethylene is produced by cracking, which will be discussed in detail in Sec. 4.2.2. Any naphthenic or paraffinic hydrocarbon heavier than methane can be cracked to produce ethylene.

4.2.1 Feedstocks

Feedstocks generally are classified by their boiling ranges, i.e., from ethane and propane, which are gases at room temperature, to heavy gas oil, which boils at 570-750°F (300-400°C). Various sources disagree on the exact definitions of the petroleum fractions; a typical set of boiling ranges, together with the numbers of carbon atoms in the constituent molecules, is shown in Table 4.1. The gaseous feeds (light aliphatic hydrocarbons, i.e., natural gas "liquids" and "liquid" petroleum gas) are preferred in the United States. Ethane is produced almost entirely at natural gas processing plants, as is at least 50% of the propane and 75% of the butane that is cracked for olefins production. Until recently, these feeds were unavailable in Europe and Japan, where naphtha is generally cracked. The light feeds are easiest to crack (see Sec. 4.2.2) and yield the fewest by-products. The heavier the feed, the higher the boiling point; less ethylene and more by-products are produced per pound. Table 4.2 shows the quantities of various feeds required and the by-products (propylene, butadiene, pyrolysis gasoline, and fuel oil) produced per billion pounds of ethylene. A plant cracking liquid feeds produced at petroleum refineries produces approximately equal quantities of the higher olefins and ethylene. Such a plant is, therefore, properly called an olefins unit. Development of technology to crack crude oil for ethylene is underway (see Sec. 4.2.3).

Table 4.1. Boiling Ranges of Petroleum Fractions

Product	Boiling Range (°C)	Hydrocarbon Molecule
Gas and liquefied gas	up to 25	C_1-C_4
Gasoline (petrol, naphtha)	20-200	C_4-C_{12}
Kerosene	175-275	C_9-C_{16}
Gas oil and diesel oil	200-400	C_{15}-C_{25}
Lubricating oil	-	C_{20}-C_{70}
Fuel oil	-	C_{10+}
Bitumen and coke	-	Large molecules

Source: Ref. 56.

Table 4.2. Typical Gross Product Distributions for Various Feedstocks

	Feedstock (10^6 lb/yr)			
Product	Ethane	Propane	Naphtha	Heavy Gas Oil
Ethylene	1000	1000	1000	1000
Propylene (chemical grade)	25	410	530	600
C_4				
Butadiene	20	50	160	220
Butylene, butane	13	30	150	200
Pyrolysis gasoline				
C_5, 204°C nonaromatics	–	–	230	400
C_6–C_8 aromatics	10	80	500	360
Total C_{5+}	28	160		
Fuel oil	–	–	140	900
Off gas	164	680	540	450
Total products	1260	2410	3250	4130
Feed rate	1260	2410	3250	4130

Source: Ref. 9.

Ethane available for petrochemical manufacture is expected to increase by about 15% by 1986, in spite of falling natural gas production and lower ethane content. This can be attributed to the use of cryogenic techniques that recover up to 70% of the ethane; currently only 20% is recovered. Further expansions of ethylene capacity will rely increasingly on heavy liquids. About 95% of the new ethylene capacity expected to come on-line by 1980 will crack naphtha or gas oil.[20] These units will have the flexibility to crack either naphtha or gas oil, depending on the prices and supplies of these materials. Figure 4.1 shows the trend in feedstocks, with heavy liquids, for which olefins production competes with gasoline and heating oil, expected to account for more than 45% of ethylene capacity in 1980 (which is up from less than 25% in 1970). This implies a large increase in the quantities of propylene and butadiene available from cracking. Thus, the percentage of propylene produced from cracking will increase from 25% in 1972[77] to over 80% by 1985. (The rest of the propylene is derived from refinery by-product streams and is used in gasoline production.) The butadiene produced on purpose from refinery streams by dehydrogenation of n-butane or butenes ("swing" butadiene) will continue to decline from 65% in 1973 to less than 29% in 1985.[31] In 1980, 50% of butadiene is expected to come from ethylene production, 17% from imports, and 33% from primary or swing sources.[36]

Olefins and their derivatives can be made from nonpetroleum sources. Ethylene originally was made by dehydration of ethanol, and commercial polyethylene in England was made from ethylene produced this way until about 1950.[27] It is possible to make almost any ethylene derivative from fermentation alcohol. During World War II, large quantities of synthetic rubber

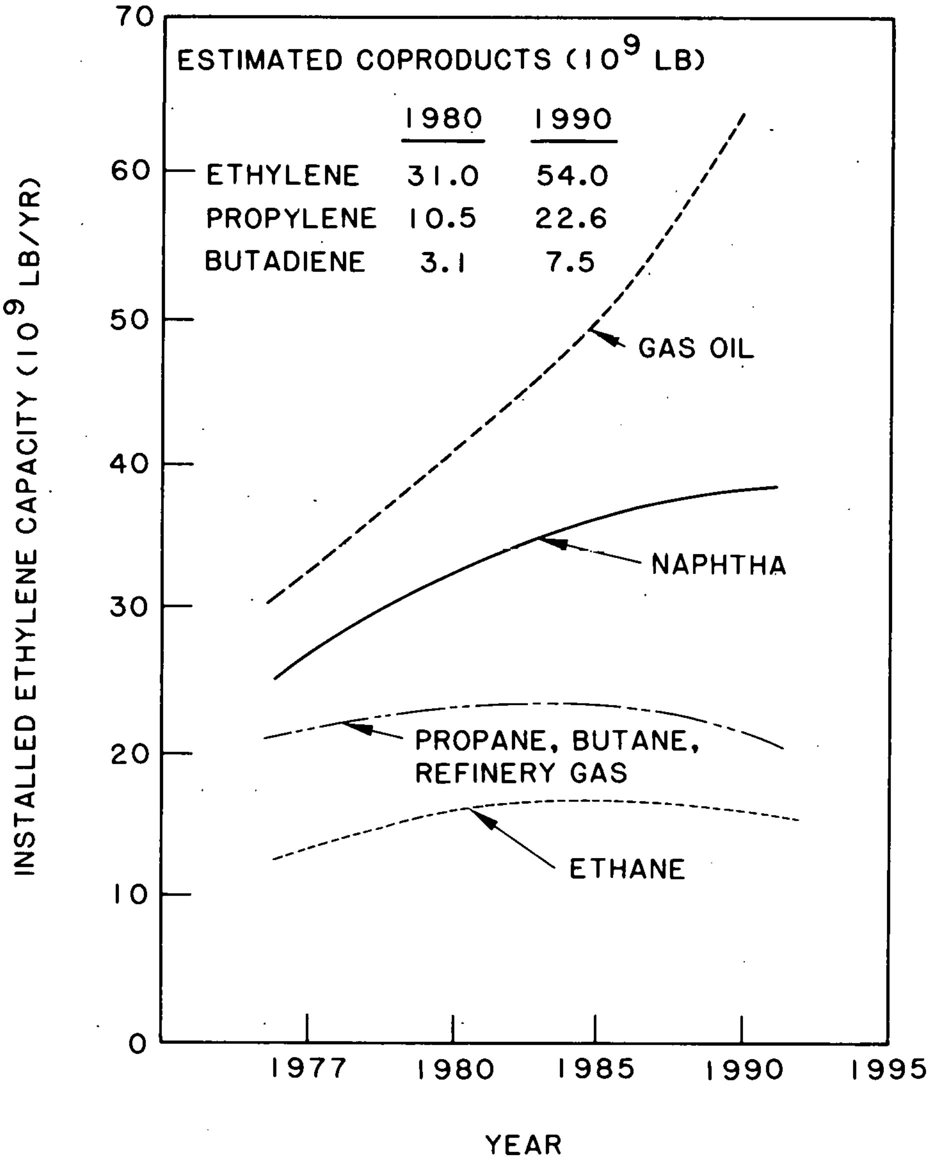


Fig. 4.1. Ethylene Feedstock Trend (Source: Ref. 20)

were made from alcohol. The relative economics of production for a specific chemical will depend both on petroleum, grain, and molasses prices, and on the number and complexity of process steps. Fermentation alcohol is almost competitive with the synthetic product right now.

It is also possible to synthesize most major petrochemicals from coal, although, as of 1978, only 2% of U.S. feedstocks were coal-derived.[2] Two intermediates that can be produced readily from coal are acetylene and synthesis gas ($CO + H_2$). Acetylene can be produced by adding water to calcium carbide, which, in turn, is produced from lime and coke in an electric furnace. Major organic chemicals that have been made from acetylene include acetaldehyde, acetic acid, and vinyl chloride, but reintroduction of these technologies may not occur until about 1990.[38] Manufacturers are seriously looking at coal-based acetylene as a feedstock after demand for ethylene grows to fill current capacity.

Synthesis gas can be made from coal and steam, although it is usually obtained from natural gas. Before World War II, olefins, paraffins, ammonia, and gasoline were made via gasification of coal. Ethylene glycol, for example, was made this way commercially by DuPont. Figure 4.2 illustrates how various ethylene derivatives can be produced from nonpetroleum substances.

4.2.2 Cracking of Oil and Gas

The basic process for making olefins from heavier hydrocarbons is called pyrolysis. It is essentially the same for all feedstocks -- ethane to gas oil -- although capital and energy requirements depend on both the feed and the desired products. Process flowcharts for ethane, naphtha, and gas oil feeds are shown in Figs. 4.3-4.5. The pyrolysis process begins when hydrocarbon feed and steam are introduced into a tubular pyrolysis furnace and heated to cracking temperature (≈1500°F or 800°C). Ethane feed gives up hydrogen to form ethylene, while longer molecular chains break at carbon-carbon bonds to form ethylene and other products. In order to minimize further reactions, the pyrolysis products are cooled rapidly (quenched); heat is recovered as high-pressure steam. Since the critical temperature of the major products is below ambient, the product stream is compressed and cooled until everything but hydrogen liquefies. Acid gases (hydrogen sulfide [H_2S]

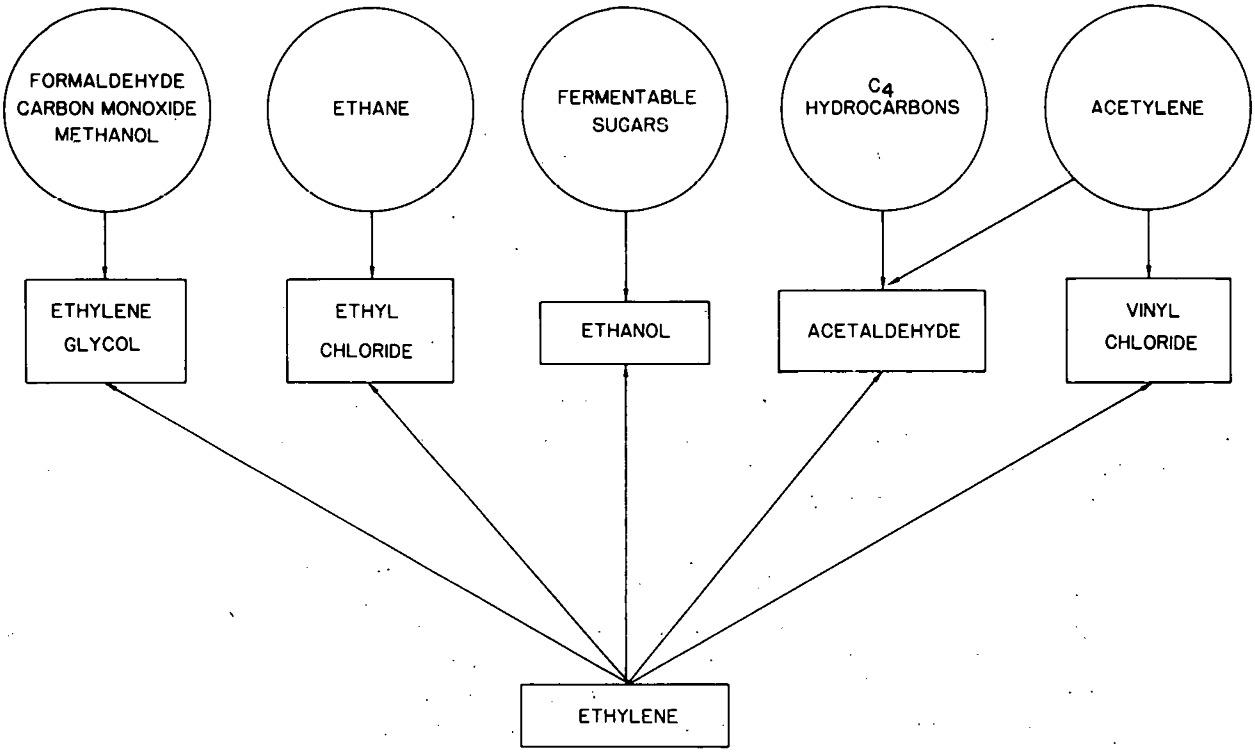


Fig. 4.2. Alternative Routes to Ethylene Derivatives (Source: Ref. 78)

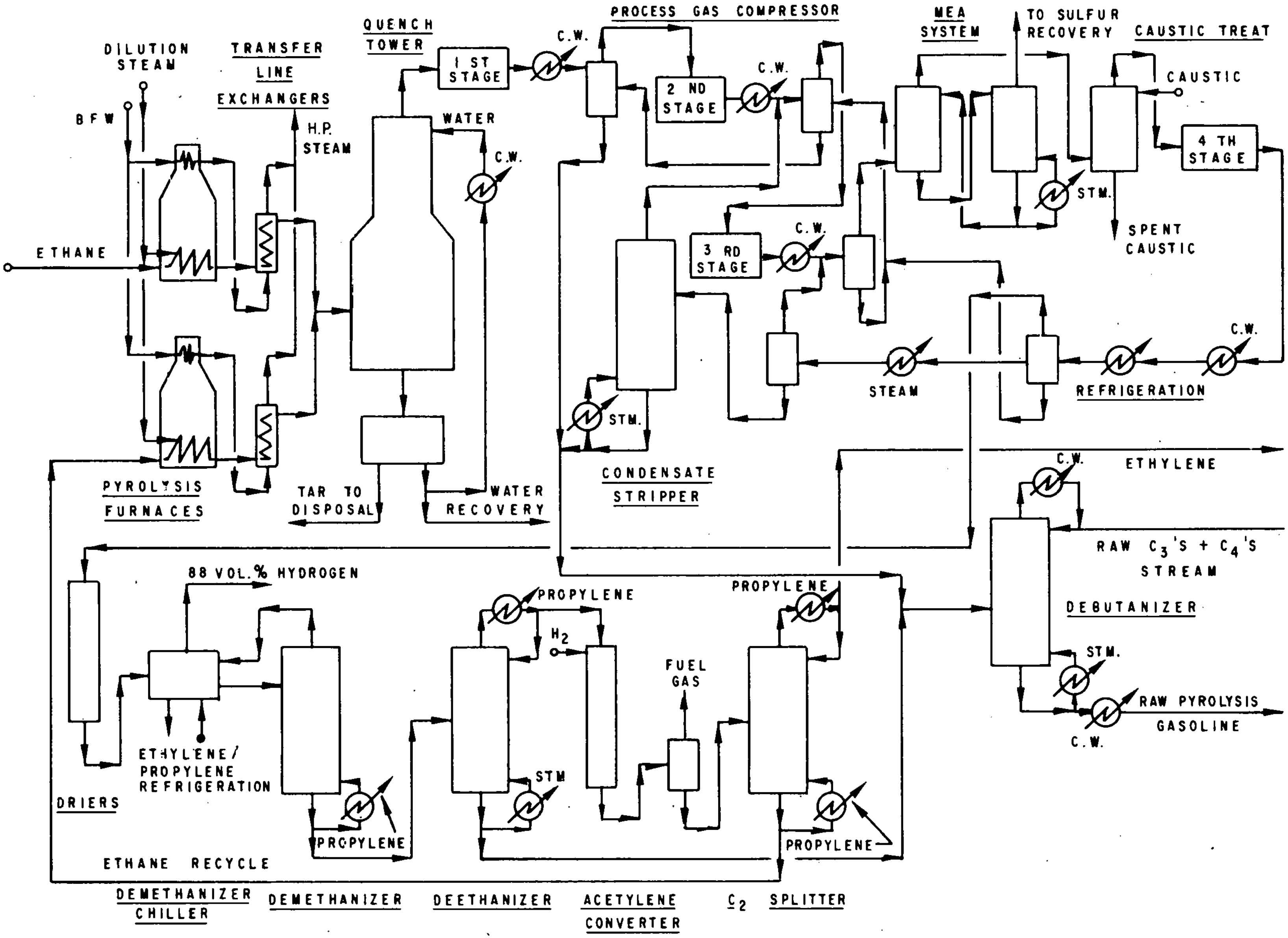


Fig. 4.3. Process Flow for Production of Ethylene from Ethane
(Source: Ref. 72)

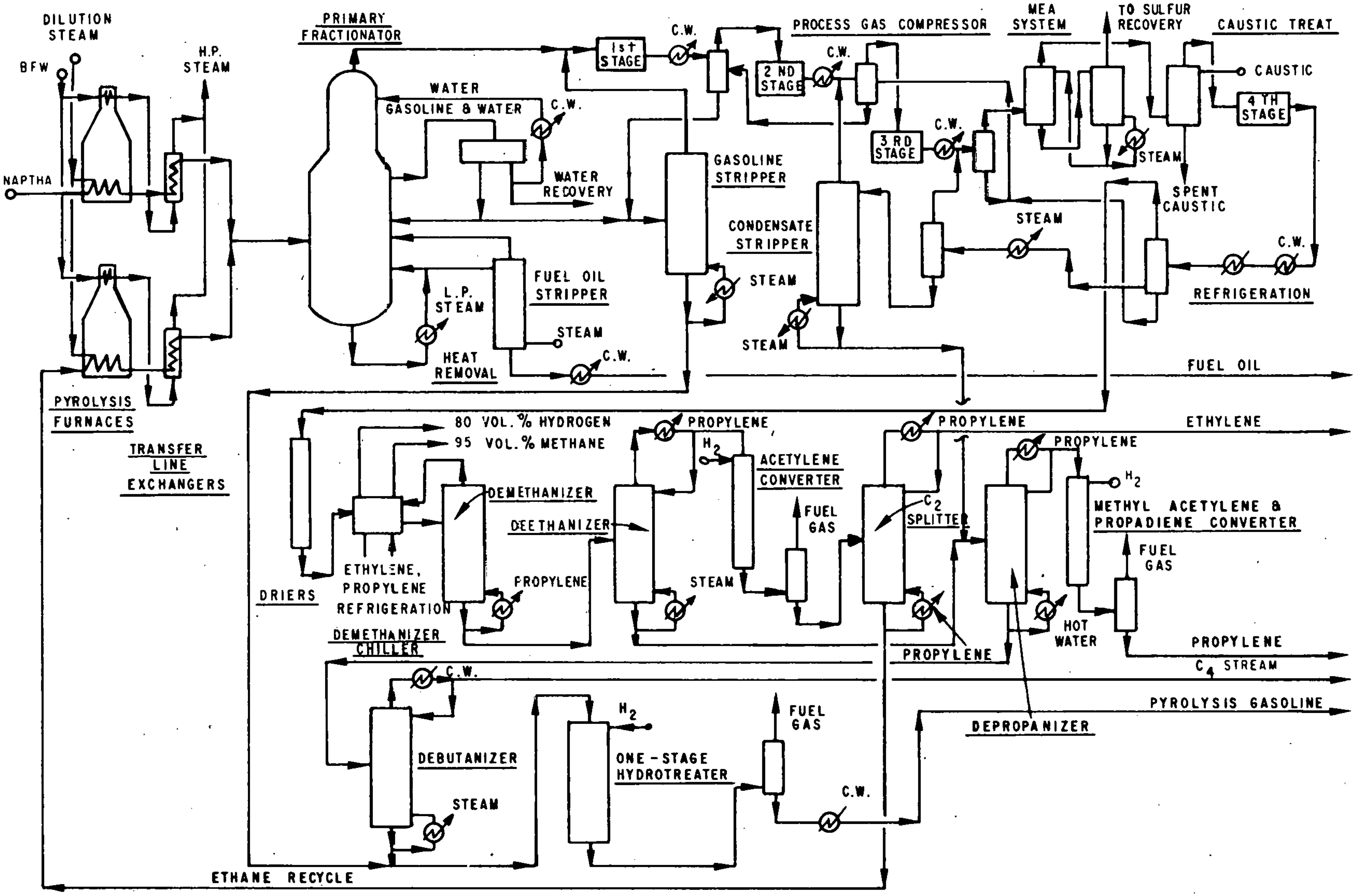


Fig. 4.4. Process Flow for Production of Ethylene from Naphtha (Source: Ref. 72)

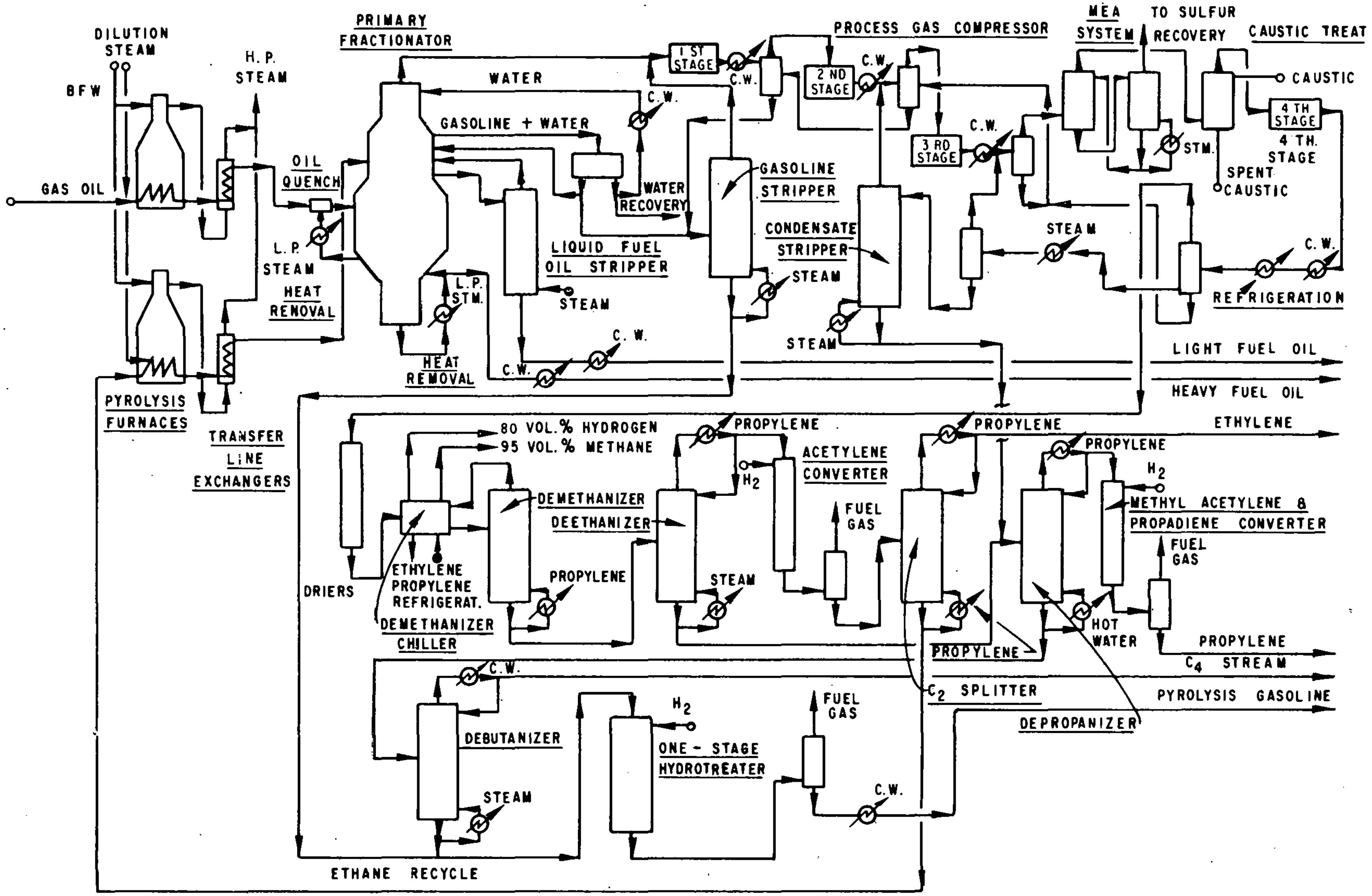
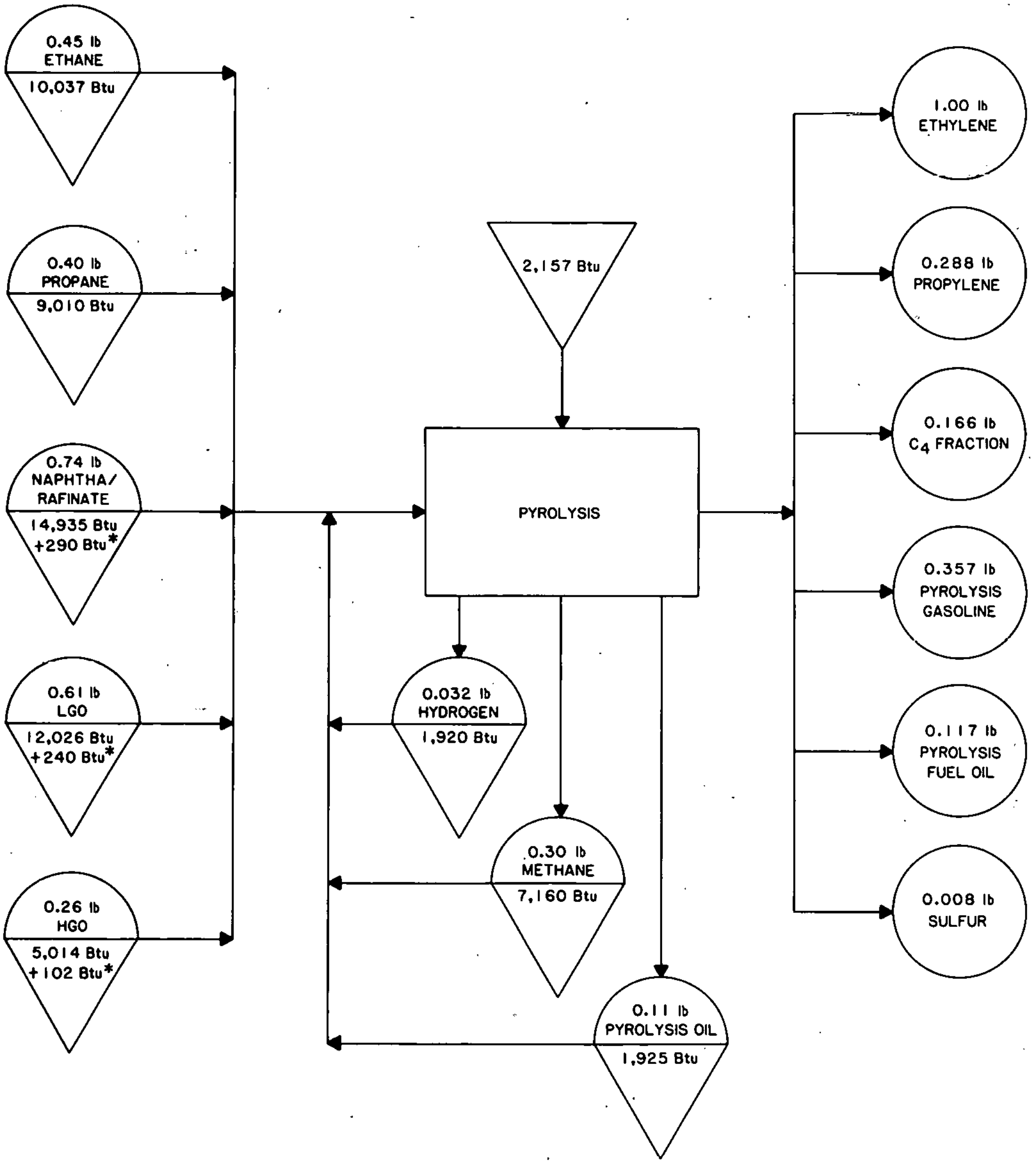


Fig. 4.5. Process Flow for Production of Ethylene from Gas Oil (Source: Ref. 72)

and carbon dioxide [CO_2]) and water are removed during this process to avoid corrosion and freeze-ups in the series of distillation towers (fractionation train) in which products are separated out. Ethane (and sometimes propane) is recycled back to the furnace. All or part of the product stream is reacted with hydrogen over a selective catalyst to remove alkynes (acetylene and methyl acetylene) and diolefins (propadiene and possibly butadiene), which cannot be present in a polymer-grade product.

An energy and materials flow for 1980 production of one pound of ethylene, weighted by percentage produced from each cracking feed, is shown in Fig. 4.6. The energy inputs to manufacturing ethylene are shown in



*Crude distillation at 390 Btu/lb.

Fig. 4.6. Energy and Materials Flow for the Production of Olefins (Sources: Refs. 20, 69, and 72)

Table 4.3 for each feedstock. The total demand for fuel and feedstock per pound of ethylene produced increases with feedstock weight, with fuel almost doubling and feedstock tripling from ethane to gas oil, as can be seen in Table 4.3. The energy actually lost or consumed in the process (energy foregone) is 10,000-20,000 Btu/lb (23-46 kJ/g) ethylene. Since other products besides ethylene are produced, the energy consumed by the process should be allocated to coproducts on an equal weight basis. Pyrolysis gasoline is included in the coproducts, because it contains more than 50% by weight aromatics and is therefore a valuable chemical feedstock. A small quantity of pyrolysis fuel oil also is included to simplify this approximate calculation. This allocation of inputs per pound of net products is given in Table 4.4. Feedstock consumption per pound of net products* decreases slightly with heavier feedstocks, and the energy foregone per pound of net products goes down by more than a factor of two.

The energy input (E_{in}) per pound of net products for each feed is used to calculate the average energy input per pound of each of the coproducts (see Table 4.5). The energy inputs are weighted by the fraction of the coproduct produced by each feed** and summed to give the total E_{in} for that product. The results are not quite equal for each product, since more of the heavier products are produced from the heavier feeds. Total energy input per pound of ethylene is 29,360 Btu/lb (68.29 kJ/g) and that of propylene, mixed C_4, and pyrolysis gasoline is 27,717, 27,048, and 27,328 Btu/lb (64.47, 62.91, and 63.56 kJ/g), respectively.

Manufacturing costs for olefins vary in a way similar to energy costs, generally increasing per pound of ethylene as feedstock weight increases (see Table 4.6). Capital investment, utility, maintenance, and labor costs increase by about 50% from ethane to gas oil due to increases in material to be handled and the more complex separation train. Total costs do the same. Feedstock costs go up by a factor of three, but this is partially offset by the by-product credit, which is determined by market value. The percentage of net production cost made up by net materials† decreases from 60% to 44% (as of January, 1980) when a mixture of 50% naphtha and 50% gas oil is used instead of a 70% ethane and 30% propane feed mixture (and even lower for heavy gas oil). For the same two plants,[36] utility cost (gross utilities as a percentage of net production cost) increases from 23% to 28%.

4.2.2.1 Pyrolysis

In the pyrolysis process, a mixture of hydrocarbon feed and steam is fed into each of several (on the order of tens) tubular pyrolysis furnaces. Where possible, a different furnace is used for each feed or recycle stream in order to optimize furnace conditions for maximum ethylene production. Steam is added to the feed as a diluent for two reasons. First, it reduces

---

*Total products minus those burned as process fuels.

**Determined by the fraction of 1980 capacity cracking that feed times the number of pounds of coproduct per pound of ethylene for that same feed.

†Net materials cost = raw materials cost minus all coproduct credits.

Table 4.3. Feed and Energy Requirements for Typical Olefins Production

			Btu/lb Ethylene					
Feedstock	lb Feed / lb C_2H_4	% C_2H_4 Yield	Feed[a]	Purchased Fuel	Total Fuel[b]	Energy In[c]	Net HC Products[d]	Energy Foregone[e]
Ethane	1.22	82	27,210	5,910	9,960	33,120	22,596	10,524
Propane	2.24	45	50,454	2,705	7,399	53,159	33,107	20,052
50% naphtha/ 50% raffinate	3.13	32	63,170 +1,220	0	17,600	64,390	49,700	14,690
Light gas oil (LGO)	3.94	25	77,673 +1,537	0	19,700	79,210	61,300	17,910
Heavy gas oil (HGO)	4.50	22	86,773 +1,755	0	19,085	88,528	71,670	16,858

[a] Heat of combustion of feedstock (HHV) + crude distillation energy, which will hereafter be included in process fuel (390 Btu/lb feed).

[b] Purchased fuel + fuel value of by-products burned within process.

[c] Heat of combustion of feedstock + purchased fuel.

[d] Heat of combustion of net process products (HHV).

[e] Heat of combustion of feedstock + purchased fuel - heat of combustion of net products.

Sources: Refs. 20, 69, and 72.

Table 4.4. Feed and Energy Requirements for Typical Olefins Production

Feedstock	lb Net HC Products / lb C_2H_4[a]	% Yield Net HC	Btu/lb Net Products					
			Feed[b]	Purchased Fuel	Total Fuel[c]	Energy In[d]	Net HC Products[e]	Energy Foregone[f]
Ethane	1.07	88	25,430	5,545	9,340	30,975	21,170	9,805
Propane	1.54	69	32,762	1,757	4,805	34,519	21,498	13,021
50% naphtha/ 50% raffinate	2.42	77	26,103 + 504	0	7,285	26,607	20,540	6,067
Light gas oil (LGO)	3.08	78	25,218 + 499	0	6,390	25,717	19,900	5,817
Heavy gas oil (HGO)	3.64	81	23,839 + 482	0	5,245	24,321	19,690	4,631

[a] Products not used as internal process fuel.

[b] Heat of combustion of feedstock (HHV) + crude distillation energy, which will hereafter be included in process fuel (390 Btu/lb feed).

[c] Purchased fuel + fuel value of by-products burned within process.

[d] Heat of combustion of feedstock + purchased fuel.

[e] Heat of combustion of net process products (HHV).

[f] Heat of combustion of feedstock + purchased fuel - heat of combustion of net products.

Sources: Refs. 20, 69, and 72.

Table 4.5. Energy Allocation to Coproducts of Ethylene Production

			Product				
Feedstock	Btu/lb Feed[a]	Net E_{in}/lb Products[b]	Ethylene	Propylene	Mixed C_4 Fraction	Pyrolysis Gasoline	Pyrolsis Fuel Oil
Ethane	22,304	30,975	0.365	0.00913/[c] 0.0316	0.0073/ 0.0441	0.00767/ 0.021	0/ 0
Propane	22,524	34,519	0.1795	0.0545/ 0.189	0.0184/ 0.111	0.0237/ 0.066	0/ 0
50% naphtha/ 50% raffinate	20,572	26,607	0.238	0.1074/ 0.372	0.0631/ 0.381	0.167/ 0.468	0/ 0
Light gas oil (LGO)	20,104	25,717	0.156	0.0839/ 0.116	0.0515/ 0.311	0.1115/ 0.312	0.073/ 0.63
Heavy gas oil (HGO)	19,628	24,321	0.058	0.0336/ 0.116	0.0255/ 0.154	0.048/ 0.134	0.043/ 0.37
		lb Product	1.0	0.289	0.166	0.357	0.116
		Btu/lb Product	29,360	27,717	27,048	26,400	25,200

[a] Heat of combustion + 390 Btu/lb for crude distillaion of refinery streams.

[b] From Table 4.4.

[c] Pounds product by feed per pound C_2H_4/fraction by feed.

Sources: Refs. 20, 69, 72, and 79.

Table 4.6. Typical 1978 Ethylene Economics

Cost	Feed			
	Ethane	Naphtha	Light Gas Oil	Heavy Gas Oil
Variable cost (¢/lb)				
Feedstock	5.8	17.6	19.3	20
Other materials	0.3	0.5	0.6	0.7
Net by-product credit	(0.2)	(12.4)	(15.7)	(19.5)
Purchased utilities	1.2	0.1	0.3	0.3
Labor and indirect	2.5	4.5	4.9	5.1
Net product cost	9.6	10.3	9.4	6.6
Return on investment	4.5	6.3	6.5	7.2
Product value	14.1	16.6	15.9	13.8
Net materials per product cost	0.61	0.56	0.45	0.18
Capital costs (\$ 10^6 for 10^9 lb/yr capacity)				
Inside battery limits	125	160	180	210
Total (inside plus outside battery limits)	170	240	270	310

Source: Ref. 72.

the partial pressure of the feed in the furnace. This serves to drive the feedstock reaction towards ethylene and inhibits the secondary reactions of polymerization and cyclization. Second, steam slows the buildup of coke (carbon) on furnace surfaces by reacting with the coke to form carbon monoxide. Since the tendency for coke buildup increases with heavier feeds, the quantity of dilution steam per unit weight of feedstock must be increased by about a factor of three from ethane to gas oil (see Table 4.7). In addition, since yields of ethylene per pound of feedstock decrease as feed weight increases, more feed must be cracked for a given ethylene yield, and the quantity of material passing through the furnaces increases by about a factor of 10 from ethane to gas oil. Gross process fuel requirements also increase, but this is generally supplied by process by-products burned as furnace fuel, rather than by purchased fuel (see Tables 4.3 and 4.4).

The mixed steam and hydrocarbon feed stream first enters the convective section of the furnace, where it is preheated (with heat recovered from the hot flue gases) to the temperature at which cracking begins (about 1500-1650°F [800-900°C]). The temperature required to crack heavier feeds is lower than that needed to crack ethane (see Table 4.7). Temperature and residence time in the radiative zone of the furnace can be adjusted to change the relative yields of various products. For instance, when cracking propane at high severity (high temperature -- 1470-1600°F [800-870°C] -- and short residence time), the propylene-to-ethylene ratio is 0.3 lb of propylene per

Table 4.7. Pyrolysis Furnace Operating Parameters

Feed	Typical (Range) (lb steam/ lb feed)	lb Feed/ lb Ethylene	Exit Temperature (°F)	Process Fuel (Btu/lb ethylene)	Residence Time (sec)	Overall Conversion (%)
Ethane	0.3 (0.2-0.5)	1.56	1650	7,800	<0.5	60-70
Propane	0.4 (0.3-0.5)					75-90
Naphtha	0.5 (0.3-1)	3.05	1560	10,300	<0.4	33
Gas oil	0.9 (0.5-1)	4.95	1470	14,700		25

Source: Refs. 19, 63, and 80.

pound of ethylene produced, while low-severity cracking (slightly lower temperature -- 1300-1470°F [700-800°C] -- but longer residence time) produces 0.7 lb (0.3 kg) of propylene. The percentage of feed converted per pass is higher at high severity (90% versus 70% in the example above), thereby minimizing the quantity of unreacted feed to be recycled, but the overall yield of desired products is less. Thus, choice of temperature and residence time in the furnace depends on feedstock and desired products. Since the objective is usually to maximize ethylene production, most cracking is done at high severity.

The principal reactions that occur in the cracking furnace are dehydrogenation and demethylation. These are illustrated in Fig. 4.7 for ethane and propane feeds. Both types of reaction are endothermic and occur by a free-radical mechanism. The heat of reaction for ethane going to ethylene is 2220 Btu/lb (5.15 kJ/g).[81] The reaction goes spontaneously above 1580°F (860°C), as can be seen from Fig. 4.8. Note that the temperature should be below 2000°F (1090°C) to avoid excessive acetylene production and to maximize furnace tube life. The exact reactions that occur for the cracking of liquid feeds are difficult to characterize because of the large variety of chemical compounds in the feed. Each compound yields a different spectrum of products, and one material called "naphtha" may be very unlike another "naphtha." The product stream leaving the pyrolysis furnace is a mixture of hydrocarbons from hydrogen to heavy fuel oil, with the composition depending on feed and cracking conditions.

A large quantity of fuel is consumed in the pyrolysis furnace, with the radiative zone of the furnace consuming more than any other single area of the plant (see Table 4.8). Energy use increases sharply for heavier feeds; however, about 70% of this energy can be recovered from hot flue gases, with additional energy recoverable from the hot products.

4.2.2.2 Quenching

Quenching is the term for the rapid cooling that hot reaction products undergo as they emerge from pyrolysis furnaces. Quenching serves two purposes: (1) the cooling arrests chemical reaction and prevents secondary reactions, such as polymerization, which decrease olefin yield and foul equipment and (2) heat is recovered as high-pressure steam (1500 psi [100

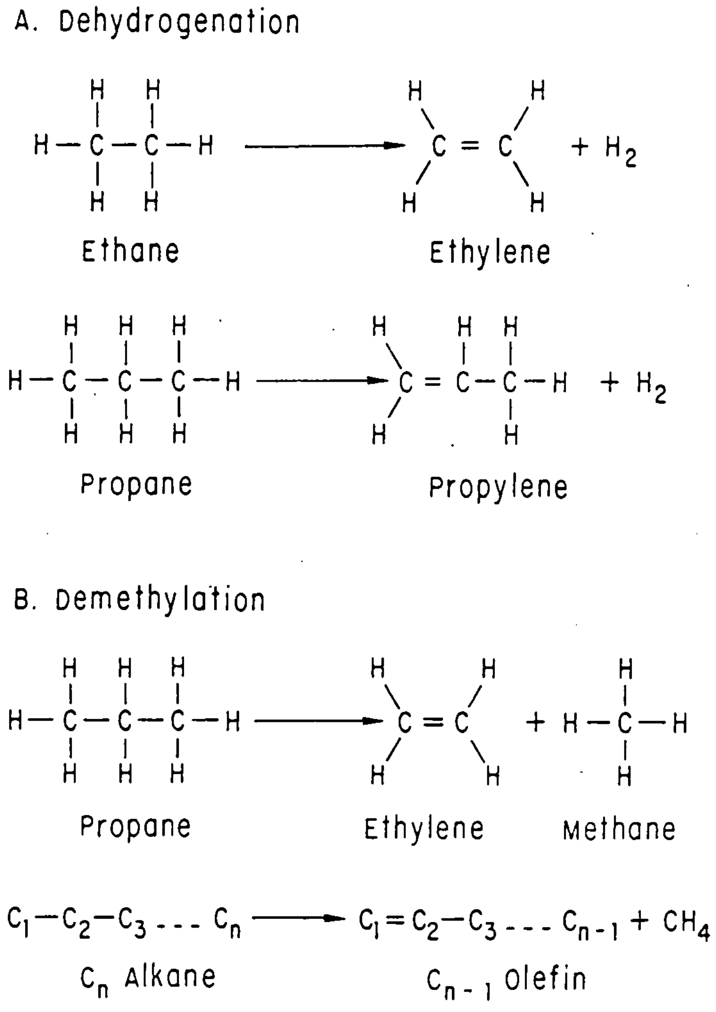


Fig. 4.7. Principal Cracking Reactions

atm)), which is used to drive process gas and refrigeration compressors at considerable utility savings.

Quench Exchangers

The first stage of quenching is accomplished in quench exchangers commonly called transfer line exchangers. These have become standard equipment for new plants within the last 10 years. Less heat is recovered than from flue gases, but the two sources combined supply more than half of the plant's energy requirements (see Table 4.9). For all feedstocks, heat is recovered as high-pressure steam via indirect heat exchange with water. The transfer line exchangers are attached to the back of the furnaces to minimize product degradation and heat loss.

The exact temperatures and pressures of the steam depend on feedstock, design, and operating conditions. For example, depending on when the tubes

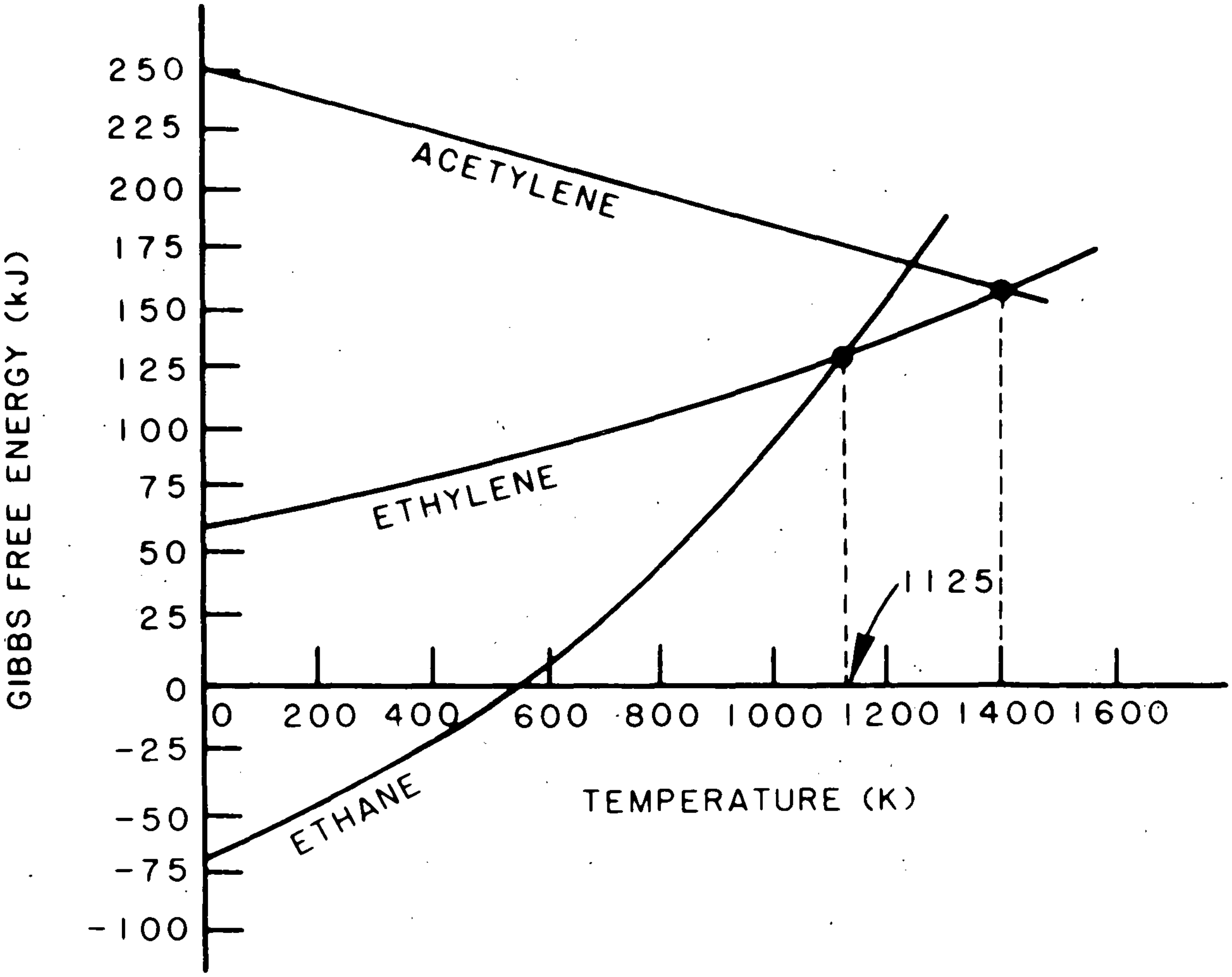


Fig. 4.8. Stability of C_2 Hydrocarbons with Temperature (Source: Ref. 82)

Table 4.8. Fuel Use in Pyrolysis Furnace (10^3 Btu/lb ethylene)

Feed	Energy Demand as Fuel	Area Demand					
		Preheat	Radiative Zone	Compress	Refrig.	Medium Pressure Dilution Steam	Misc. Steam
Ethane	11.71	1.70	3.95	2.31	2.56	0.93	0.26
Propane	14.84	2.55	3.98	2.73	3.13	0.97	1.49
Naphtha	16.21	3.38	5.66	2.23	2.27	1.93	0.74
Gas oil	21.87	5.36	6.32	2.23	2.28	4.95	0.74

Source: Ref. 19.

Table 4.9. Energy Recovery (10^3 Btu/lb ethylene)

Feed	Flue Gases	Transfer Line Exchanger	Primary Fractionator	Total	% of Demand
Ethane	4.73	2.30	0.28	7.31	62
Propane	4.45	1.81	1.18	7.44	51
Naphtha	6.82	3.69	1.81	12.32	76
Gas oil	7.51	4.38	2.99	14.88	68

Source: Ref. 19.

were last cleaned, there may be more than a 100°F (55°C) temperature difference. For ethane or propane feeds, most of the sensible heat in the pyrolysis products can be recovered. Heavier feeds, however, produce considerable quantities of products with higher dew points. Therefore, the gas stream cannot be cooled as far in the transfer line exchangers without condensation fouling the tubes. Furnace effluent gases from ethane or propane feed can be cooled to 550°F (300°C), but only to 700°F (375°C) from naphtha or 1000°F (550°C) from gas oil feeds. More energy is recovered in transfer line exchangers per pound of ethylene produced from heavy feeds than from light feeds (in spite of the smaller temperature drop) because of the larger quantity of gas handled. Steam pressures of 200-2000 psi (13.5-135 atm) have been reported, with somewhat higher pressures for heavy feeds.

Countercurrent Quench Towers

Gases from the transfer line exchangers are cooled further in one or more vertical countercurrent quench towers. Details of tower design depend on feed and desired products, but the basic idea is always the same. The hot gases enter the bottom of the tower and rise, coming into direct contact with water or oil entering from the top. Gasoline and lighter materials are separated from water (recovered dilution steam), fuel oil, and tars. When the feed is naphtha or gas oil, the product gases generally are sent from the transfer line exchangers to an oil quench tower, which is called the pyrolysis effluent fractionator or gasoline fractionator. This tower is actually a distillation column, which becomes larger and more elaborate as heavier feeds are cracked. The temperature is regulated by adjusting the reflux rate so that steam does not condense out. (This tower is not needed for ethane or propane feedstocks.)

Heat is recovered as low- or medium-pressure steam (<200 psig [<14 atm]) that can be used for small pump turbines or as dilution steam, or as low-temperature heat for use in downstream reboilers. Two separate water streams are usually maintained: one for oily water and the other for clean boiler water for the turbine-drive steam system. The quench oil removes entrained hydrocarbon liquids from the pyrolysis products. Tarry material from the bottom is sent to disposal, although it could be used as a fuel.

Heavy fuel oil (which makes up 15-20% of the product from gas oil) is stripped in a side stream to remove any entrained olefins and gasoline, and is either recovered as a by-product or burned to generate process steam.

Almost all ethylene plants include a water quench tower in which process gases are cooled to about 100°F (40°C) in preparation for compression. For a heavy feed, this process may occur in the top of the primary fractionator. Hydrocarbons are recovered from the water (combined condensed dilution steam and quench water) in a settling drum (140°F [80°C]) and stripped of light oils. For ethane or propane feeds, fuel oil is recovered and tar is disposed of. Water is recycled to the quench tower and dilution steam boilers after recovery of low-level heat.

4.2.2.3 Gas Preparation

Compression

The cooled pyrolysis products, from which tars and heavy fuel oil have been removed, enter a multistage, single-train, centrifugal compressor in which they are compressed from atmospheric pressure to 500-550 psig (35-40 atm). Four or five stages of compression are commonly used, with cooling to about 100°F (40°C) to inhibit polymer formation and with liquid removal between the stages. Refinery gas composed of light ends (C_4 and lighter mixed olefins and paraffins) may enter the process stream before compression. The compressors account for 15% of the plant capital cost and 30-40% of the process energy use.[19] Because of the high reliability and high capital cost of the compressors, there are no backup units.

Heavy hydrocarbons condensing in the interstage coolers contain dissolved light gases, which are recovered by heating and flashing the condensate. Gases are recycled to the compressor, and the liquid (sometimes called "dripolene") either becomes part of a gasoline product or is sent to the depropanizer (see Sec. 4.2.2.4). Small quantities of condensate produced during compression of ethane or propane pyrolysis products may not be recovered. The quantities of condensate and light gas recycled for various feeds are shown in Table 4.10, along with the composition of the input gas to the compressors.

About once a year, the compression train is cleaned by flushing with gas oil to dissolve the polymers that foul the surfaces.

Acid Gas Removal

In order to meet the stringent product specifications for polymer-grade ethylene, the hydrogen sulfide concentration must be reduced to 1-2 ppm and carbon dioxide to 10-15 ppm. Removal of these gases also is necessary to avoid corrosion, poisoning of the catalyst in the acetylene removal section, and condensation of carbon dioxide in the low-temperature fractionation train.

Table 4.10. Gas Composition to Process Gas Compressor

	Cracking Feedstock		
	Ethane	Propane	Naphtha
Gas compositon (Wt. %)			
Hydrogen	3.1	1.6	1.3
Methane	6.5	21.2	16.5
Ethylene and ethane	81.8	48.5	42.0
Propylene and propane	3.8	19.9	15.4
Butylene, butane, and butadiene	1.4	2.3	8.5
Gasoline	3.4	6.5	16.3
Total	100.0	100.0	100.0
Hydrocarbon condensate (Wt. % of net feed up to 17 atm)	0	1.2	16.5
Light gas recycle (Vol. % of net feed)	0	1.4	2.2

Source: Ref. 19.

Acid gas removal generally occurs after the final or sometimes after the third compression stage for ethane feed and after the third stage for propane or naphtha feeds. First, an amine absorption step brings the carbon dioxide concentration down to 50-150 ppm. In the amine absorber tower, process gases come into countercurrent contact with a regenerable sorbent, such as diethanolamine at 160-180°F (70-80°C). The sorbents have a temperature-dependent affinity for hydrogen sulfide; heating to 200°F (90°C) releases the hydrogen sulfide. This gas is usually vented or flared, although it can be recovered.[63] The remaining acid gases are removed with a caustic scrub. Process gases enter the lowest section of a multistage tower and directly contact a countercurrent flow of dilute sodium hydroxide (NaOH) solution. The gas is kept hot enough to prevent condensation. Two stages are often required to bring the carbon dioxide concentration down to 15-20 ppm, while three or more are needed to reduce the concentration below 5 ppm. The concentration of caustic is controlled by the addition of dilute sodium hydroxide to the last (top) stage. Partially depleted caustic flows down, stage by stage, and is discharged at the bottom and neutralized. Gas leaving the final stage is scrubbed with large quantities of water to remove entrained caustic and foreign matter.

Drying

Process gases must be dried to prevent ice formation during low-temperature distillation, since ice would block lines and force shutdowns. Gases from the caustic scrub are chilled with propane or propylene refrigeration to remove most of the water and thereby minimize dryer size and costs. The temperature to which the gases are cooled depends on the feedstock and must be higher than the point at which hydrates (solid hydrocarbon-water phase) form (55-60°F [13-16°C]). The gases are further dried in a tower by adsorption on a solid desiccant -- either activated alumina or molecular sieves at 65-85°F (15-30°C).. The desiccant is regenerated by passing heated tail gas (from the recovery plant or ethane recycle) through it. The gas is then cooled and the water discarded. The desiccant is eventually spent and is landfilled at the rate of about 30 tons/yr for a 1 billion lb/yr (0.45 billion kg/yr) olefins plant.

A typical arrangement has three drying towers: one on-line, one being regenerated, and the third ready to go back on-line. Water concentration in the process gas is reduced to 1-2 ppm, where the slight amounts of ice formed can be removed (without plant shutdown) by the addition of an antifreeze like methanol.

Refrigeration

An integrated ethylene-propylene cascade system is used to chill the compressed process gases to -150°F (-100°C) in several refrigeration stages. Ethylene and propylene are used because of their availability and their appropriate boiling points. Propylene refrigerant is used for temperatures of +48°F to -29°F (+9°C to -34°C). This is sufficient for all process cooling loads except the demethanizer feed and condenser, which require ethylene refrigerant to reduce the temperature to -150°F (-100°C). At this temperature, most of the process gases have liquefied, except for a hydrogen-rich stream that can be sold as a product, burned as fuel, or purified. This stream can be further cooled in turbo-expanders if temperatures lower than -150°F (-100°C) are required.

Each refrigerant is contained in a closed circuit in which liquid is evaporated and let down to different pressures, depending on the refrigeration level required. The resultant vapors are compressed by centrifugal compressors and steam-turbine drivers, and cooled until they liquefy; the liquid is then returned to the evaporator. Propylene is cooled with cooling water (whose temperature will determine operation of the propylene system), and ethylene is cooled by the coldest propylene. Each circuit consists of several stages, or temperature levels. This helps to achieve high thermodynamic efficiency in two ways. Process streams can be cooled in a series of steps in order to minimize the available work lost, and reflux duty can be performed by refrigeration at the appropriate constant temperature (for the same reason). The refrigeration system is cascaded by utilizing the slightly warmed refrigerant from a cold stream to cool another slightly less cold stream, and so on. There is a complex system of heat exchangers to recover refrigeration from cold streams leaving the recovery section. The energy required for refrigeration, about 2000 Btu/lb (5 kJ/g) of ethylene product, is usually supplied by high-pressure steam generated during pyrolysis gas quenching.

4.2.2.4 Product Separation

The product fractionation train is similar for all feedstocks but becomes larger and more complex for heavier feeds because of the larger quantity and wider spectrum of products to be separated. In all cases, a series of low-temperature distillation columns is employed to remove methane and hydrogen from the liquid product stream, to separate the remaining C_2 hydrocarbons from heavier components, and to recover ethylene product from the C_2 hydrocarbons. Acetylene is removed from the product stream at a location dependent on the feedstock. Operating conditions for the various towers are listed in Table 4.11. As the fraction taken overhead* in the tower becomes heavier from the demethanizer to the depropanizer, the tower temperature rises and the pressure is permitted to fall below the initial 450-600 psi (30-40 atm). In addition, refrigeration requirements for reflux condensers become less stringent, and heat recovered at higher temperatures is used for reboiling the bottoms.* Process integration accomplishes these tasks with minimum energy consumption and minimum loss of availability.

Although there is some flexibility in the order of fractionation towers, most modern plants use the following order: demethanizer, de-ethanizer, and C_2 splitter. (Subsequent towers are needed for feedstocks heavier than ethane.)

Demethanizer

For efficient operation, condensates from different refrigeration levels enter the demethanizer tower at the appropriate levels, depending on their composition. The gaseous methane and hydrogen stream is taken overhead, while a heavier C_{2+} stream (compounds with two or more carbons) becomes the bottoms. The methane-hydrogen stream (called "tail gas") is used as a fuel in the pyrolysis furnaces or in an on-site utility after refrigeration recovery by heat exchange or expansion. A separate hydrogen stream may be taken for use in the acetylene-removal step. Unless there is a large temperature difference from the top to the bottom of the column, it is difficult to separate methane from ethylene, since much ethylene stays in the vapor and a considerable quantity of methane condenses in the liquid.

The minimum amount of ethylene is lost overhead when the temperature at the top of the column is kept at or below the critical temperature of methane (-114°F or -81°C) by -140°F (-95°C) ethylene refrigerant. Because hydrogen lowers the methane partial pressure, the temperature must be lower when hydrogen is present. Refrigeration to -200°F (-130°C) is accomplished by heat exchange with the overhead stream, which has been expanded to low pressure using a throttle valve, turbine, or reciprocating expander. Little heat recovery is possible from the bottoms, which are at close to room temperature.

De-ethanizer

Bottoms from the demethanizer are sent to the de-ethanizer, where a C_2 stream (ethylene, ethane, and acetylene) is separated overhead from C_{3+}

---

*The lower-boiling stream coming out of the top of a distillation column is called the "overhead," while the higher-boiling liquids remaining are called the "bottoms."

Table 4.11. Fractionator Operating Data

Column	Number of Plates	Pressure (atm)	Temperature Range		Reflux Condensor	Reboil
			Tower (°C)	Reboil (°C)		
Demethanizer	20-40	30-35	-70/-130	+2/+18	Ethylene	Condensing propylene
De-ethanizer	30-100	22-31	-12/-1.1	+66/+88	Propylene refrigerant	Low-pressure steam
Acetylene converter	-	5-25	+40/+260	-	-	-
C_2 splitter	50-65	19-24	-18/-29	-10/+4	Propylene	Propylene
Depropanizer	-	10-15	+24/+43	+107/+135	Water	Steam
C_3 splitter	$\leq$200	19	+40/+50	-	Water	Steam
Debutanizer	-	-	-	-	Water	Steam

Source: Refs. 1, 78, and 80.

compounds. Acetylene, typically 0.1-1% of the C_{2+} stream, must be removed, since it adversely affects ethylene polymerization and forms azeotropic mixtures that interfere with separation of ethane from ethylene. Similarly, methyl acetylene (propyne) and propadiene must be removed. Removal to less than 10 ppm is accomplished by selective hydrogenation (to minimize ethylene conversion to ethane) over a noble-metal catalyst in a packed-bed reactor. This can be accomplished two ways: (1) two reactors in parallel (one regenerated by heating with air and steam, and one on-line) or (2) a single reactor with a long-lived catalyst. The temperature in the bed rises as catalyst activity decreases, with regeneration needed after 3-12 mo of operation. For ethane or propane cracking, removal of acetylenes can take place before demethanizing (front-end removal) over a nickel/cobalt/chromium catalyst. Although rarely used, this front-end removal method has the advantage that hydrogen is already present in the stream and only a single conversion unit is required. The more common practice is to hydrogenate streams from which C_4 compounds have been removed; otherwise, substantial quantities of butadiene product would be lost. Acetylene removal, therefore, takes place in the C_2 stream after depropanization, using palladium as a catalyst. This tail-end removal has the advantage that impurities (C_{4+}) that might poison the catalyst are absent and that a reduced volume of gas with a higher acetylene concentration can be processed in a smaller unit. To minimize ethylene loss, hydrogen for the process from the demethanizer off-gas is supplied in approximately stoichiometric quantities of 2-2.5 times the acetylene molar concentration.

Further Separations

The C_2 stream from which acetylene has been removed is sent to the C_2 splitter to separate a 99+% pure ethylene product from ethane bottoms. Refrigeration is recovered from the bottoms, which are usually recycled to the pyrolysis furnaces but can be sold. If ethane feed is used, the fractionation train may end here (with C_{3+} compounds sold or burned) or the train may continue through one more step. Bottoms from the de-ethanizer can be sent to the depropanizer, which separates C_3 compounds overhead from C_{4+} bottoms. Note that there is no refrigeration load from this point on in the fractionation train; cooling is supplied by water. The C_3 stream directly from ethane or propane cracking or from liquid cracking via methyl acetylene and propadiene removal generally is suitable for sale as chemical-grade propylene (93+% pure) and requires no further processing unless it is less than 92% pure or polymer-grade propylene (99+%) is the desired product. In both cases, the C_3 stream is sent to the C_3 splitter. Since propane and propylene have such similar boiling points (-43.8°F and -53.9°F or -42.1°C and -47.7°C, respectively), this is the most difficult separation performed in a distillation column. (C_4 separation requires special techniques described in Sec. 4.2.4.1.) Propane is recycled to the pyrolysis furnaces. Energy for the C_3 splitter reboiler is provided by low-level heat from the primary fractionator condensor, reducing its cooling requirements. This is an example of process integration to conserve energy.

The bottoms from the depropanizer may be either sold as a C_{4+} product or burned for ethane or propane cracking. However, for naphtha or gas oil cracking, this stream is sent to the debutanizer, which separates a C_4 stream from a heavier bottom stream. The C_4 stream contains 25-60% butadiene and may be sold or separated on site. The bottoms from the debutanizer are further split to produce a fuel oil (as well as a gasoline product) or mixed directly with the bottoms from the pyrolysis effluent fractionator to form a pyrolysis gasoline product. The pyrolysis gasoline, which is 50-70% aromatics, can be sent to an aromatics recovery unit, where these valuable chemical feedstocks are separated out. Alternatively, the pyrolysis gasoline can be hydrotreated to decrease diolefin, alkyne, sulfur, and nitrogen content. The result is improved gasoline stability for blending.

4.2.3 Ethylene from Crude Oil

Several companies have developed processes that crack crude oil to produce ethylene. All employ a specialized pyrolysis unit with a conventional compression and fractionation train. Some were taken to the production stage but later discontinued because of technical or economic problems. None is commercial today. Dow and Union Carbide are now building prototype plants and are expected to build commercial units in the mid-1980s. A $15 million prototype of the Union Carbide-Kureha advanced cracking reactor (ACR), with a capacity of 5 million pounds (2300 t) of ethylene per year,[2] is scheduled to be in production by the end of 1980 in Seadrift, Texas.[36] Dow's unit, with a capacity of 25 million lb (11,000 t) of ethylene per year, is expected to be completed in early 1981.[20] The Dow and Union Carbide technologies are similar.

Gulf Oil and Stone & Webster Engineering also are building a $15 million pilot demonstration plant of their thermal regenerative cracking (TRC) process, at Cedar Bayou, Texas, scheduled for late-1980 operation. They plan to prove the process commercially with a full-scale module by the mid-1980s. The novel feature of their process, which can accept a wide variety of feedstocks (including crude oil), is that, in contrast to conventional cracking: "pyrolysis occurs by heat transfer directly from hot micron-sized solid particles in a moving stream rather than indirectly in a heated metal tube."[84] Advantages cited for the process are: product flexibility, lower energy use, lower capital costs, and the ability to use low-grade fuels, including coal, for process heat.[83] No further details are available.

The ACR (see Fig. 4.9) is discussed in more detail here, because the most information is available. It differs from conventional tubular cracking units in several important respects. The feed, which can be deasphalted crude* (1050°F or 565°C endpoint) or distillate, is preheated to 660°F (350°C) and then sprayed into the reaction chamber. There it is rapidly vaporized and cracked as it comes into direct contact with about two times its weight of superheated steam at 3600°F (2000°C). The steam is superheated in a fired heater and then further heated by injection into a flame, where by-product fuel gas is burned with oxygen. Excessive coking problems, which would ordinarily be present at such high temperatures for heavy feed, are avoided by direct contact of the feed with the gaseous energy carrier and by the extremely short residence times (about 20 ms). Quench oil is sprayed directly into the furnace outlet to stop the reaction. In the unique Ozaki quench cooler, waste heat is recovered efficiently, and coke and polymer buildup on the walls is prevented by a curtain of gas. Pitch is removed from the bottom of the quench, and the rest of the products are sent to the primary fractionator, where C_{5+} compounds are removed.

The rest of the process train is the same as a conventional tubular cracker, except that the acid gas removal section is designed to handle the large quantities of sulfur compounds that might result from cracking crude oil. Acetylene is recovered rather than hydrogenated, because of the substantial quantities of acetylene produced in the process. Ethylene-to-acetylene ratios of 8:1 to 25:1 can be selected. Note that the ethylene-to-propylene ratio can also be varied over a larger range (1.5 to 6:1)[20] than from tubular cracking. Typical process yields are shown in Table 4.12. Useful chemical products form 60-70% of the yield, with ethylene comprising 22-27%. Energy and materials use and reaction conditions are shown in Table 4.13. There are several important advantages to the process. First, the chemical producer no longer depends on the petroleum refiner for raw materials. Second, there is flexibility in the choice of feedstock and in the ability to buy crude oil or a distillate fraction at less-than-premium prices (e.g., heating oil in the summer). In addition, the product slate is flexible. Although the cracking section of the plant may be more than twice as expensive as a conventional unit (because of the steam superheaters and the special quench), the process is reported to have an overall economic advantage of about $0.03/lb ($0.07/kg) of ethylene. To summarize, energy consumption is comparable to conventional processes, but crude is used instead of the more valuable lighter fractions.

Some questions remain to be answered. What is the best use of the 30% of the product slate that is fuel residues or pitch? Could better use be made of the crude by refining and then using the fractions separately? The answers will depend on how the process is run, as well as on the operating results from the prototype plants. In the meantime, ethylene producers are building conventional units to crack naphtha and gas oil.

---

*The Dow design does not include a deasphalting unit.

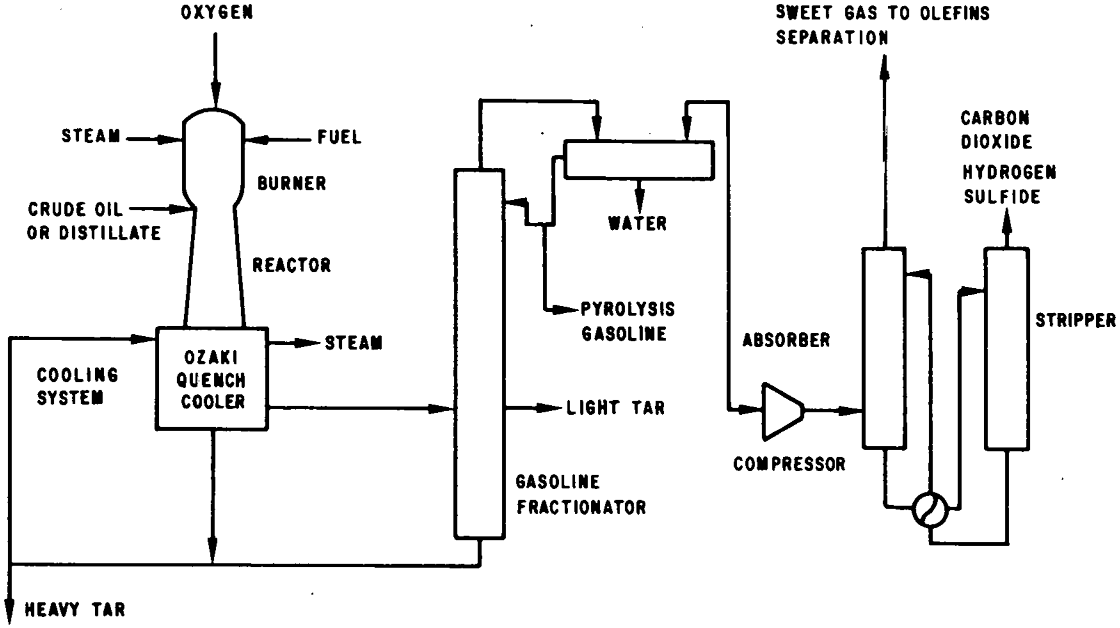


Fig. 4.9. Process Flow for Union Carbide's Crude Oil Cracking
(Source: Ref. 83)

4.2.4 Butadiene Production

Butadiene is produced in the United States in two ways: (1) as a by-product of ethylene manufacture and (2) as the desired product of dehyrogenation of butane or butene (see Fig. 4.10). Butadiene produced by the latter route is called "swing" butadiene, since it is sensitive to changes in demand. In view of the increasing quantities of butadiene that are and will be produced in olefins plants given the trend toward cracking heavier feedstocks, the outlook for swing butadiene is poor (see Table 4.14). However, since considerable quantities of butadiene are currently produced by this method, a brief process description is included in Sec. 4.2.4.2. A flowchart of energy and materials in butadiene production is shown in Fig. 4.11.

Table 4.12. Yields from Crude Oil vs. Naphtha Cracking

	Relative Output by Weight via	
Product	Crude Oil Cracking	Naphtha Cracking
Ethylene	1000	1000
Acetylene	60	15
Propylene	200-300	590
Butadiene	400-500	360

Source: Ref. 86.

4.2.4.1 Separation of Butadiene from Mixed C_4 Streams

The C_4 fraction separated from the products of thermal cracking contains 25-60% 1,3-butadiene. A typical composition is butadiene 30%, isobutene 33%, 1-butene 21%, 2-butene 12.5%, n-butane and isobutane 3.5%, and 1,2-butadiene and acetylenics (compounds with triple bonds) in trace amounts. This mixture cannot be separated by conventional distillation because of the similar boiling points of the individual compounds (see Table 4.15) and because of the azeotrope formed by butadiene and butane.[67] There are several solvents that alter the relative volatilities of the C_4 compounds and make fractionation possible by extractive distillation in a solvent environment. The configuration of the separation system depends on the gas composition and on the solvent used. Solvents used commercially include N-methylpyrrolidone, dimethylformamide, furfural, dimethyl acetamide, and acetonitrile. A typical arrangement using furfural first splits the feed in a conventional distillation tower into a bottoms stream of n-butane and mixed butenes and an overhead stream of butadiene and 1-butene (see Fig. 4.12). The overhead is sent to an extractive distillation column, which produces a butadiene-solvent bottoms. This is stripped of solvent, and the butadiene product is further purified by conventional distillation to remove all traces of solvent. Solvent is recovered and recycled. The butane-butene bottoms fraction from the feed splitter is separated by a combination of conventional and extractive distillation, and then either sold or sent to butadiene production (see Sec. 4.2.4.2).

Isobutylene must be removed from the butanes and butenes, since it does not hydrogenate in the butadiene production process and, therefore, builds up in the reactor. Isobutylene is extracted with 60-65% cold sulfuric acid and is then stripped from the acid. The sulfuric acid is recycled, and

Table 4.13. Union Carbide Crude Cracking Process, Estimated Operating Parameters

Parameter	Per lb Ethylene Plus Acetylene
Reactants (lb)	
Crude oil feed	2.54
Process steam (1.5:1)	3.81
Oxygen	2.06
Reactor products (lb)	
Carbon dioxide	1.42
Water	4.97
Pyrolysis products	2.44
Acid gas (yield)	0.10
Cracking conditions	
Reactor pressure (atm)	20-25
Burner temperature (°F)	3,992
Reactor outlet (°F)	2,125
Process steam inlet (°F)	1,000
Energy consumption	
Input (Btu)	
Burner fuel	11,100
Compressors[a]	10,740
Process steam[b]	2,580
Electric power	1,500
Credit (Btu) TLX steam generation	(7,915)
Total consumed (Btu)	18,005

[a] Ethylene recovery and oxygen plant.

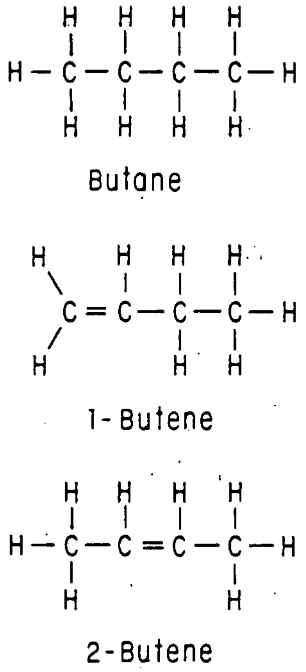
[b] Superheat only; assumes latent heat supplied by waste heat.

Source: Ref. 63.

the isobutylene is sold. Alternatively, isobutylene can be made to form oligomers (low polymers suitable for gasoline blending), which are insoluble in acid.

Unless extraction is carried out with N-methylpyrrolidone or dimethylformamide, acetylenics must be removed from all streams by selective hydrogenation. These compounds, which may be present in quantities up to 5000 ppm in thermal cracking C_4 streams, interfere with rubber formation and form coke deposits on the dehydrogenation catalyst.

The process energy required for separation is about 4350 Btu/lb (10.1 kJ/g)[36] butadiene produced (with about 14% in the form of electric energy), which is allocated only to the butadiene stream.


Butane

1-Butene

2-Butene

Fig. 4.10. Butadiene Feeds

4.2.4.2 Dehydrogenation of Butane and Butene

The basic catalytic process is similar for the saturated and unsaturated feeds, although a more active catalyst is required for dehydrogenating the less reactive butane. The heat of reaction for butene to butadiene is 722 Btu/lb (1.7 kJ/g); that for butane to butadiene is 1000 Btu/lb (2.3 kJ/g).[6] The industrial processes are very fuel intensive. Purchased fuel for dehydrogenation of butene and butane is about 8000 Btu/lb (19 kJ/g) and 17,000 Btu/lb (40 kJ/g), respectively. Additional energy is consumed in the form of by-product fuels. A process flowchart for butadiene production from butane is shown in Fig. 4.13. In both cases, the feed is passed through a fixed catalyst bed at about 1100°F (600°C), and the reactor effluent is quenched, cooled, and compressed. The resultant liquid mixture goes through a standard C_4 separation unit that recycles unreacted feed. (About 20% is converted per pass, with overall product yields of about 75%. These numbers vary by as much as 10% from plant to plant.) Major differences between the

Table 4.14. Sources of Butadiene (%)

Source	Year			
	1965[a]	1970[b]	1976[c]	1985[c]
Butane dehydrogenation	40	34	46	5-29
Butene dehydrogenation	43	46		
Olefins manufacture	17	20	40	78-58
Imports	-	-	14	17-13

[a] Ref. 30.

[b] Ref. 25.

[c] Ref. 31.

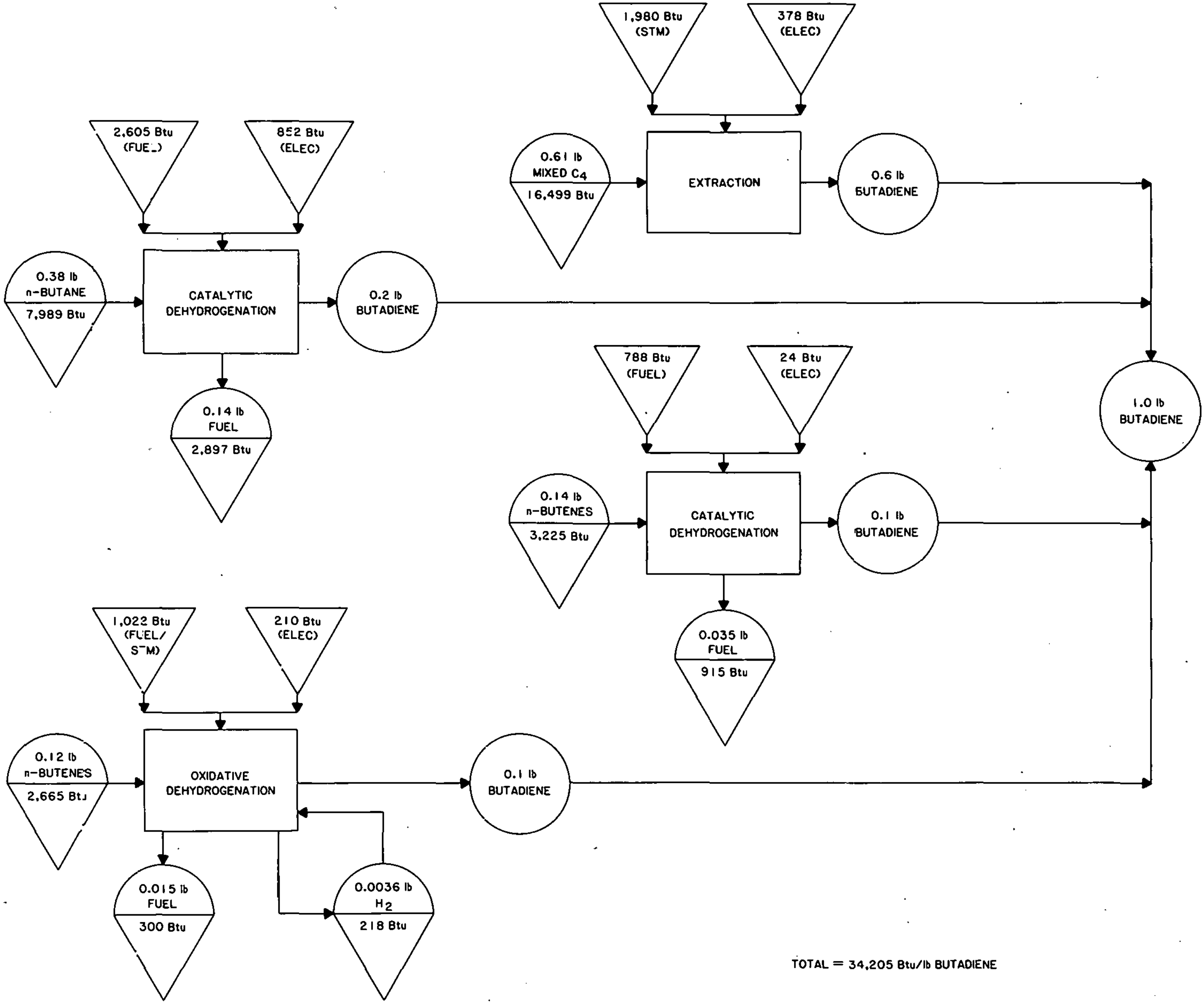


Fig. 4.11. Energy and Materials Flows for 1980 Production of Butadiene (Sources: Refs. 21, 36, and 87)

two feeds are the use of steam diluent in butene dehydrogenation and the use of a cyclic system in butane dehydrogenation, which keeps one reactor on-line while another is regenerated by burning off coke deposits.

Plants built since 1970 for on-purpose production of butadiene are based on oxidative dehydrogenation of butene. In this process, oxygen combines with the hydrogen from the butene and removes it as water in an exothermic reaction. This removal allows the reaction to proceed to completion. The major advantage of this technology is lower feedstock consumption. As swing butadiene demand decreases, the older catalytic dehydrogenation plants will close, leaving oxidative dehydrogenation of butenes as the only production route for swing butadiene.

Table 4.15. Boiling Points of C_4 Hydrocarbon Isomers

Isomer	BP(°C)
n-Butane	- 0.5
Isobutane	- 6.9
n-Butene-1	- 6.3
Cis-n-Butene-2	+ 3.7
Trans-n-Butene-2	+ 0.9
Isobutene	- 0.9
1,3-Butadiene	- 4.4
1,2-Butadiene	+10.3

Source: Ref. 88.

4.3 PRODUCTION OF DERIVATIVES

4.3.1 Polymerization

There are two basic types of reactions leading to the formation of polymers -- condensation and addition. Condensation is a slow process whereby

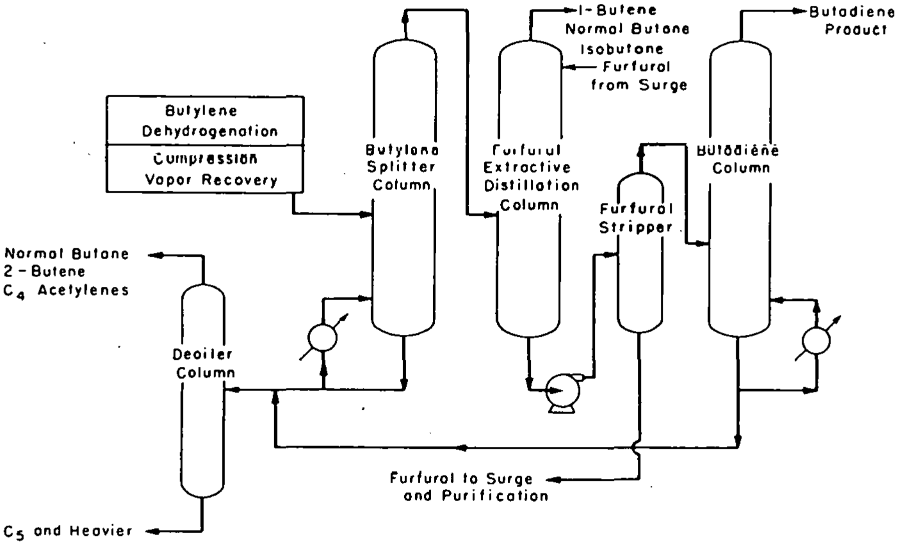


Fig. 4.12. Process Flow for Butadiene Extraction from Isomers (Source: Ref. 35)

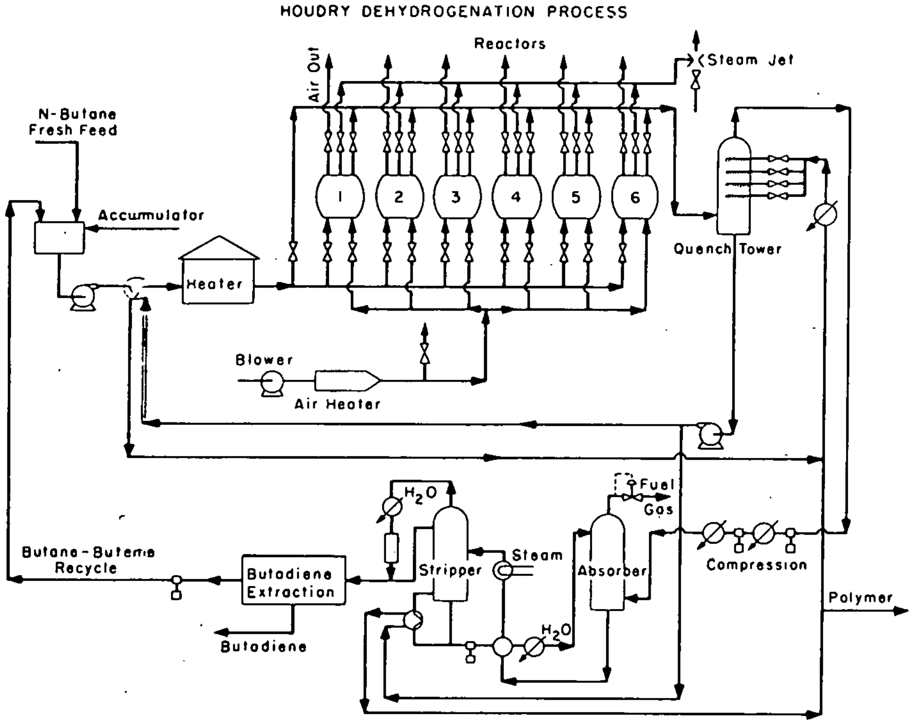


Fig. 4.13. Process Flow for Production of Butadiene from Butane (Source: Ref. 35)

two comonomer molecules join, with the resultant elimination of a small by-product molecule, such as water. Since the process is reversible, the by-product is removed by boiling or entraining in a solvent, which favors the forward reaction. A typical condensation reaction, the formation of polyethylene terephthalate (polyester), is shown in Fig. 4.14. Most common thermosetting materials are condensation polymers, as are some thermoplastics (e.g., nylon).

Addition polymerization is the rapid, end-to-end joining of monomer (or comonomer) units by the rupturing of a bond within one unit followed by the formation of another bond with the next unit. The empirical formula of the polymer is the same as that of the monomer. The reaction is highly exothermic (18,000-36,000 Btu/lb-mole [42-84 kJ/g mole]),[29] because a double bond is weaker than two singles, and leads to the formation of long chains with molecular weights up to several hundred thousand.[27] Most thermoplastics are addition polymers (e.g., polyethylene, polypropylene, polystyrene, polyvinyl chloride, and polyacrylonitrile).

Although addition reactions are spontaneous, a catalyst or initiator is usually added to run polymerizations most economically. Two major types of initiators are in common use: free-radical and ionic. The initiator decomposes to form an active agent (free radical or ion), which attaches to a monomer and transfers its activity. Ultraviolet light or heat also can act as an initiator by decomposing monomer molecules. The activated monomer can then link up with another monomer, and so on, leading to a long

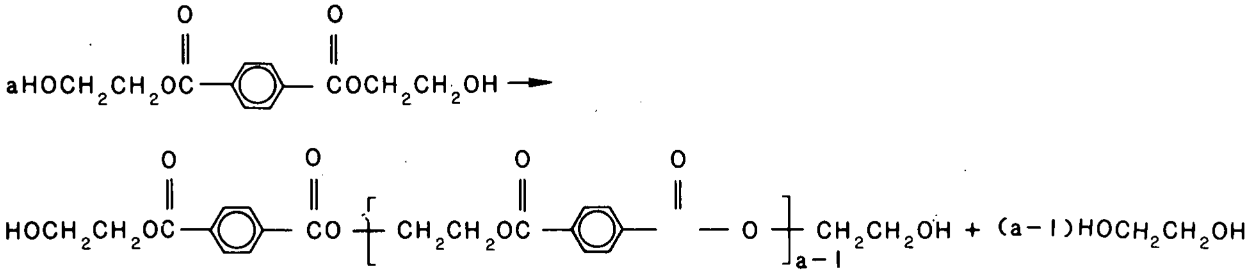


Fig. 4.14. Process Flow for Polyester Production by Condensation Polymerization (Source: Ref. 9)

chain called a polymer. Chains are terminated when one meets another free radical or oppositely charged ion and transfers its activity to another molecule (chain transfer). The free-radical mechanism is suitable for most olefinic monomers, while the ionic mechanism is suitable for others as well. Certain addition polymerizations, most notably production of high-density polyethylene and polypropylene, are carried out with the aid of special catalysts developed by Ziegler and Natta in the 1950s. These catalysts allow polymerization at relatively low temperatures and pressures, and permit selection of preferred spatial configurations.

Several types of unit processes are used for polymerization reactions. Table 4.16 lists common polymers with the production processes and initiators used for their production. The simplest process conceptually is bulk polymerization, in which liquid or vapor monomer and initiator are introduced into a reaction vessel and may be stirred. The polymer may be soluble in the monomer or it may be insoluble and settle out. The mixture often becomes very viscous, which impedes the heat removal necessary to maintain control of the process. The major advantage of bulk or mass polymerization is the product purity, which confers excellent optical clarity and electrical insulating properties.

Dissolving the monomer and initator in an inert solvent allows easy heat removal via the refluxing solvent and lowers the mixture viscosity to permit easy stirring. The polymer may be insoluble in the solvent or may require separation. In either case, traces of solvent remain in the product. Molecular weights are lower for solution polymers than for bulk polymers because of chain transfer to the solvent. An example of solution polymerization is high-density polyethylene production. The solvent used is cyclohexane, as water destroys the catalyst.

Another variant is emulsion polymerization, in which monomer droplets called micelles are held in water by an emulsifying agent like soap. As with solution polymerization, heat removal is easy, but product purity is not as good as that of the bulk product. Rate and average molecular weight are

Table 4.16. Polymerization Techniques

					Anionic			
Monomer	Bulk	Solution	Suspension	Emulsion	Conventional	Ziegler	Cationic	Free Radical
Ethylene	A[a]	B[b]	B	B		*[c]		*
Propylene		A				*		
Vinyl chloride	B	B	A	B				*
Styrene	A	B	A	B	*	*	*	*
Vinyl acetate	B	B	B	A				*
Acrylonitrile	B	B	A		*			*
Acrylates and methyacrylates	A	A	B	B[d]	*	*		*
Butadiene		A		B[e]	*	*		*
Isoprene		A			*	*		
Isobutene		A					*	
Chloroprene				A				*
Ethylene propylene terpolymer		A				*		

[a] Commonly used method.

[b] Occasionally used method.

[c] Applicable reaction mechanism.

[d] Emulsion polymerization is important for acrylates.

[e] A redox system is used for SBR rubbers.

Source: Ref. 22.

higher for emulsion polymers than for solution or bulk process polymers. Purchasing of the emulsifying agent and drying of the finely divided product are major expenses.

Suspension or pearl polymerization is carried out in a manner similar to emulsion polymerization. Monomer droplets $\lesssim$ 10 μ in diameter are suspended by agitation in water in which they are insoluble. The water serves to remove heat and reduce viscosity. A stabilizer, such as gelatin or diatomaceous earth, prevents polymer globules from sticking together as they are formed. The size of these "pearls" depends on the rate of agitation and the stabilizer used. The product is separated with screens and dried. Purity is similar to that of bulk polymers, but the molecular weight is lower.

4.3.1.1 Production of Elastomers

Polybutadiene Rubber

Several isomers of polybutadiene are possible, depending on where addition of one monomer unit to the next takes place. All retain one double bond per monomer unit, allowing vulcanization with sulfur. Two possible isomers consist of saturated chains, with ethenyl branches ($-CH = CH_2$) either on every other carbon (1,2-polybutadiene) or on the first two of every four (3,4-polybutadiene). A third configuration consists of a single unbranched chain, with every fourth bond double (1,4-polybutadiene). This latter compound can be formed in either of two distinct stereoisomers. The carbon chain can lie entirely on one side of the double bond (cis-1,4-polybutadiene) (see Fig. 4.15) or across each double bond (trans-1,4-polybutadiene). Products consisting of isomeric mixtures have poor properties, so stereo-specific catalysts are used to produce the most abrasion-resistant species (preferably cis-1,4-polybutadiene). Most catalysts are of the Ziegler type, consisting of alkylated aluminum and titanium halides, although uranium catalysts have been reported recently.[89] An exemplary process (patented by Phillips in 1962) uses $Al(i\text{-}C_4H_9)_3$ and TiI_4 to produce a rubber with 400-4000 butadiene units per chain.[89] The reaction is carried out in toluene solution in a stirred, jacketed kettle reactor from which water and oxygen must be excluded to protect the catalyst. The solvent-to-monomer ratio is high enough to keep the viscosity in a range that can be handled by a conventional reactor.

More recent variations employ a series of cooled reactors in a train to achieve the desired residence time of about 20 hr with a continuous

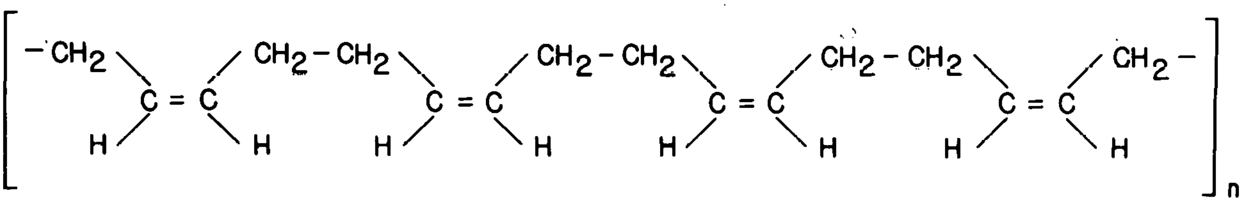


Fig. 4.15. Cis-Polybutadiene (Source: Ref. 82)

process. The reaction temperature is between 5°F and 175°F (-15°C and +80°C), and the pressure is about three atmospheres. Yields of 90% to over 98% have been reported. An antioxidant and a "shortstop" to terminate the polymerization are added to the reactor effluent, which flows through a heat exchanger to the concentrator. Here, unreacted butadiene and part of the solvent, both of which get recycled, are removed from the solution before it is blended. The solution, now called a latex (defined as a suspension of particles 400-2000 Å)[1] is sent to a steam stripper where any remaining solvent is removed overhead. Solvent and water are separated by decanting and are recycled. The crumb rubber-water slurry is pumped to the drying section, where it is dried first on shaker screens and then in an extrusion dryer prior to being weighed, baled, and wrapped in polyethylene (see Fig. 4.16). Energy and material flows in the production of polybutadiene are shown in Fig. 4.17.

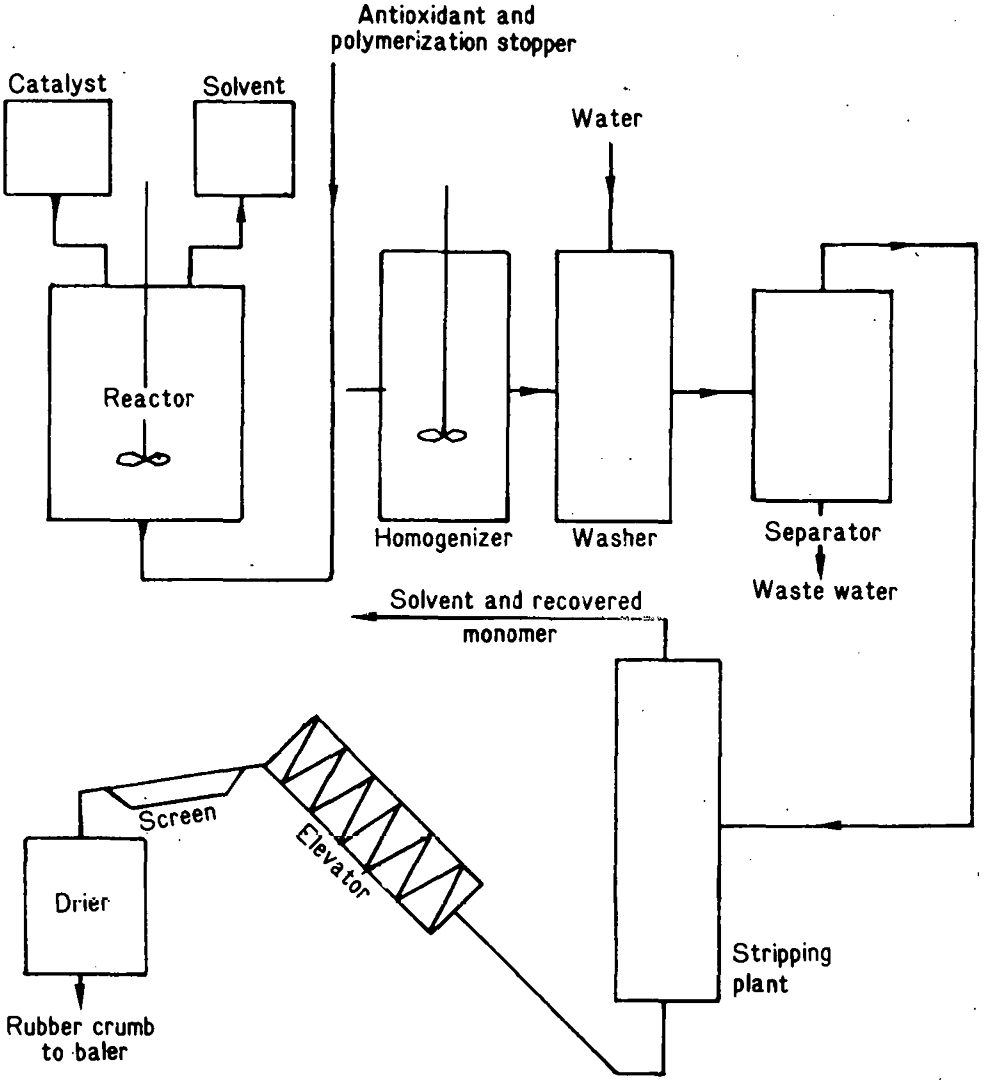


Fig. 4.16. Process Flow for Butadiene Rubber Production
(Source: Ref. 27)

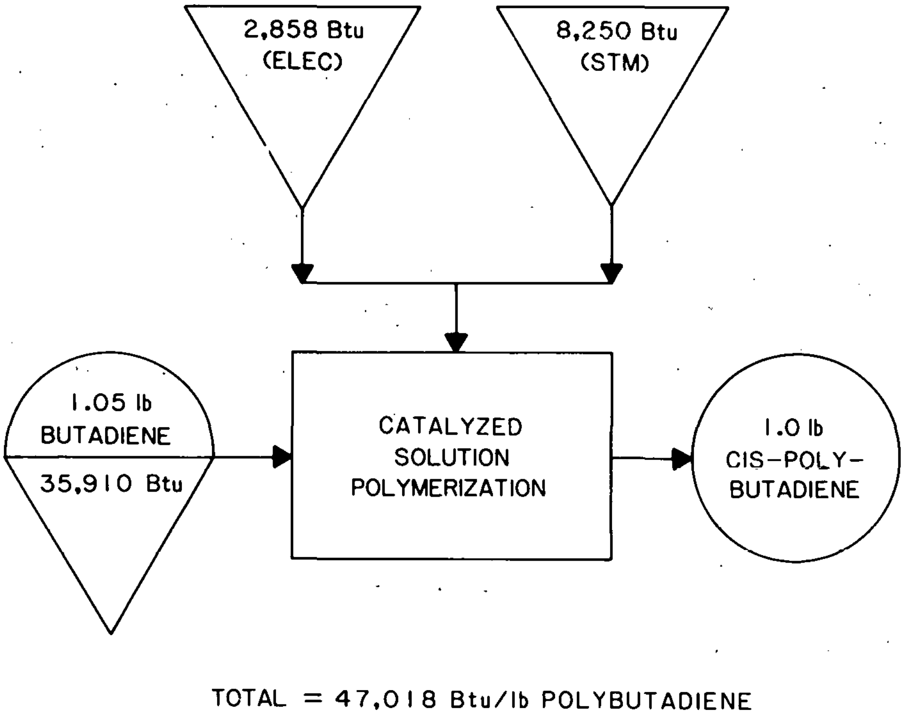
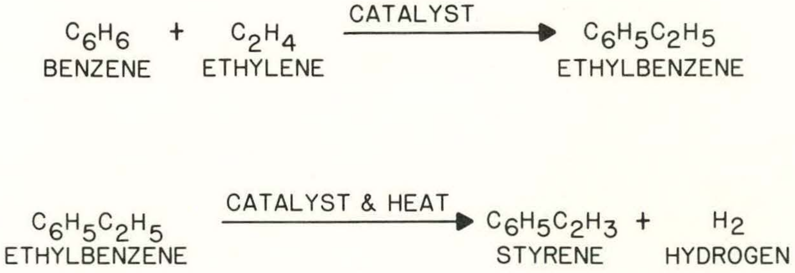


Fig. 4.17. Energy and Materials Flow for Polybutadiene Production (Source: Ref. 90)

Styrene-Butadiene Rubber

Styrene-butadiene rubber is an addition polymer containing about 75% butadiene by weight that is generally produced in an emulsion process. (Butadiene production is described in Sec. 4.2.4.) Styrene for SBR or polystyrene is produced by catalytic dehydrogenation of ethyl benzene, which, in turn, is made by alkylation of benzene with ethylene. The relevant chemical reactions are shown in Fig. 4.18, and process flow diagrams are shown in Figs. 4.19 and 4.20.

Benzene is produced largely by catalytic reforming at petroleum refineries; this process is described in some detail in Ref. 79. It represented 85% of the supply in 1970, with 12% supplied from coke ovens and 3% supplied as a by-product of ethylene production.[25] Alkylation of benzene with ethylene is carried out catalytically, with the product washed to remove traces of catalyst and separated by distillation from unreacted benzene and polyethyl benzenes, which are recycled to the reactor. The reaction is exothermic (550 Btu/lb or 1.28 kJ/g),[81] and heat is recovered as low-pressure steam. About 50% more heat is recovered than is needed for the distillation; hence, the process is a net energy producer. In order to save fuel and operating expenses, this process is generally integrated with the dehydrogenation, which is very fuel intensive. Ethylbenzene is heated to 1200°F (650°C) or higher by superheated steam over a chromium-promoted iron oxide catalyst. The reaction is endothermic, and conversion to styrene per pass is 40-60%, necessitating ethylbenzene recyle and increasing energy use. By-product



$$\underset{\text{BENZENE}}{C_6H_6} + \underset{\text{ETHYLENE}}{C_2H_4} \xrightarrow{\text{CATALYST}} \underset{\text{ETHYLBENZENE}}{C_6H_5C_2H_5}$$

$$\underset{\text{ETHYLBENZENE}}{C_6H_5C_2H_5} \xrightarrow{\text{CATALYST \& HEAT}} \underset{\text{STYRENE}}{C_6H_5C_2H_3} + \underset{\text{HYDROGEN}}{H_2}$$

Fig. 4.18. Chemical Reactions for Production of Styrene

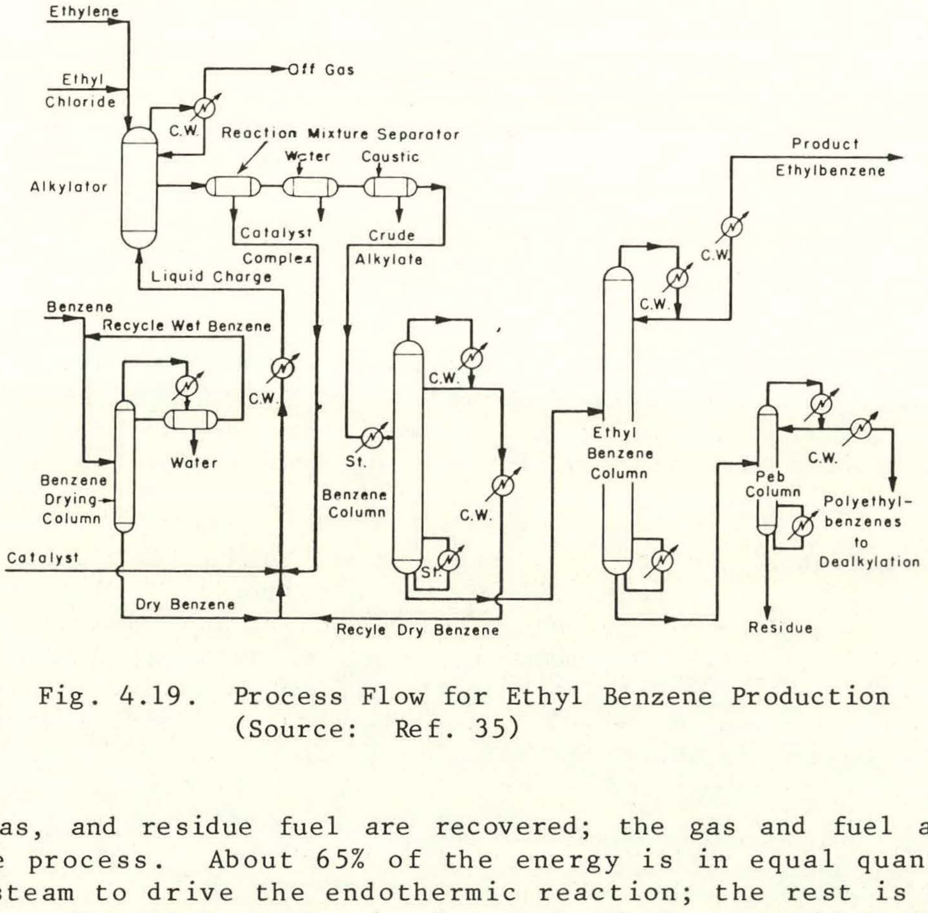


Fig. 4.19. Process Flow for Ethyl Benzene Production
(Source: Ref. 35)

toluene, gas, and residue fuel are recovered; the gas and fuel are burned within the process. About 65% of the energy is in equal quantities of fuel and steam to drive the endothermic reaction; the rest is steam for distillation. Note that styrene is also produced as a coproduct of propylene oxide production (see Sec. 4.3.2.2).

Styrene-butadiene rubber can be produced in emulsion or solution, with emulsion polymerization representing 93% of 1973 production.[26] The emulsion process can be carried out at either 120°F (50°C) or 40°F (5°C). The former is called "hot rubber" and represented 15% of 1973 production; the latter is called "cold rubber" and represented 78% of 1973 production. The lower temperature method was discovered in the 1950s and rapidly dominated production because of superior product properties. Lower temperatures favor

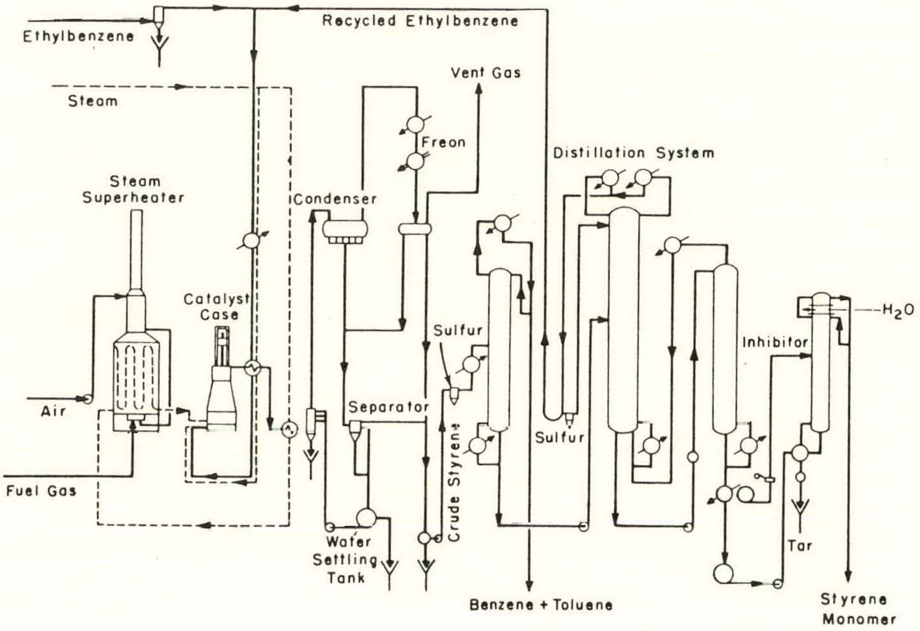


Fig. 4.20. Process Flow for Styrene Production
(Source: Ref. 35)

the production of the long-chain 1,4-addition product over the branched-chain 1,2-product. The temperature chosen for the cold process (40°F or 5°C) actually represents a compromise to avoid the need for antifreeze in the emulsion. Process flow diagrams for hot and cold methods are shown in Figs. 4.21 and 4.22.

Ingredients for the cold process are precooled, while those that are water-soluble are preheated for the hot process. Monomers are added at ambient temperature and the batch heated to reaction temperature with steam in the vessel jacket. The monomers, together with appropriate emulsifier (soap or detergent), free-radical initiator, and molecular weight modifiers, enter a stirred reaction vessel (batch process) or a series of 6-10 vessels (continuous process), where the reaction proceeds for 6-12 hr. Since butadiene is more reactive and enters the polymer faster, a weight ratio of 71:29 butadiene to styrene in the charge is used to form a 23.5% styrene polymer.[26] Initial pressures are 80 psi and 10 psi (6 atm and 1.7 atm) and final pressures are 50 psi and 5 psi (4.4 atm and 1.3 atm) for hot and cold processes, respectively.

The polymerization is exothermic (550 Btu/lb [1.3 kJ/g] rubber), and heat dissipation requires cooling in the reactor jacket, with water cooling for the hot process and high-capacity refrigeration for the cold. In addition, there are sometimes ammonia coils within the vessel for heat exchange. Since further reaction is slow due to monomer depletion and leads to an inferior product because of increased side-chain formation, the reaction is terminated by the addition of a "short-stop" at 72% conversion for the hot process and at 60% conversion for the cold.

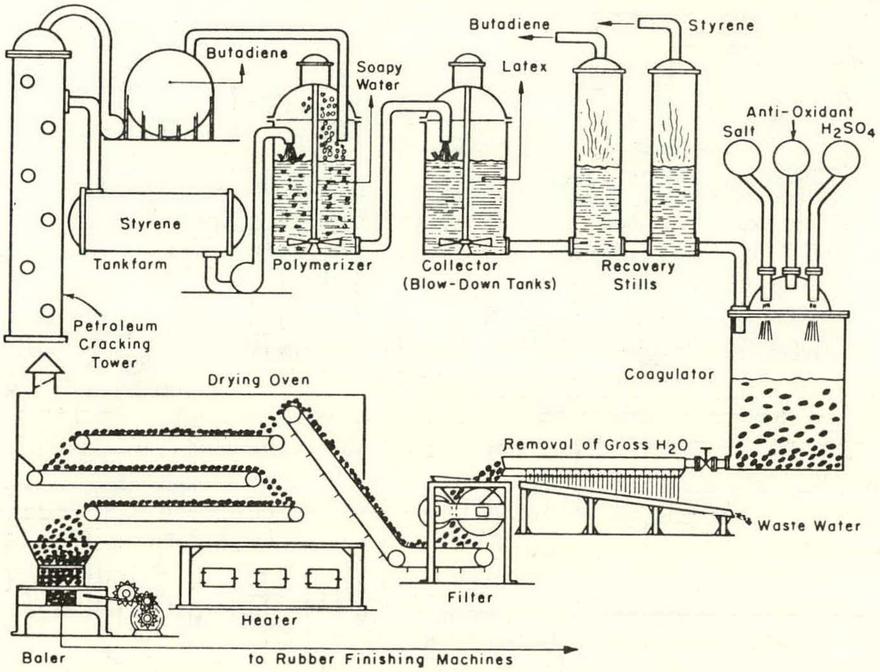


Fig. 4.21. Process Flow for Production of Hot Rubber (Source: Ref. 35)

Unreacted butadiene is recovered by flashing from the reactor effluent at 120°F (50°C) and by reducing pressure in two stages. Styrene is removed in a vacuum stripping column with steam and then separated from the water in a decanter. These processes use low-pressure steam. Monomers are recovered at about 80% purity, which is less than is required for the reaction (91.5% for butadiene, 95.5% for styrene); hence, they must be mixed with fresh high-purity feed (99% butadiene, 98% styrene). All the monomer recovered in the hot process can be recycled in this way, but the lower conversion in the cold process results in more unreacted monomer. About 18% must be repurified before recycle to achieve necessary feed purity. This is done most economically by the monomer supplier.

The rubber emulsion or latex is sent to large tanks, where it is blended to achieve greater uniformity and where antioxidants, carbon black (to toughen) or extender oil, are added. General Tire and Rubber Co. first added petroleum oils to their high-molecular-weight rubbers in 1950. The oil serves to plasticize the rough product and make it more readily processible without any deterioration of properties and to extend it, thereby making it less expensive to produce. From 25 to 75 parts of oil per 100 parts rubber hydrocarbon are added to approximately 70% of SBR produced.[1] The blended latex is coagulated in two steps. First, a 5% solution of sodium chloride (or another electrolyte) is added to cream the latex. A small percentage of SBR latex is concentrated and sold in that form for paints and foam rubber. If a solid product is to be produced, 0.25% sulfuric acid (or other dilute acid) is added with vigorous agitation to prevent agglomeration of the rubber crumbs that form. The crumb rubber is filtered off and washed on vibrating screens or rotating filters to remove water-soluble impurities, such as soap and

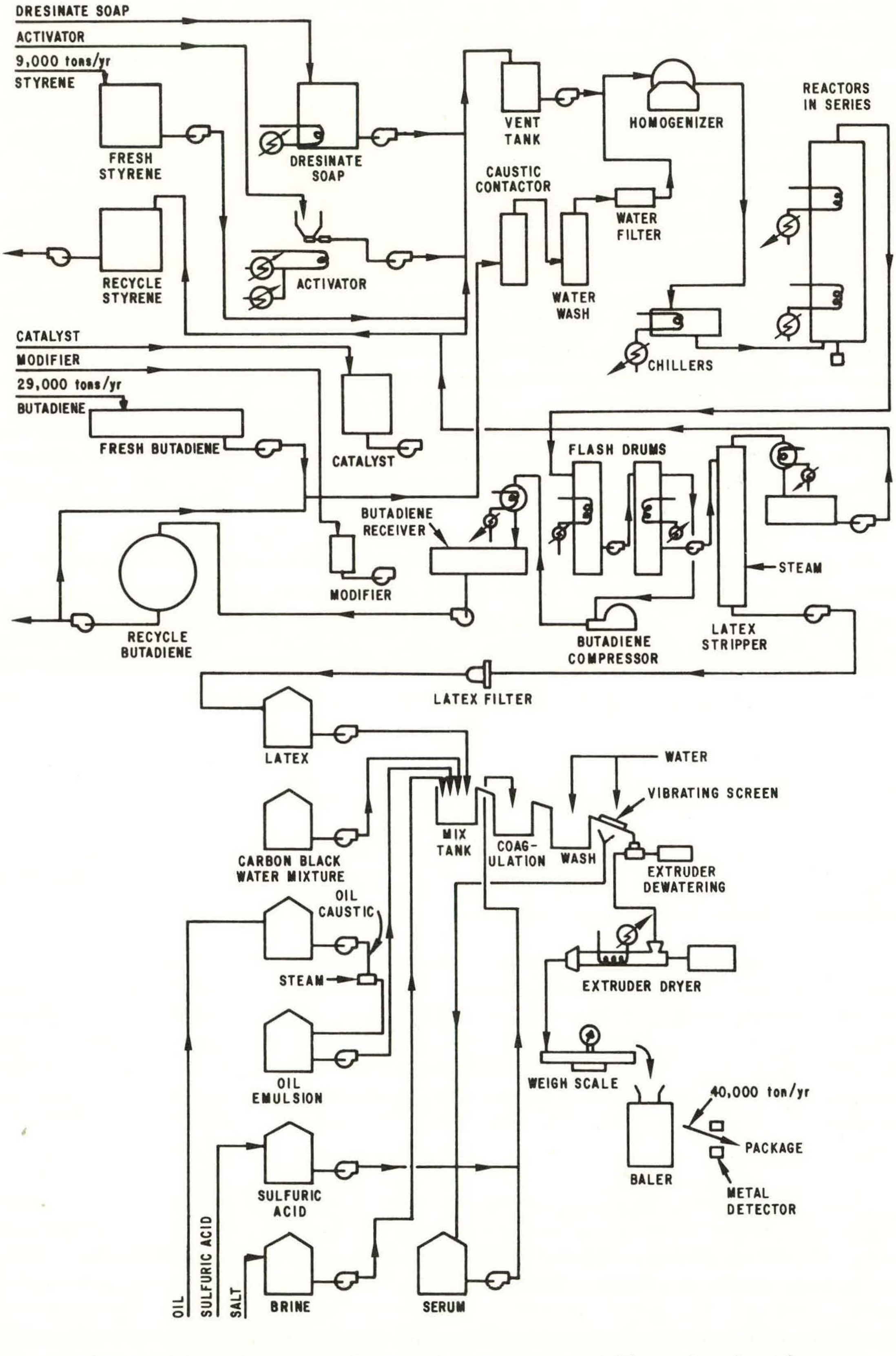


Fig. 4.22. Process Flow for Styrene-Butadiene Production
(Source: Ref. 1)

coagulent. Finally, the crumb is dried and wrapped in 75-lb (34-kg) bales covered with polyethylene. Drying by vacuum has been replaced in most plants by mechanical drying, which is less energy consuming. With the mechanical method, the material first enters a screw-pass dryer, which reduces the moisture content to 15%. The material then enters an extruder dryer where shearing action heats the rubber to 325°F (163°C) under pressure. When the material is forced out of the dryer, the pressure drop flashes the water from the hot product.

Solution polymerization of SBR is very similar to the emulsion processes in most respects, except that a hydrocarbon solvent replaces the water (necessitating solvent recovery), and a stereospecific catalyst like lithium butyl (LiC_4H_9) is used in place of the initiator. No other additives are required. The reaction temperature (140-158°F [60-70°C])[20] may increase as the reaction proceeds, necessitating water or refrigeration cooling. The monomer concentration in solution is 15%, and the per-pass conversion is 10-15%. The rubber in solution, called a "cement," is precipitated by adding hot water to the tank and agitating violently. It is washed, dried, and baled, as is the emulsion product. Solution SBR has more cis-linkages than the emulsion product and, therefore, has better abrasion and heat build-up properties.

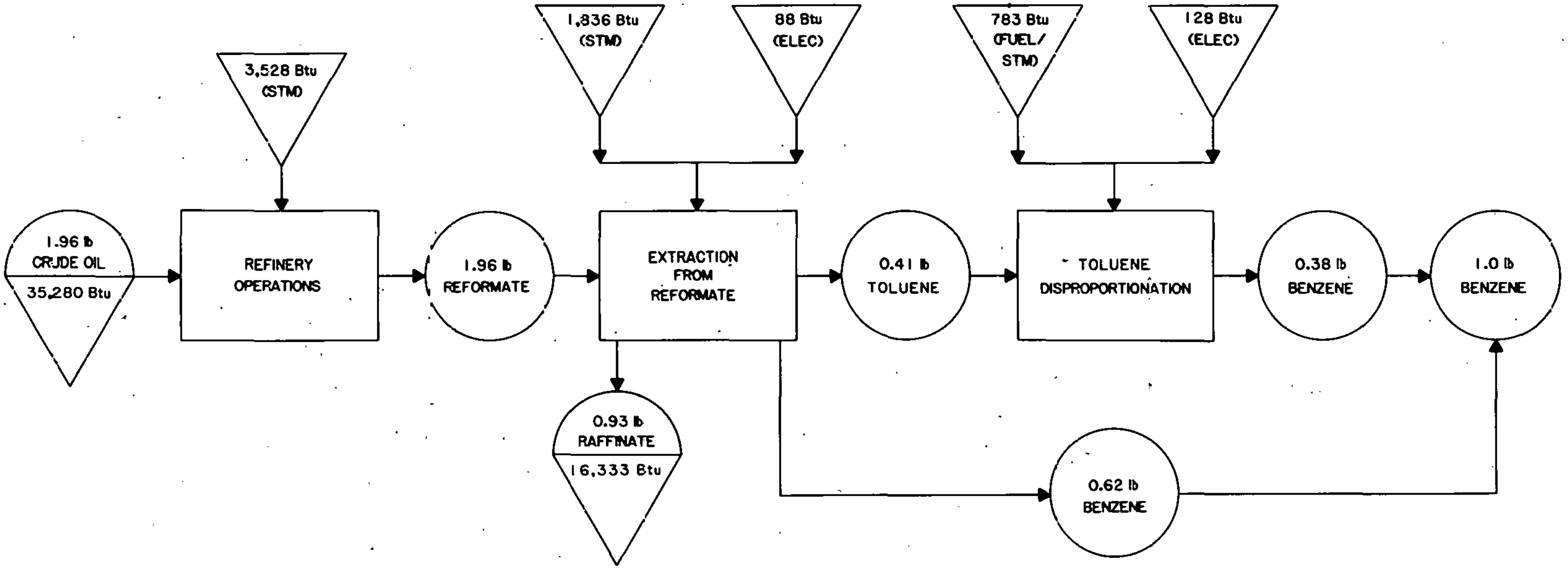
Energy and materials flows for the production of benzene, ethyl benzene, styrene, and SBR are shown in Figs. 4.23-4.26. In Fig. 4.23, refinery processing is represented as a single box with only the desired output. This simplification can be made, because the process energy is allocated per pound of product. Details of refinery processing can be found in Ref. 79. The same simplification (ignoring coproducts charged with their share of the energy) is made for the extraction step, which produces xylenes (not shown here). In addition, raffinate is credited as a fuel; therefore, it is not charged with any of the extraction process energy. Since its market value is higher than its fuel value but considerbly lower than the value of the benzene, toluene, xylene fraction (BTX), the decision to call it a byproduct is somewhat arbitrary. In the styrene flow chart, toluene is credited to the process with the energy that would have been required to make it by the conventional method (see Fig. 4.47).

The total net energy required for production of an average pound of SBR from primary oil and gas feeds (about 38,300 Btu/lb or 89 kJ/g, including the feed) is broken down by process in Fig. 4.26. The gross heat of combustion of the product is 19,000 Btu/lb (44 kJ/g), so the net energy foregone is 19,300 Btu/lb (45 kJ/g). The energy required by the hot and cold polymerization processes is calculated to be 2000 and 2500 Btu/lb (4.6 and 5.8 kJ/g),[26] respectively, compared with the actual average of 5300 Btu/lb (12.3 kJ/g).

4.3.1.2 Production of Plastics

Low-Density Polyethylene

The high-pressure process for production of LDPE was discovered in 1933. It was commercialized in the United States in 1943 and was the only



TOTAL = 25,266 Btu/lb BENZENE

Fig. 4.23. Energy and Materials Flow for Benzene Production (Source: Ref. 72)

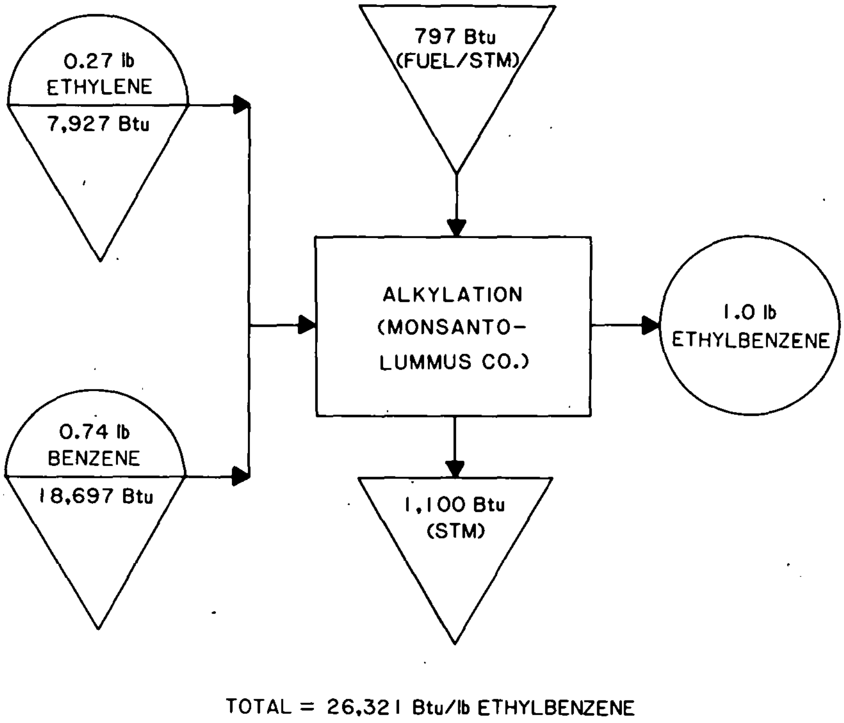


Fig. 4.24. Energy and Materials Flow for Ethylbenzene Production (Source: Ref. 89)

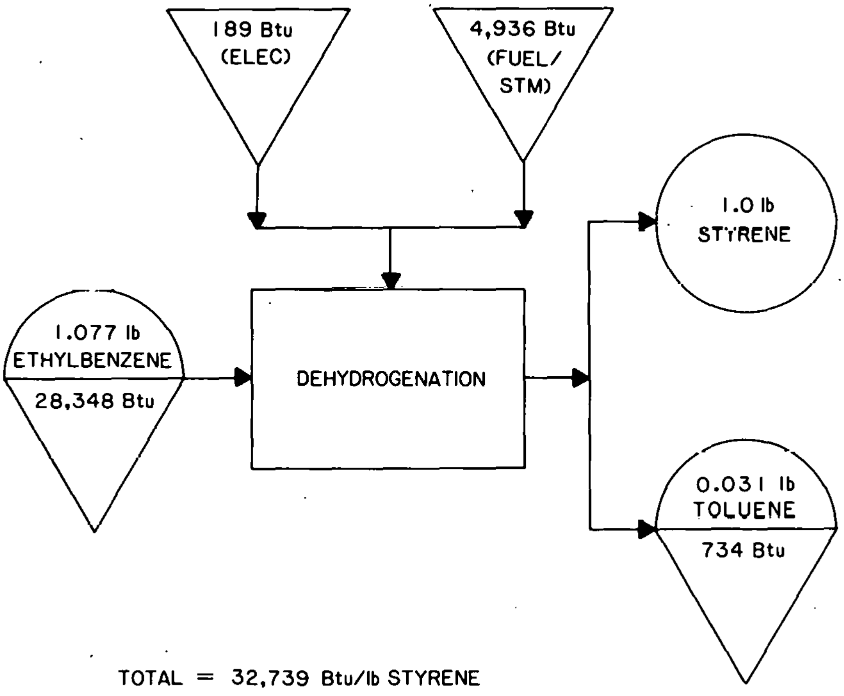


Fig. 4.25. Energy and Materials Flow for Styrene Production (Source: Ref. 89)

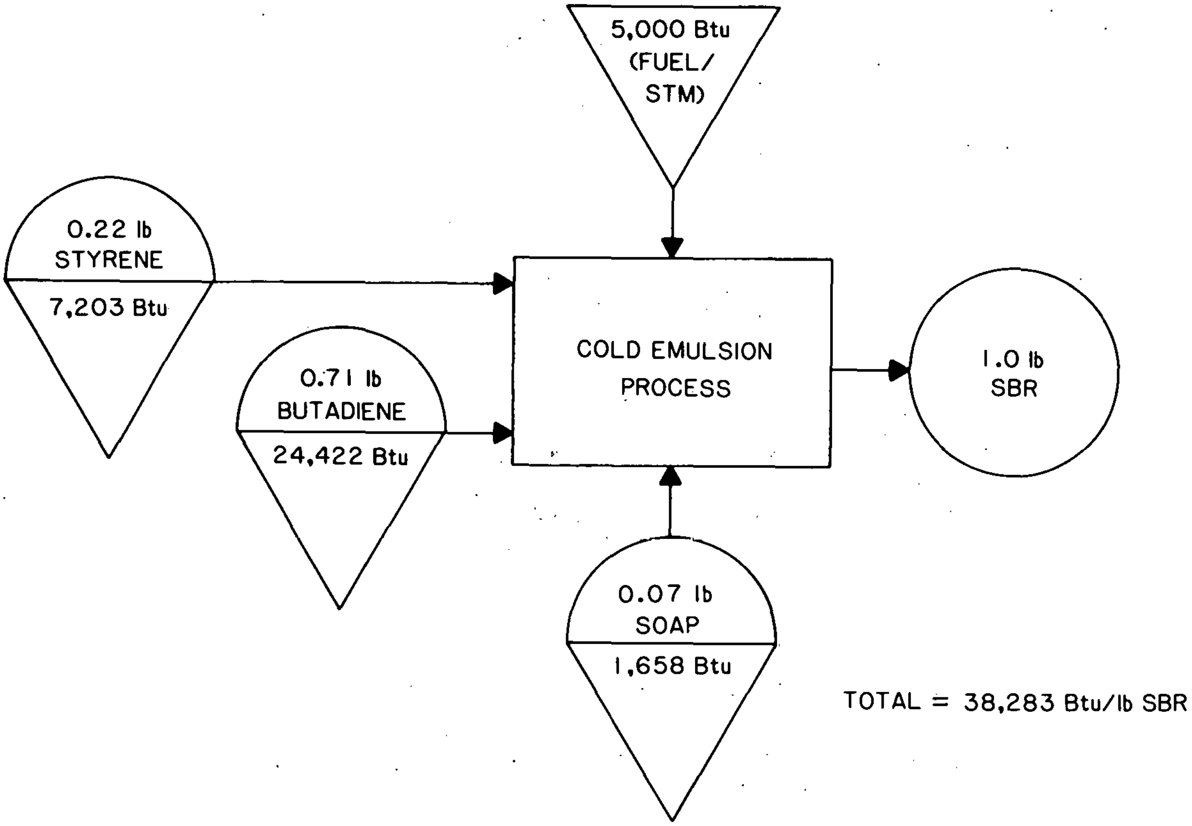


Fig. 4.26. Energy and Materials Flow for SBR Production (Source: Ref. 91)

process in use until 1956, when low-pressure processes (which produce HDPE) were introduced. Most LDPE is produced in bulk, as shown in Fig. 4.27, but some is produced using a solvent like benzene. The addition polymerization process is favored by high pressures, and pressures of 15,000-50,000 psi (1000-3400 atm) have been reported, with 19,000-32,000 psi (1300-2200 atm) the most common range. Temperatures range from 300 to 570°F (150 to 300°C), with many reports of 390-480°F (200-250°C). At these conditions, ethylene is in the fluid phase, with a density of 0.4-0.6 g/cc, as it is above its critical temperature. Higher temperatures increase the reaction rate and decrease the deposition of polymer on the reactor walls. However, careful temperature control is essential, as the reaction is highly exothermic (1430 Btu/lb or 3.2 kJ/g), and ethylene is unstable under reactor conditions, decomposing to carbon, hydrogen, and methane. Locally high temperatures or initiator concentrations can trigger an explosion or "decomp" when the temperature is greater than 480°F (250°C). All reactors have safety discs to release sudden pressure bursts, but the problem is usually avoided by keeping the reactants well mixed and by removing excess heat.

High-purity ethylene (at least 99.8% pure) is compressed in two stages. This is the largest energy-consuming step (75% of the total) in LDPE manufacture. The first stage, raising the pressure to about 1980 psi (135 atm), may be accomplished by either centrifugal compressors or multistage, piston-type

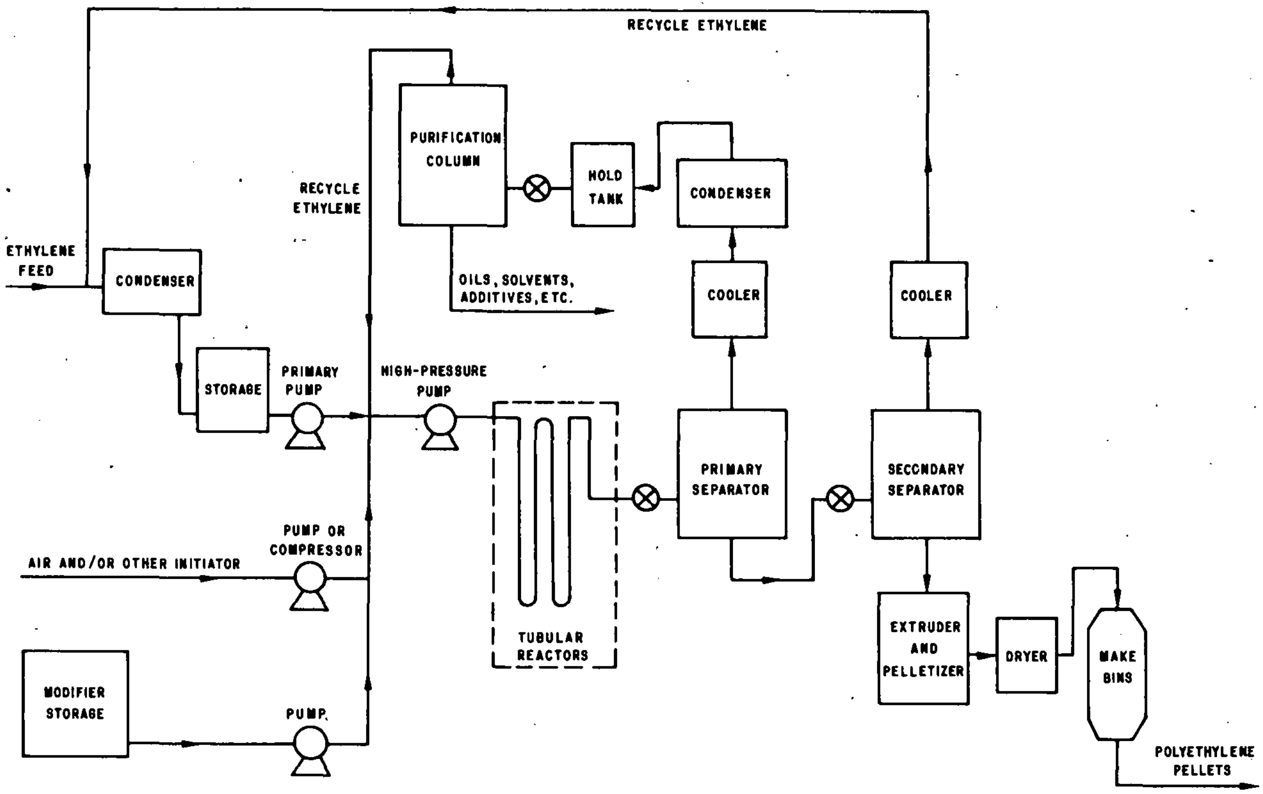


Fig. 4.27. Process Flow for Production of LDPE in Tubular Reactor (Source: Ref. 92)

compressors (positive displacement compressors). The latter type always is used for the second stage. Compressed ethylene is sent to the reactor, where it is mixed with a free-radical initiator (such as benzoyl peroxide in concentrations of about 0.06%). A telogen or chain-transfer agent to limit polymer molecular weight, such as light paraffins (which may already be present as impurities in the feed), is added in concentrations of up to a few percent. Tubular reactors and continuous-flow stirred, autoclave reactors are both in common usage. In a typical tubular reactor, the tubes have an inner diameter of 1 in. (2.5 cm) and may be 2000 ft (610 m) long. Such a reactor would have a material residence time of up to 45 sec and would produce 20-40 million lb/yr (9,000-18,000 t/yr). Ethylene enters the reactor below the reaction temperature and is heated to 210-390°F (100-200°C) via co-current flow of a heat-exchange fluid such as Dowtherm® in the reactor jacket. As the reaction proceeds, the mixture heats to 480-570°F (250-300°C) and cooling must be provided in the jacket. An alternative method is the use of multiple feed points within the tube. New feed is heated by the excess heat of the polymerization already in progress. Pressure drops from one end of the tube to the other are 1,000-10,000 psi (70-700 atm). Per-pass conversions and, therefore, the concentration of polymer at the end of the tube may be as high as 25%. Overall ethylene-to-polyethylene yield is greater than 95%.

Large autoclave reactors can have internal diameters up to 2 ft, with the outer diameter three or four times as large, and can produce 5-15 million lb/yr (2300-6800 t/yr). The length-to-diameter ratio is between 2:1 and 20:1, with many possible design variations. Longer reactors may use multiple feed points. One type of design consists of two zones, each with a different initiator and temperature. Residence times are several minutes, and per-pass conversion is 15-20%.

Reactor effluent enters a series of separators in which the pressure is dropped to flash off unreacted ethylene. In a typical arrangement, pressure in the first separator is 900-4000 psi (60-270 atm). This flashes off 95% of the ethylene, which is recycled to the second compressor. A second separator operates near atmospheric pressure, and the rest of the ethylene is removed and sent to the low-pressure compressor. The separators may be steam-jacketed to prevent excessive heat loss. More separators allow ethylene recycle at higher pressures thereby saving energy,[89] but the additional capital expense of more separators and purifying units is large. Recycled ethylene is cooled by air or water to remove waxes and oils, and usually is fractionated to remove other impurities that would otherwise build up. If the LDPE plant is colocated with the ethylene plant, some of the ethylene may be sent back to the ethylene fractionation train for purification.

Semiliquid polymer from the separator is sent to a screw extruder, where it is forced through 1/8-in. (3-mm) diameter dies, cooled with a water bath, and cut with a rotating knife into pellets. The pellets are dried over screens (with the water going to recycle) and then dried further with a countercurrent flow of hot air. Dried pellets are sent to "make hoppers" or storage silos that hold 30,000-100,000 lb (13.6-45.5 t). Samples are taken periodically to check on polymer quality. Off-grade material or wide specification lots (less than 10% of total plant output) are generated during reactor condition changes or upsets. These are blended and sometimes reextruded and sold as nonprime. A small percentage of the production is badly contaminated material (e.g., floor sweepings). This is sold to scrap buyers. Additives such as antioxidants, slip agents (to give final products a desired coefficient of friction), and sometimes pigments are blended with the pellets. Finished pellets can be shipped in lots from 50-lb (23-kg) lined paper bags to 200,000-lb (91-t) railroad cars.

Energy use in LDPE production is cited in previous reports as 6,600-10,000 Btu/lb (15.3-23 kJ/g) electricity, plus a quantity of steam.[25,26] (An industrial source judges these numbers rather high.[68]) In the mid-1970s, a specific operating plant consumed 10,000-15,000 Btu/lb (23-34 kJ/g), of which 75% typically was for compression and 25% for extrusion. Retrofitting the plant with electric compressors (now complete) was expected to save half of the compression energy, yielding an overall process energy of 6200-9500 Btu/lb (14.4-22 kJ/g). Such a large change in energy requirements with a single equipment modification implies the possibility of large plant-to-plant variations. It is interesting to note that about 2.5% of the process energy could be saved through reduced reextrusion by lowering product optical specifications. Current best estimates of the energy and materials flow in modern LDPE production plants using industrial flow sheets are summarized in Fig. 4.28.

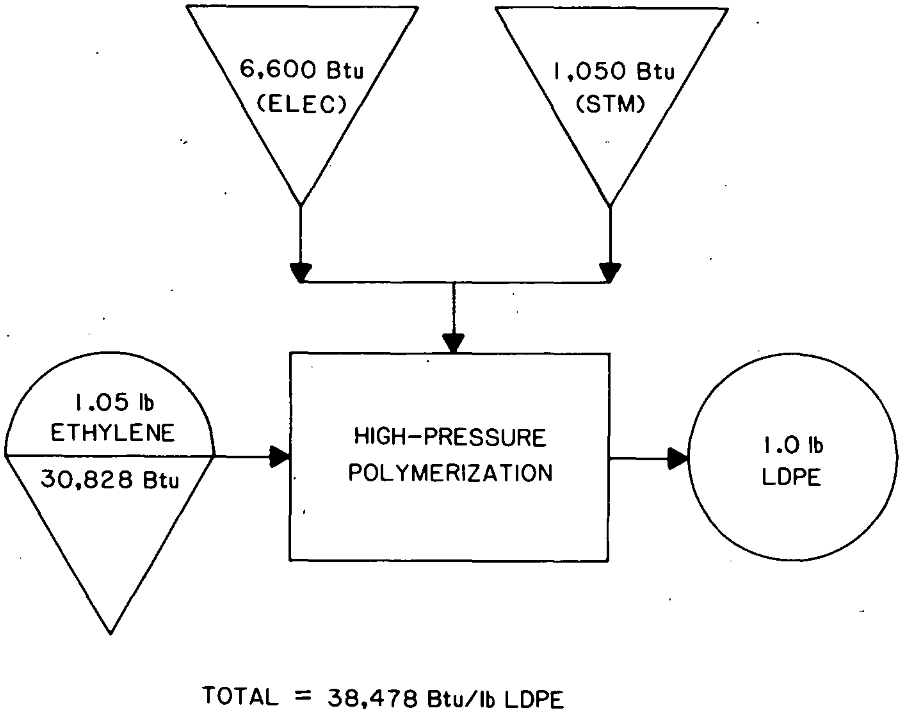


Fig. 4.28. Energy and Materials Flow for LDPE Production (Sources: Refs. 69 and 89)

High-Density Polyethylene

High-density polyethylene is manufactured by polymerizing ethylene in the presence of one of the following basic catalyst systems: (1) chromium oxide on silica or silica/alumina or (2) titanium tetrachloride partially reduced and activated by an aluminum alkyl (Ziegler-type catalyst). Recent process research has developed highly active catalysts that leave negligible residue, thus eliminating the need to remove catalysts from the product. Progress has also been made to control the properties of the product by varying catalyst composition and by regulating the reactor operating conditions.

Major commercial processes are distinguished by reactor type. Reactors operate in either the liquid phase or the gas phase. Those operating in the liquid phase produce polymer either as a solution or as a slurry, depending on temperature, pressure, and diluent.

Liquid-phase solution processes using metal oxide catalysts were originally developed by Phillips Petroleum Co. (supported chromium oxide) and Standard Oil Co. (supported molybdenum oxide). Although some of the plants are still in operation, the processes are considered obsolete. Modern liquid-phase solution processes use high-activity Ziegler catalysts and are operated by Dow, DuPont, and Stamicarbon.

Figure 4.29 shows the flow of a typical liquid-phase, Ziegler-Natta process. The Ziegler catalyst is prepared in two steps from titanium tetrachloride and diethyl aluminum chloride in a hydrocarbon diluent. The catalyst slurry is fed, together with ethylene and hydrogen (to control molecular

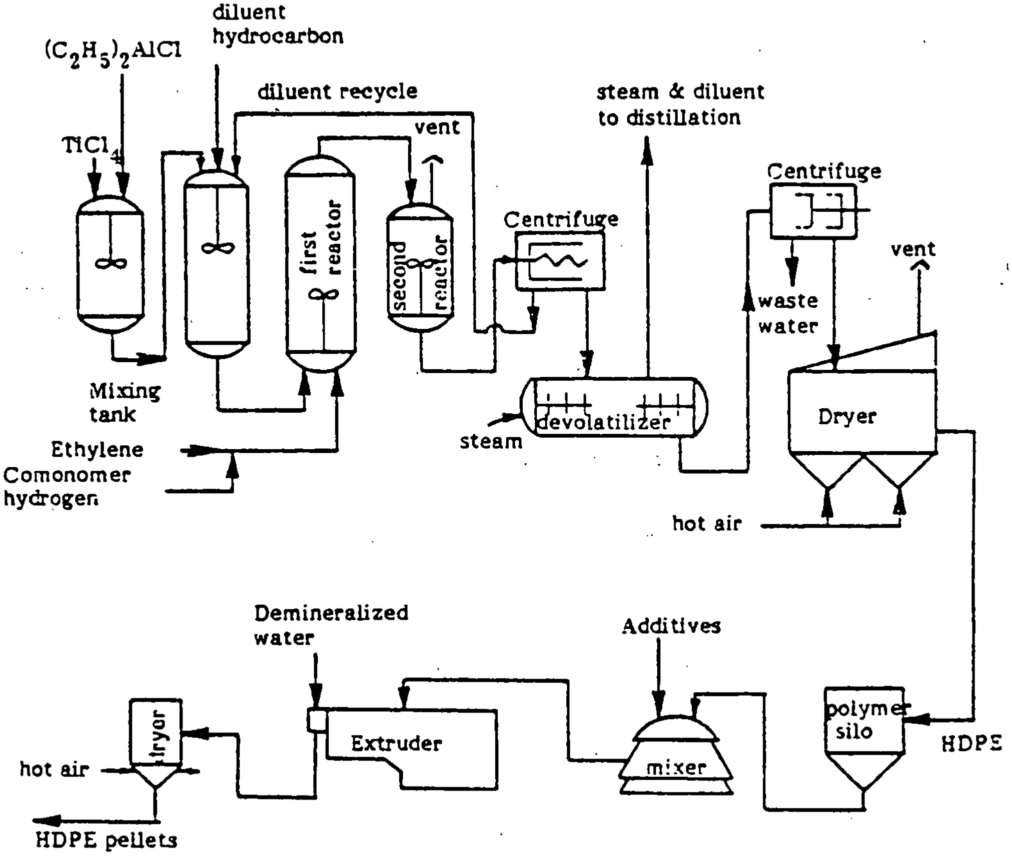


Fig. 4.29. Process Flow for Liquid-Phase Production of HDPE Films Resins (Source: Ref. 69)

weight), into the agitated first polymerization reactor maintained at 175-195°F (80-90°C) and 100 psi (7 atm). The polymeric suspension formed flows continuously into a second reactor of one-tenth the size of the first. A high-activity catalyst has made it possible to eliminate the catalyst residue removal section and to produce 2200 lb (1000 kg) of HDPE per 1 g of titanium. Due to almost complete conversion of ethylene (98-99%), this process does not require any ethylene recycle or monomer recovery system.

The HDPE/diluent stream is transferred to a centrifuge, where about 90% of the diluent is separated at atmospheric pressure and recycled. The remaining diluent is stripped out by steam. The water-wet HDPE is centrifuged and dried in a fluidized bed air dryer. The HDPE powder can then be processed as such, but it is more common for it to be blended and extruded into colored, modified or stabilized pellets for shipment to film producers. The extrusion section accounts for a large portion of the total plant construction cost. There is a growing tendency to use large, twin-screw extruders with capacities up to 40,000 lb/hr (18 t/hr), apparently allowing a single extruder for each reactor line.

Gas-phase processes using high-activity catalysts are operated by Union Carbide (supported chromium oxide), Napthachimie (supported Ziegler catalyst), BASF, Amoco, and Cities Service. Patents on gas-phase polymerization of ethylene using chromium as a catalyst were filed by Phillips Petroleum Co. as early as 1957. The Union Carbide Corp., however, first brought such a process into commercial operation and now claims a savings of about 25% in plant investment and 15% in operating cost over liquid-phase HDPE processes. The process flow is shown in Fig. 4.30. Gaseous ethylene, with or without comonomers, is fed into the fluidized bed reactor maintained at 185-220°F (85-105°C) and 300 psi (20 atm), where catalyst is added. Circulating ethylene fluidizes the reactor contents, acts as a monomer source, and is a medium for heat removal in external coolers. Granular polymer, consisting of 95% HDPE and 5% monomer is discharged intermittently into the degassifying bin. Polymer density may be controlled between 0.94 g/cc and 0.966 g/cc, and melt indices range from 0.1 to above 30. Union Carbide reports that use of a high-efficiency catalyst in rigidly controlled conditions and elimination of solvents and high-temperature drying offers several advantages for film grades. First, heat history is reduced by bypassing a pelletizing step, since the process can produce resin in granular form. Second, there are no gels (large polymer masses of high molecular weight) to disrupt film blowing. Finally, the process is claimed to result in less discoloration and contamination, since monomer and traces of catalyst are the only materials added to the reactor.

Electricity required in the production of HDPE is reported to be approximately 0.3-0.4 kWh/lb (7-10 kJ/g), and total energy associated with polymerization processes is approximately 6000-8000 Btu/lb (13.9-18.6 kJ/g).[93,94] A weighted average of the total process energy based on current

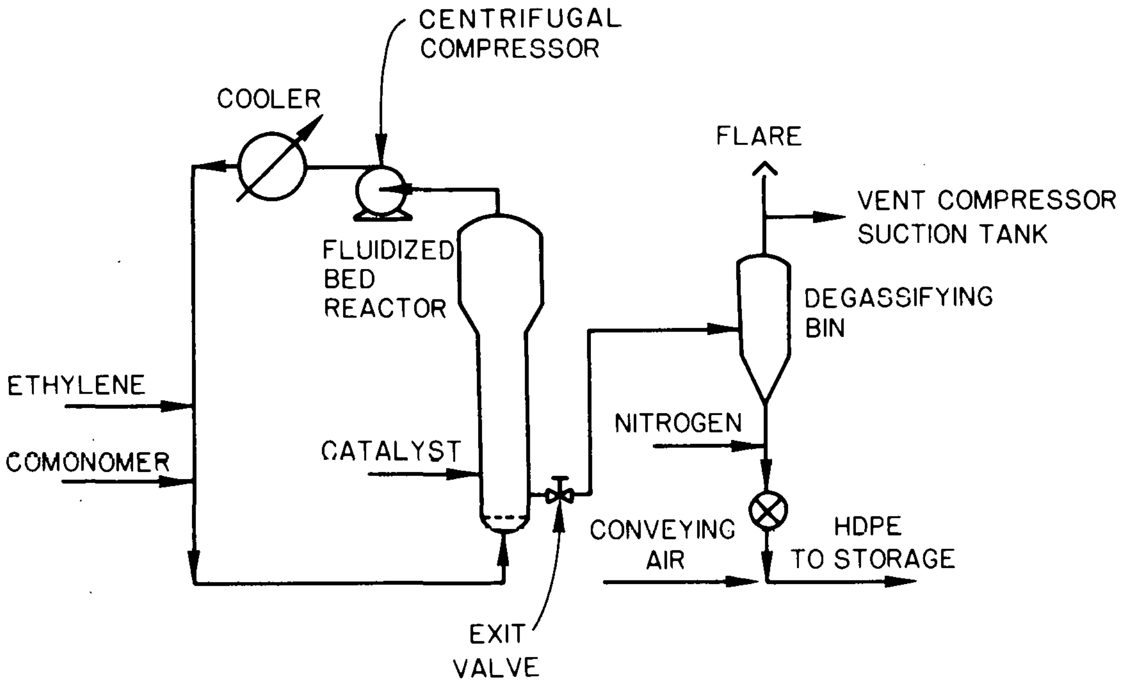


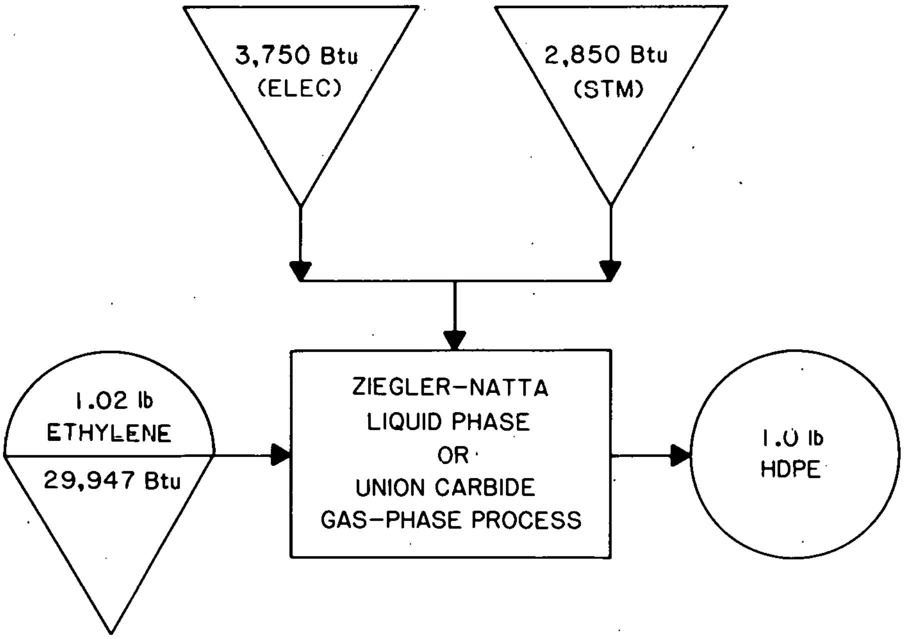
Fig. 4.30. Process Flow of the Union Carbide Vapor-Phase Process for HDPE (Source: Ref. 89)

process flow sheets and capacities is estimated to be 6600 Btu/lb (15.3 kJ/g (see Fig. 4.31).

Polypropylene

Polypropylene is produced only by a Ziegler-type catalyst. Two types of polymerization processes are in use: (1) liquid-phase polymerization of polymer-grade (99+%) propylene over titanium chlorides and alkyl aluminum compounds and (2) gas-phase polymerization.

Liquid-phase polymerization is the more conventional process and is still popular. Propylene is polymerized near room temperature in a hydrocarbon solvent employing just enough pressure to insure the concentration of propylene in the solvent necessary for efficient propagation. If the methyl branches on the resultant polymer chain are oriented in the same direction (stereospecificity), the chains form highly crystalline regions (also called isotactic polymer). If the methyl groups have varying orientations, the product in that molecular region is an amorphous polymer (called atactic) of much less desirable properties for many applications. The best polypropylene technology produces highly isotactic polymers, which have only minor amounts of atactic polymer randomly distributed. Historically, producers have been unable to limit production of atactic polymer to an acceptable level. Therefore, considerable amounts of atactic have to be removed and disposed of in order to upgrade the physical properties of the product. Less than half of the atactic is sold at low prices for use in hot melt adhesives, some is burned as fuel, and some is buried in landfills. DOE is funding a demonstration of the conversion of atactic polypropylene to fuel oil.



TOTAL = 36,547 Btu/lb HDPE

Fig. 4.31. Energy and Materials Flow for HDPE Production (Source: Ref. 72)

Most of the catalyst residue also must be removed, once the polymer particles have grown to the desired molecular weight. Residual titanium and aluminum could cause degradation and poor electrical properties.

A general liquid-phase process involves the following process steps:

1. Reaction in a hydrocarbon solvent (needed to reduce viscosity).
2. Flashing and recycling of some unreacted propylene.
3. Removal and recycle of hydrocarbon solvent by atactic polymer removal.
4. Alcohol extraction of metallic catalyst residues ("deashing").
5. Drying.
6. Compounding and pelletizing.

An important element of recent polypropylene technology development is the constant effort to reduce the number of steps. Each of the processing steps listed above has been eliminated or considerably simplified in at least one process now under construction or final development for the U.S. market.

The product mix of a typical U.S. polypropylene producer also includes ethylene copolymers, which are required to give improved low-temperature flexibility and higher impact resistance for certain applications. Ethylene is much more reactive in contact with a Ziegler catalyst. There is a considerable amount of proprietary technology concerning how best to add this comonomer to achieve block and random copolymers. Older processes resort to blending elastomers into polypropylene homopolymer. In later processes, prepolymers were combined and reacted to final molecular weight. The latest technology claims superior copolymer performance through novel reactor design.

Each individual line of operation generally achieves the desired range of performance properties required of polypropylene resins in four ways:

- Comonomers or polymer alloys are used to incorporate ethylene for low-temperature flexibility.
- Molecular weight is controlled by adding hydrogen to terminate chains.
- Additives enhance color, stability, flame retardancy, and clarity.
- Reinforcement and filling adds strength and rigidity.

Typical ratios of raw materials to end products for copolymerization are 0.93 lb (0.42 kg) of polymer-grade propylene and 0.15 lb (0.06 kg) of ethylene to produce 1.00 lb (0.45 kg) of high-impact copolymer. For homopolymer, about 1.08 lb (0.48 kg) of propylene would be required.

BASF has a number of patents on gas-phase polymerization of propylene. As with Union Carbide, the patents for gas-phase polymerization of ethylene use chromium catalysts.[95,96] The patents for gas-phase polymerization of propylene use titanium trichloride mostly in the widely used $TiCl_3 \cdot 1/3AlCl_3$ form. According to the patent literature, the catalyst appears to be little different from that typically used in liquid-phase operation. The success of BASF's gas-phase process appears to depend mainly on development of a reactor that uses liquid propylene injection to absorb the heat of polymerization. According to industrial estimates, the gas-phase polymerization process uses about as much energy as the liquid-phase process; the average process energy consumption is estimated at about 5200 Btu/lb (12.09 kJ/g) polypropylene produced. At current capacities, each pound of polypropylene consumes about 1.045 lb (0.47 kg) of propylene. The energy and materials flow based on averages of modern Ziegler-catalyst (liquid-phase) processes is summarized in Fig. 4.32.

Linear Low-Density Polyethylene

The most significant new development in polyethylene processes is the use of low-pressure routes to produce the medium- and low-density polyethylenes with a straight backbone that are known by the generic name of linear low-density polyethylene. Several processes commercially output grades of polyethylene that fall in the LLDPE category:

- DuPont Canada (late 1950s) produces Sclair LLDPE and HDPE.
- Phillips Chemical (late 1960s) produces Marles LLDPE and HDPE.

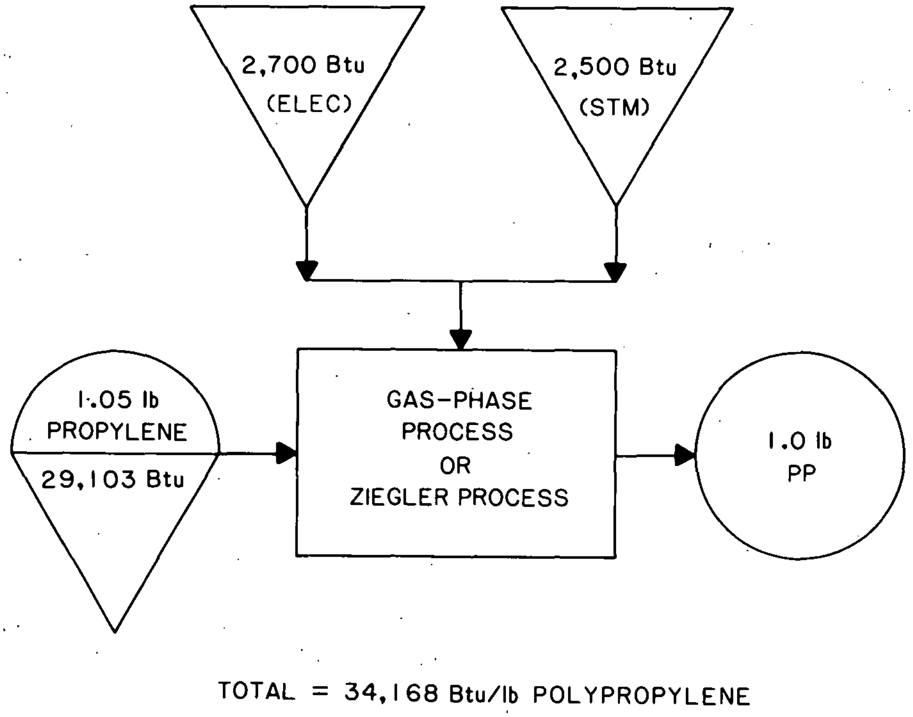


Fig. 4.32. Energy and Materials Flow for Polypropylene Production (Source: Ref. 72)

- Union Carbide (1977) uses gas-phase Unipol processes to produce LLDPE.
- Dow Chemical (1977) yields Dowlex LLDPE.

Other processes not yet commercialized include the gas-phase HDPE processes of Amoco and Cities Service.

The low-pressure gas-phase LLDPE process is an extension of the linear HDPE technology. The Dow process uses the liquid-phase (solution) route and Ziegler catalysts. The use of lower pressure in the production of LLDPE compared to LDPE leads to lower plant costs and lower energy usage. The product is a coarse powder unlike the conventional LDPE pellets, and its processing properties differ from those of the LDPE resins.

In Union Carbide's Unipol process, described in detail here, gaseous ethylene and comonomer are fed continuously into a fluidized-bed reactor (see Fig. 4.33). Catalyst is added separately. The pressure inside the Unipol reactor is only about 100-300 psia (6.8-20.4 atm), and the temperature is controlled at about 212°F (100°C). A small compressor circulates the gas stream through a cooler, which removes the exothermic heat of reaction from the fluidized bed of polymer. Cooled monomer is then recycled to the reactor. Polyethylene is removed directly from the reactor through a gas-lock chamber -- a major difference from the conventional process for LDPE. This

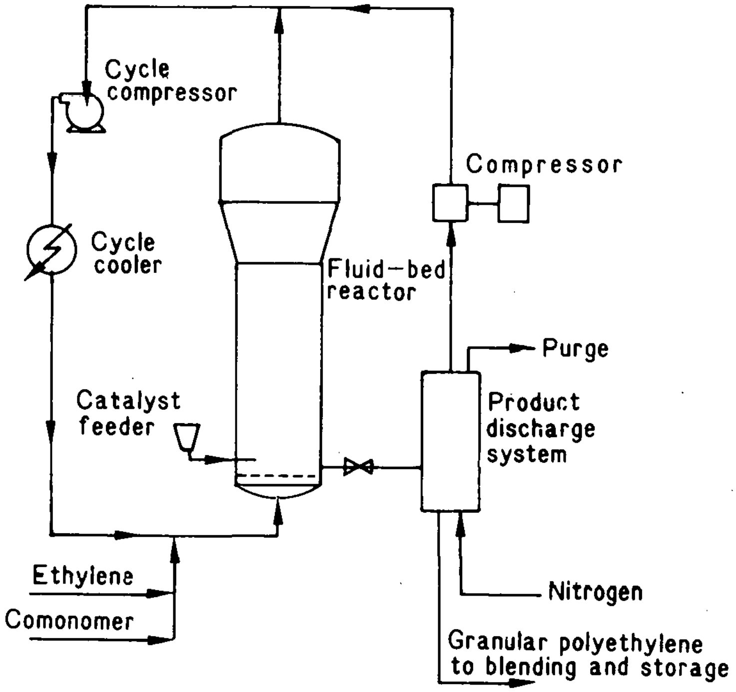


Fig. 4.33. Process Flow for Low-Pressure Fluidized-Bed Production of LLDPE (Source: Ref. 97)

chamber purges the small amount of residual monomer that accompanies the granular polymer. Catalyst productivity is high, so there is no need to remove catalyst residue. The low-molecular-weight fraction also need not be removed, as it is produced in extremely small quantities. The product is sold not as pellets but as a granular powder resembling laundry detergent. Particle size varies but averages 0.05-0.1 mm.

The family of catalysts, which is the key to the low-pressure process, is made batchwise because of the quantities required. Any interbatch change in activity in the catalyst results in variations in the polymer. The catalysts based on chromium oxide are supported on finely divided silica of critical particle size and porosity. Union Carbide's patent recommends the use of microspheroidal silica with a surface area of 300 m^2/g, a pore diameter of about 200 Å, and an average particle size of 70 μ.[98]

An example of catalyst preparation begins with slurrying the finely divided silica in a solution of chromium oxide in water for 15 min. The wet silica is dried under a stream of nitrogen for 4 hr at 392°F (200°C), slurried with isopentane and tetraisopropyl titanate, and further dried in nitrogen. The activation of the catalyst is performed in several steps: (1) replacement of the nitrogen blanket by dry air, (2) activation at 572°F (300°C) for 2 hr, (3) activation at 1472°F (800°C) for 8 hr, (4) cooling to 302°F (150°C) with dry air, and (5) cooling to room temperature with pure nitrogen.

Nitrogen is used to inject the catalyst continuously into the reactor about half way up the fluidized bed to insure rapid mixing. The temperature is kept constant, and the rate of injection is controlled to balance the required rate of polymer production.

Since only one compressor is used to feed the fluidized reactor, total horsepower is cut by about a factor of six when compared with conventional tubular-reactor LDPE processes. Union Carbide reports overall energy savings of 75% and a capital costs reduction of 50%. The latter advantage is a result of the lack of monomer-stripping equipment and pelletizing machinery.

Liquid-phase LLDPE suppliers say that resins based on the gas-phase process present a processing complication because of their granular form. Plastics processors are unable to deal with both granular and pelletized products. Therefore, slip and antiblock additions in conventional LDPE and liquid-phase LLDPE are incorporated during pelletizing at the resin plant. A possible alternative seems to be blending ground additive masterbatch with the granules. Otherwise, the energy savings in not having to pelletize may be lost.

The catalysts allow polymerization with one or more alpha-olefins: 1 lb (0.45 kg) of LLDPE requires an input of 0.99 lb (0.44 kg) of ethylene and 0.04 lb (0.01 kg) of butene-1. The energy required for the low-pressure processes is mostly electrical and is estimated to be 1800 Btu/lb (4.1 kJ/g) (see Fig. 4.34).

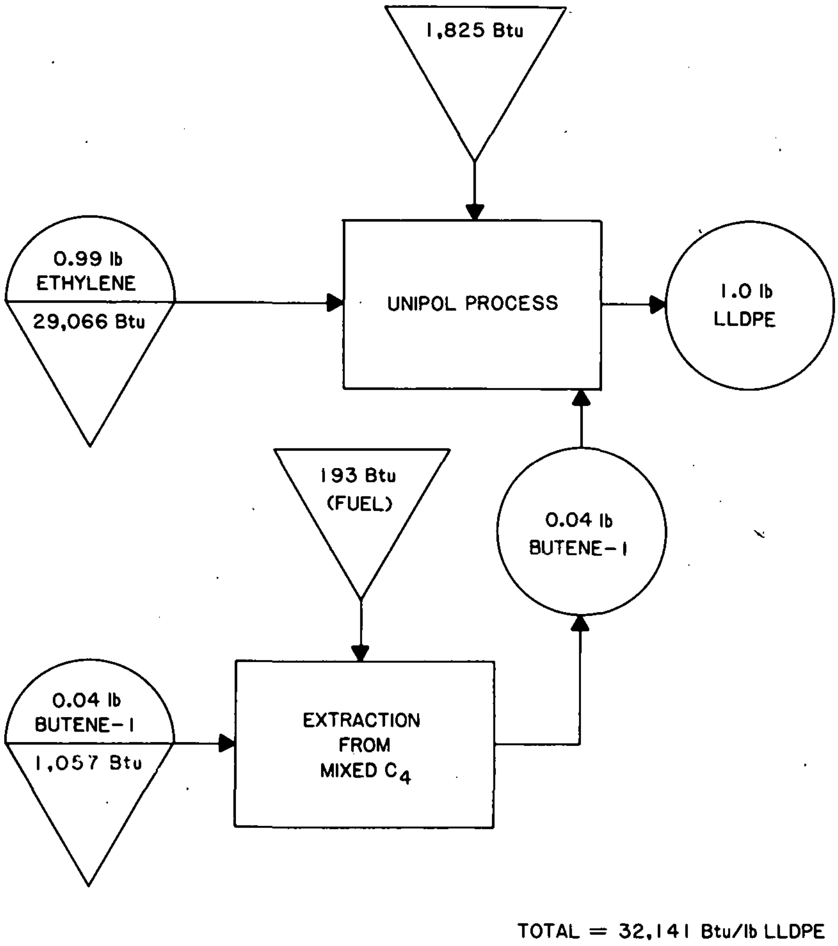


Fig. 4.34. Energy and Materials Flows for LLDPE Production

Polystyrene

Polystyrene can be made by any of the standard polymerization techniques described above, but production is dominated by bulk processes and modified bulk processes in which a small quantity of solvent, such as cyclohexane, is added to reduce viscosity and improve heat transfer (see Fig. 4.35). Suspension polymerization is the second most important process and is used for the production of polystyrene foam. The various production methods differ in cost, energy use, and polymer properties, although the latter are also affected by reaction conditions. Bulk processes are cheapest and probably the least energy intensive.[26] Even though no solvent removal or drying is necessary, some energy is required to agitate the viscous liquid. No additives are required to produce a high-purity product. Suspension and solution polymers are of lower purity, but the reactor is simple and inexpensive, and the conversion cost is low. Total cost and energy use may be higher because of water or solvent removal. Emulsion polymerization requires the least initial capital investment, but energy use is high due to water removal. The product has a high molecular weight, which is desirable for some

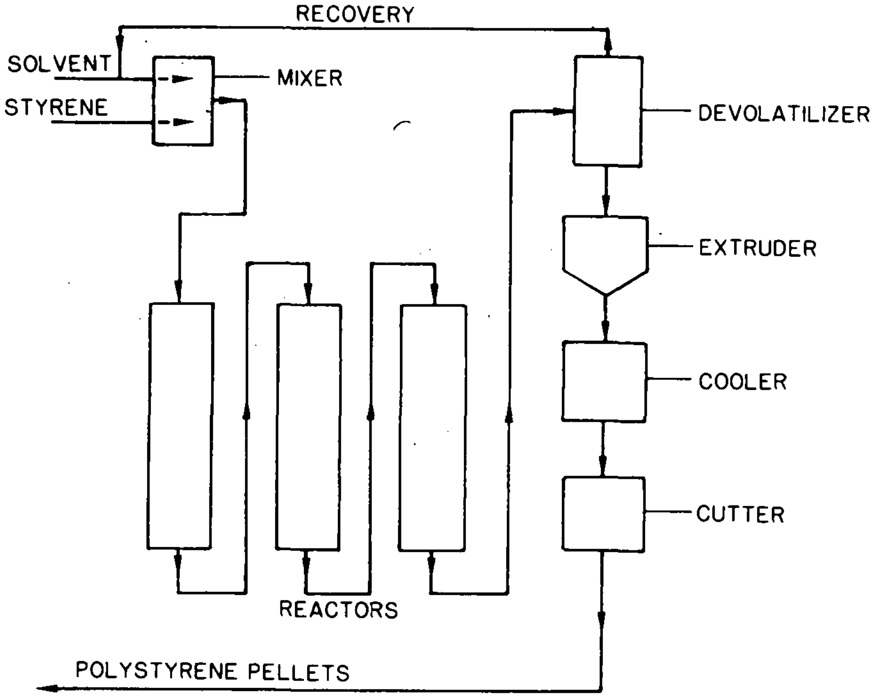


Fig. 4.35. Process Flow for Polystyrene Production
(Source: Ref. 9)

applications. Clarity and color are inferior. To summarize, the technique used for production of polystyrene will be dictated by costs and product requirements.

Polymerization of styrene occurs at normal room temperature and pressure with no initiator. However, the rate increases exponentially with temperature.[35] The reaction takes months at room temperature and hours at 300°F (150°C). Presence of an initiator increases the rate even further, with the reaction going to completion in 90 min at 160°F (70°C). An initiator generally is used at moderate temperatures, since polystyrene produced at high temperatures tends to have a low molecular weight and be weak and brittle. In addition, temperature control to avoid runaway reaction is more difficult and expensive at higher temperatures.

Bulk polymerization of styrene is performed continuously or in batches; overall conversion to polymer is over 97%. The continuous processes used by large manufacturers differ in detail, but all conform to the same pattern. Styrene monomer is sent to a prepolymerizer, where it is heated. A viscous solution of polymer in monomer is formed, and the viscous mass is pumped to the top of a tower and passed down through regions of carefully controlled increasing temperature. The reaction is completed at the bottom of the tower, where the temperature is about 390°F (200°C). In the Dow process, the prepolymerizer is a stirred reactor or tower, and the mixture is taken to 11-15% conversion before being sent to two agitated towers, where 85-90% conversion is achieved.[26] The BASF process employs an autoclave prepolymerizer and sends a 50% polymer solution to a tower with six heated zones ranging from 212-360°F (100-180°C). The tower product is 95% polystyrene. Union Carbide uses a series of small autoclaves (allowing high heat transfer) to send 85% polymer to a tower where temperatures are 350-420°F (175-215°C) and conversion reaches 95-98%.[26]

The viscous molten polymer is pumped by a screw out of the bottom of the tower (possibly after heating to 536°F [280°C]) through 1/4-in.-diameter die holes to form strands. Unreacted styrene monomer (along with any other volatiles) flashes into vacuum and is recovered for separation and recycle. The strands are cooled and chopped. This product, which is about 99% polystyrene, may be blended with additives and reextruded. Other methods of separating unreacted styrene from the polymer include:

- Vacuum rolling, whereby mechanical work raises the temperature to 435°F (225°C) and low ends are volatilized, and
- Screw devolatilization, which is rapid and minimizes thermal degradation.[26]

When styrene is bulk-polymerized in batches, an autoclave prepolymerizer is used. This increases the product molecular weight. The 30-35% polymer is sent to a chamber reactor, where solid polystyrene blocks are formed. These must be broken up before fabrication.

Suspension polymerization of styrene is carried out in batches in stirred kettle reactors, ranging to over 15,000-gal (57,000-L) capacity, or in jacketed cylinders. Styrene, an initiator (e.g., benzoyl peroxide), stabilizers, and water are added, with water-to-styrene weight ratios of 1:1 to 3:1. This small amount of water is sufficient for heat removal, since the heat of polymerization is only 290 Btu/lb (0.67 kJ/g)[26] (as compared with 1430 Btu/lb or 3.3 kJ/g for ethylene).* Overall conversion is 92.5%. The small beads from suspension polymerization are centrifuged, dried, and stored. They can be molded directly or compounded first.

If a volatile hydrocarbon such as pentane, propylene, or methylene chloride is absorbed during polymerization, the beads will expand on heating with steam or boiling water to produce a foam product. All polystyrene foam, except for Dow's Styrofoam®, is made this way.[30]

Energy use in the polymerization processes is about 1600 Btu/lb (3.75 kJ/g) of polymer,[89] as can be seen in the energy and material flowchart in Fig. 4.36.

Polyvinyl Chloride

The production of polyvinyl chloride from ethylene has three steps:

---

*The molar heats of polymerization are similar (22.35 kcal/mole for polyethylene and 16.5 for polystyrene), but the monomer molecular weights are quite different (28 for ethylene and 104 for styrene).

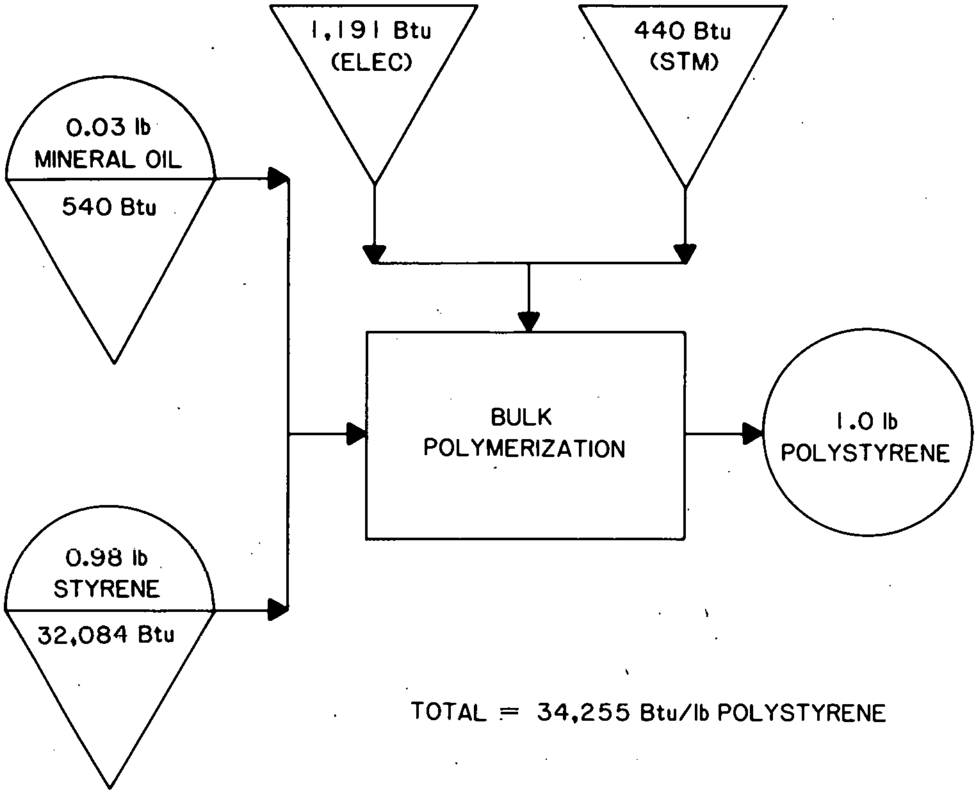


Fig. 4.36. Energy and Materials Flow for Polystyrene Production (Source: Ref. 89)

- Chlorination of ethylene to ethylene dichloride (EDC) (proper name: 1,2-dichloroethane).
- Dehydrochlorination of ethylene dichloride to vinyl chloride monomer (VCM).
- Polymerization of the monomer.

A process flow sheet for monomer production is shown in Fig. 4.37. There are two basic chemical reactions with 92% or better yield used in the production of ethylene dichloride from ethylene (see Eqs. 1 and 3 in Fig. 4.38).

The direct chlorination of ethylene is exothermic (43.9 kcal/mole = 800 Btu/lb or 1.86 kJ/g ethylene dichloride), and cooling is used to keep the temperature at 122°F (50°C). The reaction is carried out at atmospheric pressure in liquid ethylene dichloride in the presence of a metallic chloride catalyst, which, along with the lower temperature, inhibits the formation of more highly chlorinated products. The reactor effluent is washed in corrosion-resistant equipment to remove hydrochloric acid, and the ethylene dichloride, which may be as high as 99.8% purity, is distilled.[30]

Oxychlorination (also called oxidation-chlorination or oxhydrochlorination) of ethylene to ethylene dichloride is also exothermic (57.5 kcal/mole = 1048 Btu/lb or 2.43 kJ/g). Stoichiometric quantities of ethylene,

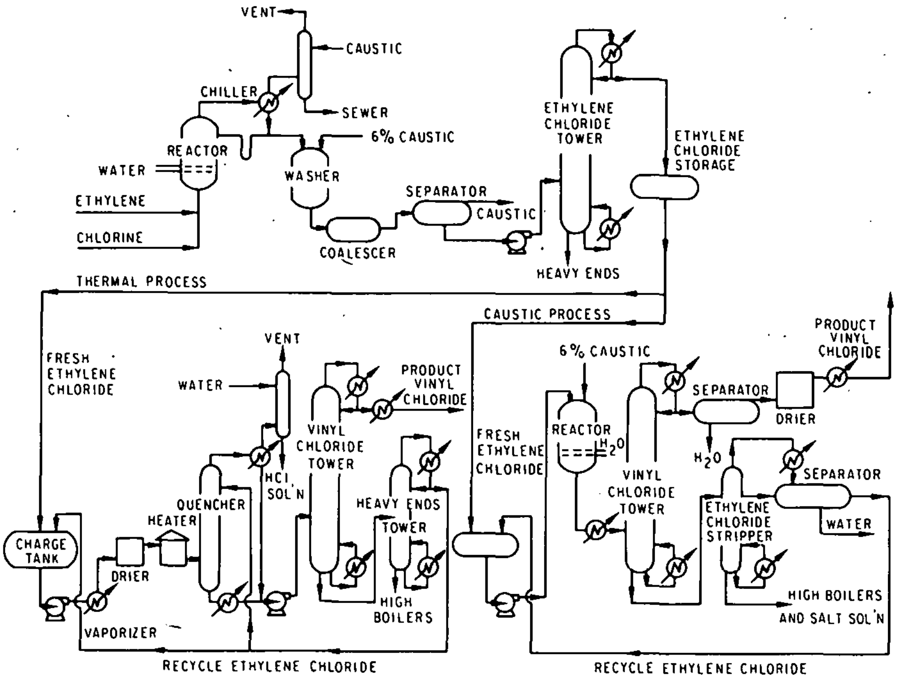


Fig. 4.37. Process Flow for Production of Vinyl Chloride from Ethylene (Source: Ref. 35)

Direct chlorination of ethylene:

$$C_2H_4 + Cl_2 \longrightarrow ClC_2H_4Cl \qquad (1)$$

Thermal dehydrochlorination of EDC (EDC cracking):

$$ClC_2H_4Cl \longrightarrow CH_2 = CHCl + HCl \qquad (2)$$

Oxhydrochlorination of ethylene:

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \longrightarrow ClC_2H_4Cl + H_2O \qquad (3)$$

Fig. 4.38. Chemical Reactions in the Production of Vinyl Chloride (Source: Ref. 9)

hydrochloric acid, and oxygen are reacted in the vapor phase at about 480°F (250°C), at atmospheric (or higher) pressure in a fixed copper chloride catalyst reactor or a fluid catalyst bed.[9] The fixed catalyst must be replaced periodically as activity is lost, but the fluid catalyst bed, which eliminates some corrosion problems, is maintained, with small quantities of fresh catalyst replacing the continuous losses. The catalyst has high thermal conductivity and high heat transfer with the cooling surfaces, leading to the production of one pound of steam at up to 185 psig (13 atm) per pound of ethylene dichloride. Reactor effluent is quenched and scrubbed with water, which absorbs unreacted hydrochloric acid and is treated for disposal. The scrubbed gas is condensed, and ethylene dichloride for distillation is separated from water in a decanter. Alternatively, the reactor effluent may be refrigerated and the water/hydrochloric acid layer decanted off, with ethylene dichloride washed with caustic and distilled. Ethylene dichloride from direct chlorination and oxychlorination may be distilled together to give a high-purity (99.8%) product.

Ethylene dichloride is then cracked thermally (pyrolyzed) to produce vinyl chloride and hydrochloric acid (Eq. 2, Fig. 4.38). The endothermic reaction (16.8 kcal/mole or 306 Btu/lb [0.710 kJ/g EDC]) is carried out at 600-1000°F (315-540°C) and 15-45 psi (1-3 atm) in directly heated tubes, with or without a catalyst. Conversion per pass generally is limited to 50-60% to minimize coke deposition on the tubes from side reactions. Yield of the reaction is 92%,[1] so yield of vinyl chloride from ethylene in the two-stage reaction is about 85%. Several schemes may be used to separate products and ethylene dichloride for recycle from the reactor effluent. A typical procedure is to quench the gases with cold ethylene dichloride, which preheats the ethylene dichloride before reaction. The gas from the quench is scrubbed with water to recover hydrochloric acid and distilled at 73 psi (5 atm) to yield pure vinyl chloride monomer (VCM). Another scheme employs two distillations: the first removing hydrochloric acid overhead and the second VCM overhead with ethylene dichloride bottoms for recycle. In either scheme, hydrochloric acid can be used for oxychlorination of ethylene or chlorine gas regenerated. The energy required for production of VCM from ethylene is about 4100 Btu/lb (9.5 kJ/g), most of which is consumed in the cracking step. The energy and materials flow for VCM production is shown in Fig. 4.39.

It should be noted that the chlorination and dehydrochlorination steps can in principle be combined into a single oxidation-chlorination step that produces vinyl chloride and water from ethylene, chlorine, and oxygen. The reaction takes place at 930°F (500°C) over a $CuCl_2$ catalyst but was not commercial as of 1977 because of low yields.[99]

The most widely used method for the production of polyvinyl chloride in the United States is suspension polymerization. This method has the lowest capital and operating costs, and most fabricated PVC products can be made from the suspension polymer.[9] Suspension polymerization of PVC is typically carried out batchwise in 5-10 parallel reaction trains, each with 5-10 stirred, jacketed reactors feeding a stripper, blending and storage tanks, and a finishing system. Reactor size (2000-6000 gal [7,600-23,000 L]) is determined by reaction rate, temperature, water-to-monomer ratio, and vessel heat transfer characteristics.

Demineralized water containing a suspending agent (gelatin, methyl cellulose, polyvinyl alcohol, or sodium lauryl sulfate) is charged to the reactor, followed by VCM and a peroxide or persulfate free-radical initiator. The water-to-monomer ratio is between 1 and 3.5, and total additives are less than 1%. The temperature is raised to 105-160°F (40-70°C) by hot water in the reactor jacket to start the polymerization. Cooling is required for the remainder of the 10-20 hr of reaction time to remove the 670 Btu/lb (1.6 kJ/g) polymerization energy. Initial pressure is 70-120 psi (5-8 atm), dropping to about 44 psi (3 atm) as monomer is consumed. The reaction is terminated at

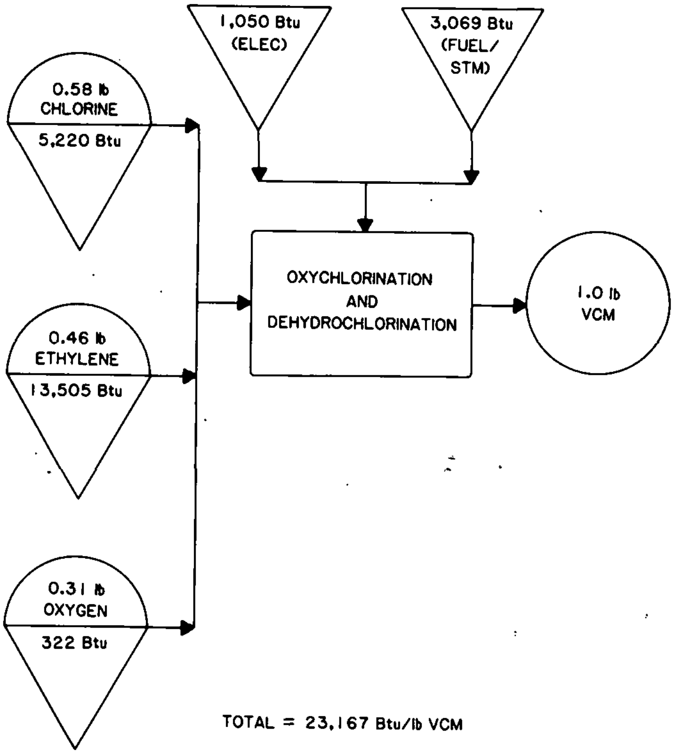
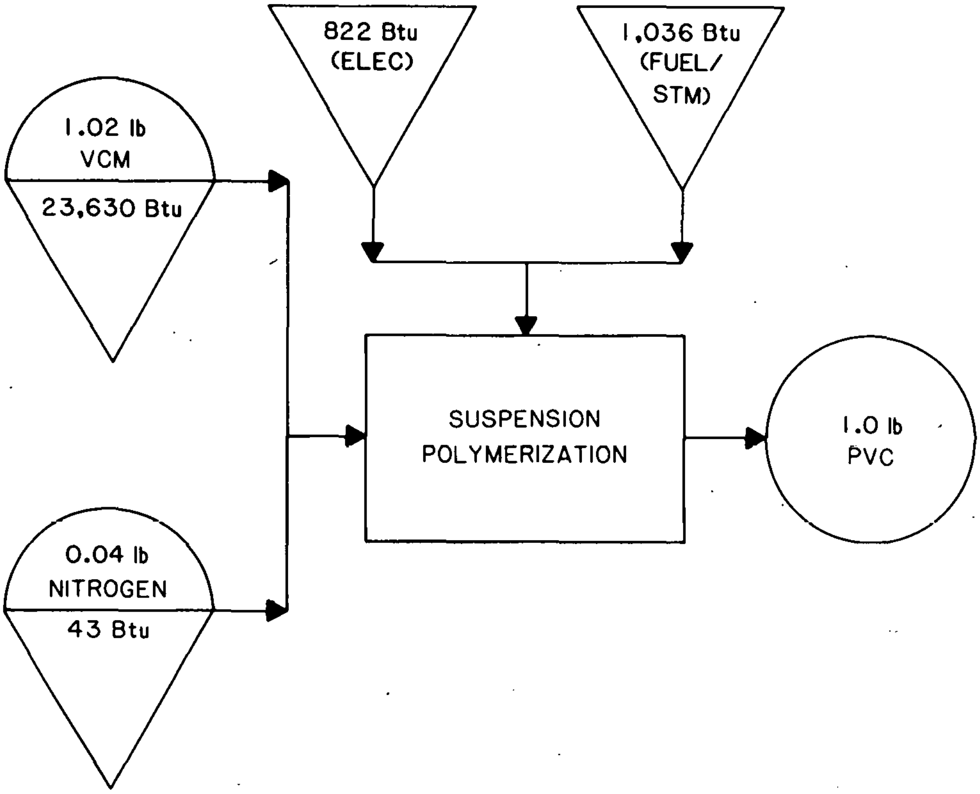


Fig. 4.39. Energy and Materials Flow for Vinyl Chloride Monomer Production (Source: Ref. 69)

90% conversion, since further reaction adversely affects resin color and porosity.[100] The batch is dropped to a stripper, where the 8-10% unreacted monomer is recovered by heating and agitating or under vacuum. Recovered monomer is condensed, distilled, and recycled. Several batches of polymer slurry are blended and stored in an agitated tank prior to being centrifuged, washed, and fed to rotary hot air driers. The polymer is carried by hot air to a collector, where oversized particles are removed by screen, and the product is bagged. The yield of prime resin is 95%.[9] Most sources cite process energy requirements for suspension polymerization of PVC as 3200-6600 Btu/lb (9.7-15.3 kJ/g). A modern plant can achieve energy requirements as low as 1860 Btu/lb (4.3 kJ/g) (see Fig. 4.40).

Energy required by bulk polymerization should be less because no water removal is required. In a typical bulk process, the reaction is initiated by heat in a prepolymerizer, where half the batch reaches 10% conversion. This material serves as a seed for the entire batch in a stirred, jacketed autoclave, which is kept at 140°F (60°C) under pressure. The reaction is stopped at low conversion by evaporating unreacted monomer (for recycle) and removing monomer dissolved in the product under vacuum.

Emulsion polymerization of vinyl chloride is a continuous process and therefore has lower labor costs. The product is too fine to filter off and must be used as an emulsion or must be spray-dried to a powder at considerable energy cost. The emulsifying agents are difficult to remove, but they act as lubricants and make the product easier to process.



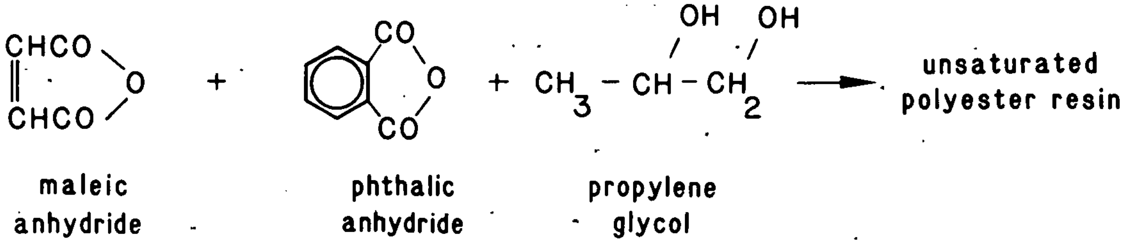
TOTAL = 25,631 Btu/lb PVC

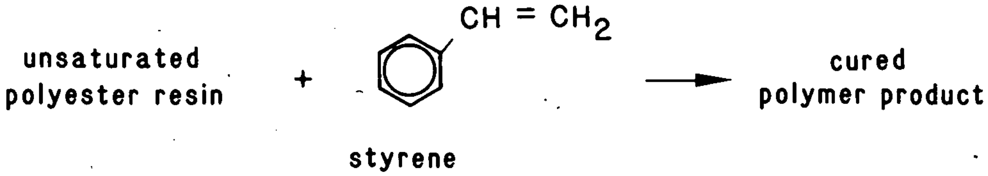
Fig. 4.40. Energy and Materials Flow for Polyvinyl Chloride Production (Source: Ref. 69)

Fiber-Reinforced Plastics

The majority of fiber-reinforced plastics employs an unsaturated polyester resin with glass fiber reinforcement. An inert filler, usually calcium carbonate, is often used to reduce costs and to improve material flow characteristics. The filler reduces the composite's viscosity so that complete, uniform molding can be achieved at a lower pressure. Some fillers, such as aluminum trihydroxide, also improve product flame resistance and electrical properties. Typically, the plastic resin represents 25-30% of the total composite weight. Chemically, unsaturated polyester resin products are thermosetting plastics formed in a two-step chemical sequence. First, a mixture of saturated and unsaturated dibasic acids (or anhydrides) combines with a polyhydric alcohol to form the unsaturated polyester resin. Second, reactive monomer combines with the unsaturated polyester resin to form the cured product. During the latter step, the reacting material is shaped under pressure to the desired product shape (molding) while the curing reaction takes place.

The most widely used unsaturated polyester resins are formed from: (1) maleic anhydride, as the unsaturated anhydride; (2) phthalic anhydride, as the saturated anhydride; (3) propylene glycol, as the polyhydric alcohol; and (4) styrene, as the reactive monomer. The chemical reaction sequence is:





4.3.1.3 Production of Fibers

Acrylics

Polyacrylonitrile (PAN) is an addition polymer of acrylonitrile (vinyl cyanide), which is produced in the United States exclusively from propylene and ammonia. All plants constructed since the early 1960s, when the Standard Oil of Ohio (Sohio) process was commercialized, are based on this process. The Sohio process, illustrated in Fig. 4.41, employs the following chemical reaction:

$$\underset{\text{propylene}}{CH_2{=}CH{-}CH_3} + \underset{\text{ammonia}}{NH_3} + 1.5O_2 \longrightarrow \underset{\text{acrylonitrile}}{CH_2{=}CH{-}C{\equiv}N} + 3H_2O$$

The vapor-phase reactants (chemical-grade propylene and anhydrous fertilizer-grade ammonia) are fed in approximately stoichiometric quantities to a catalytic, fluidized-bed reactor, where contact time is on the order of several seconds. Originally, the catalyst was based on molybdenum and bismuth, but it has been improved to increase yields and selectivity (details are proprietary). The reaction, which is carried out at 750-950°F (400-510°C) and 15-44 psi (1-3 atm) is exothermic, and high-pressure steam is generated from cooling water passing through the reactor in tubes. Effluent from the reactor is neutralized and scrubbed with water in a counter-current absorber to remove unreacted ammonia. The temperature in the absorber is below 75°F (24°C) to prevent the reaction of acrylonitrile with aqueous ammonia. The organic products are stripped from the water solution, and hydrogen cyanide (HCN) by-product is fractionated off. Acrylonitrile and acetonitrile are separated and purified in a series of conventional and azeotropic or extractive distillation columns. Conversion of propylene to

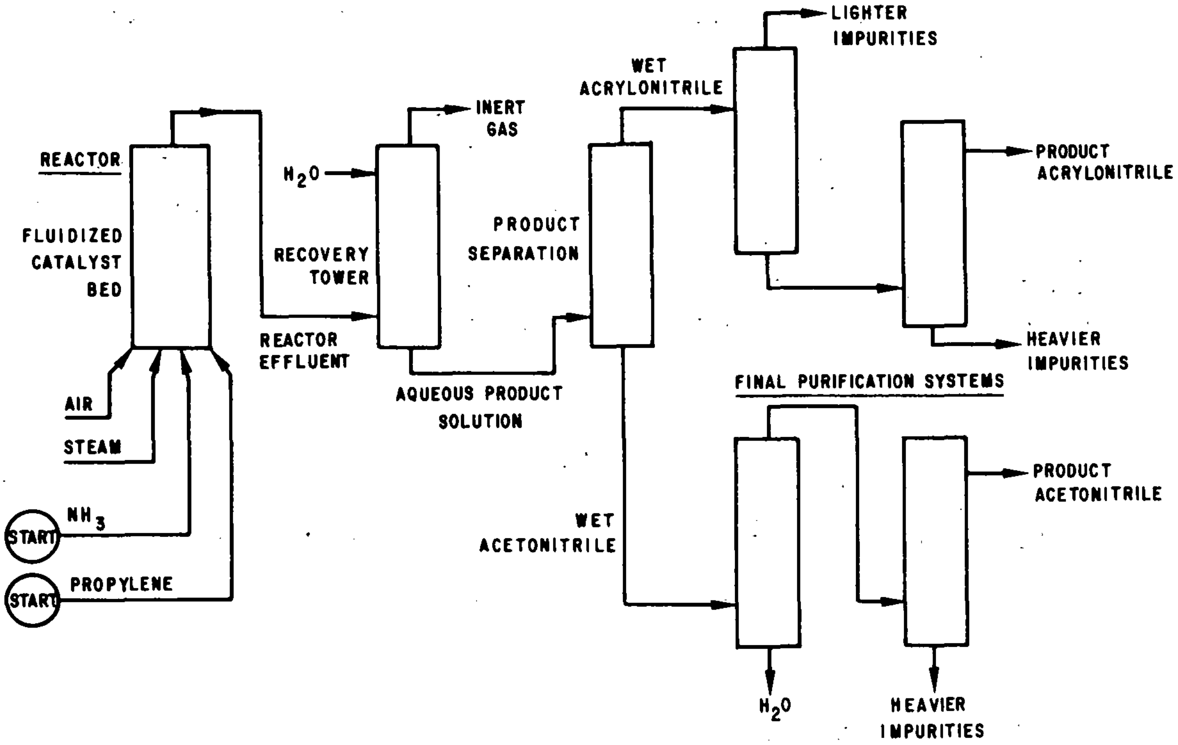


Fig. 4.41. Process Flow for Production of Acrylonitrile from Propylene (Source: Ref. 100)

products is complete, with a yield of about 0.85 lb (0.39 kg) acrylonitrile per pound of feed or about 70%. About 0.1 lb (0.004 kg) acetonitrile and 0.1 lb (0.004 kg) hydrogen cyanide per pound of acrylonitrile are produced from competing reactions.

Acrylonitrile is moderately soluble in water and is usually polymerized in water solution or suspension using a water-soluble, free-radical or anionic initiator to start and accelerate the reaction. In a typical process, sulfuric acid is added to a water solution of 6% acrylonitrile and 0.1% initiator in sufficient quantity to lower the pH to 3.2. The reaction is exothermic by 18.5 kcal/mole (630 Btu/lb or 1.5 kJ/g), and cooling is required to maintain the temperature at 100-120°F (38-50°C). The polymer is insoluble in water and precipitates as an ivory-white powder, which is separated and dried. Commercial production of acrylic fibers had to wait until 1950, when suitable solvents for the polymer were discovered. Highly polar organic solvents such as dimethyl formamide, strong mineral acids, or concentrated inorganic salts, such as lithium bromide, are used for dissolving the polymer, which is then filtered and spun. Acrylic fibers may be either dry-spun (Orlon) or wet-spun (Acrilan). In the dry-spinning method, the viscous solution is forced through spinnerets, with the solvent evaporating to leave a dry fiber. In the wet-spinning method (see Fig. 4.42), the fiber from spinnerets is coagulated in a bath. Acrylic fibers cannot be melt-spun, as they degrade at or below the melting point. The weak fibers are drawn at elevated temperature to three to eight times their length in order to orient

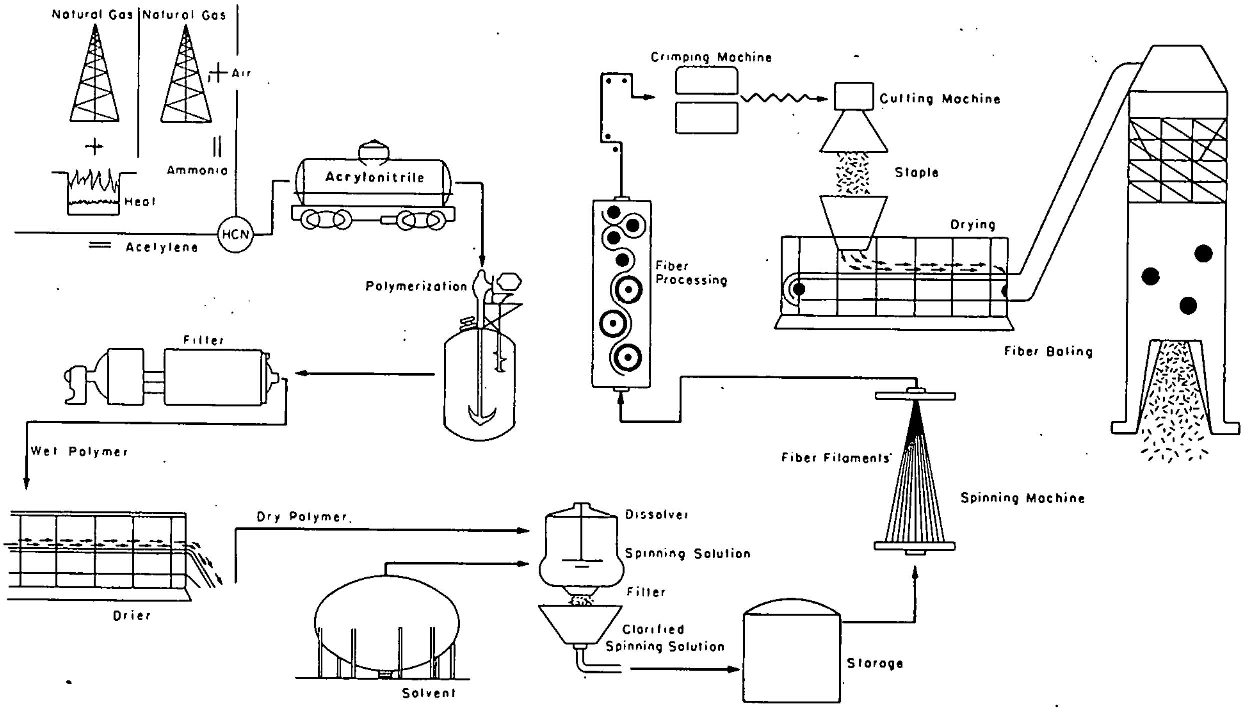


Fig. 4.42. Process Flow for Acrylic Fiber Production (Source: Ref. 35)

the molecules parallel to the fiber axis for greater strength. Product properties depend on spinning and stretching methods, as well as on modifiers added during polymerization.

Recent developments in acrylic fiber manufacture center on finding solvents, such as dimethyl sulfoxide, in which both monomer and polymer are soluble. Such a solvent would eliminate the polymer separation, drying, and redissolution steps, thereby reducing both energy use and financial costs. It is not known whether this process improvement is currently in use.

Energy and material requirements for the production and polymerization of acrylonitrile are shown in Figs. 4.43 and 4.44. Note that the energy consumed for monomer production is allocated uniformly on a weight basis to the coproducts as well as the main product. This is because the coproducts are of substantially greater unit value as products rather than as fuels.

Polyester

Polyethylene terephthalate is a condensation polymer made from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). TPA is made by oxidation with air or nitric acid of p-xylene, which is obtained from BTX production at refineries, or recovered from olefin plant coproducts, while DMT is produced by esterification of TPA with methanol. These two reactions are shown in Fig. 4.45. Either compound (DMT or TPA)

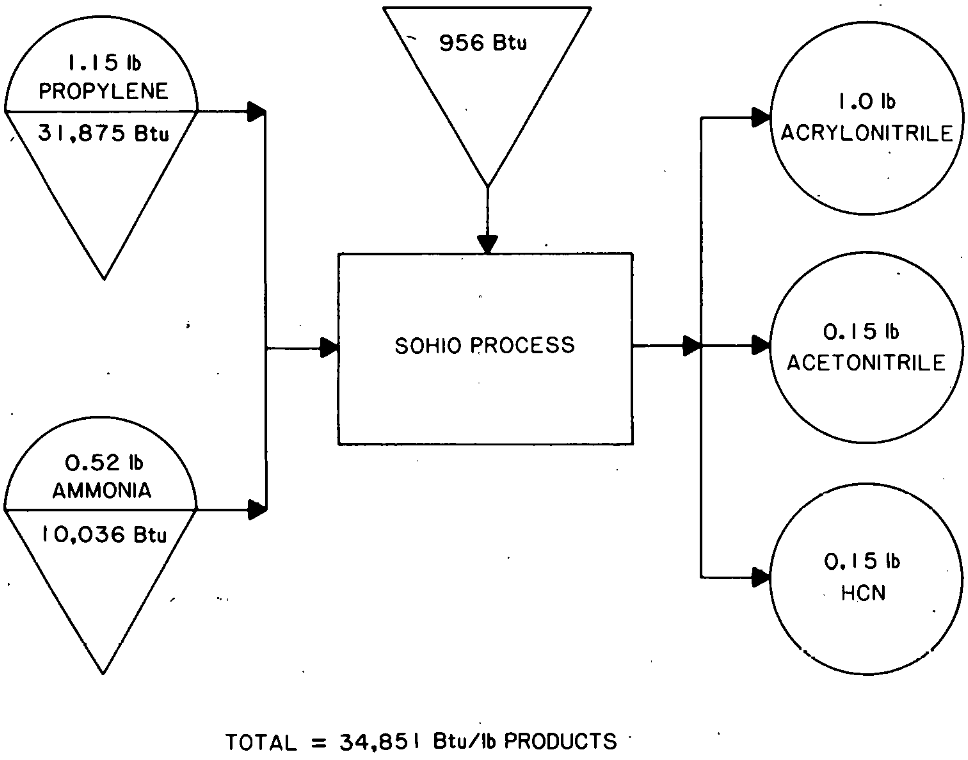


Fig. 4.43. Energy and Materials Flow for Acrylonitrile Production (Sources: Refs. 89, 101, and 102)

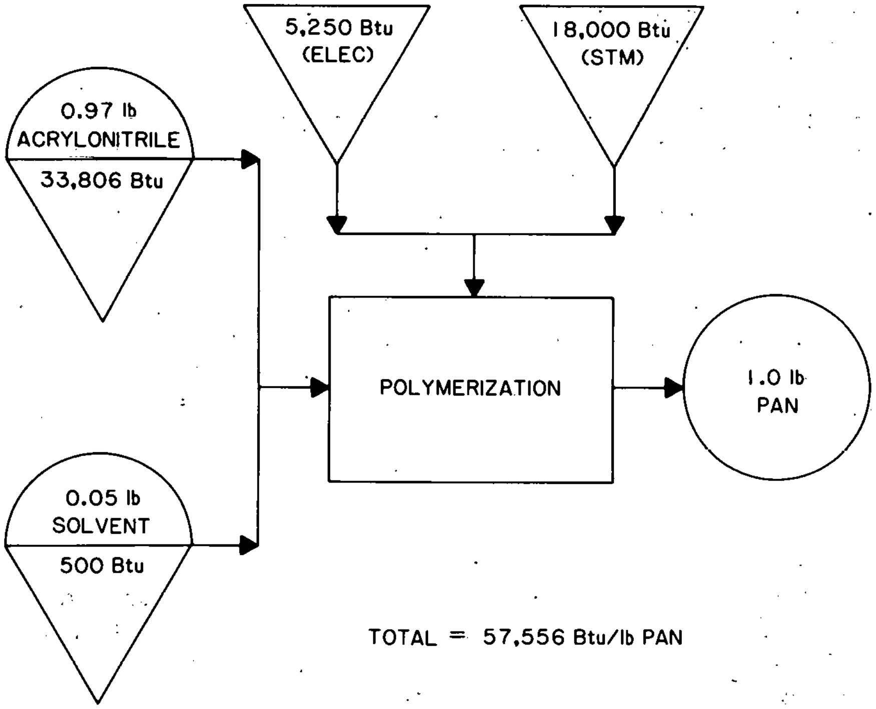


Fig. 4.44. Energy and Materials Flow for Polyacrylonitrile (Source: Ref. 89)

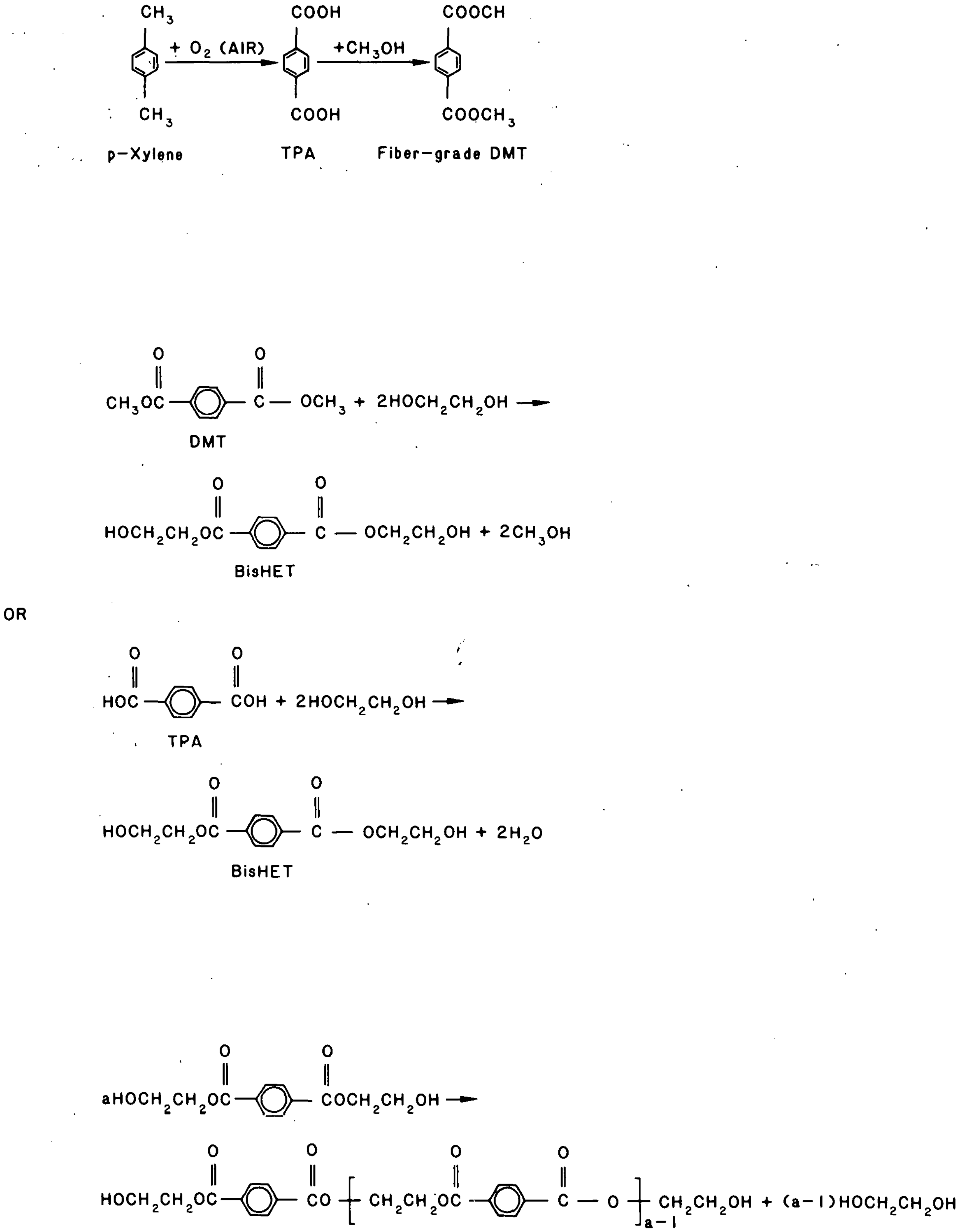


Fig. 4.45. Chemical Reactions for Polyester Production
(Source: Ref. 9)

can be reacted with ethylene glycol to produce the di-ester monomer bishydroxyethyl terephthalate (bis-HET), as shown in Fig. 4.45. The monomer then undergoes polycondensation to polyester, with the elimination of ethylene glycol (see Fig. 4.45). Figure 4.46 is a flowchart for these processes.

Terephthalic acid is difficult to purify because of its high melting point and its general insolubility. The method for production of a reactant sufficiently pure for polymer manufacture was originally esterification of

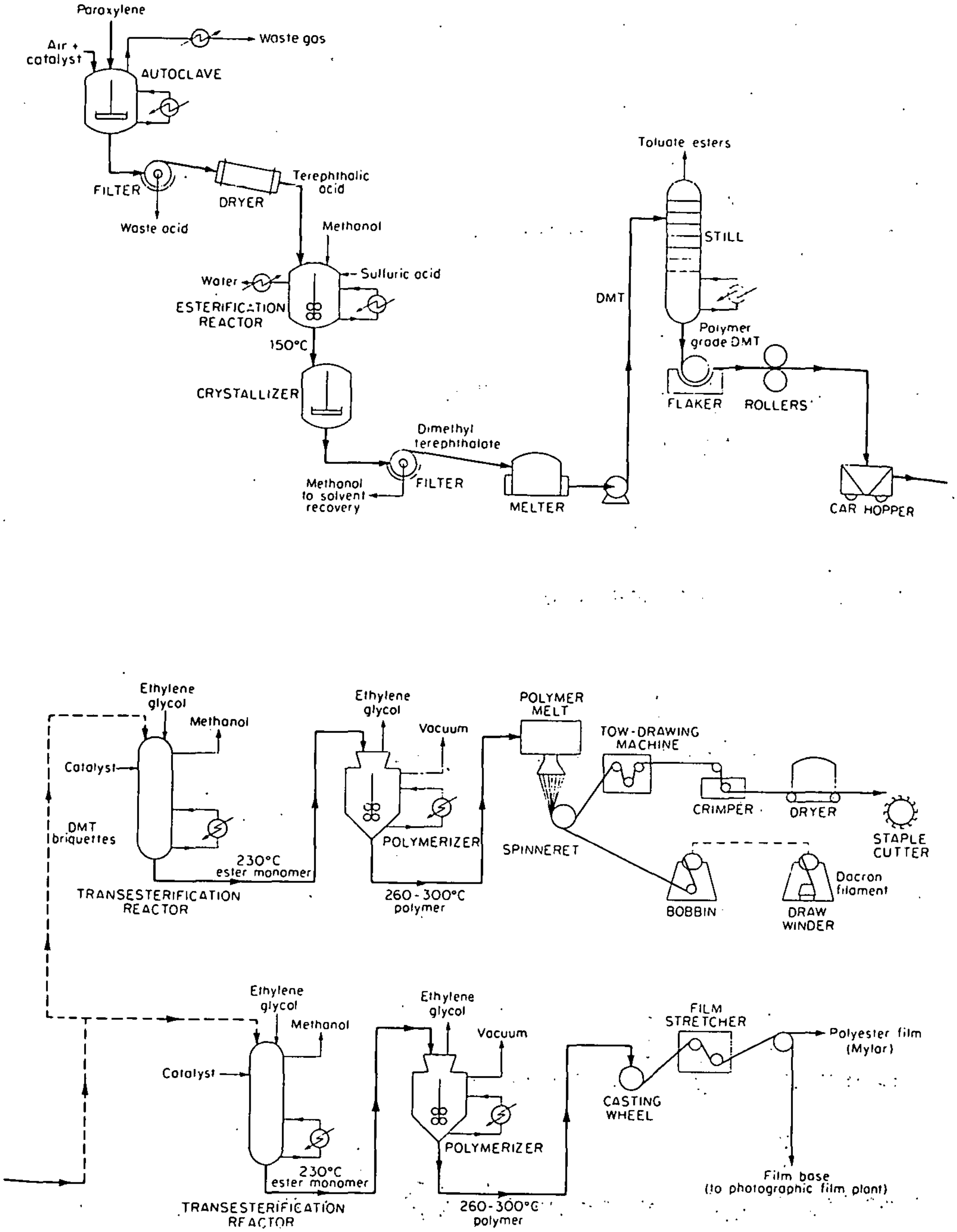


Fig. 4.46. Process Flow for Production of Polyester Fiber (Dacron) or Film (Mylar) (Source: Ref. 1)

impure TPA with methanol to form DMT, which can be purified by vacuum distillation or recrystallization from solution. The pure DMT can then be used to produce the di-ester in a more rapid reaction than esterification with TPA. The process for monomer production based on DMT is still in wide use. However, it is now possible to obtain TPA in sufficient purity for polyester production without the intermediate steps of DMT production and purification. A process with fewer steps usually has an economic and energy use advantage and, in 1974, 20% of polyester was made via the direct TPA method.[101] This percentage increased to over 60% with the completion of a new Hercules facility in North Carolina.

Monomer production from DMT and ethylene glycol is an ester-interchange reaction carried out at about 390°F (200°C) with excess glycol in the presence of a few parts per million of one or more catalysts (generally oxides or organic salts of alkali, alkaline earth, or transition metals). As it is formed, methanol is distilled off to drive the reaction to the right. The methanol is then either recovered and sold or recycled to DMT production. The colorless liquid product, referred to as "prepolymer" because it contains some dimer and trimer along with the monomer, is purified by filtration before it enters the polymerizer. The prepolymer product of direct esterification of TPA with ethylene glycol contains a larger percentage of low polymers. No catalyst is required, but the temperature is elevated to 390-480°F (200-250°C) to increase the reaction rate. The reaction pressure of 30-150 psi (2-10 atm) is high enough to prevent evaporation of glycol but low enough to distill the water produced.

The prepolymer produced by either method is charged to the stirred polymerization reactor (with a catalyst such as antimony trioxide) where the temperature is 500-570°F (260-300°C). The pressure is reduced to about 0.015 psi (10^{-3} atm) to drive the reaction to the right (towards polymer formation). Ethylene glycol distills off as it is produced. The reaction is allowed to proceed for four to six hours until the proper molecular weight is attained (about 80 rings per chain). This is determined by the power needed to stir the viscous liquid. The vacuum is released, and the clear, pale-yellow molten polymer mass is then either (1) melt-spun by forcing it through spinnerets and quenching with cool air or (2) quenched in cold water and cut into small pieces that are later reheated to about 510°F (285°C), filtered, and melt-spun. The weak and highly extensible spun fiber is heated and stretched to three to six times its length in order to give it strength and dimensional stability. The direct spinning method, which is less energy consuming and requires less capital equipment, can conveniently be used for continuous polyester production, while the chip method is usually used for batch processes. Continuous processing is used in most new installations because of reduced capital and operating costs as well as higher yields.

Energy and material flows in the production of BTX, a necessary input for TPA, and in polyester production via the DMT route are shown in Figs. 4.47 and 4.48. (The only data available for the TPA route were judged unreliable.)

Nylon

Nylon 66 is a condensation polymer formed from hexamethylene diammonium adipate or "nylon" salt by the elimination of water. The salt is produced

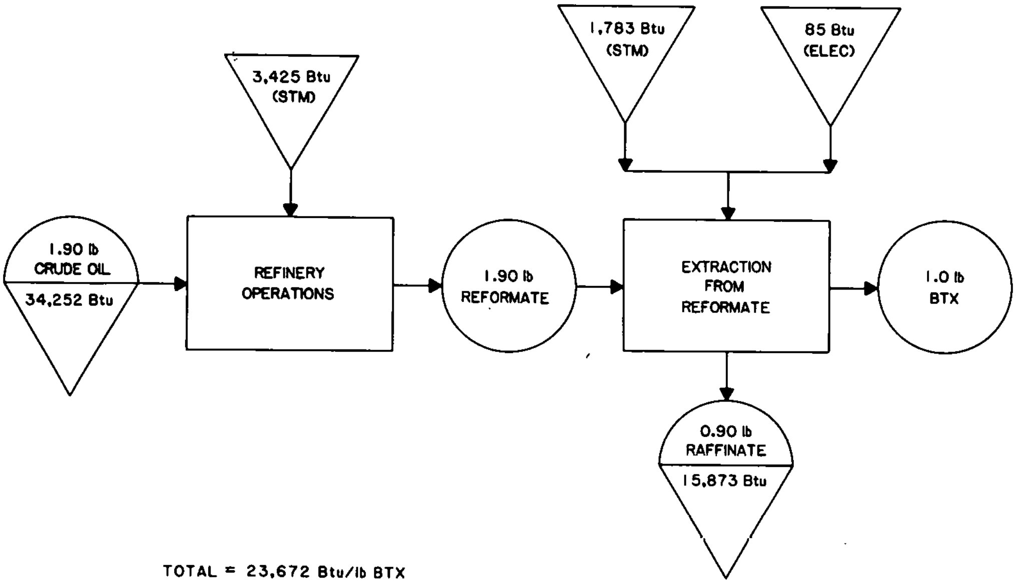
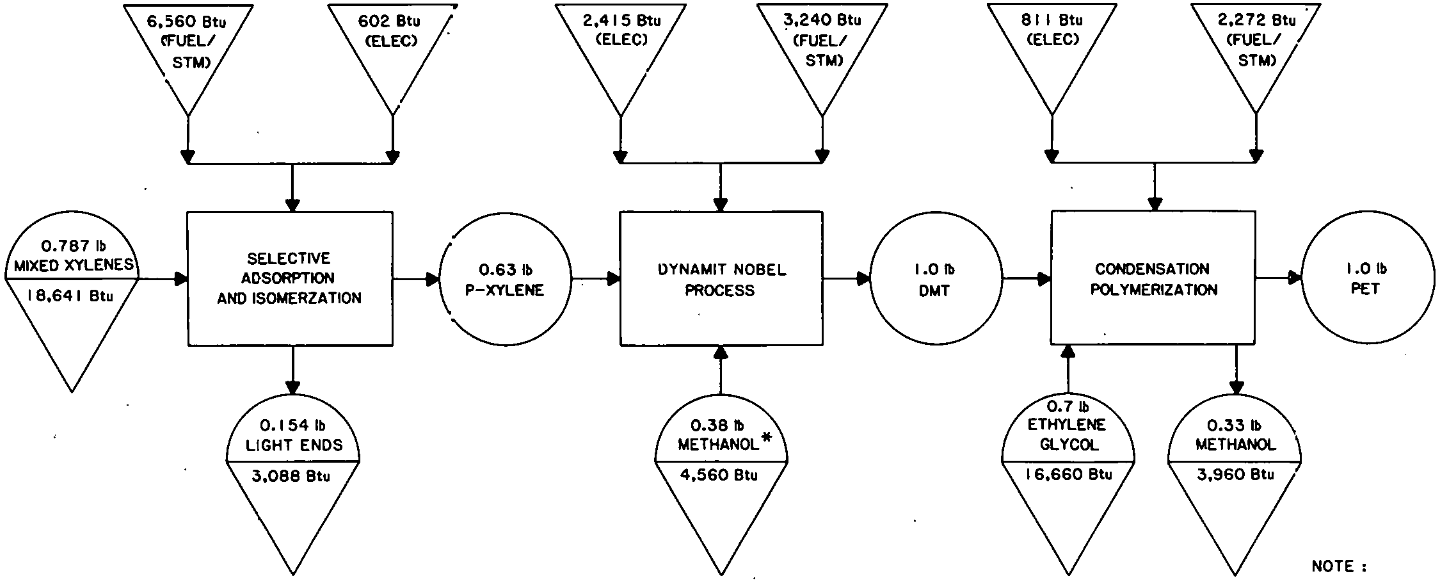


Fig. 4.47. Energy and Materials Flow for Separated BTX Production (Source: Ref. 72)

from hexamethylene diamine (derived from butadiene) and adipic acid (derived from cyclohexane). The series of chemical reactions utilized in nylon manufacture (see Fig. 4.49) is considerably more complex than most industrial processes. Nylon salt production and polymerization are described here and illustrated in Fig. 4.50. Other means of producing Nylon 66 are shown in Fig. 4.51. It is interesting to note that nylon could be produced from biomass.

Hexamethylene diamine and adipic acid are dissolved in water at pH 7.8 ±0.1 in stoichiometric quantities to produce the highest molecular weight polymer (6,000-10,000). Both reactants must be of high purity, since the salt remains in solution and is not purified prior to polymerization (older processes produced a crystalline salt). The 20% salt solution is concentrated to 60% in a vacuum evaporator, and 0.5-1 mole % acetic acid is added as a viscosity stabilizer. The solution flows by gravity to a jacketed, agitated autoclave, which is purged of air with steam and heated to 530°F (280°C) at about 265 psi (18 atm) for three hours until all of the water is evolved as steam. A pigment dispersion agent (TiO_2) is added, and the polymerization reaction is completed under vacuum at 570°F (300°C) in an inert atmosphere to prevent oxidation. Alternatively, the pressure can be maintained at 265 psi (18 atm) until completion of the reaction and then reduced to atmospheric. The water evaporates and agitates the polymer to leave a polymer melt (mp 507°F or 264°C), which is heated for one hour to establish equilibrium. The molten polymer is extruded after vacuum release as a ribbon 12 in. wide and 0.25 in. thick onto a casting wheel, cooled with air and water sprays, and cut into flakes.

If it is a batch operation, the polymer flakes are blended with those from other 2000-lb (0.91-t) batches for greater uniformity and melted in a

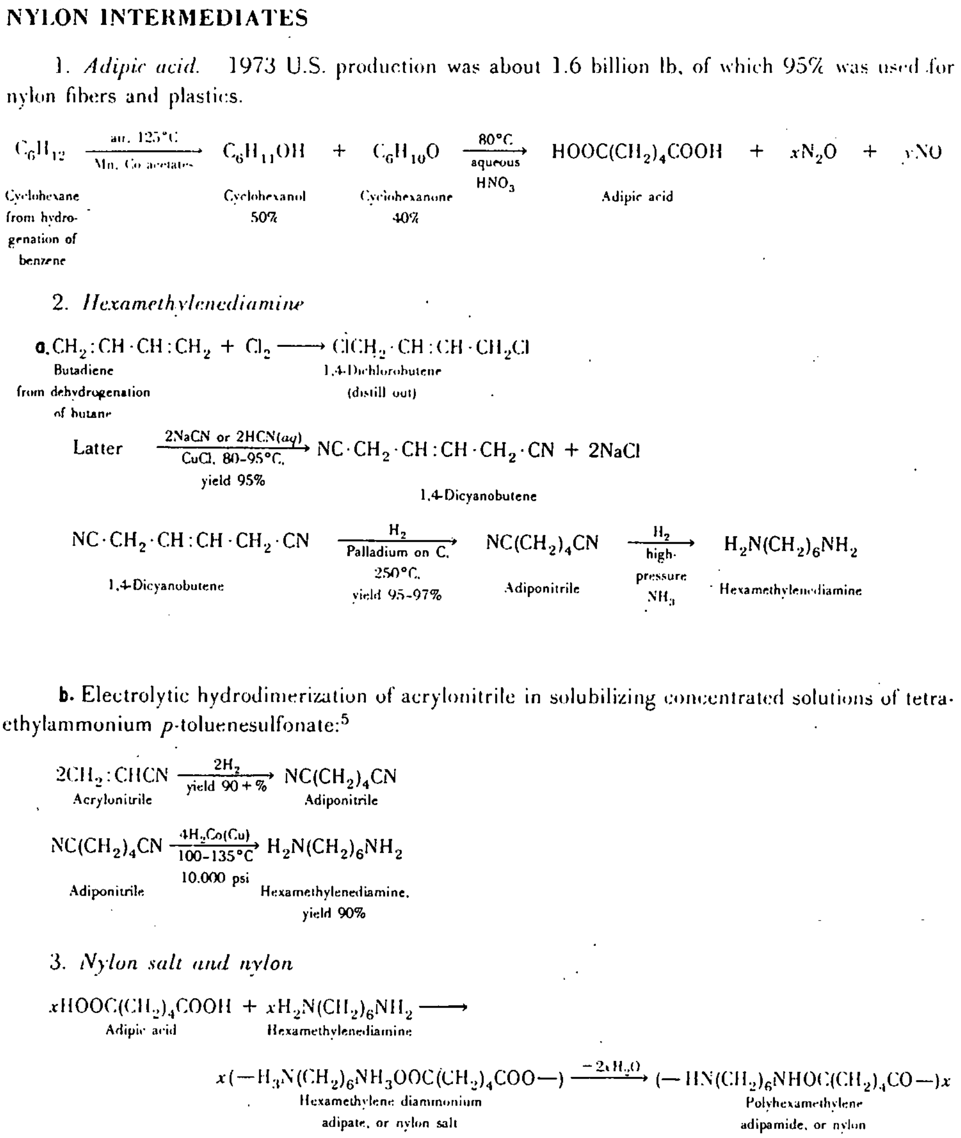


NOTE :
EXCLUDES SPIN & DRAW

TOTAL = 48,713 Btu/lb PET

* EST. 12,000 Btu/lb

Fig. 4.48. Energy and Materials Flow for Polyester Production (Sources: Refs. 72 and 89)



NYLON INTERMEDIATES

1. *Adipic acid.* 1973 U.S. production was about 1.6 billion lb, of which 95% was used for nylon fibers and plastics.

$$\underset{\text{Cyclohexane from hydrogenation of benzene}}{C_6H_{12}} \xrightarrow[\text{Mn, Co acetates}]{\text{air, 125°C}} \underset{\substack{\text{Cyclohexanol}\\ 50\%}}{C_6H_{11}OH} + \underset{\substack{\text{Cyclohexanone}\\ 40\%}}{C_6H_{10}O} \xrightarrow[\substack{\text{aqueous}\\ HNO_3}]{80°C} \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + xN_2O + yNO$$

2. *Hexamethylenediamine*

a. $$\underset{\substack{\text{Butadiene}\\ \text{from dehydrogenation}\\ \text{of butane}}}{CH_2{:}CH\cdot CH{:}CH_2} + Cl_2 \longrightarrow \underset{\substack{\text{1,4-Dichlorobutene}\\ \text{(distill out)}}}{ClCH_2\cdot CH{:}CH\cdot CH_2Cl}$$

$$\text{Latter} \xrightarrow[\substack{CuCl,\ 80\text{–}95°C,\\ \text{yield 95\%}}]{2NaCN \text{ or } 2HCN(aq)} \underset{\text{1,4-Dicyanobutene}}{NC\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CN} + 2NaCl$$

$$\underset{\text{1,4-Dicyanobutene}}{NC\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CN} \xrightarrow[\substack{\text{Palladium on C,}\\ 250°C,\\ \text{yield 95–97\%}}]{H_2} \underset{\text{Adiponitrile}}{NC(CH_2)_4CN} \xrightarrow[\substack{\text{high-}\\ \text{pressure}\\ NH_3}]{H_2} \underset{\text{Hexamethylenediamine}}{H_2N(CH_2)_6NH_2}$$

b. Electrolytic hydrodimerization of acrylonitrile in solubilizing concentrated solutions of tetraethylammonium *p*-toluenesulfonate:[5]

$$\underset{\text{Acrylonitrile}}{2CH_2{:}CHCN} \xrightarrow[\text{yield } 90+\%]{2H_2} \underset{\text{Adiponitrile}}{NC(CH_2)_4CN}$$

$$\underset{\text{Adiponitrile}}{NC(CH_2)_4CN} \xrightarrow[\substack{100\text{–}135°C\\ 10{,}000 \text{ psi}}]{4H_2,Co(Cu)} \underset{\substack{\text{Hexamethylenediamine,}\\ \text{yield 90\%}}}{H_2N(CH_2)_6NH_2}$$

3. *Nylon salt and nylon*

$$x\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + x\underset{\text{Hexamethylenediamine}}{H_2N(CH_2)_6NH_2} \longrightarrow$$

$$x\underset{\substack{\text{Hexamethylene diammonium}\\ \text{adipate, or nylon salt}}}{(-H_3N(CH_2)_6NH_3OOC(CH_2)_4COO-)} \xrightarrow{-2xH_2O} \underset{\substack{\text{Polyhexamethylene}\\ \text{adipamide, or nylon}}}{(-HN(CH_2)_6NHOC(CH_2)_4CO-)x}$$

Fig. 4.49. Chemical Reactions for Nylon Manufacture (Source: Ref. 1 [used with the permission of McGraw-Hill Book Company])

heating-jacketed metal vessel in an oxygen-free environment. Flakes hit a hot grid in the vessel and dribble through to a sand filter, after which the melt can be molded or spun. In the latter case, fiber filaments are frozen by cool air as they emerge from spinnerets. Then they are cold-drawn by stretching to three to six times their original length to orient the molecules and strengthen the product.

Energy and materials flow in the production of nylon 66 is shown in Fig. 4.52. Note that process energies may be overestimated; the only

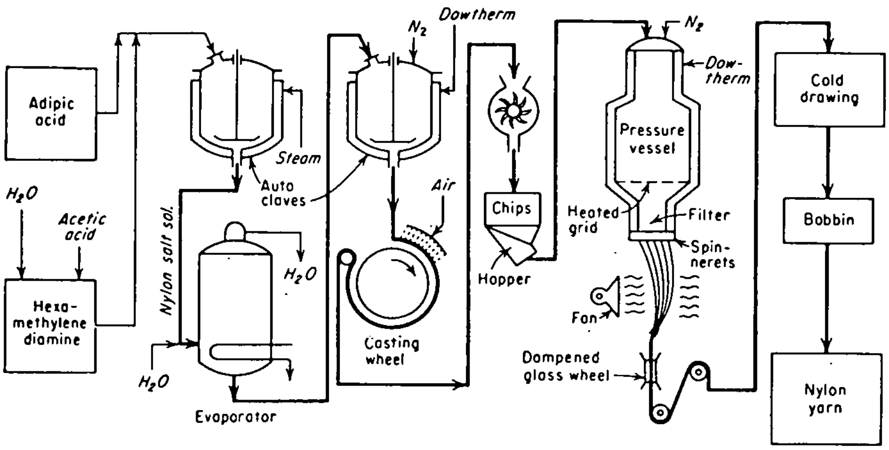


Fig. 4.50. Process Flow for Nylon Yarn Production (Source: Ref. 1 [used with the permission of McGraw-Hill Book Company])

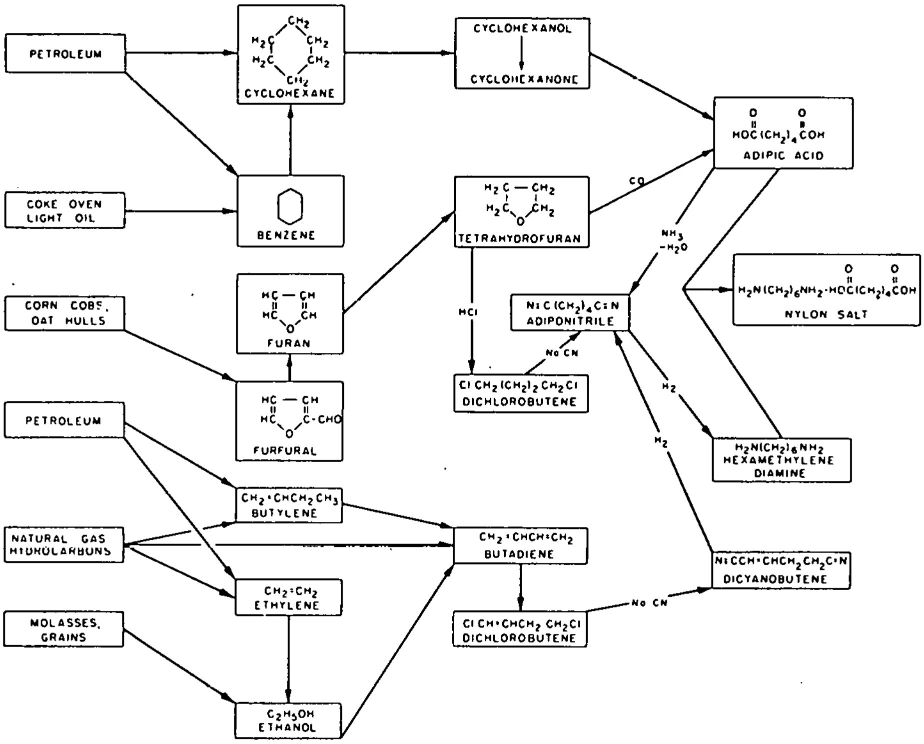


Fig. 4.51. Synthesis Routes to the Manufacture of Nylon (Source: Ref. 35)

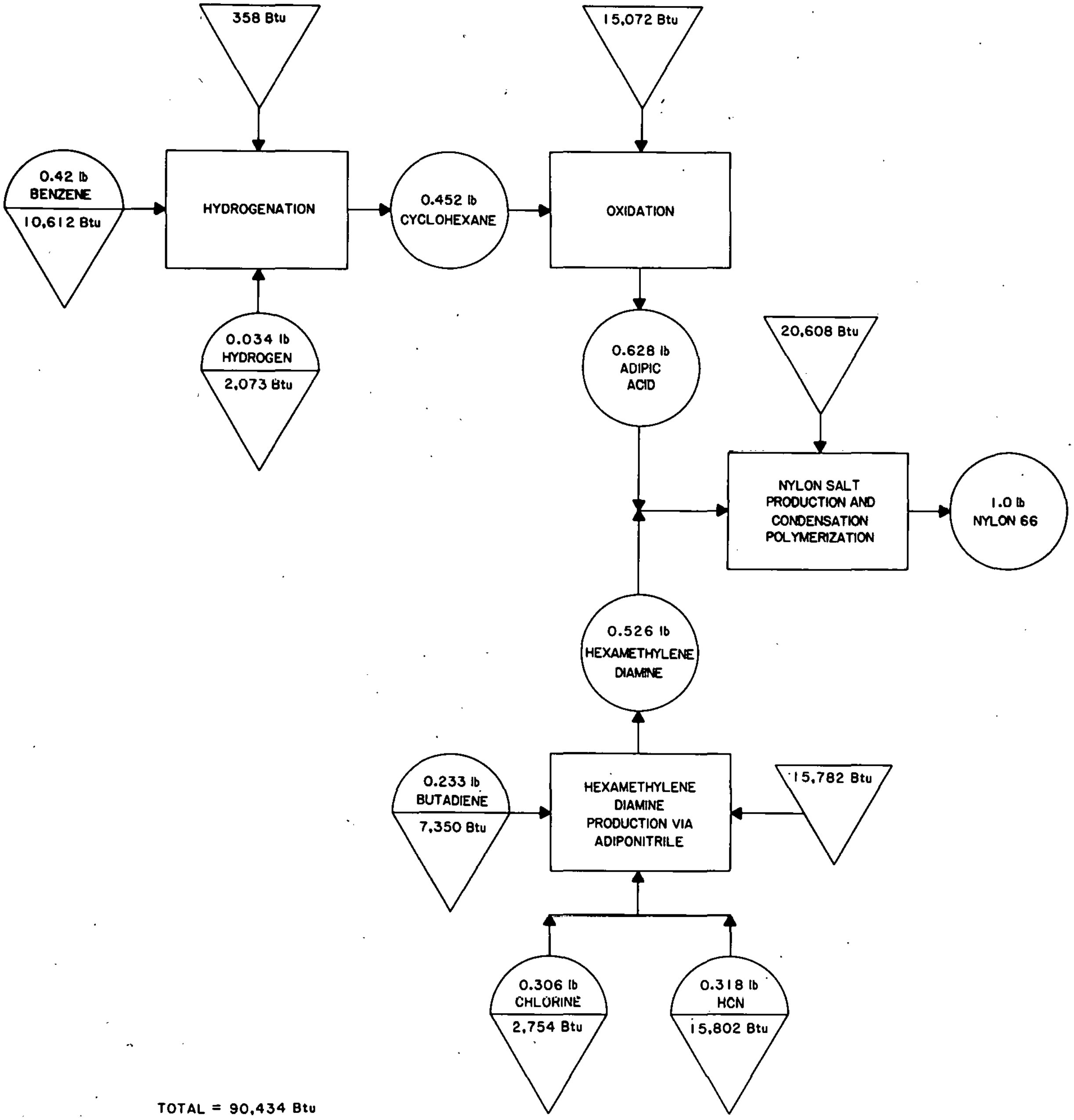


Fig. 4.52. Energy and Materials Flow in Nylon 66 Production (Sources: Refs. 101 and 102)

source of data available was high for PET and PAN on comparison with reliable sources.

4.3.2 Oxidation and Hydration

4.3.2.1 Production of Ethylene Oxide

Ethylene oxide is produced by the direct oxidation of ethylene over a catalyst. A process flow diagram is shown in Fig. 4.53. Ethylene and air or oxygen are preheated by hot reactor effluent, which contains the finely divided silver oxide catalyst. Temperatures of 390-570°F (200-300°C) and pressures of 150-440 psi (10-30 atm) have been reported, with temperatures for oxidation by air (500-550°F or 260-290°C) somewhat higher than for oxygen (450°F or 230°C). Typical reaction parameters are shown in Table 4.17. High pressure does not change the percentage of feed converted to product but does decrease the plant size and cost for a given output.[19] Heat from the exothermic reactions is removed by heat exchange with coolant that surrounds the more than 3000 reactor tubes. The coolant may be water, in which case high-pressure steam is generated directly, or an organic (like Dowtherm®), in which case the coolant is cooled by indirect contact with water in a moderately high-pressure steam boiler. Two competing processes occur in the reactor. The oxidation, producing 1615 Btu/lb (3.71 kJ/g) ethylene at 1100°F (600°C), is enhanced by the catalyst over combustion of ethylene to carbon dioxide and water, producing 21,790 Btu/lb (50.5 kJ/g).[103] Selectivity (percentage of molecules undergoing a particular reaction) for combustion increases with temperature. Since combustion produces 15 times as much energy as direct oxidation, an increase in combustion raises the temperature, which causes more combustion and a runaway effect. As temperatures decrease,

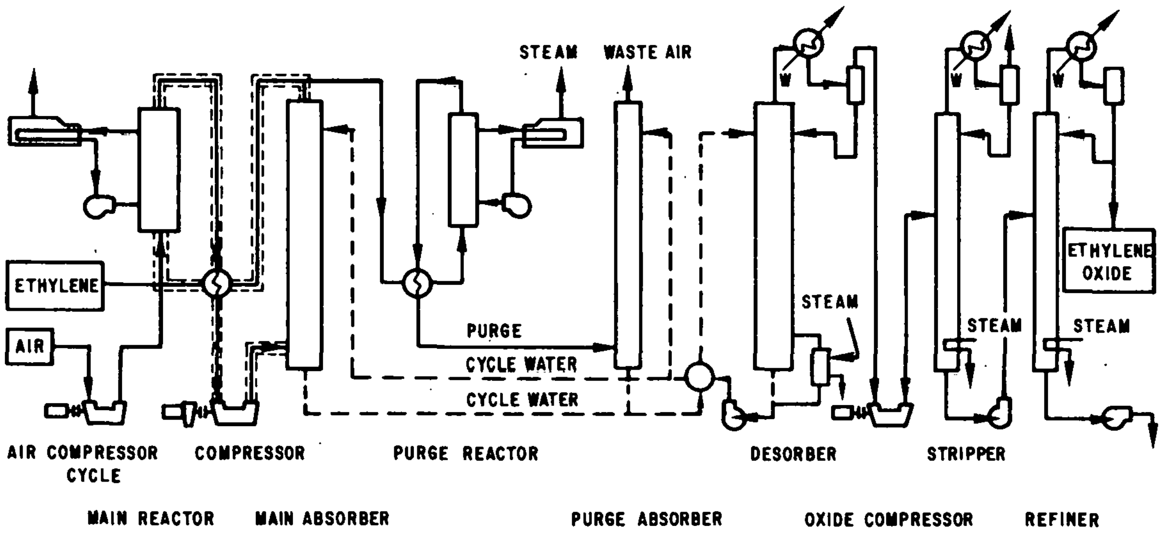


Fig. 4.53. Process Flow for Ethylene Oxide Production by Direct Oxidation (Source: Ref. 19)

Table 4.17. Reaction Parameters for the Direct Oxidation of Ethylene to Ethylene Oxide

	Broad Range	For a Specific Catalyst
Ethylene (mol %)	1.5-5	5.0
Oxygen (mol %)	5-8	6.0
Carbon dioxide (mol %)	10	7.0
Ethane (mol %, maximum)	-	0.1
1,2-Dichloroethane (ppm)	-	0.05
Temperature (°C)	220-280	250.0
Pressure (atm)	10-15	20.0
Flow rate (m/sec)	61-4	-
(L/hr/tube)	-	18.395
Residence time (sec)	0.4-1.5	-
Reactor pressure drop (atm)	0.4-3.4	-
Selectivity (%)	63-70	73.0
Conversion (%)	30-65	27.0

Source: Ref. 20.

the opposite happens, i.e., the reactor temperature falls dramatically. Thus, control of temperature is of crucial importance in ethylene oxide manufacture.

Gases from the reactor are cooled by heat exchange and enter the bottom of the counter-current absorber, where they are contacted with a downward flow of water, which dissolves the ethylene oxide and some carbon dioxide, nitrogen, and aldehydes. This oxide-rich water is sent either to a glycol plant or to the top of a desorber column where a counter-current flow of steam frees the oxide from the water as a result of decreased solubility at higher temperature. The water is recycled, and the ethylene oxide enters the stripper to remove light gases. The ethylene oxide product is then distilled to the desired purity.

Gases leaving the water absorber contain large quantities of ethylene due to the low per-pass conversion to product (<50%). Feedstock at $0.06/lb ($0.13/kg) represented 75% of ethylene oxide cost in 1975 and was predicted to be 86% of the cost at the 1978 price of $0.12/lb ($0.26/kg).[72] Therefore, recycling of the gases is critical. Even so, overall yields are less than 75%, and new process research is aimed at improving yields. An important difference between the air and oxygen processes occurs in the recycle stream. Inert gases tend to build up with continued recycle and must be purged (vented). If oxygen is used, relatively small quantities must be purged. Carbon dioxide is permitted to build up to a concentration of 2-10% to minimize the danger of explosion and help heat removal. Excess carbon dioxide is removed from a side stream. When air is used, large quantities of nitrogen build up, and a purge reactor is needed. A side stream of the recycle gas is sent to the purge reactor, where most of the remaining ethylene is oxidized.

In 1969, about 75% of U.S. ethylene oxide was produced using air and 20% using oxygen.[19] However, since today's technology can separate oxygen from nitrogen relatively inexpensively, oxygen oxidation is favored for large plants. The advantages are that: (1) a purge reactor and absorber are not needed (allowing more of the gases to be recycled) and (2) the entire plant can be smaller and less expensive to operate. These advantages are partially offset by the oxygen plant costs and the carbon dioxide removal cost.

Energy and materials used in oxide manufacture by oxygen oxidation are shown in Fig. 4.54.

4.3.2.2 Production of Propylene Oxide

In 1979 most propylene oxide in the United States was made by the chlorohydrin process,[105] a two-stage process requiring chlorine as a raw

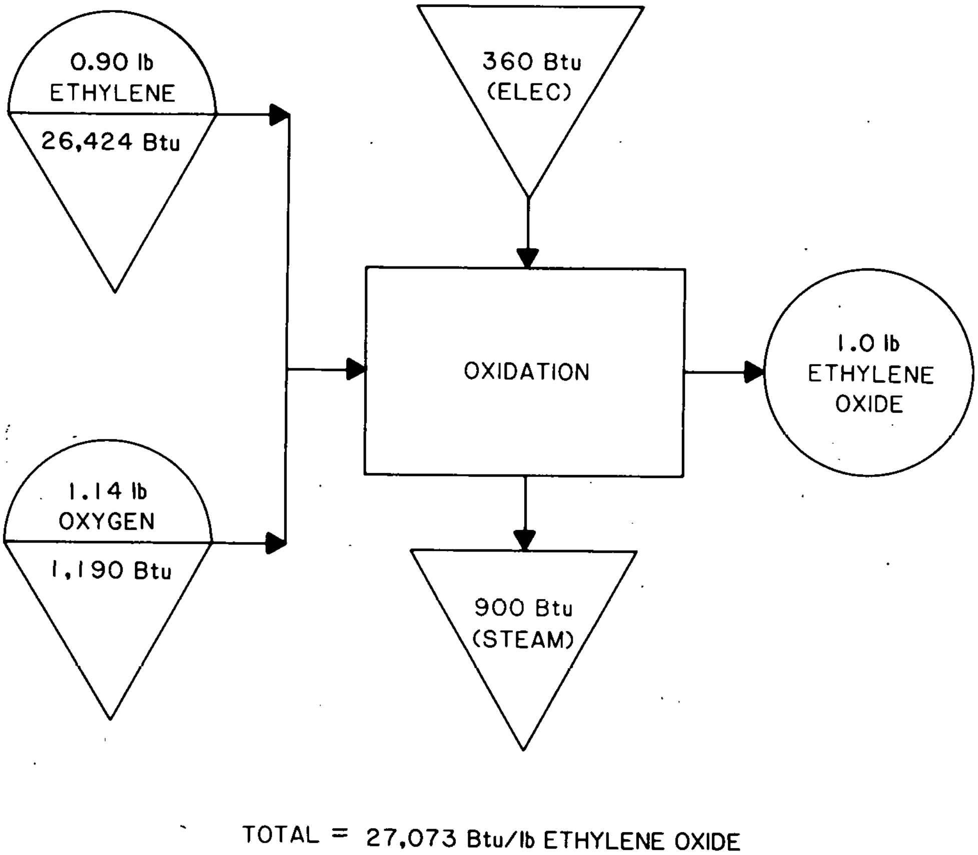
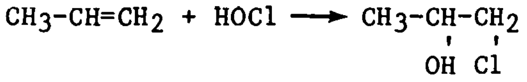


Fig. 4.54. Energy and Materials Flow for Ethylene Oxide Production (Sources: Refs. 72 and 104)

material. In 1950, 75% of ethylene oxide was made by the chlorohydrin process[82] (see Fig. 4.55). The direct oxidation method was discovered and rapidly adopted in the 1950s. Most obsolete ethylene chlorohydrin plants have either been converted to propylene-oxide manufacture (representing a large fraction of capacity) or scrapped; hence, new propylene oxide capacity will have to be dedicated. The major drawback of the chlorohydrin process is the large consumption of chlorine, which accounts for more than 40% of ethylene oxide costs. A direct oxidation route to propylene oxide (analogous to that for ethylene oxide) has long been sought. However, the methyl group is vulnerable to attack, and most attempts at direct oxidation lead to acrolein ($CH_2{=}CHCH{=}O$).

Propylene, chlorine, and water are fed into a tower, where the temperature is maintained at about 120°F (50°C) by controlling materials flows. Chlorine dissolves in water to form hydrochloric and hypochlorous acids, the latter reacting with propylene to form propylene chlorohydrin.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$



$$CH_3{-}CH{=}CH_2 + HOCl \longrightarrow CH_3{-}\underset{OH}{CH}{-}\underset{Cl}{CH_2}$$

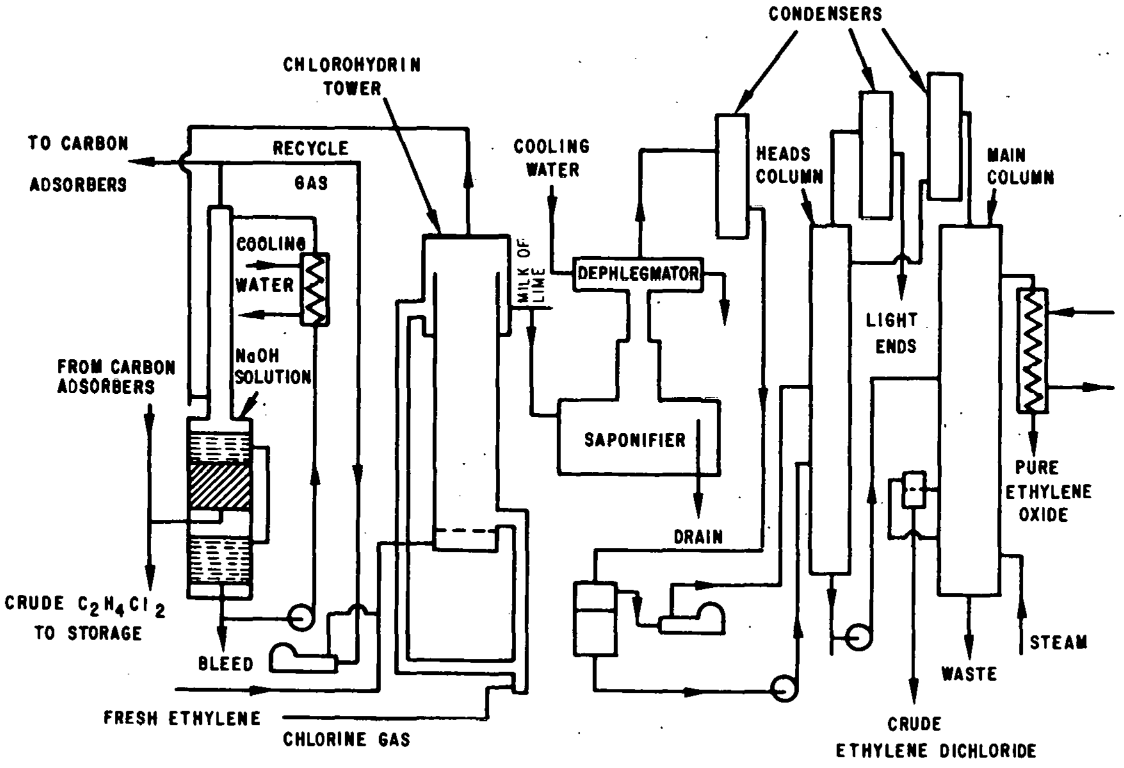
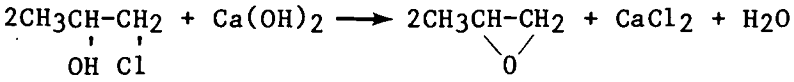


Fig. 4.55. Process Flow for Ethylene Oxide Production by Chlorohydrin Process (Sources: Refs. 72 and 104)

Propylene is maintained in excess, away from the chlorine source, and the chlorohydrin concentration is kept low (≤6%) to minimize by-product production. The major by-product is propylene dichloride, which is formed by the addition of chlorine to propylene. These reactions occur more readily for propylene than ethylene and, therefore, produce more by-products, which accounted for over 20% of the yield by product weight in the ethylene chlorohydrin process. Unreacted propylene is scrubbed with caustic and recycled.

In the second process step (hydrolysis or saponification), propylene chlorohydrin is drawn off the top of the chlorohydrin tower and then steam-heated and agitated with excess alkali (10% milk of lime) to form propylene oxide product and calcium chloride waste.

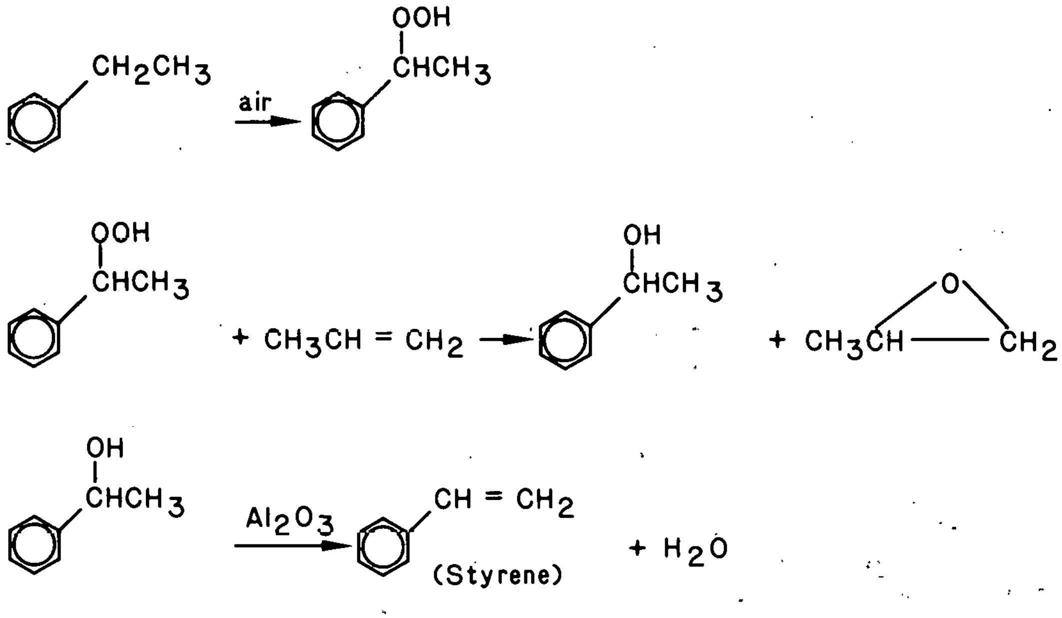


$$2CH_3\underset{OH}{CH}-\underset{Cl}{CH_2} + Ca(OH)_2 \longrightarrow 2CH_3\underset{\diagdown O \diagup}{CH-CH_2} + CaCl_2 + H_2O$$

The propylene oxide vapors are removed from the reaction zone, condensed, and distilled to remove water and by-products.

Propylene oxide process technology has undergone a dramatic change in recent years due to the introduction of the Oxirane process, a joint development by Halcon International and Arco Chemical Co. More than 40% of U.S. propylene oxide capacity uses the hydroperoxide process of Oxirane.

The Oxirane process comprises two distinct steps. First, a hydrocarbon, such as isobutane or ethylbenzene, is oxidized at 255-300°F (125-150°C) and 50 psig (3.4 atm) with air to the corresponding tertiary or secondary hydroperoxide. The hydroperoxide is then reacted with propylene at 175-230°F (80-110°C) and 550 psig (37 atm) to produce propylene oxide in 82% selectivity at 22% propylene conversion. Epoxidation occcurs in the liquid phase via a tungsten, vanadium, or molybdenum catalyst system, such as $Mo(CO)_6$. The reaction sequence is summarized by the following equations, and the process flow is illustrated in Fig. 4.56.



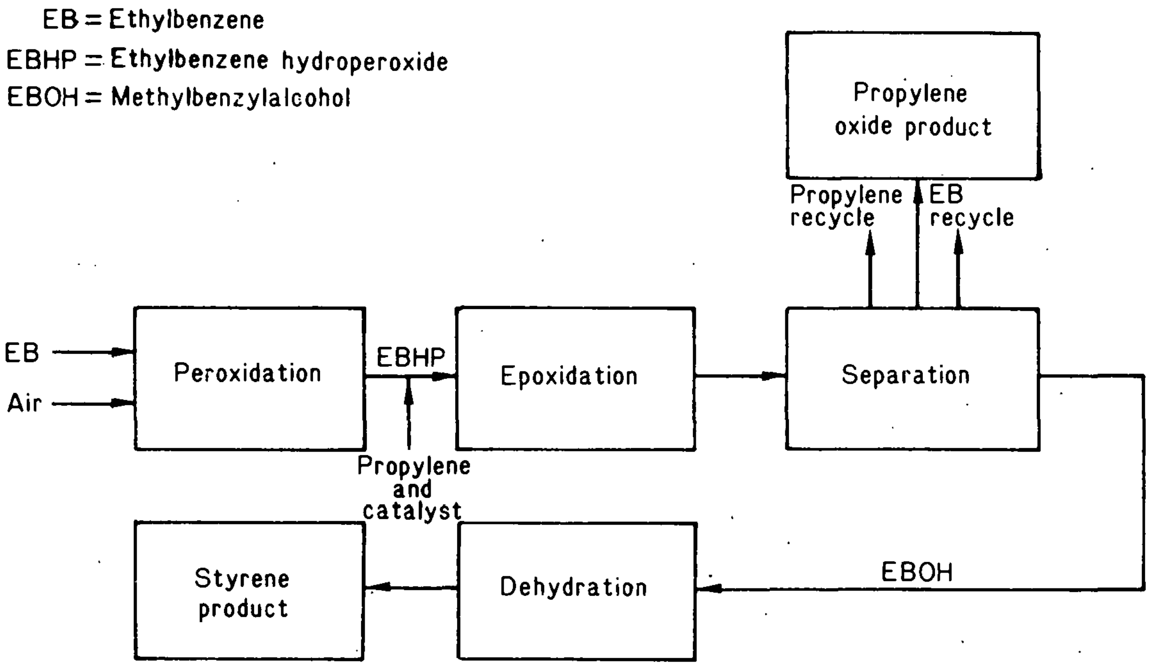


Fig. 4.56. Process Flow for Coproduction of Propylene Oxide and Styrene (Oxirane process) (Source: Ref. 106)

Methylbenzyl alcohol is a by-product (18% by weight total products for that step) in the initial ethylbenzene hydroperoxidation step, as well as a coproduct during propylene oxide formation. Dehydration to styrene is virtually quantitative.

Initial commercialization of this technology employed isobutane (t-butylhydroperoxide) as a coreactant. The t-butanol (isobutylene) coproduct was recovered and sent to the gasoline pool. Shortages in isobutane supply have led to substitution of ethylbenzene.

A principal factor in the success of the Oxirane technology is its large styrene credit (about 2.5 lb [1.13 kg] of styrene per pound of propylene oxide). This almost entirely offsets total raw material costs. Furthermore, chlorohydrin technology is encumbered by a high cost for chlorine. This does not appear in the final product and represents a sizable disposal problem in the form of calcium chloride. The attractive economics of the Oxirane process is the basis for its increasingly greater share of U.S. production capacity.

Oxirane technology proceeds via homogeneous catalysis. Recently, Shell Oil introduced a heterogeneous system; molybdenum, vanadium, or titanium are supported on silica gel, and the composite is treated with trimethylchlorosilane.[107] Other than the character of the peroxidation catalyst, the Shell system appears to be substantially the same as Oxirane's.

The energy and materials flows for the chlorohydrin and the peroxidation methods of propylene oxide manufacture as estimated from industrial flow sheets are shown in Figs. 4.57 and 4.58. Note that the total energy

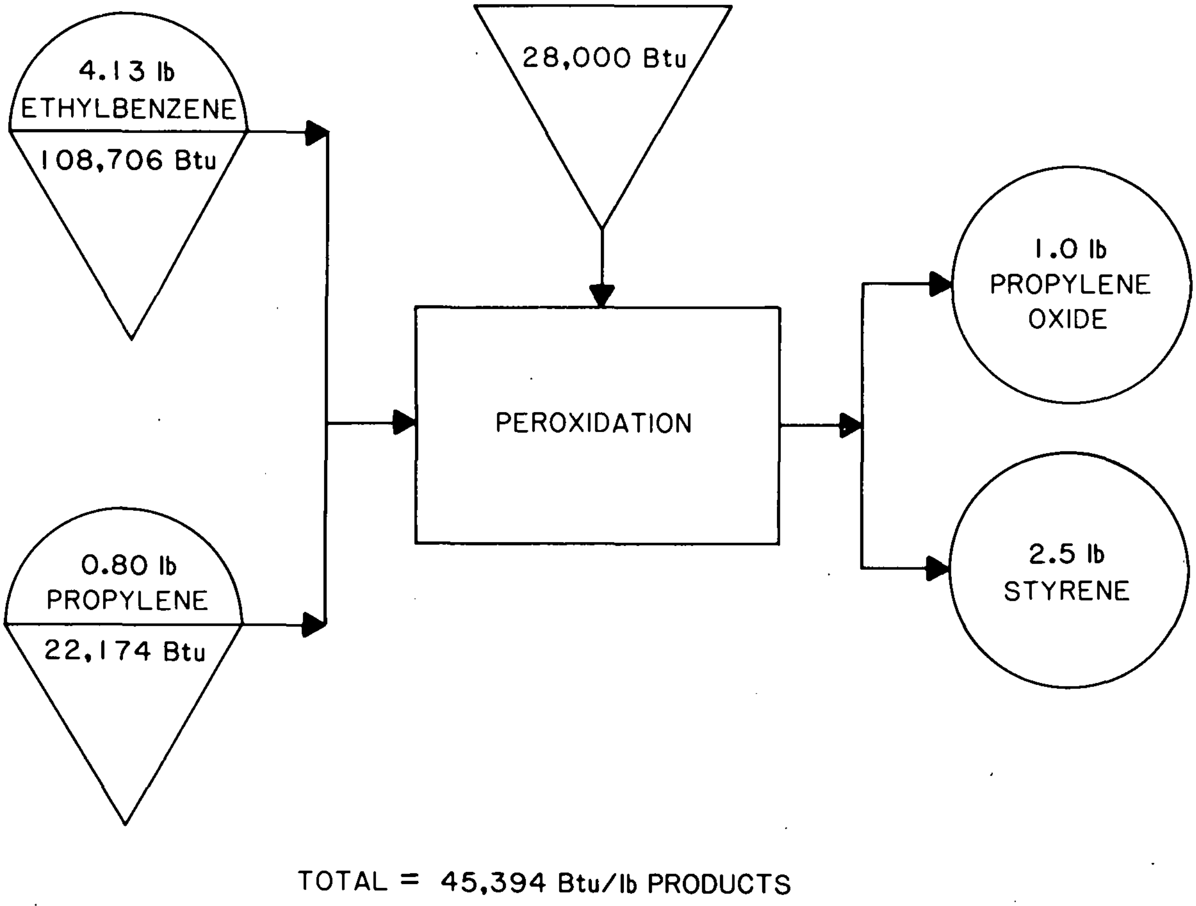


Fig. 4.57. Energy and Materials Flow for Coproduction of Propylene Oxide and Styrene (Sources: Refs. 89, 102, and 106)

input for the 3.5 lb of coproducts of the peroxidation process is about 159,000 Btu. This is equal, to the accuracy of these numbers, to the 146,000 Btu required to produce these same outputs by conventional processes.

4.3.2.3 Production of Glycol

Until 1978, ethylene glycol was commercially produced almost entirely by a two-step process (see Fig. 4.59): (1) the vapor phase oxidation of ethylene to ethylene oxide and (2) the liquid phase hydrolysis of ethylene oxide to ethylene glycol. Beginning in 1978, ethylene glycol has been produced directly from ethylene.[69,108]

The process for making ethylene or propylene glycol in liquid-phase direct hydration of the olefin oxide yields a mixture of the monoglycol and higher glycols. Water adds to the oxide to yield the monoglycol, which can in turn react with the oxide to form higher glycols, according to the following net reaction (shown for ethylene glycols; n = 1 for monoglycol, 2 for di-, etc.).

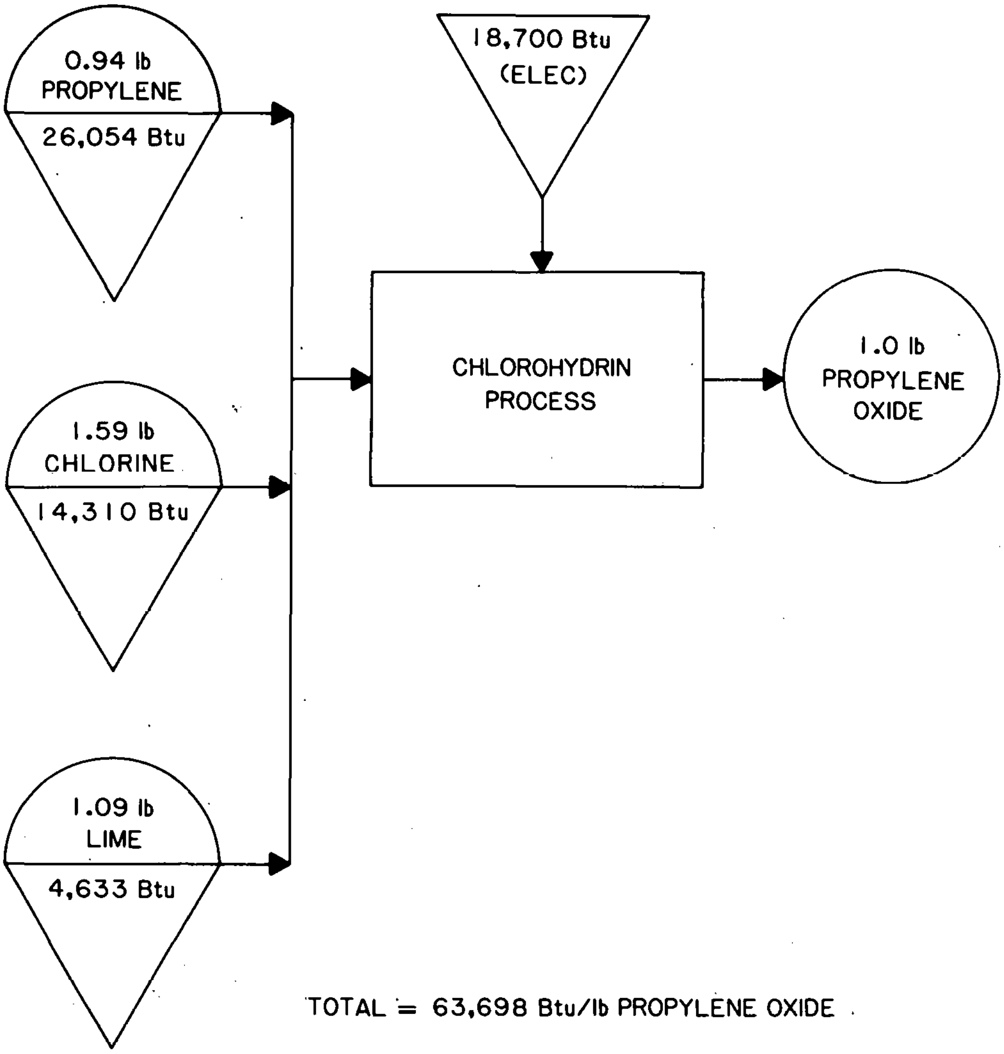
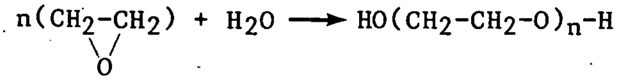


Fig. 4.58. Energy and Materials Flow for Propylene Oxide Production (chlorohydrin process) (Source: Ref. 106)



$$n(\underbrace{CH_2-CH_2}_{O}) + H_2O \longrightarrow HO(CH_2-CH_2-O)_n-H$$

Conversion of the oxide to glycols is reported to be better than 95%. Excess water favors formation of the monoglycol, but separating large quantities of water from products is expensive, and a balance between selectivity to monoglycol and plant size must be achieved. One source cites a reasonable balance as 15 moles of water per mole of oxide,[88] resulting in a yield of 86% ethylene glycol, 12% diethylene glycol, and 2% triethylene glycol.

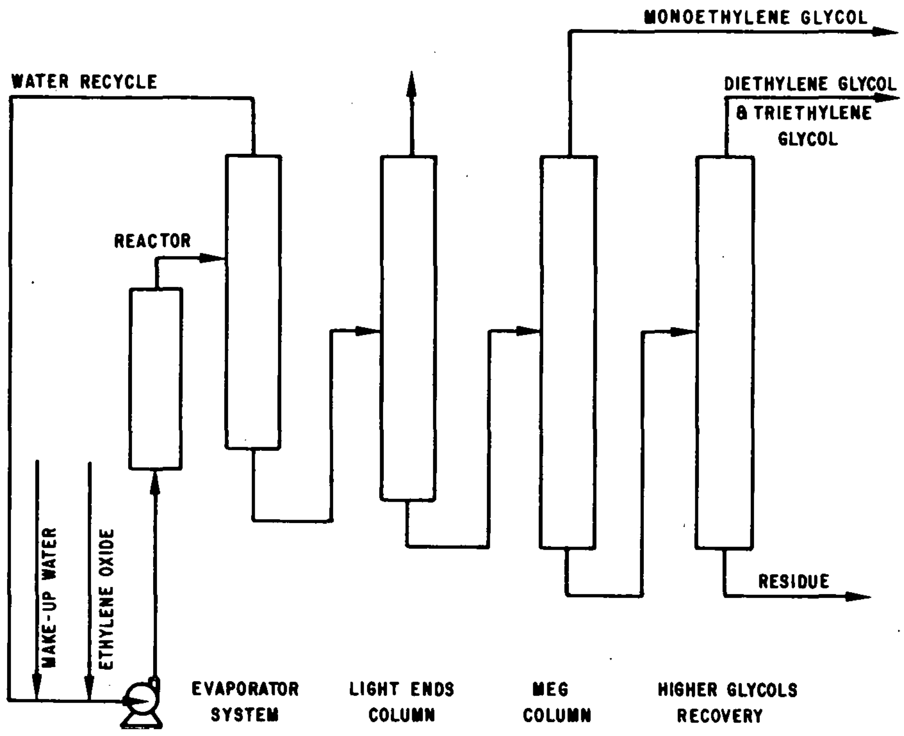
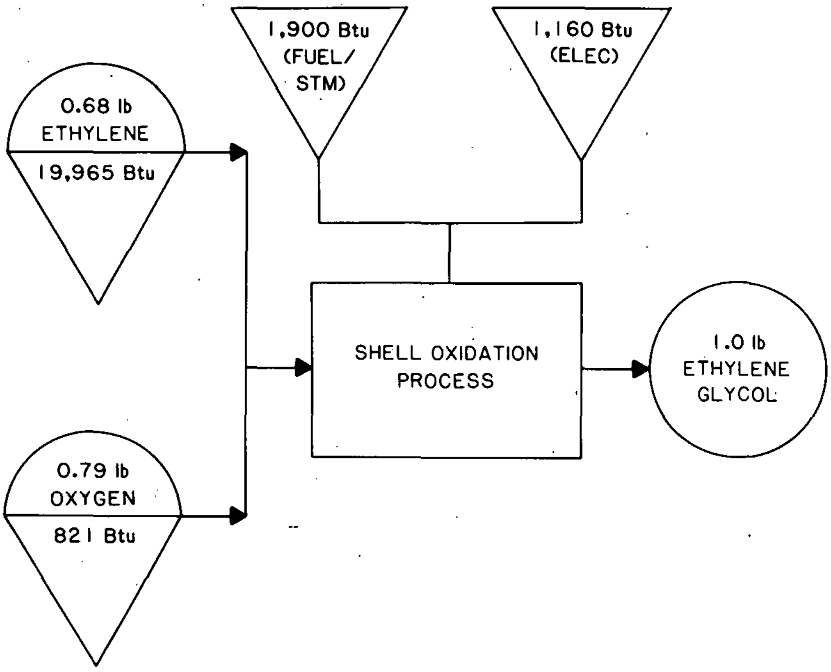


Fig. 4.59. Process Flow for Ethylene Glycol Production (Source: Ref. 19)

Reaction conditions depend on whether a catalyst is employed. If a dilute strong acid is present, the reaction is carried out at atmospheric pressure and 120-210°F (50-100°C). More severe conditions, with pressures over 190 psi (13 atm) and temperatures of 300-390°F (150-200°C), are required when no catalyst is used. The noncatalytic process is preferred in the United States, as it avoids dealing with corrosives and separating acid from products. The reaction is exothermic and is carried out in a reactor tube with continuous flow. Reactor effluent is sent to a multistage evaporator with each stage at successively higher vacuum to remove the excess water, which is recycled to the reactor. A three-column still separates the mono-, di-, and tri-glycol products from a small quantity of polyglycol waste. Because of the large quantities of water evaporated and the low volatilities of the liquids distilled, careful energy conservation is required to produce glycols economically. One source reports that costs for glycol manufacture are minimized when this process is integrated with oxide manufacture.[56]

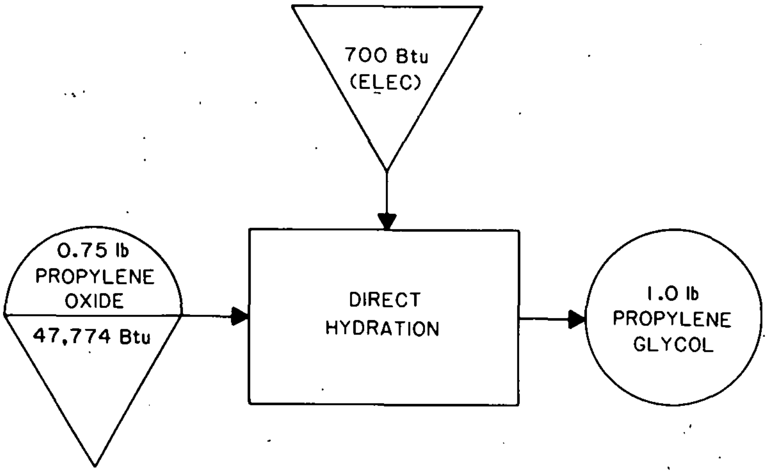
Union Carbide is carrying out extensive research on producing ethylene glycol from coal-derived synthesis gas (CO and H_2). The process is expected to be commercialized this decade.

Estimated energy and materials flow in typical production processes for ethylene glycol and propylene glycol are shown in Figs. 4.60 and 4.61.



TOTAL = 23,846 Btu/lb ETHYLENE GLYCOL

Fig. 4.60. Energy and Materials Flow for Production of Ethylene Glycol (Source: Ref. 108)

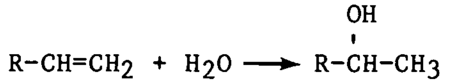


TOTAL = 48,474 Btu/lb PROPYLENE GLYCOL

Fig. 4.61. Energy and Materials Flow for Production of Propylene Glycol (Source: Ref. 6)

4.3.2.4 Production of Alcohol

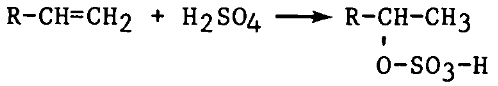
The general chemical reaction for the hydration of an olefin to an alcohol can be written as follows, where R represents an alkyl group (H in the case of ethylene and CH_3 in the case of propylene):



$$R\text{-}CH{=}CH_2 + H_2O \longrightarrow R\text{-}\overset{OH}{CH}\text{-}CH_3$$

The reaction (for R with few carbons) is exothermic, with the heat of reaction about 415 Btu/lb (1 kJ/g) for ethanol.[9] Note that the hydroxyl group (OH) adds to the secondary carbon atom rather than the end or primary carbon. This is in accordance with Markownikov's rule, which says that additions to double or triple bonds occur in such a way that substituted carbons become more so. The two carbons in ethylene are equivalent, but this is not true for propylene. This implies that isopropyl alcohol (i-propanol) is produced by hydration rather than n-propanol.

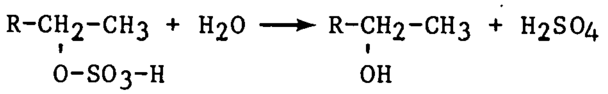
Two processes are available commercially for the manufacture of ethanol and isopropanol: the direct hydration process and the sulfate process. Most new plants use the direct hydration process, which was developed by Shell in the 1940s. However, the indirect process using a sulfate intermediate is still a factor in industry and will be discussed first. The two processes are shown in Figs. 4.62 and 4.63. In the first stage of the sulfate process, a feed stream of olefin is absorbed in a counter-current flow of concentrated sulfuric acid in a tower or stirred pot reactor to give the alkyl sulfate or disulfate:



$$R\text{-}CH{=}CH_2 + H_2SO_4 \longrightarrow R\text{-}\underset{O\text{-}SO_3\text{-}H}{CH}\text{-}CH_3$$

Low olefin concentrations discourage disulfate and, thereby, by-product formation. The lighter the olefin, the higher the temperature and acid concentration required for sulfation (see Table 4.18). Typical conditions for ethyl sulfate formation are 200-600 psig (15-40 atm)[56] and 130-170°F (55-75°C), with an acid concentration of 96%. Corresponding conditions for propyl sulfate formation are 290-440 psi (20-30 atm), 70-90°F (20-30°C), and 75-85% acid concentration. Conversion to sulfates is high (100% for ethylene), and no feed recycle is needed.

The sulfate is then hydrolyzed with steam heating to give the alcohol plus sulfuric acid:



$$R\text{-}\underset{O\text{-}SO_3\text{-}H}{CH_2}\text{-}CH_3 + H_2O \longrightarrow R\text{-}\underset{OH}{CH_2}\text{-}CH_3 + H_2SO_4$$

Excess water, which dilutes the acid to about 40%, is added to drive the reaction forward. Crude alcohol and other volatiles are stripped (with steam) from the dilute acid and scrubbed with sodium hydroxide to remove traces of acid. The acid, left at the bottom of the stripper column, is reconcentrated by evaporation and recycled to the reactor. The polymers and tar that form as reaction by-products eventually build up in the acid, which must be replaced.

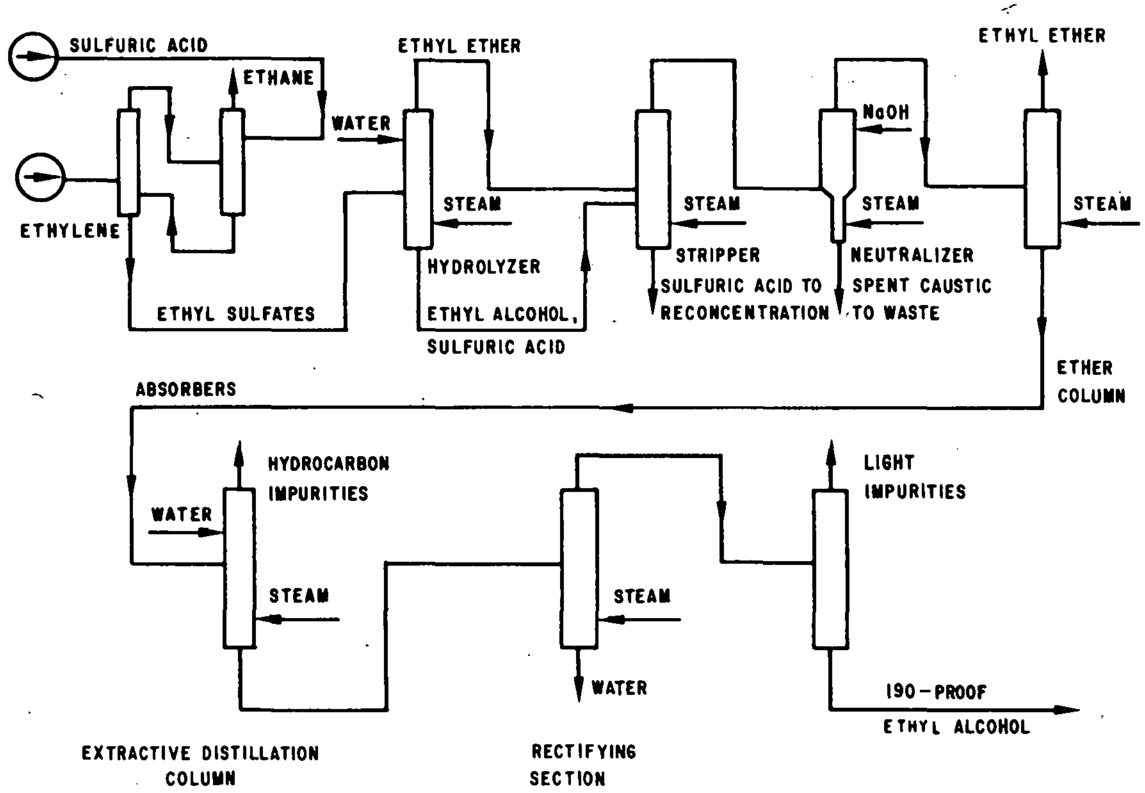


Fig. 4.62. Process Flow for Ethanol Production (Source: Ref. 30 [used with the permission of McGraw-Hill Book Company])

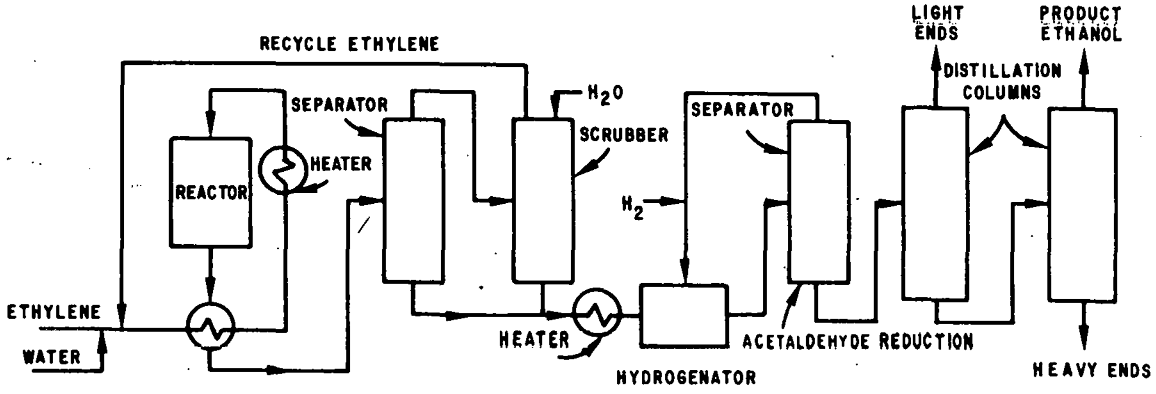
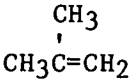


Fig. 4.63. Process Flow for Ethanol Production by Direct Hydration (Shell Development Process) (Source: Ref. 88 [used with the permission of Chemical Engineering, McGraw-Hill, Inc.])

Table 4.18. Acid Concentrations and Temperatures for the Sulfation of Various Olefins

Olefin	Formula	Acid Concentration Range (%)	Temperature Range (°C)
Ethylene	$CH_2=CH_2$	90-98	60-80
Propylene	$CH_3CH=CH_2$	75-90	25-30
Butylenes	$CH_3CH=CHCH_3$ $CH_3CH_2CH=CH_2$	75-85	15-30
Isobutylene	 $CH_3\overset{CH_3}{C}=CH_2$	50-65	0-25

Source: Ref. 109.

Spent acid is either used for low-grade uses or concentrated and cleaned for reuse by oxidation of carbonaceous material.[88] The crude alcohol is distilled to yield a pure alcohol-water azeotrope (a mixture with a single boiling point) that is 95% alcohol by weight for ethanol and 87.7% for isopropanol.[56] This can be sold as a high-quality product or azeotropically distilled if anhydrous alcohol is required. For azeotropic distillation, a third component or entraining agent (e.g., benzene) is added to the column, where it forms either a lower-boiling binary azeotrope with water or a ternary azeotrope containing only a small amount of water.* The alcohol can thereby be separated from the water, while the entraining agent remains in the column; this requires only a small quantity of makeup entraining agent.

Yields from the sulfate process are high, with about 90% of the feed converted to alcohol and most of the rest to the major by-product, which is diethyl (or di-isopropyl) ether. Most of the diethyl ether consumed in the United States is produced in this way at ethylene sulfation facilities. The major advantage of this process, and an important factor in its initial adoption in the 1930s, is the ability to handle dilute feed streams. The original production at Union Carbide used ethylene concentrations as low as 35%. The major disadvantages of the process are connected with handling and reconcentrating the acid. High maintenance costs accrue and special equipment (e.g., lead-lined vessels) is needed when large quantities of corrosive materials are handled. In addition, the cost in dollars and energy of acid reconcentration is high and will increase as U.S. Environmental Protection Agency regulations become more stringent.[9]

The direct hydration process was introduced in the 1940s by the Shell Development Company and now dominates U.S. ethanol and isopropanol production. Fresh feed plus recycled olefin and demineralized water (molar ratio of

---

*In the actual case of ethanol distillation using benzene, a ternary azeotrope boiling at 157.5°F (69.7°C) and a binary azeotrope of benzene and ethanol boiling at 162.5°F (72.5°C) are separated from the anhydrous ethanol at 173.1°F (78.4°C).

1:6[88]) are preheated by exchange with reactor effluent and enter the reactor vessel, which is packed with a phosphoric acid catalyst on an inert support, such as diatomaceous earth or Celite. Typical reactor conditions for ethanol production are 570-630°F (300-330°C) and 880-1000 psi (60-68 atm). For isopropanol production, the values are 360-500°F (180-260°C) and 370-955 psi (25-65 atm).[9,56] The exothermic reactions are favored by high pressure and low temperature (LeChatlier's principle) but are run at elevated temperatures to increase the reaction rates. Conversion per pass for ethylene to ethanol is 4-5%; typically, the ratio of recycled to new feed is 23:1. Conversions of up to 20% per pass are possible with very high pressure, low temperature, and excess water, but the capital costs would be prohibitive. Gases from the reactor are cooled and partially condensed in a separator. The vapor is sent to a water or caustic scrubber to remove traces of acid catalyst in the product, which is now in the liquid phase. If there are significant quantities of unsaturated compounds or aldehydes in the product, they are hydrogenated in the vapor phase over a nickel catalyst.

The product plus the liquid from the separator are sent to a series of distillation towers, the first of which is a "light ends" or wash column. Here, low-boiling impurities, such as ethers, are removed. (Diethyl ether is also the major by-product of direct ethylene hydration.) The next column removes most water and leaves an alcohol-water azeotrope, which may be dehydrated as described above or sold as a high-quality, low-odor product. The unreacted olefin is taken overhead from the scrubber and compressed for recycle. Because of the extensive recycle, inert contaminants in the feed tend to build up, necessitating a purge (venting) of part of the recycle stream and resultant loss of material.

Unit processes described above for ethanol are identical for isopropanol with two exceptions. The order of scrubber and separator may be reversed and the separator replaced by a flash drum, where unreacted propylene is vaporized and separated from water and product. In addition, an extractive distillation step may be necessary before the azeotropic distillation stage to separate product from impurities with similar boiling points.

Yield of ethanol from ethylene is about 97%. The direct hydration process is less capital intensive and has lower maintenance costs than the sulfate process but does require high-purity feed. In addition, the direct hydration process employs high temperature and pressure, plus power to recirculate the feed and, therefore, has high utility requirements.

Energy and materials flows are shown in Figs. 4.64 for ethanol and 4.65 for isopropanol.

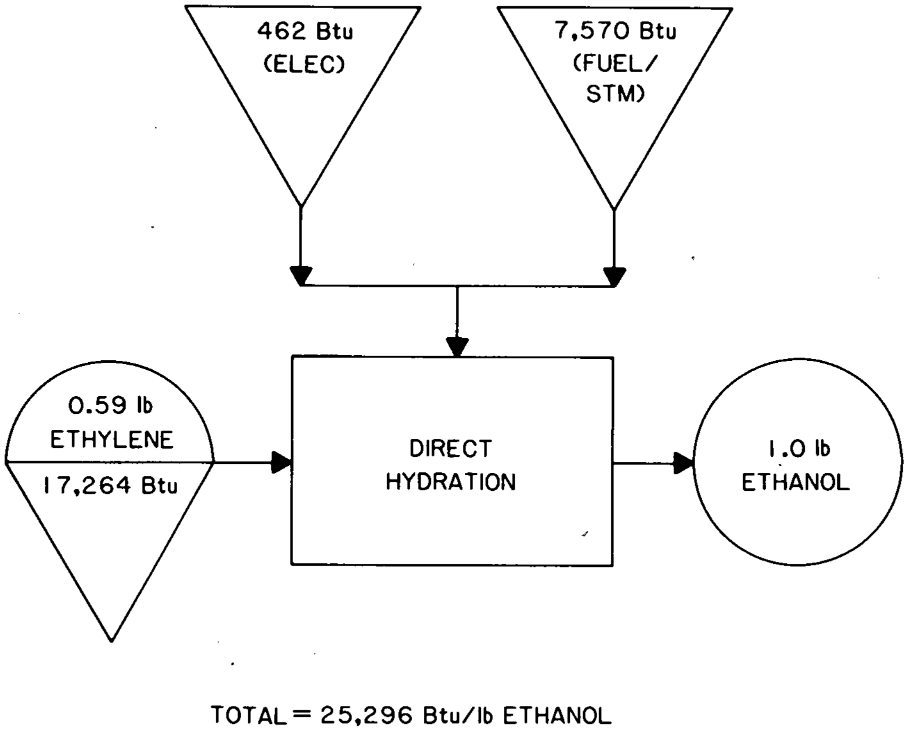


Fig. 4.64. Energy and Materials Flow for Ethanol Production via Direct Hydration (Source: Ref. 72)

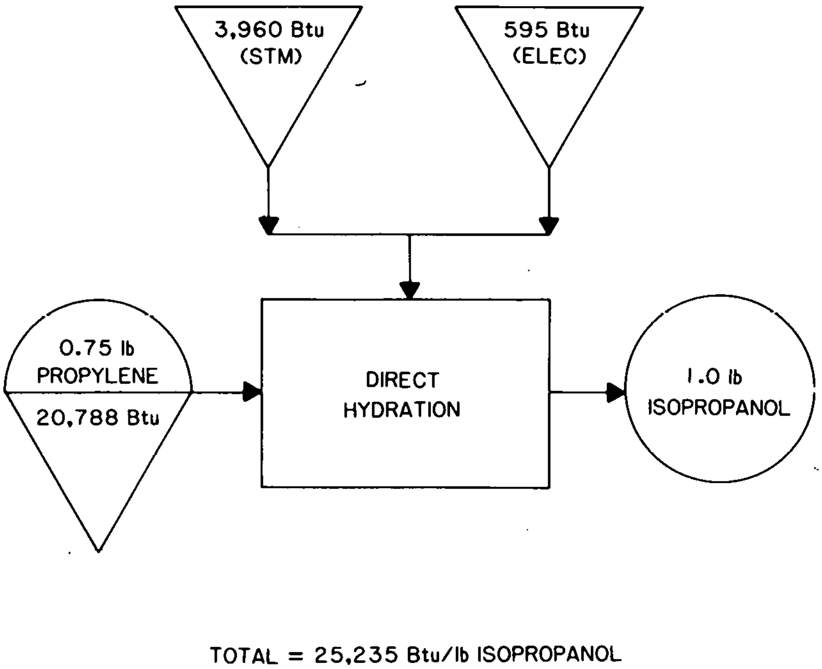


Fig. 4.65. Energy and Materials Flow for Isopropanol Production (Source: Ref. 89)

5 ENERGY SAVINGS THROUGH RECYCLING

Chemical intermediates generally are consumed in the manufacture of products that may be recyclable. Ethylene glycol, for example, is used for automotive antifreeze but is normally discarded after a year's use due to acidic contaminants formed by oxidation. Antifreeze could be recovered and purified, and the unoxidized ethylene glycol reused. Solvents in industrial processes often are reused, but those in consumer products (e.g., cosmetics and rubbing alcohol) are dispersed with no possibility of recovery.

Several significant energy- and material-conserving alternatives to the present throwaway system are possible for petrochemically derived consumer goods. Since the average product lifetime for polymeric materials is short, large volumes of material and embodied energy are quickly part of the waste stream. And, although the consumer product may no longer be usable, the material has often lost little of its original usefulness. A metal like copper has a 17-yr average product lifetime, whereas fibers, the longest-lived class of polymers, are usually discarded after less than 10 yr. Rubbers are used perhaps three years and the largest volume of polymers, plastics, may be used for days or months. Considerable quantities of plastic packaging are discarded as soon as the product reaches the consumer. Note that the maximum quantity of material that can be supplied by recycle is equal to the quantity going out of use, i.e., the demand one product lifetime ago. For short-lived products, this is virtually equivalent to present demand.

The simplest alternative to discarding an item is reuse. Energy consumption per use decreases with this alternative. When the product is no longer reusable, the material can sometimes be refabricated. Another possibility for recycling polymeric materials involves breaking them down chemically into smaller building-block molecules that can be reused. The final possibility for reclaiming part of the energy embodied in waste materials is combustion. A good example of this option is when mixed municipal waste is co-fired with coal in power plants, as against incineration simply for waste disposal. These three options have been listed in decreasing order of energy recovered. Reuse recovers all of the energy required to produce the product, while combustion of the plastics most often found in municipal waste recovers an average of 17,000 Btu/lb (39 kJ/g)[110] or about half of the total embodied energy. While this represents a considerable loss of energy and availability, combustion is feasible now and is preferable, at least from an energy conservation point of view, to the total loss associated with landfilling.

The possibilities for recycling a given material depend on its purity, its value, and the amount available at a given location. Prompt industrial scrap is easiest to recycle. Pure thermoplastic wastes generated in a fabrication process usually can be remelted and returned to the same or a similar process, either directly or via a plastics reprocessor. Thermoplastics typically can be remelted and reused at an energy cost of only 1000 Btu/lb (2.3 kJ/g).[111] Most of the synthetic polymers now recycled fall into this category.

Thermosetting scrap generated during manufacture cannot simply be remelted. It is most often landfilled but can be used as filler. There are some processes now being developed for breaking down thermosets into their constituent molecules. For example, several companies are working on a process for hydrolyzing polyurethane foam scrap from the manufacture of auto seat cushions back into the feedstocks for new polyurethane.

Post-consumer scrap is very difficult to recycle for a number of reasons. The most important is that a mixture of melted polymers generally produces a very low quality product, although there is a report of a mixed-plastic refabrication operation producing toys in Taiwan.[112] Separation of plastic wastes is mechanically impossible with present technology. Manual separation is also unfeasible, except for large, recognizable items like milk containers, because of the labor required and the large variety of apparently similar plastics that would need to be distinguished. Therefore, considerable experimental work has been done on methods for separating mixed wastes and on making mixtures of plastics compatible. However, concentrations of polymers in municipal wastes are low (a few percent by weight), and their separation would need to "piggyback" on the recovery of higher-volume or more valuable components. For these reasons, commercial recycling operations for post-consumer polymer scrap are all based on some source separation. For example, telephone manufacturers recycle obsolete or broken phone bodies made of ABS plastic. Rather than expending the labor and capital necessary to segregate and remelt different colors separately, used phone bodies are melted together to give a gray product. This is then used: (1) for the interior of new phone bodies, (2) to make new parts where appearance is unimportant (e.g., connector blocks), or (3) in a mixture with polyvinyl chloride to form a new material usable for central office equipment. The Bell System also recovers polyvinyl chloride and copper from old cables and wires for reuse in similar products.[113]

There are several other large, recognizable, post-consumer scrap items that can be diverted from the solid-waste stream that are already being recycled to a small extent. One example is polyester bottles, which can be ground up and remelted for use in fiber and film, or broken down into simpler molecules for manufacture of unsaturated polyester. Another is automobile tires, which can be: (1) burned whole or shredded, (2) pyrolyzed to yield an oil product and a solid char, (3) ground up and mixed with asphalt paving material (asphalt-rubber), or (4) digested with alkali to produce traditional rubber reclaim. The average quantity of reclaim rubber used in tire manufacture in 1979 was only 1.6% of the weight of a bias tire; no reclaim was used in radials. The energy required to produce one pound of reclaimed rubber is 4600 Btu (10.6 kJ/g), considerably less than the total primary energy embodied in a pound of SBR compound (43,000 Btu/lb or 99.7 kJ/g).[91] However, total reclaim produced in the United States decreased from 291,000 tons (265,000 t) in 1958 to 119,000 tons (108,000 t) in 1977 because tire manufacturers consider it an inferior product.[114] This trend could be reversed as rubber raw materials become more expensive. Preliminary studies show that use of discarded tires in asphalt-rubber recovers the most energy of all of the known options.[91] The major economic problems that recycling options for nonretreadable tires share are the high costs of collection and size reduction. Demonstration projects for energy recovery from discarded tires are currently being funded by DOE.

A somewhat less promising area for post-consumer waste recycling is specific waste streams having a higher-than-average plastics concentration and containing relatively few components. Examples of this type of waste stream include wastes from airports, hospitals, and fast-food chains. This is an entirely new area for investigation.

In summary, although a solution to the very difficult problem of recovering polymers from general municipal solid waste is not in sight, some commercial recycling operations for certain waste streams have proved feasible.

6 CONCLUSIONS

This report analyzes the manufacture of ethylene, the cornerstone of the petrochemical industry, and its coproducts and derivatives. The energy and materials flows in the various manufacturing processes are used as the basis to study the energy implications of producing and recycling olefin-derived materials, and to compare these products with competing products. Countless consumer and industrial products are manufactured from olefin derivatives. The volume of product is enormous. For example, the five major thermoplastics (LDPE, HDPE, PP, PS, and PVC) accounted for over 20 billion lb in 1979.

The industries producing olefins and their derivatives are major consumers of oil and gas, both for feedstock and process fuel. Present manufacturing technology for conserving energy involves extensive use of heat (or cold) recovery. Processes and even whole petrochemical complexes are integrated and use techniques like cascading to make a given quantity of energy perform as much work as possible. Because materials make up a large part of the costs and energy into a process, extreme care also is taken to prevent the waste of materials. By-products are used as chemicals whenever possible or else burned as fuel. Unreacted feed is usually recycled to extinction. If there are impurities building up after repeated recycling, a small loss will occur as a result of using a purge stream. The largest materials losses come from competing reactions, and considerable research is dedicated to creating more selective catalysts. The catalysts are regenerable, thereby saving materials. Alternatively, new processes can be sought to avoid a reaction with poor selectivity, as in the development of direct routes to ethylene glycol.

New technology allows ethylene manufacturers to crack either crude oil or various refined products. While not specifically directed towards energy conservation, this development allows chemical plants to use gas oil feed in the summer (when it is not needed as heating oil) and naphtha in the winter (when demand for gasoline, of which it is a component, is relatively low). Competition for refined streams is thereby eased. Ethylene production is growing much more rapidly than U.S. refinery output; without the capability to crack crude oil, chemical producers would quickly strain the capacity of refineries to produce streams for cracking.

The economy is basically a system for transforming resources into final products. From the point of view of materials and energy inputs, it is possible to consider changes on three levels: (1) adjustments at the feedstock level, (2) changes in the transformation process employed, and (3) substitution of an entirely new product for a given end use. In the petrochemical industry, energy and materials are a substantial portion of costs. Therefore, energy-conserving retrofits are installed because they pay. And, as the industry is expanding rapidly, new and more efficient units are installed. Thus, energy and materials usage per pound of product should become even lower in the future. This is not to imply, however, that there is no room for further conservation efforts, for all of the subject processes are far from their theoretical thermodynamic efficiencies.

Some important areas requiring further investigation are:

1. After any petrochemical product has fulfilled its purpose for the consumer, it still has substantial energy value. It can be recycled as a material to recover some part of the processing energy required to make it, while still allowing recovery of the heat of combustion by later burning. However, even the combustion of polymer wastes is seldom performed now, and this potential resource is being lost. Therefore, recycling and ultimate combustion of these and other petroleum-derived products require further investigation.

2. From the point of view of available national resources, it is important to study the impacts on the economy of using coal- and biomass-derived chemicals as feedstocks in the olefins industry. This would involve process analysis combined with input-output techniques.

3. Efforts to make optimum use of the available heat embodied in process steam are indicated, because this energy is a major fraction of the energy input of many of the production processes.

REFERENCES

1. Shreve, R.N., and J.A. Brink, *Chemical Process Industries*, McGraw-Hill, New York City (1977).

2. Wishart, R.S., *Industrial Energy in Transition: A Petrochemical Perspective*, Science, *199*:614-618 (Feb. 10, 1978).

3. *The Petroleum Handbook*, 5th ed., Shell International Petroleum Company, Ltd., London (1966).

4. *Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals (including Synthetic Plastics and Resin Materials), November, December, and Cumulative Totals, 1979,* U.S. International Trade Commission, SOC Series C/P-79-12 (Feb. 14, 1980).

5. Sax, N.I., *Dangerous Properties of Industrial Materials*, Reinhold Publishing Corp., New York City (1962).

6. Lowenheim, F.A., and M.R. Moran, *Faith, Keys, and Clark's Industrial Chemicals*, 4th ed., Wiley-Interscience, John Wiley and Sons, New York City (1975).

7. Edmister, W.C., *Applied Hydrocarbon Thermodynamics*, Gulf Publishing Co., Houston (1961).

8. *Materials Reference Issue 1976*, Machine Design, *48*(5):120 (March 4, 1976).

9. *Chemical and Process Technology Encyclopedia*, McGraw-Hill, New York City (1974).

10. *Chemical Origins and Markets*, G.M. Lawler, ed., 5th ed., Chemical Information Services, Stanford Research Institute, Menlo Park, Calif. (1977).

11. *Surge in Petrochemicals Due to Subside*, Chemical and Engineering News, *57*(47):10-21 (Nov. 19, 1979).

12. *What's Ahead for Propylene and Ethylene Oxide*, Chemical Engineering Progress, *76*(1):5356 (Jan. 1980).

13. O'Neill, K.S., and M.G. Marbach, *Future Effects of Energy Values on Propylene*, and Michalicek, S.G., *The Effect of Changing Energy Values and Government Regulation on Butadiene Production and Demand*, in The Future Effect of Changing Energy Values on the CPI, Proc. Meeting of Chemical Marketing Research Assn., New Orleans (Nov. 1978).

14. *Plastics Monomers Business is Thriving,* Chemical and Engineering News, *57*(25):8-11 (June 18, 1979).

15. *Facts and Figures of the Plastics Industry*, 1977 and 1979 eds., The Society of the Plastics Industry, Inc., New York City (1977, 1979).

16. *The Outlook for High Density Polyethylene*, Chemical Engineering Progress, *76*(1):74-77 (Jan. 1980).

17. *Thermoplastics Boom May Be Easing*, Chemical and Engineering News, *57*(36): 10-16 (Aug. 3, 1979).

18. *Downturn Looms for Synthetic Elastomers*, Chemical and Engineering News, *57*(10):8-9 (March 5, 1979).

19. *Ethylene and Its Industrial Derivatives*, S.A. Miller, ed., E. Benn, Ltd., London (1969).

20. Stinson, S., *Ethylene Technology Moves to Liquid Feeds*, Chemical and Engineering News, *57*(22):32 (May 28, 1979).

21. *Butadiene Isn't All It's Cracked Up to Be*, Chemical Week, *123*(7):33 (Aug. 16, 1978).

22. Reuben, B.G., and M.L. Burstall, *The Chemical Economy*, Longman Group, Ltd., London, p. 614 (1973).

23. *Chemical Industry Facts and Figures*, Chemical and Engineering News, *58*(23):33 (June 9, 1980).

24. *Our Industry Petroleum*, British Petroleum Co., Ltd., London (1976).

25. *The Potential for Energy Conservation in Nine Selected Industries. The Data Base*, Gordian Associates, Inc., New York City (June 1974).

26. *Evaluation of the Theoretical Potential for Energy Conservation in Several Basic Industries*, Battelle Columbus Laboratories (July 1975).

27. Gait, A.J., and E.G. Hancock, *Plastics and Synthetic Rubbers*, Pergamon Press, Oxford, England (1970).

28. *Handbook of Chemistry and Physics*, R.C. Weast and S.M. Selby, eds., 48th ed., CRC Press, Boca Raton, Fla. (1967-68).

29. Arnold, L., *Introduction to Plastics*, Iowa State University Press, Ames (1968).

30. Hahn, A.V., *The Petrochemical Industry*, McGraw-Hill, New York City (1970).

31. *Petrochemical Outlook*, Chemical Engineering Progress, *73*(7):25 (July 1977).

32. DuBois, J.H., and F.W. John, *Plastics*, Van Nostrand Reinhold Co., New York City (1967).

33. Cummings-Saxton, J., Argonne National Laboratory, unpublished information (1980).

34. *Webster's New Collegiate Dictionary*, G. & C. Merriam Co., Springfield, Mass. (1976).

35. Golding, B., *Polymers and Resins*, D. Van Nostrand Co., Princeton, N.J. (1959).

36. Stern, K., Chem Systems, Inc., New York City, personal communication (1980).

37. Compton, W.D., Ford Motor Co., unpublished information presented at American Society of Metals Materials Substitute Conf., Chicago (Sept. 1977).

38. Mai, K., *Energy and Petrochemical Raw Materials through 1990*, Chemical Engineering, *84*(12):122 (June 6, 1977).

39. *ABS*, Plastics Design Forum, *1*(6):53 (Nov./Dec. 1976).

40. *Acetal*, Plastics Design Forum, *3*(1):85 (Jan./Feb. 1978).

41. *Acrylic*, Plastics Design Forum, *3*(6):87 (Nov./Dec. 1978).

42. *Cellulosics*, Plastics Design Forum, *2*(2):65 (March/April 1977).

43. *Fluoropolymers*, Plastics Design Forum, *5*(1):81 (Jan./Feb. 1980).

44. *Phenolic*, Plastics Design Forum, *3*(4):107 (July/Aug. 1978).

45. *Polycarbonate*, Plastics Design Forum, *3*(3):89 (May/June 1978).

46. *Polyethylene*, Plastics Design Forum, *5*(2):85 (March/April 1980).

47. *Polypropylene*, Plastics Design Forum, *4*(1):71 (Jan./Feb. 1979).

48. *Polystyrene*, Plastics Design Forum, *3*(2):77 (March/April 1978).

49. *Polysulfone*, Plastics Design Forum, *4*(5):97 (Sept./Oct. 1979).

50. *PPO-Based Resin*, Plastics Design Forum, *4*(6):75 (Nov./Dec. 1979).

51. *PVC*, Plastics Design Forum, *2*(1):41 (Jan./Feb. 1977).

52. *Rigid Urethane*, Plastics Design Forum, *2*(5):61 (Sept./Oct. 1977).

53. *The Case for Nylon 6*, Plastics Design Forum, *2*(4):60 (July/Aug. 1977).

54. *Thermoplastic Polyester*, Plastics Design Forum, *2*(3):55 (May/June 1977).

55. *Unsaturated Polyester*, Plastics Design Forum, *4*(3):109 (May/June 1979).

56. Waddams, A.L., *Chemicals from Petroleum*, 3rd ed., John Wiley and Sons, New York City (1973).

57. *Chemical Industry Facts and Figures*, Chemical and Engineering News, *57*(24):32-68 (June 11, 1979).

58. *Chemical Industry Facts and Figures*, Chemical and Engineering News, *55*(23):40 (June 6, 1977).

59. *Chemical Industry Facts and Figures*, Chemical and Engineering News, *56*(24):45 (June 12, 1978).

60. *Synthetic Organic Chemicals, U.S. Production and Sales, 1976*, U.S. International Trade Commission Pub. 833, U.S. Government Printing Office (1977).

61. *Key Chemicals*, Chemical and Engineering News, *55*(45):11 (Nov. 7, 1977).

62. *Current Prices of Chemicals and Related Materials*, Chemical Marketing Reporter, *217*(19):46-55 (May 12, 1980).

63. *Environmental Considerations of Selected Energy Conserving Manufacturing Process Options, Vol. VI, Olefins Industry Report*, U.S. Environmental Protection Agency Report EPA-600/7-76-034f (Dec. 1976).

64. *Overcapacity Still Hurting Petrochemicals*, Chemical and Engineering News, *56*(47):12-17 (Nov. 20, 1978).

65. *Petrochemical Pickup Still Around the Corner*, Chemical and Engineering News, *55*(45):8 (Nov. 7, 1977).

66. *Petrochemicals Wait for the End of the Pause*, Chemical and Engineering News, *54*(47):11-18 (Nov. 15, 1976).

67. Stobaugh, R.B., Jr., *Petrochemical Manufacturing and Marketing Guide, Vol. II - Olefins, Diolefins and Acetylene*, Gulf Publishing Co., Houston (1968).

68. Dow Chemical, USA, personal communication (Jan. 1979).

69. *The Impact of Energy Costs, Technological Change and Capital Equipment Costs upon Raw Materials Competition, 1978-1983-1988*, Springborn Laboratories, Inc., and Phillip Townsend Associates, Inc. (March 1979).

70. *Fuels and Electric Energy Consumed*, 1977 Census of Manufactures, U.S. Bureau of the Census preliminary report MC77-SR-4(P) (May 1979).

71. *Annual Report, Industrial Energy Efficiency Program*, U.S. Dept. of Energy Report DOE/CS/0111 (Dec. 1979).

72. Confidential industry source.

73. Lurie, M., *Oil and Chemicals. Era of Peaceful Coexistence*, Chemical Week, *125*(16):70-92 (Oct. 17, 1979).

74. *1977 Census of Manufactures*, Industry Series, Preliminary Reports, U.S. Dept. of Commerce: Plastics Materials and Resins, SIC 2821, Report MC77-1-28B-1(P) (June 1979); Synthetic Rubber, SIC 2822, Report MC77-1-28B-2(P) (March 1979); Organic Fibers - Noncellulosic, SIC 2824, Report MC77-1-28B-4(P) (July 1979); Industrial Organic Chemicals Not Elsewhere Classified, SIC 2869, Report MC77-1-28F-3(P) (Aug. 1979).

75. *Voluntary Industrial Energy Conservation Progress Report 5 July 1977*, originally issued by U.S. Dept. of Commerce and Federal Energy Administration, reprinted by U.S. Dept. of Energy (Oct. 1977).

76. See, for example, Ahern, J.E., *The Exergy Method of Energy Systems Analysis*, John Wiley and Sons, New York City (1980).

77. *Chemical Engineering*, deskbook issue, *80*(23) (Oct. 8, 1973).

78. *Introduction to Petroleum Chemicals*, H. Steiner, ed., Pergamon Press, Oxford, England (1961).

79. Gaines, L.L., and A.M. Wolsky, *Energy and Materials Flows in Petroleum Refining*, Argonne National Laboratory Report ANL/CNSV-10 (1980).

80. *Industry Process Profiles for Environmental Use. Chapter 5: Basic Petrochemicals Industry*, Radian Corp., Austin, Tex. (Jan. 1977).

81. *Energy Consumption: The Chemical Industry*, U.S. Environmental Protection Agency Report EPA-650/2-75-032a, NTIS Order No. PB 241 927 (April 1973).

82. Stern, J.P., and E.S. Stern, *Petrochemicals Today*, Edward Arnold Publisher, Ltd., London (1971).

83. *New Ethylene Process May Cut Costs 20%*, Chemical and Engineering News, *57*(43):8 (Oct. 22, 1979).

84. Stone & Webster Engineering Corp., New York City, unpublished information (Aug. 1980).

85. *Carbide Details Ethylene-from-Crude Process*, Chemical and Engineering News, *56*(13):29 (March 27, 1978).

86. Davis, J.C., *Crude Oil Cracking Gains*, Chemical Engineering, *84*(12):78 (June 6, 1977).

87. Craig, R.G., L.C. Doelp, and A.K. Logwinuk, *Economics of Olefin and Diolefin Production*, World Petroleum, *36*(4):33 (1965).

88. Gait, A.J., *Heavy Organic Chemicals*, Pergamon Press, Oxford, England (1967).

89. *1979 Petrochemical Handbook Issue*, Hydrocarbon Processing, Gulf Publishing Co., Houston (Nov. 1979).

90. *1977 Petrochemical Handbook Issue*, Hydrocarbon Processing, Gulf Publishing Co., Houston (Nov. 1977).

91. Gaines, L.L., and A.M. Wolsky, *Discarded Tires: Energy Conservation through Alternative Uses*, Argonne National Laboratory Report ANL/CNSV-5 (Dec. 1979).

92. Albright, L.F., *High-Pressure Processes for Polymerizing Ethylene*, Chemical Engineering, *73*(26):113 (Dec. 19, 1966).

93. E.I. DuPont de Nemours & Company, personal communication (1980).

94. Boustead, I., and G.F. Hancock, *Handbook of Industrial Energy Analysis*, Halstead Press, New York City (1979).

95. U.S. Patent 370837 to Union Carbide Corporation.

96. U.S. Patent 370956 to Union Carbide Corporation.

97. Martino, R.J., New York City, personal communication (1980).

98. U.S. Patent 4011382 to Union Carbide Corporation.

99. Wittcoff, H., *How It's Really Done - I*, Chemtech, *7*(12):754 (Dec. 1977).

100. Stephenson, R.M., *Introduction to the Chemical Process Industries*, Reinhold Publishing Corp., New York City (1966).

101. Van Winkle, T.L., et al., *Cotton vs. Polyester*, American Scientist, *66*(3):281 (May-June 1978).

102. *Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing*, prepared by Battelle Columbus Laboratories for U.S. Bureau of Mines, NTIS Order No. PB 245 759 (June 1975).

103. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd ed., Wiley-Interscience, John Wiley and Sons, New York City (1965).

104. Shen, S.Y., and A.M. Wolsky, Argonne National Laboratory, unpublished information (1980).

105. *Propylene Oxide*, Chemical and Engineering News, *57*(25):11 (June 18, 1979).

106. Brownstein, A.M., *Trends in Petrochemical Technology*, Petroleum Publishing Co., Tulsa (1976).

107. U.S. Patent 3829392 to Shell Oil Company.

108. *Ethylene Glycol*, Chemical and Engineering News, *57*(13):12 (March 26, 1979).

109. Hatch, F., *The Chemistry of Petrochemical Reactions*, Gulf Publishing Co., Houston (1955).

110. Teasely, L.N., *Energy Implications of Polymer Production and Use*, master's thesis, Washington University (1974).

111. Berry, R.S., and H. Makino, *Energy Thrift in Packaging and Marketing*, Technology Review, *76*(4) (Feb. 1974).

112. Chiu, H.H., University of Illinois at Chicago Circle, personal communication (1980).

113. Donovan, R.C., et al., *Recycling PVC*, Bell Laboratories Record, p. 215 (Sept. 1977).

114. Rubber Recycling Division Bulletin 78-2, National Assn. of Recycling Industries (Aug. 31, 1978).

Distribution for ANL/CNSV-9

Internal:

J.G. Asbury
L. Burris
R.R. Cirillo
E.J. Croke
J. Dzingel
A.R. Evans
B.R.T. Frost
L.L. Gaines
B.L. Graves
P.F. Gustafson
W. Harrison
A.S. Kennedy
A.B. Krisciunas
M.L. Kyle
K.S. Macal
W.E. Massey
P.A. Nelson
E.G. Pewitt
J.J. Roberts
N.A. Sather
S.Y. Shen
W.K. Sinclair
T. Surles
A. Tevebaugh
M.W. Tisue
R.W. Weeks
A.M. Wolsky (250)
ANL Contract Copy
ANL Libraries (2)
TIS Files (6)

External:

DOE-TIC, for distribution per UC-95f (256)
Manager, Chicago Operations and Regional Office, DOE
Chief, Office of Patent Counsel, DOE-CORO
President, Argonne Universities Association
Energy and Environmental Systems Division Review Committee:
  W.C. Ackermann, U. Illinois
  E.E. Angino, U. Kansas
  B.A. Egan, Environmental Research and Technology, Inc.
  R.E. Gordon, U. Notre Dame
  W.W. Hogan, Harvard U.
  W.N. Poundstone, Consolidation Coal Company
  L.H. Roddis, Jr., Charleston, S.C.
  G.A. Rohlich, U. Texas at Austin
  R.A. Schmidt, Booz, Allen, & Hamilton
  J.J. Stukel, U. Illinois
J.H. Gibbons, Office of Technology Assessment, U.S. Congress
D.E. Kash, USGS, Reston, Va.
J.F. Collins, DOE, Chief, Alternative Materials Utilization Branch,
  Office of Industrial Programs

☆U. S. GOVERNMENT PRINTING OFFICE: 1980—750-034/32