27
5-15-81
24 exp. to NTIS

(1)
R-4348

Technical Memo

MASTER

ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, 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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

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 nor 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.

This informal report presents preliminary results of ongoing work or work that is more limited in scope and depth than that described in formal reports issued by the Energy and Environmental Systems Division.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ANL/CNSV-TM-56

ENERGY/MATERIAL FLOWS ASSOCIATED
WITH CYCLIC PETROCHEMICALS

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, 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.

prepared by

H.M. Mittelhauser Corp.
Downers Grove, Illinois

for

Argonne National Laboratory
Energy and Environmental Systems Division
under Argonne Contract 31-109-38-5345

October 1979

work sponsored by

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

TABLE OF CONTENTS

	<u>Page No.</u>
1.0 EXECUTIVE SUMMARY	1
2.0 INTRODUCTION	2
3.0 CONSUMPTION OF BTX AND CYCLOHEXANE	3
3.1 Introduction	3
3.2 Summary	3
4.0 BLOCK FLOW DIAGRAMS AND PROCESS DESCRIPTIONS	18
4.1 BTX Separation	18
4.1.1 Summary	18
4.1.2 Process Description	18
4.1.3 Alternative Processes	19
4.1.4 Conversion Factors Used in Chapter 4.0	19
4.2 Separation of O- and P-Xylene	22
4.2.1 Summary	22
4.2.2 Process Description - Separation of O-Xylene	22
4.2.3 Process Description - Separation of P-Xylene	23
4.2.4 Process Alternatives	26
4.3 Benzene from Toluene	29
4.3.1 Summary	29
4.3.2 Process Description - Toluene Hydrodealkylation	29
4.3.3 Process Description - Toluene Disproportionation	30
4.3.4 Alternative Processes	35
4.4 Benzene Hydrogenation	36
4.4.1 Summary	36
4.4.2 Process Description	36
4.5 Styrene from Benzene	39
4.5.1 Summary	39
4.5.2 Process Description - Production of Ethylbenzene (Liquid Phase Process)	39
4.5.3 Process Description - Production of Styrene	39
4.5.4 Process Alternatives	40

TABLE OF CONTENTS (Contd)

	<u>Page No.</u>
4.6 Polystyrene from Styrene	43
4.6.1 Summary	43
4.6.2 Process Description - Bulk Suspension Polymerization	43
4.6.3 Process Description - Bulk-Press Polymerization	43
4.7 ABS/SAN from Styrene	49
4.7.1 Summary	49
4.7.2 Process Description of the Emulsion Polymerization SAN Process	49
4.7.3 Process Description of the Suspension Polymeriza- tion SAN Process	49
4.7.4 Process Description of the ABS Graft by Emulsion Polymerization	52
4.7.5 Process Description of the ABS Graft Resin by Solution Polymerization	57
4.8 SBR from Styrene	60
4.8.1 Summary	60
4.8.2 Process Description for Cold Emulsion Polymeri- zation of SBR	60
4.8.3 Process Alternatives	62
4.9 Cumene from Benzene	65
4.9.1 Summary	65
4.9.2 Process Description	65
4.10 Phenol from Cumene	68
4.10.1 Summary	68
4.10.2 Process Description	68
4.11 Phenolic Resins from Phenol	71
4.11.1 Summary	71
4.11.2 Process Description for Resole Resins	71
4.11.3 Process Description for Novolak Resins	72
4.12 TDI from Toluene	76
4.12.1 Summary	76
4.12.2 Process Description	76
4.12.3 Alternative Processes	78
4.13 Urethane Foam from TDI	81
4.13.1 Summary	81
4.13.2 Process Description for Prepolymer Type Process	81
4.13.3 Process Alternatives	82

TABLE OF CONTENTS (Contd)

	<u>Page No.</u>
4.14 Dimethyl Terephthalate from PXylene	85
4.14.1 Summary	85
4.14.2 Process Description of the Dynamit Nobel AG Process	85
4.14.3 Process Description of the Toray Industries' Process	87
4.14.4 Alternative Processes	87
4.15 Polyester Fibers	93
4.15.1 Summary	93
4.15.2 Process Description	94
4.16 Caprolactam from Cyclohexane	98
4.16.1 Summary	98
4.16.2 Process Description	98
4.16.3 Process Alternatives	100
4.17 Nylon 6 from Caprolactam	103
4.17.1 Summary	103
4.17.2 Process Description	103
4.17.3 Process Alternatives	103
4.18 Adipic Acid from Cyclohexane	105
4.18.1 Summary	105
4.18.2 Process Description	105
4.19 Nylon 6,6 from Adipic Acid	109
4.19.1 Summary	109
4.19.2 Process Description	109
4.20 Phthalic Anhydride from O-Xylene	113
4.20.1 Summary	113
4.20.2 Process Description	113
4.21 Maleic Anhydride from Benzene	116
4.21.1 Summary	116
4.21.2 Process Description	116
4.22 Unsaturated Polyester Production	119
4.22.1 Summary	119
4.22.2 Process Description	119
5.0 REFERENCES	122
6.0 ADDITIONAL REFERENCES	126

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

1.0 EXECUTIVE SUMMARY

This study was prepared in support of the Argonne National Laboratory Systems Analysis for Alternative Materials Utilization Project. The principal objective was to describe and analyze the energy and material flows in the production of benzene, toluene, xylene, cyclohexane, and their derivatives.

A detailed product flow analysis, starting with the refinery reformat stream, was prepared to identify the major products of interest. The selection of the products and their derivatives for detailed analysis was based on 1978 consumption data which is reported in Section 3.0 of this report. The products selected for detailed analysis were: Benzene (from Toluene), Polystyrene, Polyester fibers, Cyclohexane, Nylon 6,6, Nylon 6, ABS + SAN, Phenolic resins, Urethane foams, Unsaturated polyesters and SBR. Data on the selling price of these products and the companies which market these products are reported in Tables 3.6 and 3.7, respectively.

Once the major products were established, the production routes were analyzed to determine the key manufacturing processes available. A detailed analysis of the important steps in the production of these materials is presented in Section 4.0. For each step in the manufacturing process a process description, a block flow diagram, the energy consumption, and the feedstock conversions are provided. If more than one process was available and was determined to be commercially important, this route was also presented in detail. If the alternate process was not as significant, then this process was noted and briefly described.

The results from this study must be integrated with the results of other studies before a comprehensive evaluation of the total energy required to produce a particular product can be determined. For example, calculation of the energy consumption required to produce butadiene (used in SBR production) was outside the scope of this study.

2.0 INTRODUCTION

This project was undertaken in support of the Argonne National Laboratory (ANL) Systems Analysis for Alternative Materials Utilization Project. The purpose of the ANL project is to study, at the unit-process level, the energy and material flows in selected energy-intensive industries in order to identify significant energy conservation opportunities. These conservation opportunities can take the form of:

- Improved efficiencies of existing processes
- New more efficient processes
- Use of alternative materials and feedstocks.

The principal objective of this report is to describe and analyze the energy and material flows, at the unit-process level, in the production of cyclic petrochemicals (aromatics and cyclohexane) and their major derivatives.

The consumption patterns of BTX and cyclohexane and their major derivatives are described in Chapter 3.0. Block flow diagrams and process descriptions for the major manufacturing processes used in production of BTX, cyclohexane, and their most significant derivatives are given in Chapter 4.0.

3.0 CONSUMPTION OF BTX AND CYCLOHEXANE

3.1 INTRODUCTION

Task I of Contract #31-109-38-5345 requires a detailed analysis of the production of aromatics (BTX), cyclohexane, and their major derivatives. The purpose of this chapter is threefold:

- To determine the ultimate use of BTX, cyclohexane and their derivatives.
- To establish market prices and major producers of BTX, cyclohexane and their derivatives
- To determine which final products constitute the major consumption of BTX and cyclohexane in order to establish which processes require a detailed process flow analysis (Chapter 4.0).

3.2 SUMMARY

BTX is separated from the petroleum reformat into Benzene, Toluene and Xylene. Cyclohexane may be separated from petroleum naphthas but the major route is manufacture from Benzene. This section summarizes the major derivatives of BTX and cyclohexane. All data is based on 1978 consumption. Figure 3.1 shows the 1978 consumption patterns for benzene (Refs. 3.2-1, 3.2-2). Very small consumptions (e.g., ethylbenzene as a solvent) are not shown. All units are billions of pounds. The numbers in brackets are the weight of benzene consumed in the product shown. For example, 3.14 billion pounds of the 11.13 billion pounds of benzene consumed in 1978 are consumed in polystyrene production. The numbers not in brackets are the weight of final product derived from the starting material. For example, in 1978, 3.41 billion pounds of polystyrene were derived from benzene. Table 3.1 summarizes 1978 benzene consumption, based on the information shown in Figure 3.1. The weight percent shown is the weight percent of the total benzene consumed. Weights of final products are not shown for "other" since all "other" final products are not known.

Figure 3.2 and Table 3.2 present the same information in the same format for Toluene. Similarly, Figure 3.3 and Table 3.3 present the same information for Xylene and Figure 3.4 and Table 3.4 present the same information for Cyclohexane.

Table 3.5 summarizes the 1978 consumption of BTX and cyclohexane. As shown in Table 3.5, the major source of cyclohexane is from Benzene, not naphtha extraction. The following end products are clearly the most significant.

<u>Material</u>	<u>Wt of BTX Component (10^9 lbs)</u>
Benzene (from Toluene)	5.72×10^9 lbs
Polystyrene	3.14
Polyester Fibers	2.69
Cyclohexane	2.06
Toluene Solvents	1.21
Toluene Export	1.19
Nylon 6,6	0.90
Styrene Export	0.89
Nylon 6	0.83
ABS + SAN	0.63
Phenolic Resins	0.51
Urethane Foams	0.39
Unsaturated Polyesters	0.27
SBR	<u>0.24</u>
	20.67×10^9 lbs

The above products consume 20.67 billion pounds, or 75 percent of the total 27.38 lbs of BTX and cyclohexane consumed in 1978. The routes to the above products have been shown in Figures 3.1 to 3.4. The processes to be analyzed for energy consumption that lead to each of the above products are shown below, using the numbering system of Chapter 4.0.

PROCESS SECTIONS

- 4.1 Separation of Benzene, Toluene, Xylene
- 4.2 Separation of Ortho, Meta and Para Xylene
- 4.3 Benzene from Toluene
- 4.4 Cyclohexane from Benzene
- 4.5 Styrene from Benzene
- 4.6 Polystyrene from Styrene
- 4.7 ABS/SAN from Styrene
- 4.8 SBR from Styrene
- 4.9 Cumene from Benzene
- 4.10 Phenol from Cumene

4.11	Phenolic Resins from Phenol
4.12	TDI from Toluene
4.13	Urethane Foams from TDI
4.14	DMT and TPA from p-Xylene
4.15	Polyester Fibers from DMT and TPA
4.16	Caprolactam from Cyclohexane
4.17	Nylon 6 from Caprolactam
4.18	Adipic Acid from Cyclohexane
4.19	Nylon 6,6 from Adipic Acid
4.20	Phthalic Anhydride from O-Xylene
4.21	Maleic Anhydride from Benzene
4.22	Unsaturated Polyester Production

The 1978 Market Prices for the above materials are shown in Table 3.6, and the major producers are shown on Table 3.7.

FIGURE 3.1
1978 CONSUMPTION OF BENZENE - 10⁹ lbs*

*Numbers in () represent wt of Benzene consumed in product shown.
Numbers not in () represent wt of Final Product produced from Benzene.

TABLE 3.1 SUMMARY - BENZENE CONSUMPTION - 1978 (Billions of Pounds)

<u>Material</u>	<u>10⁹ lbs Benzene</u>	<u>wt %</u>	<u>10⁹ lbs* Final Product</u>
Polystyrene	3.14	28.2	3.41
Cyclohexane	2.06	18.5	2.22
Export Styrene	0.89	8.0	0.97
ABS + SAN	0.63	5.7	1.19
Aniline	0.59	5.3	0.57
Phenolic Resins	0.51	4.6	0.84
SBR	0.24	2.2	1.39
Methacrylates	0.21	1.9	0.36
Bisphenol A	0.21	1.9	0.28
Caprolactam	0.19	1.7	0.25
SB Copolymer	0.17	1.5	0.80
Surface Coating Agents	0.11	1.0	0.15
MIBK	0.05	0.4	0.06
Other	<u>2.13</u>	<u>19.1</u>	-
	11.13	100.0	

*Weight of Final Product that used Benzene as a starting material.

FIGURE 3.2

1978 CONSUMPTION OF TOLUENE - 10^9 LBS*

*Numbers in () represent wt of Toluene consumed in product shown.
Numbers not in () represent wt of Final Product produced from Toluene.

TABLE 3.2 SUMMARY - TOLUENE CONSUMPTION - 1978 (Billions of Pounds)

<u>Material</u>	<u>10⁹ lbs Toluene</u>	<u>wt %</u>	<u>10⁹ lbs* Final Product</u>
Benzene	5.72	61.8	4.65
Solvents	1.21	13.1	1.21
Export	1.19	13.0	1.19
Urethane Foams	0.39	5.0	1.23
Other	<u>0.74</u>	<u>7.1</u>	-
	9.25	100.0	

*Weight of Final Product that used Toluene as a starting material.

FIGURE 3.3
1978 CONSUMPTION OF XYLENE - 10^9 LBS*

*Numbers in () represent wt of Xylene consumed in product shown.
Numbers not in () represent wt of Final Product produced from Xylene.

TABLE 3.3 SUMMARY - XYLENE CONSUMPTION - 1978 (Billions of Pounds)

<u>Material</u>	<u>10⁹ lbs Xylenes</u>	<u>wt % %</u>	<u>10⁹ lbs* Final Product</u>
Polyester Fibers	2.69	59.9	3.80
Plasticizers	0.28	6.3	0.71
Export	0.27	6.0	0.27
Unsaturated Polyesters	0.27	6.0	1.14
Alkyd Resins	0.22	5.1	0.63
Polyester Film	0.27	4.6	0.39
Other	<u>0.66</u>	<u>12.1</u>	-
	4.66	100.0	

*Weight of Final Product that used Xylene as a starting material.

FIGURE 3.4

1978 CONSUMPTION OF CYCLOHEXANE - 10^9 LBS*

*Numbers in () represent wt of Cyclohexane consumed in product shown.
Numbers not in () represent wt of Final Product produced from Cyclohexane.

TABLE 3.4 SUMMARY - CYCLOHEXANE CONSUMPTION - 1978
(Billions of Pounds)

<u>Material</u>	<u>10⁹ lbs Cyclo- hexane</u>	<u>wt %</u>	<u>10⁹ lbs* Final Product</u>
Nylon 6,6	0.90	38.3	1.66
Nylon 6	0.83	35.7	0.75
Net Export	0.39	16.7	0.39
Other	<u>0.22</u>	<u>9.3</u>	-
	2.34	100.0	

*Weight of Final Product that uses Cyclohexane as a starting material.

Table 3.5 Summary - 1978 Consumption of Benzene, Toluene, Xylene, and Cyclohexane - 10⁹ lbs

<u>Benzene Derivatives</u>		<u>Toluene Derivatives</u>		<u>Xylene Derivatives</u>		<u>Cyclohexane Derivatives</u>	
<u>Material</u>	<u>wt</u>	<u>Material</u>	<u>wt</u>	<u>Material</u>	<u>wt</u>	<u>Material</u>	<u>wt</u>
Polystyrene	3.14	Benzene	5.72	Polyester		Nylon 66	0.90
Cyclohexane	2.06	Solvents	1.21	Fibers	2.69	Nylon 6	0.83
Export		Export	1.19	Plastici-		Export	0.39
Styrene	0.89	Urethane Foams	0.39	zers	0.28	Other	<u>0.22</u>
ABS + SAN	0.63	Other	<u>0.74</u>	Export	0.27		2.34
Aniline	0.59		9.25	Unsaturated			
Phenolic				Polyesters	0.27		
Resins	0.51			Alkyd			
SBR	0.24			Resins	0.22		
Methacrylates	0.21			Polyester			
Bisphenol A	0.21			Film	0.27		
Caprolactam	0.19			Other	<u>0.66</u>		
SB Copolymer	0.17				4.66		
Surface							
Coating							
Agents	0.11						
MIBK	0.05						
Other	<u>2.13</u>						
	11.13						

TABLE 3.6 MARKET PRICES (¢/lb)^a

No.	Name	1978 Market Prices by Quarter				Arith. Avg. 1978	10/1/79
		Jan. 2	Apr. 3	July 3	Oct. 2		
1	Benzene ^b	9.91	9.10	9.51	9.91	9.61	21.05
2	Toluene ^b	6.89	6.82	6.89	7.93	7.13	15.86
3	Xylene ^b	6.96	6.69	6.89	7.72	7.07	17.65
4	Ortho-Xylene	11	11	11.25	11.50	11.19	19
5	Meta-Xylene	22	22	22	22	22	31
6	Para-Xylene	12.5	12.5	12.5	12.5	12.5	25
7	Cyclohexane ^b	12.26	11.03	11.49	11.95	11.68	24.52
8	Styrene	21	21	18	17.5	19.38	35
9	Polystyrene	28	28	30	30	29	41
10	Styrene-Acrylonitrile (SAN)	40	45	45	45	43.75	51
11	Acrylonitrile-Butadiene Styrene (ABS)	57	57	57	57	57	61
12	Styrene-Butadiene Rubber (SBR)			36.5 ^c		36.5	49.3 ^c
13	Cumene	14	14	14	11	13.25	25
14	Phenol	21	16.5	16.5	19	18.25	34
15	Phenol-Formaldehyde						
16	Toluene Di-Isocyanate (TDI)	48	48	51	51	49.5	63
17	Urethane	32.5	32.5	32.5	32.5	32.5	32.5
18	Dimethyl Terephthalate (DMT)	39	39	39	39	39	39
			20 ^d				29.16 ^d
19	Terephthalic Acid (TPA)	26	26	26	26	26	37.5
20	Unsaturated Polyester Resin	36	36	36	36	36	51 ^e
21	Caprolactam Monomer	51	51	51	51	51	69
22	Nylon 6					116	124 ^f
23	Nylon 6,6		116 ^g			116	124 ^g
24	Polyester, Dacron		72 ^h			72	80 ^h
25	Adipic Acid	40.5	40.5	40.5	40.5	40.5	47
26	Maleic Anhydride	37	37	28	27	32.25	44

^aNos. 10, 11, 17, 21, 25 at lower prices; i.e., medium impact or tank car sizes

^bPriced on gallon basis, expressed in ¢/lb here; prices f.o.b.

^cTelephone, Goodyear Tire, 10/11/79; 1978 Average approximate

^dTelephone, DuPont, 10/11/79, 1978 Avg approx. No explanation for diff from Ref. 3.2-3

^eWas 53.5 on 9/17/79

^fTelephone, Allied Chemical; Nylon 6 to 134

^gTelephone, DuPont, 10/11/79, 1978 Average approximate; Nylon 6,6 to 132 on 11/1/79

^hTelephone, DuPont, 10/25/79

TABLE 3.7 MAJOR PRODUCERS OF BTX, CYCLOHEXANES AND POLYMER DERIVATIVES (Ref. 3.2-1)

<u>Producer</u>	<u>Location</u>	<u>Capacity (lbs x 10⁶)</u>
<u>ABS/SAN</u>		
Borg-Warner	Washington	335
	Ottawa	235
Monsanto	Addyston	390
	Muscantine	125
<u>Benzene</u>		
Snell	Deer Park	990
	Wood River	325
	Odessa	100
Commonwealth Petrochemicals	Penuelas	1350
Gulf	Port Arthur	550
	Alliance	475
	Philadelphia	280
Sun	Toledo	650
	Corpus Christi	275
	Marcus Hook	220
	Tulsa	175
Phillips	Guayama, P.R.	800
	Sweeny	160
Amoco Oil	Texas City	625
<u>Caprolactam</u>		
Allied	Hopewell	425
Nipro	Augusta	350
Dow	Freeport	350
<u>Cumene</u>		
Gulf	Philadelphia	450
	Port Arthur	450
Georgia-Pacific	Houston	750
Monsanto	Alvin	750
Snell	Deer Park	720
<u>Cyclohexane</u>		
Phillips	Sweeney	725
	Guayama, P.R.	575
	Borger	260
<u>DMT/TPA</u>		
DuPont	Wilmington	1250
	Old Hickory	550
Hercofina	Wilmington	1300
<u>Ethylbenzene</u>		
Dow	Freeport	1750
Monsanto	Texas City	1650
	Alvin	60
Crs-Mar	Carville	1500
American Hoechst	Baton Rouge	1150
Oxirane	Channelview	1150
<u>Nylon 6</u>		
Allied	Columbia	225
	Chesterfield	175
American Enka	Lowland	145
	Enka	75
	Central	30
Dow Badische	Anderson	135
<u>Nylon 6.6</u>		
DuPont	Camden	1100
Monsanto	Pensacola	575
<u>Ortho Xylene</u>		
ARCO	Houston	200
Exxon	Baytown	200
Commonwealth Petrochemicals	Penuelas	175
<u>Para-Xylene</u>		
Amoco	Decatur	1300
	Texas City	900
Hercor	Guayanilla Bay	600
St. Croix Petrochemicals	St. Croix	600
<u>Phenol</u>		
Allied	Frankford	600
Monsanto	Alvin	500
Shell	Deer Park	500
Dow	Oyster Creek	465

TABLE 3.7 (Contd)

<u>Phthalic Anhydride</u>		
Koppers	Cicero	235
	Bridgeville	90
Monsanto	Texas City	150
	Bridgeport	85
USS Chemicals	Neville Island	205
BASF Wyandotte	South Kearny	150
<u>Polyester Fiber</u>		
DuPont	Numerous	1600
Fiber Industries	Numerous	1275
Carolina Eastman	Columbia	520
<u>Polystyrene</u>		
Dow	Midland	220
	Allyn's Point	200
	Torrance	200
	Hanging Rock	175
	Joliet	125
ARCO	Beaver Valley	435
Amoco	Joliet	300
	Willow Springs	90
	Torrance	35
Cosden	Calumet City	265
	Big Spring	160
<u>Styrene</u>		
Dow	Freeport	1500
	Midland	325
Monsanto	Texas City	1500
Cos-Mer	Carville	1300
Oxirane	Channelview	1000
American Hoechst	Baton Rouge	985
<u>Styrene Butadiene Rubber</u>		
Goodyear Tire	Houston	865
	Akron	170
	Calhoun	90
Firestone Synthetic Rubber	Lake Charles	650
	Akron	135
	Orange	100
B.F. Goodrich	Port Neches	335
	Louisville	15
<u>TDI</u>		
Mobay	Cedar Bayou	125
	New Martinsville	100
Olin Chemicals	Lake Charles	100
	Ashtabula	30
BASF-Wyandotte	Geismar	100
Dow	Freeport	100
<u>Toluene</u>		
Amoco	Texas City	1875
Sun	Toledo	475
	Marcus Hook	230
	Corpus Christi	300
	Tulsa	150
Commonwealth Petrochemicals	Penueles	1100
Hess Oil	St. Croix	1015

4.0 BLOCK FLOW DIAGRAMS AND PROCESS DESCRIPTIONS

4.1 BTX SEPARATION

4.1.1 Summary

Benzene, toluene, and xylene, commonly termed BTX aromatics, are produced as components in reformat and as a by-product from olefin production. Most BTX produced is from the reformat. The BTX must be removed from the reformat and the components separated in order to be of further process use. The most common method of separating BTX from reformat is solvent extraction. Although many processes and solvents exist, currently the most widely used extraction process is sulfolane extraction (Fig. 4.1). The final products from the process are benzene, toluene, and a mixture of all isomers of xylene (Table 4.1).

4.1.2 Process Description

Reformat containing 59% (molar) aromatics and 41% (molar) paraffins is heated to 212°F and fed to the main extraction column. Here, it is mixed with recycled sulfolane solvent. The extract (containing sulfolane and aromatics) is removed from the bottom of the tower and the raffinate (containing mostly paraffins) is removed overhead. The extract then is pumped to the extract stripper where further removal of saturated hydrocarbons takes place. The extract, now essentially free of paraffins, leaves the bottom of the extractive stripper and passes to the solvent stripper where the aromatics are separated from the sulfolane. The aromatics stream which is essentially 100% aromatics pass overhead out of the column and the sulfolane which is free of aromatics is recycled to the extractor. The aromatic stream is then condensed and pumped to a series of fractionation columns. In the first column, benzene is removed overhead and the bottoms pumped to the second column which removes toluene overhead. The bottoms from the toluene tower are pumped to the final tower for xylene separation. Bottoms from the xylene tower are heavy aromatics which are commonly used in blending gasoline.

4.1.3 Alternative Processes

Another commercial BTX extraction process is NMP/EG extraction (N-Methylpyrrolidone/Ethylene Glycol). The process is virtually identical to sulfolane extraction, with the exception of the use of a dual solvent. As with sulfolane extraction, the final products are benzene, toluene, and a mixture of xylene isomers.

Udex extraction is another common process used to separate BTX from reformat. Like the other extraction processes, the basic process is the same with the exception that glycols are used as the solvent.

4.1.4 Conversion Factors Used in Chapter 4.0

Throughout Chapter 4.0, the conversion of KWH to BTU used is 10,000. Based on an 80% efficiency for generation of steam, the following conversion factors for lbs of steam to BTU were used.

<u>PSIG Steam</u>	<u>BTU/lb</u>
10	1191
15	1181
30	1161
35	1155
50	1139
75	1181
100	1101
150	1071
175	1059
200	1046
250	1025
300	1004
400	970
450	956
600	913
850	846

When no steam pressure is given, it is assumed to be 200 lb steam.

FIGURE 4.1 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE SOLVENT EXTRACTION OF AROMATICS (Sulfolane Processes)

Energy Summary⁽¹⁾

	<u>Extraction Section</u>		<u>Fractionation Section</u>		<u>Totals</u>
Steam (lb)	0.65	(680.0)	0.80	(1208.6)	
Electricity (kWh)	0.0039	(39.0)	0.0021	(21.0)	
Total BTU		(719.0)		(1229.6)	(1948.6)

Note: (1) First number in table is units shown per pound of total aromatics produced. Second number in parentheses is the BTU equivalent.

Table 4.1 Sulfolane Extraction

Mass Conversion*

$$(A) \quad \frac{\text{lb Benzene Produced}}{\text{lb Reformate Feed}} = 0.096$$

$$(B) \quad \frac{\text{lb Toluene Produced}}{\text{lb Reformate Feed}} = 0.33$$

$$(C) \quad \frac{\text{lb Xylene Produced}}{\text{lb Reformate Feed}} = 0.16$$

*Will be variable depending upon composition of reformate feed.

Refs. 4.1-1, 4.1-2

4.2 SEPARATION OF O- AND P-XYLENE

4.2.1 Summary

When xylene is produced, either by solvent extraction of reformate or by conversion of toluene, all isomers of xylene (ortho, meta, and para) are present although the meta isomer is predominant.

Of primary importance to polymer production are the o- and p-xylenes. These two isomers must, therefore, be selectively separated from the xylene mixture. Processes can be once-through systems which separate only those products present in the feed or they can include an isomerization section which will convert m-xylene to o- and p-xylene and thus increase the product yield. In some instances, only p-xylene is desired and the o-xylene is also isomerized. O-xylene is most commonly removed from xylene mixtures by simple fractionation. P-xylene is commonly separated by adsorption. O-xylene's primary use is in the manufacture of phthalic anhydride and p-xylene is used to produce dimethyl terephthalate. (Ref. 4.1-2)

4.2.2 Process Description - Separation of O-Xylene

This process usually employs two fractionation columns in series. The first column separates the feed into m- and p-xylene (overhead) and o-xylene and heavier aromatics (bottoms). The second column then splits the o-xylene/heavy aromatics stream into o-xylene (overhead) and heavy aromatics (bottom). If the feed is high quality (~100% xylene), the second column may not be required.

Mixed feed containing o-, p-, and m-xylene plus heavy aromatics is heated by heat exchange with the o-xylene product and fed to the first fractionating column commonly called the "xylene splitter." Heat for the column is commonly supplied by a fired reboiler. The overhead product from the splitter containing primarily m- and p-xylene is sent to further processing for the recovery of p-xylene. The bottoms, containing o-xylene and heavier aromatics, are sent to the heavy ends column for separation of the o-xylene and heavier aromatics. Here the o-xylene is collected as the overhead product and the heavy aromatics are collected from the bottom of the column. A schematic diagram is shown in Figure 4.2 and mass conversions are presented in Table 4.2.

4.2.3 Process Description - Separation of p-xylene

This process uses molecular sieves to selectively adsorb p-xylene from xylene mixtures. The adsorbed p-xylene is continuously extracted from the sieves and recovered by fractionation.

The fresh feed is combined with recycle from the isomerization section and fed to a fractionation column to remove heavy (C_9^+) hydrocarbons. The feed is then pumped to the molecular sieve column where p-xylene is selectively removed from the feed. A desorbent is also pumped into the sieve bed to remove (extract) the recovered p-xylene. By continuously changing the xylene mixture, feed and desorbent feed points as well as the extract and raffinate (feed minus p-xylene) draw off points to different areas of the bed, the process is made to be continuous.

The extract, containing p-xylene and desorbent is pumped to a fractionation column to separate the p-xylene (overhead) and desorbent (bottoms). The p-xylene is condensed and fed to the light ends stripper to remove light hydrocarbons (overhead). The p-xylene is then cooled and pumped to storage.

FIGURE 4.2 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR O-XYLENE RECOVERY

Energy Summary⁽¹⁾

Total Process

Electricity (kWh)	0.016	(160.0)
Fuel (BTU)	-	(7568.0)
Steam (lb) 100 psig	0.347	(382.0)
Total BTU		(8110.0)

Note: (1) First number in table is units shown per pound of o-xylene produced. Second number in parentheses is the BTU equivalent.

Table 4.2 O-Xylene Separation

Mass Conversion

$$(A) \quad \frac{\text{lb O-Xylene Produced}}{\text{lb Xylene Mixture Feed}} = 0.17$$

Ref. 4.2-1

The raffinate containing primarily o, m-xylene and some desorbent is pumped to a fractionation column, which separates the desorbent (bottoms) from the xylene mixture. The mixture is condensed and pumped to the isomerization where the m- and o-xylenes are isomerized to p-xylene. This stream is recycled and combined with the fresh feed. A flow schematic and energy requirements for this process are shown in Figure 4.3 and the mass conversions are presented in Table 4.3.

4.2.4 Process Alternatives

In some p-xylene adsorption operations, o-xylene may also be recovered. In this system, the isomerate is mixed with fresh feed and, like the p-xylene only process, is pumped to a fractionation system at the head of the process. However, in this case, instead of a single tower to separate only C_9^+ aromatics from the xylenes, the fractionation system is a two tower o-xylene recovery system (see Sec. 4.2.2). This allows for both o-xylene and p-xylene recovery.

Another method of separating p-xylene is through a low temperature, selective crystallization. While this process has been largely replaced by adsorption, it is still a viable commercial process. Due to the necessity for refrigeration and steam for melting the p-xylene crystals, this process is somewhat more energy intensive than the adsorption system, which does not require refrigeration or steam. A typical system employs a two-stage crystallization in which p-xylene is the primary product. The remaining material may be sent to isomerization and returned to the process or may be collected as o- and m-xylene.

Fresh feed is dried, usually in desiccant beds, and mixed with a portion of the recycled "mother liquor" from the second stage crystallizer (mother liquor is the material remaining after the p-xylene has been removed). The feed is cooled against the first stage mother liquor and fed to a chiller in which p-xylene crystallization begins, and finally to a hold tank where the crystals grow in size. The slurry formed in the hold tank is then filtered. The mother liquor is used to cool the incoming feed before being sent to storage, further separation, or isomerization. The filter cake is melted in a steam jacketed vessel and may be mixed with a

FIGURE 4.3. FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR RECOVERY OF P-XYLENE BY SELECTIVE ADSORPTION

Energy Summary(1)

	<u>Recycle Section</u>		<u>Adsorption Section</u>		<u>Isomerization Section</u>		<u>Totals</u>
Electricity (kWh)	0.01	(100.0)	0.038	(380.0)	0.043	(430.0)	
Fuel (BTU)	-	(3042.3)	-	(4328.2)	-	(3042.3)	
Total BTU		(3142.3)		(4708.2)		(3472.3)	(11322.8)

Note: (1) First number in tables is units shown per pound of p-xylene produced. Second number in parentheses is the BTU equivalent.

Table 4.3 P-Xylene Separation
Mass Conversion

(A)
$$\frac{\text{lb P-xylene Produced}}{\text{lb Xylene Mixture Feed}} = 0.80$$

Ref. 4.2-1

portion of the mother liquor from the second stage crystallization before passing to the second stage crystallizer. This is done to control the feed characteristics and therefore the operation of the second stage. The mixed stream is pumped to a second chiller and crystallizer where the p-xylene is again crystallized. The mother liquor is withdrawn and the solids (p-xylene) are melted by a heating coil in the crystallizer outlet and sent to product storage.

4.3 BENZENE FROM TOLUENE

4.3.1 Summary

Benzene is produced from toluene usually by either toluene hydrodealkylation or toluene disproportionation. The process used depends upon the desired final product mix. In the former process benzene is the only product with methane being produced as a by-product. In the latter process, the products are benzene and o-, m-, p-xylene. The latter process has a somewhat greater energy consumption due to the necessity of fractionation of the benzene-xylene mixture.

4.3.2 Process Description - Toluene Hydrodealkylation

Toluene hydrodealkylation is commonly used in the conversion of nitration grade toluene to benzene. A byproduct of the process is methane which is produced during the reaction of hydrogen and toluene. Both catalytic and non-catalytic processes have been commercialized, with non-catalytic processes being the more common and shown here.

The hydrodealkylation unit consists of three sections; namely, hydrogen pretreating, conversion, and stabilization/purification sections. In gas treating, hydrogen is treated to remove oils and other contaminants prior to being fed to the conversion reactor.

Toluene is fed to the reactor system and is mixed with recycle toluene and heated by exchange with the reactor product to 1000-1100°F. The feed is further heated in a fired heater to the reaction temperature (~1200°F) and charged to the reactor. Here it is mixed with hydrogen and the conversion reaction takes place. The reactor product is charged to a flash drum where hydrogen and methane are removed and the benzene product is pumped to a stabilizer, where final removal of hydrogen and methane from the product is accomplished. From the stabilizer, the product is pumped through a clay treater to meet color specifications and then to a benzene column where it is fractionated into benzene (overhead) and unreacted toluene (bottoms). The bottoms are then recycled to the conversion reactor. (See Figure 4.4 and Table 4.4.)

4.3.3 Process Description - Toluene Disproportionation

In contrast to toluene hydrodealkylation, toluene disproportionation is a catalytic process which effectively transfers methyl groups from toluene molecules onto other toluene molecules. Therefore, the process yields benzene and xylene instead of only benzene and a methane by-product. (See Figure 4.5 and Table 4.5.)

The process unit is divided into the reaction and fractionation sections. Toluene feed is mixed with recycle toluene (35% fresh feed, 65% recycle) and fed first through a furnace to heat the feed to the reaction temperature (~800°F) and then to the catalytic reactor. Steam (125 psig) is produced by extracting the heat produced during the catalyst regeneration. The vapor product passes from the reactor to the fractionation section where the product is condensed in a stabilization column. Here light gases (i.e. CH_4) are removed overhead. The bottoms, containing benzene, unreacted toluene and xylene are then passed through a clay treater for color removal to a series of fractionation columns. Heat for the columns is supplied by steam reboilers. In the first column, benzene is the overhead product. The bottoms from the benzene column are pumped to the next column where the overhead product is toluene. This is condensed and recycled to the reactor section. The bottoms from the toluene separation are then pumped to the final column where xylene is the overhead product. The final bottoms material consists of C_9^+ material which is sent to tankage.

FIGURE 4.4. FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR TOLUENE HYDRODEALKYLATION

Energy Summary⁽¹⁾

	<u>Hydrogen Treating</u>		<u>Conversion</u>		<u>Stabilization/Purification</u>	
Steam (400 psig) (lb)	0.0275	(26.7)	-	-	0.52	(783.0)
Electricity (kWh) ⁽²⁾	0.04	(400.0)	-	-	-	-
Fuel (BTU)	-	-	-	(185.5)	-	-
Total BTU ⁽³⁾		(1393.2)	-	-	-	-

Notes: (1) First number in tables is units shown per pound of benzene produced. Second number in parentheses is BTU equivalent.

(2) Total for entire plant - not available by unit operation.

(3) Total BTU for overall plant.

Table 4.4 Toluene Hydrodealkylation
Mass Conversions

- (A) $\frac{1b \text{ Toluene Feed}}{1b \text{ Benzene Produced}} = 1.2$
- (B) $\frac{1b \text{ H}_2 \text{ Feed}}{1b \text{ Benzene Produced}} = 0.09$
- (C) $\frac{1b \text{ Fuel Gas Produced}}{1b \text{ Benzene Produced}} = .43$
- (D) $\frac{1b \text{ Oil Produced}}{1b \text{ Benzene Produced}} = .04$

Ref. 4.3-2

FIGURE 4.5 FLOW SCHEMATIC AND ENERGY SUMMARY FOR TOLUENE DISPROPORTIONATION

Energy Summary⁽¹⁾

	<u>Reactor Section</u>	<u>Fractionation Section</u>	<u>Total</u>
Steam (lb)	-0.15 (-155.4) @ 125 psig ⁽²⁾	2.29 (2221.0) @ 400 psig	
Electricity (kWh)	0.025 (250.0)	0.006 (60.0)	
Fuel (BTU)	<u>(723.8)</u>	-	
Total BTU	(818.4)	(2281.0)	(3099.4)

Notes: (1) First number in tables is units shown per pound of total aromatics produced. Second number in parentheses is BTU equivalent.

(2) Negative sign on reactor section steam summary indicates steam produced.

Table 4.5 Toluene Disproportionation
Mass Conversion

$$(A) \quad \frac{\text{lb Benzene Produced}}{\text{lb Fresh Toluene Feed}} = 0.36$$

$$(B) \quad \frac{\text{lb Xylene Produced}}{\text{lb Fresh Toluene Feed}} = 0.54$$

Ref. 4.3-2

4.3.4 Alternative Processes

Another process that converts toluene to benzene and xylene is toluene transalkylation. While this process is commercially available, it does not have the same widespread use as does disproportionation.

Toluene transalkylation is similar to disproportionation except that C_9^+ aromatics are mixed with the feed to control the ratio of xylene to benzene in the final product. The methyl groups from the C_9^+ aromatics are effectively transferred to the toluene to form xylenes and benzenes. The process employs a feed stream of C_9^+ aromatics in addition to toluene. An additional fractionation column is also employed to separate unreacted C_9^+ aromatics from heavier hydrocarbons.

The process, like disproportionation, has a reaction and fractionation section. The reactor section is identical to disproportionation, including a catalytic reactor, and catalyst regeneration with steam generation.

Fresh toluene is mixed with recycle toluene and C_9^+ aromatics and fed through a fired heater to the catalytic reactor. From the reactor the product passes to the fractionation section and is condensed in the stabilizer. The bottoms from the stabilizer are clay treated and passed through the same fractionation system as in the disproportionation process. The bottoms from the xylene column, instead of being sent to storage, are pumped to a fourth fractionation column where the C_9^+ aromatics are also recovered and recycled back to the toluene feed.

4.4 BENZENE HYDROGENATION

4.4.1 Summary

In this process, benzene is converted to cyclohexane which in turn is the raw material used to produce nylon. The basic process is the hydrogenation of benzene in the presence of a catalyst to produce the cyclohexane product.

4.4.2 Process Description

Liquid benzene feed is mixed with recycle hydrogen, heated to the vapor state and fed to the main hydrogenation reactor. Here, in the presence of a catalyst, typically nickel, almost complete conversion of benzene to cyclohexane takes place. Operating temperatures are 350-450°F and pressures are 400 to 450 psig. The reaction is highly exothermic, and low pressure steam is produced as a byproduct. The effluent from the first reactor passes to a second reactor, where, again in the presence of a catalyst, the conversion reaction is completed.

The effluent from the second reactor is cooled against the incoming feed and then passes to a separator where the dissolved hydrogen and methane is removed. This hydrogen is recycled to the reaction system and mixed with the raw benzene feed. The liquid product from the separator is then sent to a stabilizer which completes the separation of dissolved hydrogen and methane from the cyclohexane. The cyclohexane product is then pumped to storage. Conversion of benzene to cyclohexane by this process is virtually 100%. A schematic diagram and energy requirements for this process are shown in Figure 4.6 and the mass conversions are presented in Table 4.6.

FIGURE 4.6 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE BENZENE HYDROGENATION PROCESS

Energy Summary⁽¹⁾

<u>Refrigeration</u>		
BTU @ 0°F		(3.93)
BTU @ 30°F		(4.36)
Power (kWhr)	0.031	(310.0)
<u>Steam (lb)</u>		
250 psi	0.182	(186.6)
150 psi	0.235	(251.7)
35 psi	0.924	(-1067.2) ⁽²⁾
Total BTU ⁽³⁾		(-628.9)

- Notes: (1) First number in tables is units shown per pound of cyclohexane produced. Second number in parentheses is the BTU equivalent.
 (2) Steam produced.
 (3) Negative sign on energy consumption total means a net energy producer.

Table 4.6 Benzene Hydrogenation
Mass Conversions

$$(A) \quad \frac{\text{lb of Benzene Feed}}{\text{lb of Cyclohexane Produced}} = 0.93$$

$$(B) \quad \frac{\text{lb of Hydrogen Feed}}{\text{lb Cyclohexane Produced}} = 0.073$$

Ref. 4.4-1

4.5 STYRENE FROM BENZENE

4.5.1 The production of styrene from benzene requires two processing steps. The first step catalytically reacts benzene and ethylene to form ethylbenzene. This can be either a liquid or vapor phase reaction. (The liquid phase process being more common is discussed here.) The ethylbenzene is then reacted to form the final styrene product. Process feed streams are benzene and ethylene gas. By-products are principally hydrogen and low and medium pressure steam.

4.5.2 Process Description - Production of Ethylbenzene (Liquid Phase Process)

Fresh benzene feed is mixed with recycle benzene and dried. The dried benzene is then mixed with the AlCl_3 catalyst which has been made into a slurry with recycled ethylbenzene. This benzene - AlCl_3 - ethylbenzene mixture is then charged to the alkylation reactor where ethylene gas and HCl are sparged into the liquid. The alkylate, containing benzene, ethylbenzene, polyethyl benzene and catalyst are charged to the transalkylation reactor where recycled polyethyl benzenes and benzene are also added. This reaction converts additional benzene to ethylbenzene. From this reactor, the mixture is first flashed to recover the HCl , then cooled and scrubbed with water and caustic to recover the AlCl_3 . The scrubbed product then passes to a series of fractionation column. In the first column unreacted benzene (overheads) is separated from the ethylbenzenes. The benzene is then recycled to the head of the process. The ethylbenzene (bottoms) then pass to a second column where ethylbenzene is separated (overhead) from the polyethyl benzenes. (Ref. 4.5-1) The PEB, after further fractionation to remove residual impurities is recycled to the head of the process.

4.5.3 Process Description - Production of Styrene

Fresh ethylbenzene feed is mixed with recycled ethylbenzene, and steam, vaporized and superheated in a fired heater and fed to the dehydrogenation reactor where the conversion of ethylbenzene to styrene takes place. The product mixture is then cooled and fed to a separator, where

water, organic, and vapor layers are formed. The vapor, mostly hydrogen is recovered for fuel and the water phase is treated for use as boiler feed water. The organic layer is sent to vacuum distillation where the unreacted ethylbenzene, benzene and toluene (overheads) are separated from the styrene (bottoms). (Small amounts of benzene and toluene are formed in the dehydrogenation reactor due to cracking.) The overheads are then fractionated to recover the individual components. The styrene product is sent to a second vacuum distillation where the styrene product is taken overhead, condensed and sent to storage. The bottoms from the second vacuum distillation is treated to recover polymerization inhibitor, which is added as part of the styrene recovery process. A block schematic diagram is shown in Figure 4.7 and the mass conversions are presented in Table 4.7.

4.5.4 Process Alternatives

As previously mentioned, the conversion of benzene to ethylbenzene can be carried out in the vapor phase. In this process the benzene feed, mixed with recycle benzene is vaporized and fed to fixed bed, alkylation reactors. The product stream is then condensed and the ethylbenzene and unreacted benzene are recovered by fractionation.

FIGURE 4.7. FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR STYRENE FROM BENZENE
(Monsanto/C.E. Lummus Process).

Energy Summary⁽¹⁾

Gas (BTU)				(1500)	
Electricity (KW-Hr)	.003 (30)	.001 (10)	.03 (300)	.005 (50)	
Refrigeration (BTU)				(52)	
Steam (lbs)					
PSI = 600	.006 (6.2)	1.43 (1306.2)			
PSI = 75			1.28 (1431.0)		
PSI = 30				1.50 (1741.5)	
Total BTU	(36.2)	(1316.2)	(3231.0)	(1843.5)	(6426.9) ⁽²⁾

Notes: (1) First number shown is per lb of styrene produced. Second number in parentheses is the BTU equivalent.

(2) Total BTU required by process.

Table 4.7 Styrene from Benzene
Mass Conversion

Production of Ethylbenzene

$$(A) \frac{1b \text{ Benzene Feed}}{1b \text{ Ethylbenzene Produced}} = 0.75$$

$$(B) \frac{1b \text{ Ethylene Feed}}{1b \text{ Ethylbenzene Produced}} = 0.27$$

Production of Styrene

$$(A) \frac{1b \text{ Styrene Produced}}{1b \text{ Ethylbenzene Feed}} = 0.87$$

Ref. 4.5-3

4.6 POLYSTYRENE FROM STYRENE

4.6.1 Summary

Two processes commonly used to polymerize polystyrene from styrene are bulk suspension polymerization and bulk-press polymerization. Both processes have large energy input requirements and both are liquid styrene feed.

4.6.2 Process Description - Bulk Suspension Polymerization

Styrene monomer is suspended as small beads in water. It is then fed to the polymerization reactors where it is mixed with catalyst, suspending agent (to maintain suspension) and required additives. After the reaction has been started, the material is pumped to an agitated holding tank where the reaction goes to virtual completion. The polymerized product is then sent to dewatering. The collected, solid polystyrene is then washed with demineralized water and fed to a centrifuge where the final liquid-solid separation takes place. The final step is to dry the material before going to storage or polystyrene beads.

In the finishing section, the material may be mixed with pigments, lubricants, etc. and fed to extruders, where under heat and pressure, the final product is formed. The extruded product is cut into pellets for final packaging or bulk shipping.

A great variety of basic crystal and impact polystyrene grades can be produced by changing reactor conditions and varying additive additions. The batch concept of this process permits small lots of specialty grades to be produced without capacity reduction.

4.6.3 Process Description - Bulk-Press Polymerization

Liquid styrene is fed to an inert gas blanketed prepolymerization vessel where catalyst is added. After the reaction begins, the material is fed to the press reactors. These are a plate and frame type reactor. This equipment is a type of heat exchanger which allows for the circulation

of cooling water or steam to control the reaction temperature. After holding in the press reactor for the proper temperature sequence for approximately 16 hours to complete the reaction, the polymerized product is fed to a grinder where it is formed into pellets before storage.

The finishing section of this process is similar to bulk suspension polymerization. The raw polystyrene is mixed with the desired additives and fed to the extruders where, under heat and pressure, the final product is formed. The extruded product is then cut into pellets for final storage and packaging.

A block schematic diagram of both the bulk suspension and bulk press polymerization processes and their energy requirements are shown in Figures 4.8 and 4.9, respectively. The corresponding process mass conversions are presented in Tables 4.8 and 4.9. It is recognized that the true conversion will be less than 100% due to process losses, waste scrap, etc. However, the losses are expected to be small (less than 5%) and corrections are not warranted due to the other, greater, uncertainties in this study.

FIGURE 4.8 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR POLYSTYRENE FROM STYRENE
Bulk Suspension Polymerization

Energy Summary⁽¹⁾

	<u>Polymerization Section</u>		<u>Finishing Section</u>	
Power (kWh)	0.094	(940.0)	0.246	(2460.0)
Steam (lb) @ 250 psig	4.73	(4868.8)	-	-
Total BTU		(5808.8)		(2460.8)
				(8269.6) ⁽²⁾

Notes: (1) First number shown is per lb of polystyrene produced. Second number in parentheses is the BTU equivalent.

(2) Total BTU for the process.

Table 4.8 Bulk Suspension Polymerization of Polystyrene
from Styrene

Mass Conversions

$$\frac{\text{lb Polystyrene Produced}}{\text{lb Styrene Feed}} = 1$$

Ref: 4.6-3

FIGURE 4.9 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR POLYSTYRENE FROM STYRENE
Bulk Press Polymerization

Energy Summary ⁽¹⁾

	<u>Polymerization Section</u>		<u>Finishing Section</u>	
Power (kWh)	0.126	(1260.0)	0.28	(2800.0)
Steam (lb) @ 250 psig	6.31	<u>(6467.8)</u>	-	<u> </u>
Total BTU		(7727.8)		(2800.0)
				(10527.8) ⁽²⁾

Notes: (1) First number shown is per lb of polystyrene produced. Second number in parentheses is the BTU equivalent.

(2) Total BTU for the process.

Table 4.9 Bulk Press Polymerization of Polystyrene
from Styrene
 Mass Conversions

$$\frac{\text{lb Polystyrene Produced}}{\text{lb Styrene Feed}} = 1$$

Ref. 4.6-3

4.7 ABS/SAN FROM STYRENE

4.7.1 Summary

There are two major process routes for the co-polymerization of SAN from styrene and acrylonitrile, namely emulsion and suspension polymerization. These processes are quite similar, differentiated by the location of the initiator and the size of the particles produced. These same polymerization reactions are used in the production of acrylonitrile-butadiene-styrene (ABS) polymer.

4.7.2 Process Description of the Emulsion Polymerization SAN Process

Emulsion polymerization is an heterogeneous polymerization system. The continuous reaction is characterized and differentiated from suspension polymerization described in Section 4.6, by the location of the initiator catalyst in the aqueous phase and by the small size of the product.⁶⁰ A portion of the styrene-acrylonitrile mixture is emulsified with the catalyst-water system prior to feed to the reactor vessels. The temperature, reactor residence time, initiator concentration and monomer feed point are controlled to regulate reagent conversion and product molecular weight. The product from the reaction system is called latex.

In the purification step, the latex is steam stripped with residual monomer being recycled back to the reactor. The latex is coagulated by acid addition and pumped through an orifice plate to produce thin strands. The polymer is washed and heated to harden the particles. The SAN product is dried and ready for further processing. A schematic diagram and energy requirements are shown in Figure 4.10 and the mass conversions are presented in Table 4.10.

4.7.3 Process Description of the Suspension Polymerization SAN Process

Suspension polymerization is similar to emulsion polymerization in that the monomer is dispersed in a heterogeneous reaction system. It differs by the location of the catalyst initiator in the monomer phase and the larger particle size produced. Although the reaction time is longer

FIGURE 4.10 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE EMULSION POLYMERIZATION SAN PROCESS

Energy Summary ⁽¹⁾

	<u>Reaction</u>		<u>Purification & Coagulation</u>		<u>Total</u>
Electricity, kWh	0.013	(130)	0.033	(330)	
Steam, lb @ 300 psig	0.53	(532.1)	0.53	(532.1)	
Total BTU		(662.1)		(862.1)	(1524.2)

Note: (1) First number in table is units shown per pound of SAN produced. Second number in parentheses is the BTU equivalent.

Ref. 4.7-1

Table 4.10 SAN Production by Emulsion Polymerization

Mass Conversions

$$(A) \quad \frac{\text{lb Styrene Feed}}{\text{lb SAN Produced}} = 0.73$$

$$(B) \quad \frac{\text{lb Acrylonitrile Feed}}{\text{lb SAN Feed}} = 0.26$$

Ref. 4.7-1

than emulsion polymerization, generally 3 hours compared to 2 hours for the emulsion process, the polymer product can be recovered in higher purity than the emulsion process where chemical additives are included in the product.

The reagents are fed to a batch agitated reactor. The reaction temperature is closely controlled until the gel effect begins to develop. At this point, the temperature is allowed to increase until the conversion is essentially complete. At the end of the reaction, the monomer is stripped and recovered for reuse.

The polymer slurry is cooled and washed with demineralized water. The polymer beads are separated from the water by centrifuge and heat. The SAN product is then ready for further processing. A schematic diagram and energy summary are shown in Fig. 4.11 and the mass conversions are presented in Table 4.11.

4.7.4 Process Description of the ABS Graft by Emulsion Polymerization

Butadiene is reacted by the emulsion polymerization reaction similar to the SAN process described earlier. This reaction is necessary to produce the backbone polymer, namely, polybutadiene. The styrene and acrylonitrile are then grafted onto the backbone. Polybutadiene, styrene, and acrylonitrile are fed to the batch emulsion polymerization reactor to perform the graft. After acid adjustment of the solution pH and heatup, the reaction is initiated and controlled to maximize acrylonitrile-butadiene-styrene (ABS) polymer yield.

The graft resin latex is steam stripped to recover SAN polymer and coagulated to a crumb. The crumb is washed and dewatered before drying and conveying to the blending section. The graft copolymer is metered to a batch mixer which melts the mix and discharges to a roller mill. The strips are cooled, cut, and stored ready for shipment. A schematic diagram and energy summary are shown in Fig. 4.12 and the mass conversions are presented in Table 4.12.

FIGURE 4.11 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE SUSPENSION POLYMERIZATION SAN PROCESS

Energy Summary⁽¹⁾

	<u>Reaction</u>		<u>Finishing</u>		<u>Total</u>
Electricity, kWhr	0.0053	(53)	0.026	(260)	
Steam, lb					
300 psig	0.53	<u>(532.1)</u>	0.53	<u>(532.1)</u>	
total BTU		(585.1)		(792.1)	(1377.2)

Note: (1) First number in table is units shown per pound of SAN produced. Second number in parentheses is the BTU equivalent.

Ref. 4.7-1

Table 4.11 SAN Production from Suspension Polymerization
Mass Conversions

$$(A) \quad \frac{\text{lb/Styrene Feed}}{\text{lb SAN Produced}} = 0.73$$

$$(B) \quad \frac{\text{lb Acrylonitrile Feed}}{\text{lb SAN Produced}} = 0.26$$

Ref. 4.7-1

FIGURE 4.12 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR EMULSION
POLYMERIZATION OF ABS GRAFT RESINS

Energy Summary ⁽¹⁾

	<u>Reaction</u>	<u>Coagulation</u>	<u>Blending</u>	<u>Total</u>
Electricity, kWh	0.045 (450)	0.021 (210)	0.222 (2220)	
Refrigeration, BTU	-	-	-	
Steam, lb				
300 psig	0.13 (130.5)	0.39 (391.6)	-	
Total BTU	(580.5)	(601.6)	(2220)	(3402.1)

Note: (1) First number in table is units shown per pound of ABS resin produced. Second number in parentheses is the BTU equivalent.

Ref. 4.7-1

Table 4.12 ABS Production by Emulsion Polymerization
(Mass Conversion)

$$(A) \quad \frac{1b \text{ Styrene}}{1b \text{ ABS Resin}} = 0.53$$

$$(B) \quad \frac{1b \text{ Polybutadiene}}{1b \text{ ABS Resin}} = 0.25$$

$$(C) \quad \frac{1b \text{ Acrylonitrile}}{1b \text{ ABS Resin}} = 0.22$$

Ref. 4.7-1

4.7.5 Process Description of the ABS Graft Resin by Solution Polymerization

The process described in this section is that used for production of EPSAN, a product of Capolymer Corporation. The product is not truly ABS, since ethylene propylene rubber is used instead of polybutadiene.

The polymerization is started by dissolving EP (ethylene-propylene) rubber in a benzene-hexane solvent. The mixture is fed along with styrene and acrylonitrile monomers and initiator into an agitated heated batch reactor. Temperature is controlled after the reaction proceeds. The polymer is mixed with methanol, then hot water which initiates the crumb coagulation.

The mixture is steam stripped for solvent recovery. The crumb is decanted, dewatered, and dried. The blending and storage section is similar to that section just described previously. Recovery of the several solvents and water is practiced to reduce cost and effluents. A schematic diagram and energy summary are shown in Figure 4.13 and the mass conversion is presented in Table 4.13.

FIGURE 4.13 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR SOLUTION POLYMERIZATION OF ABS GRAFT RESINS

Energy Summary⁽¹⁾

	<u>Reaction</u>		<u>Solvent Recovery</u>		<u>Blending</u>		<u>Total</u>
Electricity, kWh	0.021	(210)	0.002	(20)	0.215	(2150)	
Steam, lb							
300 psig	6.44	(6466)	7.75	(7781)	-		
Total BTU		(6676)		(7801)		(2150)	(16627)

Note: (1) First number in table is units shown per pound of ABS resin produced. Second number in parentheses is the BTU equivalent.

Ref. 4.7-1

Table 4.13 ABS Production by Suspension Polymerization
Mass Conversions

$$(A) \quad \frac{1b \text{ Styrene}}{1b \text{ ABS Resin}} = .66$$

$$(B) \quad \frac{1b \text{ EP Rubber}}{1b \text{ ABS Resin}} = .12$$

$$(C) \quad \frac{1b \text{ Acrylonitrile}}{1b \text{ ABS Resin}} = .22$$

Above assumes 100% conversion. True conversion ~95%.

Ref. 4.7-1

4.8 SBR FROM STYRENE

4.8.1 Summary

The primary polymerization process used in the manufacture of styrene butadiene rubber (SBR) is emulsion polymerization. A large majority is produced using the cold emulsion technology which is discussed in the following section.

4.8.2 Process Description for Cold Emulsion Polymerization of SBR

Butadiene and styrene monomers are either piped or tanked into elastomer plants and stored in tank farms. Low-boiling monomers such as butadiene must be stored in pressure vessels containing safety valves which discharge to a flare. Inhibitors are usually added by the monomer producing plants to prevent premature polymerization during shipment or storage.

The inhibited monomer from storage must be treated to lower the inhibitor concentration to a level which will allow polymerization to occur. The inhibitor concentration in monomers such as styrene is low enough to permit the inhibited monomer to be used directly. Easily polymerized monomers such as butadiene, however, require a scrubbing with a caustic wash to decrease the inhibitor to polymerizable levels. The inhibitor is removed by washing the raw monomer with a caustic solution in a contactor packed with Raschig rings, followed by decantation. The uninhibited monomer is blended with recovered, lower purity monomer to give the correct purity for further processing. After blending, the combined stream is charged to the polymerization reactors.

The polymerization occurs in emulsifier micelles formed by dispersing the monomers into an aqueous soap solution. Catalysts, activators, and modifiers are used to initiate and control the reaction. Further reaction control is accomplished by careful regulation of the reaction temperature within plus or minus 0.25°C using either cooling coils containing ammonia refrigerant, chilled water or chilled brine.

Polymerization occurs in a series of reactors, any of which can be bypassed if desired. The reaction is usually terminated at around 60 percent conversion for "cold" SBR by the addition of chemicals called "shortstops." The shortstop solution is added whenever analysis of the reaction mixture indicates the correct polymer composition.

Polymerization is carried out on a continuous or batch-continuous basis with the input charge carefully metered according to standard formulations called recipes. Each batch of latex produced is stored in one of several storage tanks where it may be blended with other batches to give a more uniform product. The blended latex still contains large amounts of monomer as well as other additives.

For most plants, monomer recovery is divided into two sections. The light monomer, butadiene, is recovered by stripping the latex in a vacuum flash tank. The stripped butadiene vapors are then compressed and condensed. The butadiene vapor passes through an oil-absorption column which traps residual noncondensable impurities. These impurities are vented to the flare. The condensed butadiene is pumped to feed tanks in the monomer storage area for the preparation of blends. In some cases the recovered butadiene is routed to a butadiene purification plant before being used.

Heavy monomers such as styrene are removed using low-pressure steam stripping in a perforated plate column. The steam-monomer mixture is then sent to a receiver where the vapors are condensed and the phases separated by gravity. The top organic layer is recycled into the monomer feed supply system while the water is discharged to waste treatment. A small styrene bleed stream is sent through a gasification step to maintain product quality. The monomer-stripped latex is sent to a blend tank where it is stabilized by the addition of an antioxidant. The stabilized latex may then be blended with other latices before further processing.

Coagulation of the dispersed polymer in the latex permits separation of the product from the aqueous medium. This process also includes additions of components (extenders) to improve the quality of the rubber product.

The latex is coagulated by addition of acid and brine. The brine causes a "creaming" of the latex which is a partial flocculation of the rubber particles, causing the consistency of the latex to change from a mobile liquid to a heavy cream. The addition of the dilute sulfuric acid to a pH of 4.0 to 4.5 converts the soap molecules to organic fatty acids which causes the rubber particles to agglomerate. The particles are then separated from the coagulation liquor on a shake screen. The liquor is recycled with fresh acid and brine make-up added as needed. The screened rubber particles are slurried with water and sent to crumb washing and finishing.

Washing and finishing removes extraneous material from the rubber and processes the purified rubber into bales which can then be sold or captively used. The washing process step removes residual coagulation liquor along with catalysts, emulsifiers, oil, and other contaminants. The rinsed cream may be filtered and dewatered in a rotary vacuum filter. The filtrate is sent to a reslurry tank where blowdown of some of the wash water occurs. The remainder of the water is recycled to the crumb washing unit along with fresh makeup water. The dewatered crumb is dried with hot air in either continuous or screen dryers, weighed, and formed into bales. A schematic flow diagram and energy requirements are shown in Figure 4.14 and the mass conversions are presented in Table 4.14.

4.8.3 Process Alternatives

During the coagulation step, the addition of hydrocarbon oils (oil extending) improves processing properties and reduces cost. The addition of carbon black (masterbatching) to the latex immediately before coagulation produces an elastomer with improved physical properties such as increased tensile strength, stiffness, abrasion resistance, and tear resistance. The extender oil is added as an aqueous emulsion while the carbon black is added as an aqueous slurry. Masterbatches may also be produced in a mixer using dry rubber, oil and carbon black.

Solution polymerization using lithium catalysts and random copolymerization are other lower volume commercial methods for SBR production. The solution polymerization process has been described in Section 4.7.

FIGURE 4.14 FLOW SCHEMATIC AND ENERGY REQUIREMENTS IN COLD EMULSION POLYMERIZATION OF SBR

Energy Summary⁽¹⁾

	<u>Reaction</u>	<u>Monomer Recovery</u>		<u>Coagulation and Drying</u>		<u>Total</u>
Electricity, kWh	0.107 (1070)	0.011	(110)	0.153	(1530)	
Refrigeration, BTU	(905)	-		-		
Steam, lb						
150 psig	-	-		0.092	(98.5)	
100 psig	-	0.040	(44)	-		
15 psig	0.306 (361.4)	0.713	(842.0)	0.051	(60)	
Total BTU	(2336.4)		(996.0)		(1632.5)	(5020.9)

Note: (1) First number in table is units shown per pound of SBR produced. Second number in parentheses is the BTU equivalent.

Ref. 4.8-1

Table 4.14 Mass Conversions for SBR Production⁽¹⁾

$$(A) \quad \frac{1b \text{ Styrene Feed}}{1b \text{ SBR Produced}} = 0.25$$

$$(B) \quad \frac{1b \text{ Butadiene Feed}}{1b \text{ SBR Produced}} = 0.85$$

Note: (1) Overall Material Requirements will vary as batch recipe requirements change.

Refs. 4.8-1, 4.8-2

4.9 CUMENE FROM BENZENE

4.9.1 Summary

The major source of phenol within the U.S. industrial market is produced by the oxidation of benzene. The first step in this production process is the synthesis of cumene which is produced by the reaction of benzene with propylene. This route is by far the major industrial route in the manufacturing of synthetic phenol. (Ref. 4.9-1)

4.9.2 Process Description

A liquid mixture of chemical grade propylene and benzene is fed to the reactor. Benzene is fed in large excess to minimize the degree of product contamination from multiple substituted benzene rings. The reaction is catalyzed by phosphoric acid deposited on layers of diatomaceous earth materials. This alkylation reaction is exothermic. The heated products are sent to the fractionation step where propylene and benzene are flashed and recovered. Further fractionation steps are required to meet the cumene product purity specifications. A block schematic diagram is shown in Figure 4.15 with the energy requirements and the mass conversions are presented in Table 4.15.

The chemical equations representing the reaction are presented below. (Ref. 4.9-2)

FIGURE 4.15. FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR CUMENE PRODUCTION

Energy Summary⁽¹⁾

	<u>Reactor</u>		<u>Fractionation</u>		<u>Total</u>
Electricity, kw-h	0.0018	(18)	0.0054	(54.4)	
Steam, lbs					
450 psig	0.31	(296.4)			
50 psig	-		0.99	(-1127.6) ⁽²⁾	
Fuel, BTU				1774.2	
Total BTU		(314.4)		(701.0)	(1015.4)

Notes: (1) First number in table is units shown per pound of cumene produced. Second number in parentheses is the BTU equivalent.

(2) Negative sign in the energy summary indicates the unit produced energy.

Ref. 4.9-3

Table 4.15 Cumene Production

Mass Conversion

$$(A) \quad \frac{1b \text{ Benzene Feed}}{1b \text{ Cumene Produced}} = 0.67$$

$$(B) \quad \frac{1b \text{ Propylene Feed}}{1b \text{ Cumene Produced}} = 0.38$$

Ref. 4.9-1

4.10 PHENOL FROM CUMENE

4.10.1 Summary

Cumene is an industrial intermediary in the synthetic production of phenol. This process was simultaneously developed by two licensors, BP Chemicals and Hercules, over 25 years ago and represents the major production route in present use.

4.10.2 Process Description

Cumene is oxidized with air in the reactor vessel to produce cumene hydroperoxide. The reaction is assisted by the injection of aqueous sodium carbonate. Concentrated sulfuric acid is added to cumene hydroperoxide in the cleavage step. This material breaks down to form phenol and acetone. The cleavage product is neutralized and sent to fractionation. High purity phenol and acetone are produced in a series of fractionation steps. Streams are treated from both purification trains for recovery of phenol or cumene. A block schematic diagram is shown in Figure 4.16 with the energy requirements and the mass conversions are presented in Table 4.16.

The chemical equations representing this two-step reaction are presented below.⁶¹

FIGURE 4.16 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR PHENOL PRODUCTION

Energy Summary⁽¹⁾

	Oxidation		Cleavage		Fractionation		Total
Electricity, kWh	0.078	(780)	0.048	(480)	0.014	(140)	
Refrigeration, BTU		(31)					
Steam, lb							
450 psig	-		-		3.7	(3537.2)	
50 psig	0.16	(182)	-		0.11	(125)	
10 psig	1.02	(1214.8)	-		-		
Fuel, BTU	-		-			(158)	
Total BTU		(2207.8)		(480)		(3960.2)	(6648.0)

Note: (1) First number in table is units shown per pound of phenol produced. Second number in parentheses is the BTU equivalent.

Table 4.16 Phenol Production
Mass Conversions

$$(A) \quad \frac{\text{lb Phenol Produced}}{\text{lb Cumene Feed}} = 0.75$$

$$(B) \quad \frac{\text{lb Acetone Produced}}{\text{lb Cumene Feed}} = 0.45$$

Ref. 4.10-2

4.11 PHENOLIC RESINS FROM PHENOL (Ref. 4.11-1)

4.11.1 Summary

This section treats the formation of resins by polymerization of phenol and formaldehyde. There are two major types: resoles (one-stage resins) and novolaks (two-stage resins). The resoles are formed in an alkaline medium with an excess of formaldehyde and are marketed as thermosetting resins, bonding resins, varnishes, and laminates. Novolaks are formed in an acid medium deficient in formaldehyde. These thermoplastic resins require mixing with formaldehyde or a formaldehyde donor such as hexamethylene tetramine to produce a thermosetting product. Thermosetting resin powders, varnishes, and laminates are novolak products. Although steam and electricity are required by both processes, no quantitative data were found to establish their use.

4.11.2 Process Description for Resole Resins

Phenol and formaldehyde react in an alkaline medium in a batch process. Phenol is charged to the agitated reactor through a weigh tank before the formaldehyde is similarly added, rinsing residual phenol out of the lines. Sodium hydroxide is added, and steam is supplied to the kettle jacket and to the internal coils to initiate the reaction. As the exothermic reaction begins, cooling water is supplied to the kettle to maintain temperature control. Additional cooling is accomplished by using a reflux condenser.

The degree of polymerization is monitored by withdrawing samples and testing them. The extent of reaction determines the molecular weight of the polymer and the physical properties of the product.

If the reaction is halted at the point at which the polymer is still water-soluble, the product may be used for bonding resins. If the reaction is allowed to progress to the point at which the polymer precipitates, the water may be removed, and organic solvent may be added to form a varnish. The polymerization reaction may be allowed to continue until the resin reaches a brittle stage, at which point it may be used for a thermosetting

molding powder. Rapid cooling and neutralization with H_2SO_4 stop the reaction. The mixture is then distilled to purify the resin. If the resin application requires a low concentration of water, the resin is dehydrated, often under vacuum.

There are generally three types of resole products prepared in this process. Water-soluble bonding resins, varnishes and laminating resins, and dry thermosetting molding powder. The production of dry product requires discharge of the resin from the reactor through a special quick-discharge valve to prevent it from becoming an insoluble, infusible solid. Cooling must be accomplished by spreading the material in thin layers because of the low thermal conductivity. Cooling devices include water- or air-cooled floors, trays in racks, and moving belts. After cooling, the solid is ground, screened, and packaged. Some of the solid resoles require several water washing steps. This procedure necessitates drying the resin before it is packaged. The solid resin may be blended with fillers and additives before it is readied for marketing.

The water soluble bonding resins are discharged from the reactor to a filter. After filtration, the substance is packaged in drums or tanks.

The varnish and laminate resin solutions (non-water-soluble) are dissolved in a solvent, filtered, and then stored in drums or tanks for sale.

A general flow diagram is shown in Figure 4.17.

4.11.3 Process Description for Novolak Resins

In this batch process, formaldehyde and phenol are polymerized under acid conditions with a deficiency of formaldehyde to produce a thermoplastic product.

FIGURE 4.17 FLOW SCHEMATIC FOR RESOLE PHENOLIC RESINS

Notes: 1. Type of product preparation system is a function of where the reaction was stopped. Range of products include bonding resins, varnishes and laminating resins, and dry thermosetting powders.

Phenol, acid, and formaldehyde are charged to a jacketed batch-reactor. An acid, frequently sulfuric or hydrochloric acid, is added and the temperature is raised to initiate the reaction. If strongly acid conditions are used, a vacuum reflux system must be employed for cooling; for some polymerizations atmospheric reflux is sufficient. Additional cooling is provided by circulating cooling water in the jacket and in the internal coils of the reactor.

When the reaction is completed, the resin is purified by distillation and dehydrated under vacuum. The molten polymer may be neutralized before it is further processed. In making a solid resin product the charge is dumped onto cooling surfaces in thin layers. Water- or air-cooled floors, trays in racks, and moving belts are used for rapid cooling. The solid resin is then ground and screened. Fillers, coloring agents, and hexamethylenetetramine the formaldehyde donor, may be blended with the resin before it is packaged. It may then be fused on hot rollers, ground and packaged as a finished product thermosetting resin. If a product is needed in solution (varnishes and laminating agents), solvent is added in the kettle. The solution is then packaged in drums or tanks.

A generalized flow schematic is shown in Figure 4.18.

FIGURE 4.18 FLOW SCHEMATIC FOR NOVOLAK PHENOLIC RESINS

4.12 TDI FROM TOLUENE

4.12.1 Summary

Toluene diisocyanate is produced from toluene in three steps:

- 1) nitration of toluene to dinitrotoluene (DNT)
- 2) reduction of DNT to toluene diamine (TDA)
- 3) phosgenation of TDA to toluene diisocyanate (TDI).

Most TDI commercially used is a mixture of 80 parts of the 2, 4-isomer and 20 parts of the 2, 6-isomer. The major use is for the production of flexible polyurethane foam.

4.12.2 Process Description

Toluene is nitrated to dinitrotoluene (DNT) with mixed acid (nitric and sulfuric acids) in a continuous reactor. Reaction time is about 5 seconds

at atmospheric pressure and 70-90°C. The DNT typically contains about 80% of 2, 4-dinitrotoluene, the balance being mostly 2, 6-dinitrotoluene.

The DNT is reduced by H₂ at moderate pressure in the presence of a solvent and a suspended catalyst to form toluene diamine. Reduction is carried out

in a stirred, jacketed kettle at 90-110°C and 6 atmospheres pressure in a water solvent. The catalyst is a noble metal (palladium) supported on carbon, or Raney nickel. Reaction heat is removed with cooling water on the shell side of the reduction reactor.

After catalyst separation, the TDA is distilled to recycle the solvent and to remove water and heavy ends.

The TDA isomer mixture is dissolved in o-dichlorobenzene and is reacted with phosgene to produce toluene diisocyanate. The phosgene may be injected

as a gas or pre-dissolved in o-dichlorobenzene. The phosgenation occurs in two or three reaction vessels in series, each of which is held at different temperatures. The first stage operates at 50-70°C and the final stage operates at 120-150°C. Total reaction time is about 3 hours. HCl evolved during phosgenation is marketable as a by-product.

The crude TDI passes to a series of vacuum distillations to remove solvent and residue. The unreacted phosgene may be stripped from solution with N_2 or CH_4 prior to distillation. A block schematic diagram of this process is shown in Figure 4.19 and the mass conversions are presented in Table 4.17.

4.12.3 Alternative Processes

Recent developments for producing TDI have focused on eliminating phosgenation (Ref. 4.12-2). This lowers feedstock costs and eliminates a bothersome by-product, HCl.

Mitsui Toatsu Chemicals' process produces TDI by carbonylation of dinitrotoluene using palladium or selenium catalysts.

FIGURE 4.19 MANUFACTURE OF TOLUENEDIISOCYANATE FROM TOLUENE (Mitsubishi Chemical Industries)

Energy Summary⁽¹⁾

	Reduction & TDA Distillation	Phosgenation & TDA Distillation	Total (Excluding Nitration)
Electricity (kWh)	.048 (480)	.150 (1500)	.198 (1980)
Steam (lb)	3.59 (3755)	.438 (458)	4.028 (4213)
Fuel (BTU)	1540 (1540)	4850 (4850)	6390 (6390)
Total BTU	(5775)	(6808)	(12583)

Note: (1) First number in table is units shown per pound of TDI. Second number in parentheses is the BTU equivalent.

Table 4.17 Manufacture of TDI Material Requirements

	<u>lb per lb of TDI</u>
Toluene	.676 - .705
Nitric Acid	.944
Sulfuric Acid	.767
H ₂	.081 - .093
Phosgene	1.265 - 1.434

Refs. 4.12-1, 4.12-3, 4.12-4

4.13 URETHANE FOAM FROM TDI

4.13.1 Summary

Flexible polyurethane foams are produced by condensation polymerization of polyether polyols (e.g. polypropylene glycols and propylene/ethylene oxide adducts of glycerin) with polyisocyanates (chiefly toluene diisocyanate). Processing may be batch or continuous.

4.13.2 Process Description for Prepolymer Type Process

In a prepolymer-type process, a low molecular weight polymer is produced using an excess of isocyanate. Final cross-linking and foaming are performed at the point of fabrication.

In a continuous process (see Figure 4.20) polyol, TDI, catalyst, and other additives are mixed and heated to 350°F in a scraped surface heat exchanger called a Votator. Heat is supplied by 150 psig steam.

The reaction mixture is held for a specific "cook" period (about 12 minutes) during which the reaction exotherm raises the temperature to 365°F.

From the holdup unit, the material passes to a second Votator used for mixing and cooling. A second injection of TDI is performed here. The TDI addition is performed in two steps in order to obtain the necessary viscosity buildup during cooking and to provide sufficient isocyanate groups for reaction with water in the subsequent foaming step. Table 4.18 shows a typical urethane foam composition and the material requirements.

In a batch process, the above steps take place in an agitated kettle reactor under nitrogen atmosphere.

4.13.3 Process Alternatives

In the one-shot type process, the total product formulation is mixed initially and no prepolymer is formed. Continuous mixers feed the material to conveyors or molds where foaming and setting up take place.

FIGURE 4.20 MANUFACTURE OF FLEXIBLE POLYURETHANE FOAM
(General Motors' Continuous Prepolymer-type Process)

Ref. 4.13-4

Energy Summary⁽¹⁾

	<u>Continuous Process</u>		<u>Batch Process (not shown)</u>	
Electricity (kWh)	.022	(220)	.006	(60)
Steam (lb)				
150 psig	.059	(63)	.047	(50)
Total BTU		(283)		(110)

Ref. 4.13-1

Note: (1) First number in table is units shown per pound of prepolymer.
Second number in parentheses is the BTU equivalent.

TABLE 4.18 TYPICAL FORMULATION AND MASS CONVERSION FOR FLEXIBLE URETHANE FOAM

Refs. 4.13-2, 4.13-3

	<u>Parts</u>
Polyether triol ¹	100.0
Silicon copolymer stabilizer ²	1.5
Water	3.5
Catalysts ³	0.9
Foaming Catalyst	As required
Toluene diisocyanate (80:20 isomer mix)	45.0

¹Polyether triol of glycerin and propylene oxide

²Trimethylol end-blocked dimethyl polysiloxane

³Stannous octoate, N-ethyl morpholine, and organotin gel catalyst; equal parts

Material Requirements for Flexible Polyurethane Prepolymer

	<u>lb/lb Prepolymer</u>
Toluene diisocyanate	.795
Polyether	.205

4.14 DIMETHYL TEREPHTHALATE FROM P-XYLENE

4.14.1 Summary

Dimethyl terephthalate (DMT) used for production of polyester fiber, is produced by oxidation and esterification of p-xylene. Two major process routes may be defined, depending on whether terephthalic acid (TPA) is produced as an intermediate. The process without forming TPA is typified by Dynamit Nobel AG and Toray Industries' process forms a TPA intermediate.

4.14.2 Process Description of the Dynamit Nobel AG Process

Para-xylene and recycle methyl p-toluate are oxidized by air under mild conditions of temperature and pressure (150°C and 4 to 8 atm) to p-toluic acid and monomethyl terephthalate. The oxidation is performed in the presence of a cobalt and manganese catalyst in the form of an organic acid salt.

A number of oxidation reactors in series is used, with a total residence time of about 14 hours.

Conversion in the oxidation step is about 64% of p-xylene and 50% of methyl p-toluate. Spent air leaving the reactors carries with it p-xylene and water vapors, and thus provides some cooling. P-xylene is condensed and recycled from the spent air.

Heat released during oxidation is equivalent to about 3800 BTU per pound of final DMT product. Most of the cooling is provided by cooling coils in the reactors.

The p-toluic acid and monomethyl terephthalate leaving oxidation are esterified with methanol, producing methyl p-toluate and a crude DMT. The reaction is carried out by introducing superheated methanol vapor into the

bottom of valve tray reactors, operating at 260°C and 20-25 atmospheres. Liquid residence time is about 1.3 hours.

The overhead from the esterifier is distilled to recycle methanol. The distillation bottoms are mainly water and p-xylene. The p-xylene is separated and recycled to xylene oxidation.

The crude DMT from the esterifier bottoms is distilled in a column where the overhead methyl p-toluate is recycled to xylene oxidation; the bottom product is distilled again to remove residue from DMT.

Further purification is performed by crystallization from methanol. The crystallizers are operated at 330 mmHg (absolute) and are maintained at about 45°C by evaporating methanol. DMT is separated from the methanol in centrifuges and finally distilled to fiber grade DMT.

A block schematic diagram of this process is shown in Figure 4.21 and the mass conversions are presented in Table 4.19.

4.14.3 Process Description of the Toray Industries' Process

Para-xylene is oxidized in a single step at low-to-moderate temperature and pressure in acetic acid solvent. A cobalt acetate catalyst and an acetaldehyde activator are used. Granular terephthalic acid obtained in the oxidizer is washed with pure acetic acid and dried. The crude TPA product is then esterified with methanol to give DMT. Acetic acid is produced as a by-product. A block schematic of this process is shown in Figure 4.22 and the mass conversions are presented in Table 4.20.

The process chemistry is summarized below.

4.14.4 Alternative Processes

Historically, DMT has been the preferred route for producing polyester fibers because it is more easily purified than TPA. More recently, processes have been developed which oxidize p-xylene to TPA and purify the TPA without esterifying it. Processes used for TPA purification include crystallization (Standard Oil) and sublimation (Mobil).

Utilities requirements for the Mobil process are reported as follows, (Ref. 4.14-4) per pound of TPA:

Electricity (kWh)	0.11 (1100)
Steam - 400 psig (lb)	10.0 (9700)
Fuel (BTU)	5500 (<u>5500</u>)
Total BTU	(16300)

The Mobil process is reported to be no longer used (Ref. 4.14-5).

FIGURE 4.21 MANUFACTURE OF DMT (Dynamit Nobel AG Process)

Energy Summary⁽¹⁾

	<u>Xylene Oxidation</u>		<u>Esterification/ Methanol Distill.</u>		<u>Ester Distill./ DMT Purification</u>	
Electricity (kWh)	0.17	(1700)	0.02	(200)	0.04	(400)
Steam (lb) psig = 200	0.08	(84)	1.12	(1172)	-	-
Natural Gas (BTU)	-	-	680	(680)	1120	(1120)
Total BTU		(1784)		(2052)		(1520)

Refs. 4.14-1, 4.14-2

Note: (1) First number in table is units shown per pound DMT. Second number in parentheses is the BTU equivalent.

FIGURE 4.22 MANUFACTURE OF DMT
(Toray Industries' Process)

Overall
Energy Summary ⁽¹⁾

Electricity (kWh)	0.16	(1600)
Steam (lb)	7.4	(7740)
Fuel (BTU)	2340	<u>(2340)</u>
Total BTU		(11680)

Ref. 4.14-3

Note: (1) First number in table is units shown per pound of DMT produced. Second number in parentheses is the BTU equivalent.

Mass Conversions

	<u>1b/1b DMT</u>
p-Xylene	0.63
Methanol	0.38

Ref. 4.14-1

Table 4.20 Manufacture of DMT-Material Requirements
 (Toray Industries Process)

Mass Conversions

	<u>lb/lb DMT</u>
p-Xylene	0.58
Methanol	0.36
Acetaldehyde	0.20
Acetic Acid by-product	0.20

Ref. 4.14-3

4.15 POLYESTER FIBERS

4.15.1 Summary

Nearly all polyester fibers are produced by condensation polymerization of ethylene glycol with terephthalic acid (TPA) or its dimethyl ester (DMT). While most processes still start with DMT, the use of TPA is growing in importance.

Polymerization is accomplished in two steps:

- 1) DMT is esterified with ethylene glycol to produce diglycol terephthalate (i.e. bis (hydroxyethyl) terephthalate);

- 2) Diglycol terephthalate is condensation polymerized by lowering the pressure to about 1 mm Hg and raising the temperature to 270-290°C. Half of the ethylene glycol used in esterification is released.

4.15.2 Process Description

Ethylene glycol and molten DMT are fed to esterification reactors (tray columns) operating at 1 atmosphere and 170-230°C. Residence time is about 2.3 hours. The reaction is commonly performed in the presence of antimony catalyst. Methanol released by the esterification is taken from the reactor overhead and purified by distillation.

Diglycol terephthalate formed during esterification is polymerized in two stirred reactors in series. The reactors are heated by jackets containing circulating heat transfer fluid. The first reactor operates at 230-270°C and 10 mm Hg - the second at 270-290°C and 1 mm Hg. Total residence time is 4-6 hours.

Ethylene glycol evolved during polymerization is removed from the reactor overheads and purified by distillation. Distillation bottoms include aldehydes and other products of polymer decomposition. The purified ethylene glycol is recycled to esterification.

Polymer melt from the polymerization reactors is transferred by screw pumps to polymer blending vessels. From here, it can be fed directly to fiber spinning, or cooled and granulated to chips.

A block schematic diagram of this process is shown in Figure 4.23 and the mass conversions are presented in Table 4.21.

4.15.3 Alternative Processes

Material and energy requirements are shown below for an older, batch process for production of polyester fiber from DMT by Hoechst AG (Ref. 4.15-3):

	<u>lb/lb Polyester</u>
Dimethyl terephthalate	1.05
Ethylene glycol	0.40
Methanol by-product	0.33

	<u>per lb Polyester</u>
Fuel (BTU)	1980 (1980)
Electricity (kWh)	0.13 (1300)
Steam (lb)	0.90 (940)
Total BTU	(4220)

Figure 4.23 . Manufacture of Polyester Fiber (Polyethylene Terephthalate) Continuous Process

96

Energy Summary ⁽¹⁾

	<u>Esterification</u>		<u>Polycondensation</u>		<u>Ethylene Glycol Recovery</u>		<u>Polymer Blending</u>		<u>Total</u>	
Natural Gas (BTU)	304	(304)	142	(142)	209	(209)	38	(38)	693	(693)
Electricity (kWh)	.0055	(55)	.0600	(600)	.0004	(4)	.0113	(113)	.0772	(772)
Steam (lb)	0.30	(314)	0.47	(492)	0.57	(596)	.095	(100)	1.435	(1502)
Total BTU		(673)		(1234)		(809)		(251)		(2967)

Refs. 4.15-1, 4.15-2

Note: (1) First number in table is units shown per pound of polyester produced.
Second number in parentheses is the BTU equivalent.

Table 4.21 Manufacture of Polyester Fiber - Material Requirements
Continuous Process

	<u>lb/lb Polyester</u>
Dimethyl terephthalate	1.00
Ethylene glycol	0.70
Methanol by-product	0.33

Ref. 4.15-1

4.16 CAPROLACTAM FROM CYCLOHEXANE

4.16.1 Summary

The manufacture of caprolactam from cyclohexane consists of four major process steps. In the first step, cyclohexane is converted to cyclohexanone. In the second step, cyclohexanone is converted to the oxime. The oxime is converted to crude caprolactam in the third step and purified in the fourth. (See Figure 4.24.)

4.16.2 Process Description

Cyclohexane is oxidized with air in the presence of a catalyst to form a mixture of cyclohexanone and cyclohexanol (K.A. oil). The oxidation

takes place at 140-170°C and 7-9 atmospheres. The reaction is controlled to keep the per pass conversion at about 5%. Cyclohexane is separated at distillation and recycled. The cyclohexanol is separated by vacuum fractionation and then dehydrogenated to form additional cyclohexanone. Overall yields of cyclohexanone are 65%-80%.

Cyclohexanone is reacted with hydroxylamine in the presence of a solvent to form cyclohexanone oxime. The reaction which is essentially quantitative occurs at a pH of about 2, and at low temperature.

The oxime is separated from the solvent and then converted to crude caprolactam by the Beckmann rearrangement. This is done by heating the oxime with weak oleum (SO_3) under anhydrous conditions. The reaction occurs at about 100-120°C and requires 15-30 minutes.

A comparison of the Raschig route process to the Stamicarbon process is shown below (Ref. 4.16-4):

The reaction mixture is then cooled, diluted with water and neutralized with ammonia. The crude caprolactam is separated and purified

by vacuum distillation. By-product ammonium sulfate is available for processing to fertilizer grade crystals. The overall recovery, based on cyclohexanone, is over 95%. (See Table 4.22.)

4.16.3 Process Alternatives

Cyclohexane is the predominant feedstock for producing caprolactam, although originally the process was based on phenol. Currently, two significant operations are dependent upon toluene: DSM's process which uses toluene to make phenol; and Snia Viscosa's process.

Considerable development work has involved modifications to the conventional Raschig route to hydroxylamine sulfate. In its original form, this involves the production of ammonia nitrate and its subsequent reaction with SO_2 and aqueous ammonia to produce hydroxylamine disulfonic acid $[\text{NCH}(\text{SO}_3\text{NH}_4)_2]$. This is finally hydrolyzed to hydroxylamine sulfate $[(\text{NH}_3\text{OH})_2\text{SO}_4]$, producing by-product ammonium sulfate.

The material and energy requirements shown in 4.16.2 are for the Stamicarbon HPO process which produces free hydroxylamine ions (NH_3OH^+) directly and thus avoids the production of ammonium sulfate at this step. The Stamicarbon process still produces by-product ammonium sulfate during the Beckmann rearrangement.

FIGURE 4.24 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE MANUFACTURE OF CAPROLACTAM
(Conventional Process) (Stamicarbon)

Overall Energy Summary⁽¹⁾

	Ref. 4.16-1 Cyclohexane to KA Oil	Ref. 4.16-2 Cyclohexanone to to Caprolactam	Ref. 4.16-3 Total Plant (Cyclohexane to Caprolactam)	
Fuel (BTU)	- -	- --	377	(377)
Electricity (kWh)	0.17 (1700)	0.10 (1000)	0.243	(2430)
Refrigeration (BTU)	- --	- -	69	(69)
<u>Steam (lb)</u>				
psig = 450	- -	4.10 (3920)	6.22	(5946)
psig = 175	- -	1.12 (1186)	3.31	(3505)
psig = 50	- -	1.38 (1572)	3.32	(3782)
psig = Unknown	3.05 (3190)	- -	-	-
Total BTU	(4890)	(7678)	(16109)	

Note: (1) First number in table is units shown per pound of total caprolactam produced. Second number in parentheses is the BTU equivalent.

Table 4.22 Manufacture of Caprolactam - Mass Conversions

Material Requirements
(per lb caprolactam)

Cyclohexane	1.06
H ₂	0.0963
NH ₃	0.805
H ₂ SO ₄	1.360
(NH ₄) ₂ SO ₄ By-product	1.80

Refs. 4.16-2, 4.16-3

4.17 NYLON 6 FROM CAPROLACTAM

4.17.1 Summary

Caprolactam is polymerized in aqueous medium to produce Nylon-6 chips.

Pure anhydrous caprolactam does not homopolymerize.

4.17.2 Process Description

Caprolactam is polymerized in the presence of water at temperatures of 260°C. Temperature is maintained by indirect contact with circulating Dowtherm. Additives, such as dulling agents, chain terminators and catalysts are added to the polymerization mixture. The raw polymer is extruded into strands and cut into granules. Approximately 10% of the caprolactam is either unreacted or reacted to oligomers which are removed by extraction with hot water. The extracted polymer is dewatered and dried in hot nitrogen. The Nylon-6 granules may then be further formed into various products (Figure 4.25).

Monomer extracted from the chips is separated from the water by distillation and recycled to polymerization. Overall caprolactam requirement is about 1.11 pounds per pound of Nylon-6 (90% yield).

4.17.3 Process Alternatives

A second variation is producing Nylon-6 results from recovering unreacted monomer by vacuum distillation rather than the aqueous extraction route presented in 4.17.2.

FIGURE 4.25 FLOW SCHEMATIC AND ENERGY REQUIREMENTS FOR THE MANUFACTURE OF NYLON-6

Energy Summary⁽¹⁾

	<u>Polymerization</u>		<u>Chip Extrusion/ Monomer Separation</u>		<u>Monomer Recovery</u>		<u>Total</u>	
Fuel (BTU)		657	-		-		657	(657)
Electricity (kWh)	.021	(210)	.114	(1140)	.010	(100)	.145	(1450)
Steam (lb)								
psig = 100	--		-		2.4	(2642)	2.4	(2642)
psig = 100 + super- heat to 570°F	0.05	(63)	0.27	(339)	-		0.32	(402)
Total BTU		(930)		(1479)		(2740)		(5151)

Note: (1) First number in table is units shown per pound of Nylon-6 produced. Second number in parentheses is the BTU equivalent.

(2) Recycle is approximately 9.25% of the input caprolactam.

4.18 ADIPIC ACID FROM CYCLOHEXANE

4.18.1 Summary

Adipic acid is produced from cyclohexane by a two step oxidation:

- 1) Oxidation of cyclohexane by air to produce cyclohexanol and cyclohexanone (KA oil):

- 2) Oxidation of KA oil by nitric acid to produce adipic acid:

4.18.2 Process Description

Cyclohexane is air oxidized in a series of 3 to 6 stirred tank reactors⁵⁷ at temperatures in the vicinity of 160-180°C (320-356°F) and a pressure of 1100 kPa (150 psig).

A cobalt catalyst is used, with concentration in the range of 0.3 to 3 ppm.⁵⁶ Substantial quantities of cyclohexane are distilled out of the oxidizer effluent and recycled to the oxidizer feed. The recovered product is a mixture of cyclohexanol and cyclohexanone, called KA oil.

The KA oil is then catalytically oxidized with 45 to 55% nitric acid at 60-80°C (140-175°F) and 100-400 kPa (0-60 psig). The process is catalyzed by ammonium vanadate and cupric nitrate at concentrations of 0.25% copper and 0.1% vanadium. Since this reaction is highly exothermic, a high ratio (40:1) of nitric acid to KA mixture is maintained.⁵⁸ The reactor train is typically either stirred tank reactors or a circulating loop consisting of a pump, heat exchanger, and gas-liquid separator. Reaction time is 2 hours.

FIGURE 4.26 FLOW SCHEMATIC FOR ADIPIC ACID FROM CYCLOHEXANE
(Conventional Process)

Energy Summary

No information on utility requirements for adipic acid manufacture was found in the sources consulted for this study.

Table 4.23 Manufacture of Adipic Acid - Mass Conversion
Material Requirements

<u>1b/1b Adipic Acid</u>	
Cyclohexane	0.78
HNO ₃	0.266

Adipic acid product is recovered by crystallization at 30-70°C (85-160°F) and purified by recrystallization.⁵⁶ Nitrous gases from the reactor train are recovered as nitric acid and recycled to the system. The mother liquor from the crystallization is concentrated by distillation and, after nitric acid recovery; the concentrate is discarded.⁵⁹ A flow schematic is shown in Figure 4.26 and mass conversions in Table 4.23.

4.19 NYLON 6,6 FROM ADIPIC ACID

4.19.1 Summary

Nylon 6,6 is produced from the condensation polymerization of adipic acid with hexamethylenediamine (HMDA) in two steps:

- 1) Reaction of adipic acid and HMDA to produce hexamethylenediammonium adipate (AH salt)

- 2) Homopolymerization of AH salt to Nylon 6,6

4.19.2 Process Description

A 20% solution of adipic acid is neutralized with a 60-80% solution of HMDA in boiling methanol at 50°C and a pH of 7.6. The resulting aqueous solution is evaporated to precipitate AH salt. Evaporation is done on a steam heated, agitated thin-film evaporator operating at 230°F and in a vacuum mode. The precipitated AH salt is washed in methanol and centrifuged to dryness.

The centrifuge cake is redissolved in water to form a 60% solution and is filtered over activated carbon to remove impurities causing discoloration. The solution is heated to 450°F and 200 psig in a stainless steel autoclave to affect polymerization. Chain terminator (acetic acid), delustrant (TiO_2), pigments, and other additives are added at this point.

Additional water is removed by reducing pressure to atmospheric, and controlling temperature at 320°F. Next, an optional finishing step is employed. The polymer is raised to a temperature of 540°F to ensure complete polymerization.

From this step, nitrogen pressure is applied to force the molten polymer through a heated valve in the base of the autoclave. The extruded polymer is then either spun or cast.

A schematic flow diagram and energy summary are presented in Figure 4.27. The conversions of the raw materials to the Nylon 6,6 product are shown in Table 4.24.

FIGURE 4.27 FLOW SCHEMATIC AND ENERGY REQUIREMENTS
FOR THE MANUFACTURE OF NYLON 66

Overall
Energy Summary⁽¹⁾

Electricity (kWh)	0.05	(500)
Steam (lb)		
psig = 50	2.0	(2278)
Fuel (BTU)		<u>(1580)</u>
Total BTU		(4358)

Ref. 4.19-1

Note: (1) First number in table is units shown per pound of Nylon 66.
Second number in parentheses is the BTU equivalent.

Table 4.24 Manufacture of Nylon 6,6 Material Requirements

	<u>1b/1b Nylon 6,6</u>
Adipic Acid	0.65
HMDA	0.521
Methanol	0.013

Ref. 4.19-1

4.20 PHTHALIC ANHYDRIDE FROM O-XYLENE

4.20.1 Summary

Phthalic anhydride is produced from ortho-xylene and from naphthalenes by catalytic oxidation in air. The predominant feedstock is ortho-xylene and the major process is BASF's phthalic anhydride from o-xylene by Air Oxidation in a Fixed Bed Reactor. Production consists of the initial catalytic reaction followed by extensive purification to derive specification grade phthalic anhydride. Some minor amount of maleic anhydride is recovered as a by-product.

4.20.2 Process Description

O-xylene feedstock is preheated to 290°F, mixed with preheated air (at 318°F, 27 psia) and fed into the fixed-bed tube-type reactor at 300°F and 25 psia. The catalyst consists of about 6% V_2O_5 and 94% anatase on an inert ceramic ball carrier. The crude reaction product is cooled from 716°F to 370°F and is fed into the "switch-condensers" for initial separation. Crude phthalic anhydride sublimes to solid form on the cool walls of this condenser allowing other contaminants to exit. After switching the condenser is heated to reliquefy the crude anhydride which is then fed to the decomposers. Here, the remaining phthalic acid (about 4%) is converted to the anhydride. Next, the impure product is introduced into the light ends column which separates out the final benzoic acid and maleic anhydride, at about 100 mm Hg pressure and 374°F. The final purification step removes the last traces of undesired constituents at 100 mm Hg and 398°F, and the product phthalic anhydride is delivered to storage.

A schematic flow diagram and energy requirements are shown in Figure 4.28 and the mass conversions are presented in Table 4.25.

FIGURE 4.28

Energy Summary⁽¹⁾

Electricity, kWh	0.41	4100 ⁽²⁾
Steam Generated lb		
(867 psia)	(0.55)	(465)
(147 psia)	(1.75)	<u>(1892)</u>
Total Energy		1743

Notes: (1) Left column is units per pound of phthalic anhydride and right column is BTU equivalent
 (2) 10,000 BTU/kWhr

Ref. 4.20-1

Table 4.25

	Mass Conversion
	<u>1b Feed/1b Phthalic Anhydride</u>
Ortho-xylene	0.97
Air	<u>31.04</u>
	32.00

4.21 MALEIC ANHYDRIDE FROM BENZENE

4.21.1 Summary

Maleic Anhydride $[(\text{CH}=\text{CO})_2\text{O}]$ has been produced by the catalytic oxidation of benzene, n-butane, butenes and butadiene. The overwhelming bulk of this chemical is made using a benzene feedstock. Production consists of a two-stage reaction followed by separation and purification.

4.21.2 Process Description

The benzene feed is heated to 300°F and injected into a vaporizer at 100 psia where it is mixed with preheated air and fed to a fixed-bed tube-type reactor in the presence of a vanadium-titanium catalyst. The effluent from the reactor is cooled in three successive stages where approximately 40% of the crude maleic anhydride is condensed. The vapor phase is scrubbed to remove the unwanted carbon dioxides and carbon oxides and then recombined with the condensed portion. This intermediate material goes through a thin-film evaporator, at 550 mm Hg, to remove the free water and then to an evaporative filter to remove any fumaric acid and polymers. The remainder undergoes further purification to remove higher boiling point contaminants. Finally, the mix of maleic anhydride and water is sent through a barometric condenser to separate the water, and the resultant anhydride is piped to storage tanks.

A schematic diagram and the net energy requirements are shown in Figure 4.29 and the mass conversions are presented in Table 4.26.

FIGURE 4.29

Energy Summary⁽¹⁾

Net Steam Generated, lbs @ 340 psig	(6.57)	(6,544)
Electricity, kWhr	0.79	<u>7,900</u>
		1,356

Notes: (1) Left column is units per pound of maleic anhydride produced.
Right column is in BTU equivalent.

TABLE 4.26 MASS CONVERSIONS

<u>Feed Material</u>	<u>lb Feed/lb Maleic Anhydride</u>
Benzene	1.19
Air	<u>37.47</u>
	38.66

Ref. 4.21-1

4.22 UNSATURATED POLYESTER PRODUCTION

4.22.1 Summary

Polyester resins are mixtures of unsaturated polyesters and vinyl monomers. In the fabrication of thermosetting plastic products they crosslink by the addition of suitable curing agents and, perhaps, heat. Resin production consists of a linear polymerization step followed by mixing with the monomer and an inhibitor to prevent premature curing.

4.22.2 Process Description

Maleic anhydride, phthalic anhydride and a glycol are charged to an agitated reactor under an inert atmosphere in the presence of solvent xylene. The solvent and the water of reaction resulting from the polymerization are distilled out azeotropically and the solvent is recovered for recycling.

The dibasic aromatic phthalic anhydride, dibasic unsaturated maleic anhydride and the dihydric alcohols (ethylene, diethylene, propylene or similar glycols) are heated to approximately 700°F under a carbon dioxide or nitrogen atmosphere until an acid number of 60 to 65 is achieved. Then the temperature is increased to 825°F and maintained until the acid number is reduced to 45 or 50, which takes about 5 hours. The temperature is reduced to 300°F in preparation for mixing with the vinyl monomer crosslinking agent and an inhibitor to prevent undesired curing. The mixture is stored in tanks or drums for final curing at the point of use or fabrication.

Inhibitors in general use include hydroquinone, p-t-butyl catechol, phenolic resins, aromatic amines, chloranil, picric acid and quinones and are usually added in amounts of approximately 0.02 wt % of the total solution. The curing agents include benzoyl peroxide, MEK peroxide, di-t-butyl peroxide and dicumyl peroxide, and the curing process may also require the addition of heat.

A schematic diagram and energy requirements are shown in Figure 4.30 and the mass conversions are presented in Table 4.26.

FIGURE 4.30

Energy Summary ⁽¹⁾

Polymerization and Mixing

Electricity, ^(a) kWh	0.025	250
Steam, lb @ 250 psig ^(b)	0.243	249
Natural Gas, SCF ^(c)	0.291	<u>297</u>
TOTAL BTU		796

Note: (1) Left column is units per pound of unsaturated polyester resin produced. Right column is in BTU equivalent

TABLE 4.26 UNSATURATED POLYESTER RESIN PRODUCTION BY BATCH-TYPE SOLVENT
POLYMERIZATION

<u>Feed Material</u>	Mass Conversions
	<u>Resin</u>
	<u>1b Feed</u> <u>1b UPR</u>
Phthalic Anhydride	0.289
Maleic Anhydride	0.191
Propylene Glycol	0.148
Ethylene Glycol	0.121
Diethylene Glycol	-
Styrene	<u>0.300</u>
	1.049

5.0 REFERENCES

- 4.1-1 Stanford Research Institute, Process Economics Program
- 4.1-2 Hydrocarbon Processing, January 1979
- 4.2-1 Stanford Research Institute, Process Economics Program
- 4.3-1 Stanford Research Institute, Process Economics Program
- 4.4-1 Stanford Research Institute, Process Economics Program
- 4.5-1 A. Portes, et al., "Optimize Styrene Production," Hydrocarbon Processing, September 1977, V 56, No. 9, pp 154-156
- 4.5-2 "Styrene (Monsanto Co.)" Hydrocarbon Processing, November 1977, p 227
- 4.5-3 Stanford Research Institute, Process Economics Program
- 4.6-1 Wilkins, G.E., "Industrial Process Profiles for Environmental Use, Chapter 10, Plastics and Resins Industry," Radian Corporation, February 1977
- 4.6-2 Stanford Research Institute, Process Economics Program
- 4.6-3 "Polystyrene," Hydrocarbon Processing, November 1977, p 216
- 4.7-1 Stanford Research Institute, Process Economics Program
- 4.8-1 Stanford Research Institute, Process Economics Program
- 4.8-2 Hydrocarbon Processing, November 1977
- 4.9-1 P.M. Kohn, et al., "No Switch from Cumene, Say Phenol Manufacturers," Chemical Engineering, April 9, 1979, V 86, No. 8, pp 62, 64
- 4.9-2 Noller, C.R., "Chemistry of Organic Compounds," W.B. Sanders Co., Philadelphia, PA, 1957
- 4.9-3 Stanford Research Institute, Process Economics Program
- 4.10-1 Stanford Research Institute, Process Economics Program
- 4.10-2 "Phenol," Hydrocarbon Processing, November 1977, p 193
- 4.11-1 See Ref. 4.6-1

- 4.12-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.12-2 R. Ramirez, "Isocyanates on the Move," Chemical Engineering, pp 80-84, September 24, 1979
- 4.12-3 "Toluene Diisocyanate," Hydrocarbon Processing, p. 242, November 1969
- 4.12-4 "Toluene Diisocyanate," Hydrocarbon Processing, p. 213, November 1971
- 4.13-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.13-2 EPA-600/2-77-023j, G. Wilkins, "Industrial Process Profiles for Environmental Use: Chapter 10, Plastics and Resins Industry," February 1977
- 4.13-3 Y.L. Meltzer, "Foamed Plastics," p. 105, Noyes Data Corporation, Park Ridge, N.J., 1976
- 4.13-4 J.R. Wall, "Continuous Processing of Urethane Foam Prepolymers," Chem. Eng. Prog., Vol. 57, No. 10, p. 48, October 1961
- 4.14-1 "Dimethylterephthalate," Hydrocarbon Processing, p. 147, November 1977
- 4.14-2 "Process Economics Program," Stanford Research Institute
- 4.14-3 "Terephthalic Acid & DMT," Hydrocarbon Processing, p. 230, November 1977
- 4.14-4 "Terephthalic Acid," Hydrocarbon Processing, p. 211, November 1971

- 4.14-5 "Terephthalic Acid and Esters," Chemical Economics Handbook, Stanford Research Institute, p. 695.4022C, July 1977
- 4.15-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.15-2 L.M. Elkin, "Polyethylene Terephthalate," Report No. 18, Stanford Research Institute, Menlo Park, California, 1966
- 4.15-3 "Polyester," Hydrocarbon Processing, p. 202, November 1977
- 4.16-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.16-2 "Caprolactam (low sulfate process-DSM)," Hydrocarbon Processing, p. 136, November 1977
- 4.16-3 "Toluene Rivals Conventional Caprolactam Feedstocks," European Chemical News, pp 20-22, June 25, 1976
- 4.16-4 "Caprolactam Production: A Survey of Current Technology," European Chemical News, pp 24-26, April 30, 1976
- 4.17-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.17-2 "Process Economics Program," Stanford Research Institute
- 4.18-1 "Encyclopedia of Chemical Technology," Kirk-Othmer, Vol. 1, pp 518-520
- 4.18-2 J.J. McKetta and W.A. Cunningham, "Encyclopedia of Chemical Processing and Design," Volume 2, p. 134
- 4.18-3 Ibid, p. 137

- 4.18-4 "Adipic Acid," Hydrocarbon Processing, p. 124, November 1971
- 4.19-1 W.H. Hedley, et al., Monsanto Research Corporation, "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Inc., Westport, Connecticut (1975)
- 4.20-1 Stanford Research Institute, Process Economics Program
- 4.21-1 Stanford Research Institute, Process Economics Program
- 4.22-1 Stanford Research Institute, Process Economics Program
- 4.22-2 Same as 4.12-1

6.0 ADDITIONAL REFERENCES

1. Hydrocarbon Chemical Process Industries, Shreve and Brink, 4th Edition, 1977.
2. "Industrial Process Profiles for Environmental Use, Chapter 9, The Synthetic Rubber Industry," Jerry Parr, Terry B. Parsons and Nancy P. Phillips, Radian Corporation, February 1977.
3. "Industrial Process Profiles for Environmental Use, Chapter 11, The Synthetic Fiber Industry," Jerry Parr, Radian Corporation, February 1977.
4. "Phthalic Anhydride Plant Air Pollution Control," C.T. Chi and T.W. Hughes, Monsanto Research Corporation, September 1977.
5. "Environmental Considerations of Selected Energy Conserving Manufacturing Process Options," Petroleum Refining Industry Report, Volume IV, December 1976.
6. "Industrial Process Profiles for Environmental Use: Chapter 3. Petroleum Refining Industry," J.C. Dickerman, T.D. Raye, J.D. Colley, and R.H. Parsons, Radian Corporation, January 1977.
7. Chemical and Engineering News, June 11, 1979.
8. "Reducing Energy Demand of Separation Processes," W.F. Kenney, Chemical Eng. Proc. V75 N.3 68-71, March 1979.
9. "Process Efficiently Yields P-Xylene and Ethylbenzene," M. Seko, Oil Gas Journal, V77 N.27 81-86, July 2, 1979.

10. "New Process for P-Xylene and Ethylbenzene Separation from Mixed Xylene," M. Seko, T. Miyake, K. Inada, ASAHI Chemical Industry Co., Ltd., Chemical Week V124 N.15 45, April 11, 1979.
11. "The Kinetics and Mechanism of the Steam Dealkylation of Toluene on a Rhodium/Alumina Catalyst," P. Beltrame, I. Ferino, L. Forni and S. Torrazza, Chim. Ind. (Milan) V60 N. 3 191-96, March 1978.
12. "Energy Conservation in Distillation," T. J. Mix, R. C. Armstrong, J. S. Dweck and M. Weinberg, Chem. Eng. Prog. V74 N.4 49-55, April 1978.
13. "Distillation Prime Target for Energy Conservation," T. W. Mix, R. C. Armstrong and M. Weinberg, Oil Gas Journal, V76 N.16 92-94, April 17, 1978.
14. "Adsorptive Technology Ups P-Xylene Yield," S. Otani, M. Sato, M. Kanaoka, S. Akita, D. Ogawa, Y. Tsuchiya, Toray Industries, Inc., Oil Gas Journal V76 N.1 101-2, January 2, 1978.
15. "Energy Management/Distillation Pressure (Change) Ups Thruput," H. Z. Kister and I. D. Doig, Hydrocarbon Processing V56 N.7 132-136, July 1977.
16. "Cryogenics Increase Benzene Recovery," S. Dunlop, R. Banks, Petrocarbon Developments Ltd., Imperial Chemical Industries Ltd., Hydrocarbon Processing V56 N.7 147-52, July 1977.
17. "Controls Contribute to (Ethylbenzene Tower) Cost Savings," Cosden Oil & Chemical Co., R. Anderson, Instrum. Technol., V24 N.1 23, January 1977.
18. "Reducing (Distillation) Column Steam Consumption," N. G. O'Brien, Chem. Eng. Prog., V72 N.7 65-67, July 1976.
19. "Reformer Revamped for Cyclohexane," Sun Oil Co., J. McCabe, Oil Gas Journal, V74 N.11 115-16, March 15, 1976.
20. "A New Aromatics-Recovery Process Featuring Extractive Distillation," Phillips Petroleum Co., Chem. Eng. (NY), V81 N.24 71, November 11, 1974.
21. "Energy Conservation Being Pushed Hard," Goodyear Tire & Rubber Co., T. Wett, Dow Chemical Co., Oil Gas Journal, V72 N.10 67-71, March 11, 1974.
22. "Petrochemical Report/Low-Cost Paraxylene (Recovery) and Isomerization Routes Unveiled," Toray Industries, Inc., Oil Gas Journal, V70 N.36 117-18, September 4, 1972.

23. "Mobil Chemical Co.'s Zeolite-Catalyzed Low-Temperature Disproportionation of Toluene (to) Benzene and Low-Temperature Isomerization of an Extracted CB Aromatics Stream to Xylenes," Mobil Chemical Co., J. J. Wise, A. B. Schwartz, P. Grandio, F. H. Schneider, Hydrocarbon Processing V51 N.8 85-86, August 1972.
24. "Here's a Close Look at P-Xylene Processes Today--1," Institut Francais Du Petrole, Maruzen Petrochemical Co. Ltd., Phillips Petroleum Co., J. Morrison, Oil Gas Int. V10 N.12 67-68 70-74,79, December 1970.
25. "Para-Xylene via Fractional Crystallization," Phillips Petroleum Co., G. H. Dale, D. L. McKay, D. C. Tabler, Chem. Eng. Progress V62 N.11 104-112, November 1966.
26. "Dealkylation of Aromatic Hydrocarbons," R. J. Harrison, J. D. Brooks, K. M. Bowling, J. Applied Chem. (London) V15 N.2 84-91, February 1965.
27. "Polyester Technologies Reviewed," Sim-Chem Ltd., D. Markland, European Chemical News V30 N.788 32, May 27, 1977.
28. "New Styrene Plants Cut Energy Costs," Technip, K. Muenz, Badger Co. Inc., Mobil Oil Corp., Carbonnages De France Chimie, Cos-Mar, Monsanto Co., Lummus Co., Chem. Week V119 N.20 34-35, November 17, 1976.
29. "The Cheapest Route to Phenol," Universal Oil Products Co., P. R. Pujado, C. V. Berger, J. R. Salazar, Hydrocarbon Processing V55 N.3 91-96, March 1976.
30. "Adipic Acid in One Step," K. Tanaka, Chem. Technol. V4 N.9 555-559, 1974.
31. "Synthesis of Adipic Acid by Single-Stage Oxidation of Cyclohexane," Asahi Chemical Industry Co. Ltd., K. Tanaka, 167th ACS Natl. Meeting, Los Angeles, March 31 thru April 5, 1974.
32. "New (Lummus Co.) Route to Terephthalic Acid," Lummus Co., M. C. Sze, R. T. Whitehead, A. P. Gelbein, Hydrocarbon Processing V52 N.9 209, 211-212, 214-215, September 1973.
33. "Xylenes and Higher Aromatics--6. P-Xylene," N. E. Ockerbloom, Hydrocarbon Processing V51 N.1 93-99, January 1972.
34. "Mobil Chemical Co.'s Process for TPA (Terephthalic Acid)," H. S. Bryant, L. E. McMakin, J. I. Savoca, C. A. Duval, Mobil Chemical Co., Chem. Eng. Progress V67 N.9 69-75, September 1971.
35. "Compare Routes to Caprolactam," M. Chiti, M. Taverna, Hydrocarbon Processing V49 N.11 137-145, November 1970.

36. Hydrocarbon Processing, November 1973.
37. Hydrocarbon Processing, November 1971.
38. Hydrocarbon Processing, November 1969.
39. "Mobil's Process for TPA," Chem. Eng. Progress V67 N.9.
40. "Polyamides (General)," in Kirk-Othmer Encyclopedia of Chemical Technology V16 2nd Edition 29-33, 1968.
41. "Caprolactam," in Encyclopedia of Chemical Processing and Design, J. J. McUetta, W. A. Cunningham, ed., V6 72-95, 1979.
42. "Caprolactam Production: A Survey of Current Technology," European Chemical News, 20-22, April 30, 1976.
43. "Toluene Rivals Conventional Caprolactam Feedstocks," European Chemical News, 24-26, June 25, 1976.
44. "New Caprolactam Route Cuts By-Product Output by Half," Oil Gas Journal 56-58, August 24, 1970.
45. "Toluene Diisocyanate," Hydrocarbon Processing, p. 213, November 1971.
46. "Toluene Diisocyanate," Hydrocarbon Processing, p. 242, November 1969.
47. "Isocyanates on the Move," R. Ramirez, Chemical Engineering, pp 80-84, September 24, 1979.
48. "Encyclopedia of Chemical Processing and Design," J.J. McKetta and W.A. Cunningham, Volume 2, p 134.
49. Billmeyer, F.W., Textbook of Polymer Science, 2nd Edition, John Wiley and Sons, N.Y., 1971.