

Report No. 22

PHENOL

by YEN-CHEN YEN

April 1967

A private report by the

PROCESS ECONOMICS PROGRAM

STANFORD RESEARCH INSTITUTE



MENLO PARK, CALIFORNIA

CONTENTS

1	INTRODUCTION	1
2	SUMMARY	3
	General Aspects	3
	Technical Aspects	8
3	INDUSTRY STATUS	15
4	CHEMISTRY	23
	Manufacture of Phenol by the Cumene Process	23
	Oxidation of Cumene to Hydroperoxide	23
	Cleavage of Hydroperoxide	23
	Manufacture of Phenol by Raschig Process	25
	Chlorination of Benzene by Hydrochloric Acid and Air	25
	Hydrolysis of Chlorobenzene	26
	Manufacture of Phenol by Toluene Process	28
	Oxidation of Toluene to Benzoic Acid	28
	Conversion of Benzoic Acid to Phenol	31
	Manufacture of Phenol from Benzene Through Cyclohexane	
	Oxidation	34
	Hydrogenation of Benzene to Cyclohexane	34
	Oxidation of Cyclohexane to Cyclohexanol and Cyclohexanone	36
	Dehydrogenation of Cyclohexanol/Cyclohexanone	37
	Manufacture of Phenol by Chlorination Process	38
	Chlorination of Benzene	38
	Conversion of Chlorobenzene to Phenol	39
	Manufacture of Phenol by Sulfonation Process	40
	Sulfonation	40
	Conversion of Benzenesulfonic Acid to Phenol	42
	Manufacture of Phenol by Direct Oxidation of Benzene	43
	Manufacture of Phenol by Other Processes	46
5	MANUFACTURE OF PHENOL BY CUMENE PROCESS	47
	Review of Processes	47
	Oxidation of Cumene to Hydroperoxide	47
	Temperature	47
	Pressure	47
	Oxygen or Air	53
	Promoters	53
	Phase	53
	Reactors	53

CONTENTS

5	(continued)	<ul style="list-style-type: none"> Concentration of Hydroperoxide 54 Cleavage of Hydroperoxide 54 Neutralization of the Cleavage Product 55 Distillation of Cleavage Products 55 Purification of Phenol 57 Treatment of the Residue 58 Process Description 59 Process Discussion 74 Cost Estimates 76 	<ul style="list-style-type: none"> 54 54 55 55 57 58 59 74 76
6	PHENOL BY RASCHIG PROCESS	<ul style="list-style-type: none"> Review of Processes 87 The Catalyst for Oxychlorination 87 The Catalysts for Hydrolysis 88 The Oxychlorination Reactor 88 The Hydrolysis Reactor 89 The Recovery System 89 Process Description 90 Process Discussion 93 Cost Estimates 103 	<ul style="list-style-type: none"> 87 87 88 88 89 89 90 93 103
7	PHENOL BY TOLUENE PROCESS	<ul style="list-style-type: none"> Review of Processes 113 Oxidation of Toluene to Benzoic Acid 113 Conversion of Benzoic Acid to Phenol 118 A Process Based on Standard Oil and Montecatini Patents 124 <ul style="list-style-type: none"> Process Description 124 Process Discussion 137 Cost Estimate 139 A Process Based on Dow Patents 148 <ul style="list-style-type: none"> Process Description 148 Process Discussion 158 Cost Estimate 158 	<ul style="list-style-type: none"> 113 113 118 124 124 137 139 148 148 158 158
8	PHENOL BY CYCLOHEXANE PROCESS	<ul style="list-style-type: none"> Review of Processes 165 Hydrogenation of Benzene to Cyclohexane 165 Oxidation of Cyclohexane 172 Dehydrogenation of Cyclohexanol/Cyclohexanone 175 	<ul style="list-style-type: none"> 165 165 172 175

CONTENTS

8	(continued)	
	Process Description	176
	Process Discussion	193
	Cost Estimate	195
9	PHENOL BY CHLORINATION PROCESS	205
	Review of Processes	205
	Chlorination to Chlorobenzene	205
	Conversion of Chlorobenzene to Phenol	206
	Process Description	207
	Process Discussion	222
	Cost Estimate	223
10	PHENOL BY SULFONATION PROCESS	235
	Review of Processes	235
	Sulfonation	235
	Conversion of Benzenesulfonate to Phenol	238
	Process Description	239
	Process Discussion	252
	Cost Estimate	253
11	PHENOL FROM OXIDATION OF BENZENE BY MOLECULAR OXYGEN	267
	Review of Processes	267
	Phenol from Benzene--Oxidation with Irradiation	272
12	OTHER PROCESSES	285
	Oxidation by a Peroxide, Peracid, or Hydroperoxide	285
	Phenol from Acid Cleavage of Cyclohexylbenzenhydroperoxide	286
	Hydrodealkylation of Cresol	286
	Oxidation by Cupric Sulfate and Water	287
	Pyrolysis of Ortho-Benzoic Acid	287
APPENDIX A	DESIGN AND COST BASIS	291
APPENDIX B	PHYSICAL DATA	299
APPENDIX C	RAW MATERIALS AND PRODUCT SPECIFICATIONS	305

CONTENTS

CITED REFERENCES 311
SUPPLEMENTAL REFERENCES 335

ILLUSTRATIONS

5.1	Phenol by Cumene Process	61
5.2	Relationship of Production Costs of Phenol and Acetone by Cumene Process	83
5.3	Phenol by Cumene Process Production Cost for Varying Annual Production Acetone Credited at 4¢/lb, Acetophenone Credited at 20¢/lb	85
6.1	Phenol by Raschig Process	95
6.2	Phenol by Raschig Process Production Cost for Varying Annual Production	111
6.3	Effect of Conversion on Process Unit Investment and Production Cost	112
7.1	Conversion and Selectivity of Phenol from Benzoic Acid . . .	122
7.2	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents	129
7.3	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Production Cost for Varying Annual Production	147
7.4	Phenol by Toluene Process Based on Dow Patents	151
7.5	Phenol by Toluene Process Based on Dow Patents Production Cost for Varying Annual Production	164
8.1	Phenol by Cyclohexane Process	179
8.2	Phenol by Cyclohexane Process Production Cost for Varying Annual Production	204
9.1	Phenol by Chlorination Process	209
9.2	Phenol by Chlorination Process Production Cost for Varying Annual Production	232
9.3	Effect of Diphenyl Ether Production on Production Cost of Phenol	233
10.1	Phenol by Sulfonation Process	241
10.2	Relationship of Production Costs of Phenol and Sodium Sulfito by the Sulfonation Process (100 Million lb/yr Phenol)	261

ILLUSTRATIONS

10.3	Phenol by Sulfonation Process	
	Production Cost for Varying Production	263
11.1	Phenol by Direct Oxidation Process	277

TABLES

2.1	Evaluation of Processes for Producing 100 Million lb/yr of Phenol	5
2.2	Summary of Technical Data of Processes for Manufacture of Phenol	9
3.1	Synthetic Phenol Plants in North and South America	18
3.2	Synthetic Phenol Plants in Europe	19
3.3	Synthetic Phenol Plants in Asia and Australia	20
5.1	Oxidation of Cumene to Hydroperoxide Summary of Patents	49
5.2	Phenol by Cumene Process Major Process Equipment and Utilities Summary	60
5.3	Phenol by Cumene Process Stream Flows	65
5.4	Phenol by Cumene Process Process Unit and Utilities Investment	77
5.5	Phenol by Cumene Process Total Capital Investment	79
5.6	Phenol by Cumene Process Production Costs	81
6.1	Phenol by Raschig Process Major Process Equipment and Utilities Summary	94
6.2	Phenol by Raschig Process Stream Flows	99
6.3	Phenol by Raschig Process Process Unit and Utilities Investment	105
6.4	Phenol by Raschig Process Total Capital Investment	107
6.5	Phenol by Raschig Process Production Costs	109
7.1	Oxidation of Toluene by Air Summary of Patents	115
7.2	Conversion of Benzoic Acid to Phenol Summary of Patents	119

TABLES

7.3	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Major Process Equipment and Utilities Summary	128
7.4	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Stream Flows	133
7.5	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Process Unit and Utilities Investment	141
7.6	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Total Capital Investment	143
7.7	Phenol by Toluene Process Based on Standard Oil and Montecatini Patents Production Costs	145
7.8	Phenol by Toluene Process Based on Dow Patents Major Process and Utilities Summary	149
7.9	Phenol by Toluene Process Based on Dow Patents Stream Flows	153
7.10	Phenol by Toluene Process Based on Dow Patents Process Unit and Utilities Investment	159
7.11	Phenol by Toluene Process Based on Dow Patents Total Capital Investment	160
7.12	Phenol by Toluene Process Based on Dow Patents Production Costs	161
8.1	Phenol by Cyclohexane Process Summary of Patents on Hydrogenation of Benzene	167
8.2	Phenol by Cyclohexane Process Summary of Recent Patents on Oxidation of Cyclohexane	173
8.3	Phenol by Cyclohexane Process Major Process Equipment and Utilities Summary	177
8.4	Phenol by Cyclohexane Process Composition of Stream Flows	185
8.5	Phenol by Cyclohexane Process Process Unit and Utilities Investment	197

TABLES

8.6	Phenol by Cyclohexane Process Total Capital Investment	199
8.7	Phenol by Cyclohexane Process Production Costs	201
9.1	Phenol by Chlorination Process Major Process Equipment and Utilities Summary	208
9.2	Phenol by Chlorination Process Stream Flows	213
9.3	Phenol by Chlorination Process Process Unit and Utilities Investment	225
9.4	Phenol by Chlorination Process Total Capital Investment	227
9.5	Phenol by Chlorination Process Production Costs	229
10.1	Phenol by Sulfonation Process Major Process Equipment and Utilities Summary	240
10.2	Phenol by Sulfonation Process Stream Flows	245
10.3	Phenol by Sulfonation Process Process Unit and Utilities Investment	255
10.4	Phenol by Sulfonation Process Total Capital Investment	257
10.5	Phenol by Sulfonation Process Production Costs	259
11.1	Direct Oxidation of Benzene by Molecular Oxygen Summary of Patents	269
11.2	Phenol by Direct Oxidation Process Major Process Equipment and Utilities Summary	275
11.3	Phenol by Direct Oxidation Process Composition of Flow Streams	279
11.4	Phenol by Irradiated Direct Oxidation Process Total Capital Investment	282
11.5	Phenol by Irradiated Oxidation Process Production Costs	283