

Chemical Processes

dY d⊖ New forces have been at work in the investigation of chemical processes. The increased importance of thermodynamics in predicting the theoretical conversion and of process rates or kinetics to measure the rate of the chemical reaction has had an influence on the papers presented at our symposia. All the theoretical tools at our disposal should be used to bring to fruition as rapidly as possible the research ideas that must grow to the chemical process.

Another force with which we have not been concerned sufficiently in these symposia is the economic phase of the process or processing step. We hope that engineers concerned with economic balances will participate in future symposia and help introduce the dollar sign into our discussion.

With this broadened viewpoint, we hope that the Chemical Processes Symposia will continue to grow in their value to the process engineer.

KENNETH A. KOBE, Chairman

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Electrolytic Reduction of Phthalic Acid

Continuous mercury cathode cell . . .

phthalate

- Produces polymer intermediates electrolytically
- Eliminates poisoning common to lead cathodes
- Has high production capacity, current efficiency, low resistance

THE cyclohexadiene dicarboxylic acids, or dihydrophthalic acids, are of interest as intermediates for polymeric materials because they are both conjugated dienes and dibasic acids (5, 8-10). A laboratory process development program was, therefore, undertaken on their production.

The cyclohexadiene dicarboxylic acids were first described by Adolph Baeyer in the 1890's (1). He prepared 3,5cyclohexadiene-1,2-dicarboxylic acid by reducing sodium phthalate in aqueous solution with sodium amalgam:



trans-3,5-Cyclohexadiene 1,2-dicarboxylic acid The cis- isomer of this acid was made by converting the primary product to an anhydride and hydrolyzing:





The correctness of the structures assigned by Baeyer was proved by Neville (19), who resolved the *trans*-(racemic) acid. Either the *cis*- or *trans*-3,5-cyclohexadiene-1,2-dicarboxylic acids isomerize slowly to 2,6-cyclohexadiene-1,2dicarboxylic acid when refluxed in aqueous solution:





In 1906 Mettler (17) showed that a solution of phthalic acid in dilute sulfuric could be reduced electrolytically at a lead cathode. The reduction was further studied by Somlo (22). The only product isolated was the *trans*-3,5 acid.

An effort was made to adapt Mettler's method to a larger scale preparation. It was found that, in spite of all the usual precautions to avoid introducing contaminants (25), the lead cathode was rapidly poisoned, and the current efficiency suffered accordingly. The product made in the lead cathode cell was dark in color and was accompanied by varying amounts of sticky brown tar.

Batch Cell

Description. Mercury is known to have a high hydrogen overvoltage and to form a suitable cathode for many organic reductions. The cell shown in Figure 1 was, therefore, set up. It was of conventional design with the cathode, 190 sq. cm. in area, lying in the bottom of a cylindrical glass vessel 15.5 cm. in diameter. The rolled sheet-lead anode was placed inside a porous porcelain cup, 80 mm. in diameter, immersed in the catholyte. The submerged area of the anode when the cell was run with 1500 cc. of catholyte was about 480 sq. cm. (both sides), but probably only a small fraction of this was effective. The level of the anolyte was automatically maintained a little above that of the catholyte by adding distilled water from a reservoir with a single tubular opening projecting into the anode compartment. The mouth of the tube was turned to the side to keep the evolved oxygen from displacing water in the reservoir. Current was supplied by a variable-field motor-generator, and the cell was heated by an external bath.

Procedure. The materials used were C.P. sulfuric acid, distilled water, and commercial phthalic anhydride. All runs were made at 85° C., which is about the maximum that can be used conveniently with an open cell. The catholyte was 5% sulfuric acid, a concentration which provides a reasonably low resistance and is a good solvent for phthalic acid. The phthalic acid content was maintained at 4.48%, which is just under saturation at 85° C. The anolyte was 5% sulfuric acid and increased in concentration in the course of a run as a result of sulfate ion transfer from the catholyte. All of these conditions represent practical compromises, and they were not varied in the course of this work.

In making a run, catholyte was prepared by adding phthalic anhydride to dilute sulfuric in an amount of 40 grams per liter. The anhydride was dissolved and hydrolyzed by heating to 85° C.

ſable	١.	Poisoning	and	Regeneration
		of Mercury	Catl	hode

Run No.	Source of Catholyte	Reduced Acid in Product, %
49 50	Fresh Run 49 plus make-up	98 87
51	Run 50 plus make-up	84 .
52 53	Fresh ^a	101
- 0 1	1 1 1 11 0007 1	

^a Cathode washed with 20% NaOH and water after Run No. 52

Catholyte and anolyte were charged to the cell and a measured current was passed through it for a measured time. In some runs, samples were pipetted from the cell periodically for analysis. At the end of a run, the catholyte was siphoned from the cell and chilled to just above its freezing point. The crystallized product was filtered off, washed, dried, and analyzed. The filtrate was analyzed and in some cases fortified with sulfuric acid and phthalic anhydride for recycle to the cell. The product was normally light yellow, but a colorless product can be made by treating the catholyte with Norite activated carbon before chilling. The crude trans-3.5-cyclohexadiene-1.2-dicarboxylic acid can be freed from small amounts of isomeric acids by recrystallizing rapidly from water.

In occasional runs, particularly if the catholyte was chilled and filtered rapidly, a small second crop of crystals separated from the filtrate on standing. The



Figure 1. Mercury cathode batch cell

physical and chemical properties of this second crop were close to those recorded by Baeyer for cis-3,5-cyclohexadiene dicarboxylic acid (1). The cis- acid was never more than a few per cent of the total product, and was difficult to obtain free of the *trans*- acid. It is not surprising that previous investigators missed it.

Samples of catholyte withdrawn from the cell and the final dried products were analyzed for their content of reduced acid by titration in dilute sulfuric acid with bromide-bromate. Baever found that solid trans-3,5-cyclohexadiene dicarboxylic acid reacts with four atoms of bromine when exposed to its vapor (1). Under the conditions of the titration, however, both trans-3,5- and 2,6cyclohexadiene dicarboxylic acids react quantitatively with only two atoms of bromine. Phthalic acid does not react. cis-3,5-Cyclohexadiene dicarboxylic acid reacts with approximately two atoms of bromine: but in this case the reaction is not rigorously quantitative, and the analytical values are 10 to 30% high. The amount of the *cis*-acid present in the crude reaction products was so small that this inaccuracy was neglected.

In Tables I-V, the per cent of reduced acid in the product was cal-



Figure 2. Batch cell with recycling mercury cathode



Figure 3. Cross section of continuous mercury cathode cell

culated directly from the analytical values and sometimes runs slightly over 100%. This is probably due to the presence of *cis*- acid, although the values quoted are not much beyond the limits of accuracy of the analysis (within $\pm 2\%$). For calculating derived quantities such as current efficiency, the high values were corrected back to 100%.

The mercury cathode Results. proved to be more convenient for the reduction of phthalic acid than a lead cathode (4). In addition, it gave a lighter colored product and no tar. Although the mercury cathode poisoned more slowly than the lead cathode, its efficiency declined seriously when it was used repeatedly with recycled catholyte. Recycling is a practical necessity because about 25% of the product remains dissolved in the spent catholyte after crystallization is complete. The poisoning of the cathode is illustrated in Table I. Each of the runs shown was made with 1500 cc. of catholyte and a current of 20 amperes. This is a cathode current density of 11 amperes per sq. dm. Duration of each run was 2 hours. The other conditions were those pre-



Figure 4. Front view of glassware assembly for continuous cell

viously described. Run 49, made with new mercury and fresh catholyte, gave a recovered product containing 98% cyclohexadiene dicarboxylic acid. After recycling the electrolyte twice, this value fell to 84% (run 51). At least some of the poison is retained in the cathode. This is shown by the poor efficiency obtained in run 52, made with fresh catholyte and the poisoned cathode. This type of behavior was demonstrated repeatedly with both lead and mercury cathodes.

After run 52, the mercury was removed from the cell, washed with 20%aqueous sodium hydroxide and with water, and returned to the cell. Run 53, made with the washed cathode, gave the same extent of reduction as freshly distilled mercury.

In further runs, the activity of a poisoned cathode was also restored by washing with dilute nitric acid. It was not improved by washing with water, settling, and rejecting the mercury in the upper surface. By poisoning a mercury cathode in a cell with a carbon anode and a wooden cover, it was also shown that the poison was not derived from the lead in the cell.

The cathode poison formed in this reduction appears to be dissolved in the body of the mercury and must be acidic in nature. It is also attacked by an organomercury compound formed by reaction of the cathode with a partially reduced phthalic acid, but this is speculation. The cathode poison is apparently present in minute amounts; it was never isolated.

Figure 2 shows a batch cell designed to purify the mercury cathode continuously (3). Mercury is removed from the bottom of the cell through an overflow device which controls its level. It then falls through a packed column 75 cm. high containing caustic and is returned to the top of the cell by a diaphragm pump with spring-loaded ball-check valves. The pump rate was arbitrarily set to recycle all the mercury once an hour (150 cc. per hour). With this setup, a series of 10 runs similar to those in Table I was made with recycle of the spent catholyte. The content of reduced acid in the product for all the runs was 94 \pm 3%, and the recovery of product in the recycle runs was above 90%.

The above conditions are about optimum for a batch cell of this size. The production capacity is 750 cc. of catholyte, or 33.7 grams of phthalic acid, reduced per hour of electrolysis time. Neglecting handling losses, the average current efficiency (current yield) is 51%. The average voltage drop across the cell with 20 amperes applied current is 6.6 volts. The energy requirement is, therefore, 4.16 kw.-hr. per kg. of phthalic acid reduced.

Continuous Cell

The mercury cell described above is a convenient laboratory tool, but it is not well suited for scaling up to a commercial size. Some of its deficiencies are:

1. It employs a batch type of processing which requires time for emptying, filling, and heating.

2. The long residence time of the catholyte at elevated temperatures favors isomerization of the primary product.

3. Because the cathode lies flat, a large floor area per unit of capacity is necessary.

4. It is difficult to place the anode parallel and close to the cathode, and the cell resistance is consequently high.

A continuous cell of a novel design was developed to overcome these difficulties $(2, \delta)$.

Description. The cell diaphragm (Figure 3) is a porous porcelain cup submerged in a vessel full of mercury. The mercury acts as a cathode, and there is a lead anode inside the cup. The catholyte is pumped in through a jet in the bottom of the cul and impinges on the bottom of the cup at its center. The porous porcelain is wetted by aqueous solutions, but not by mercury. The catholyte, therefore, adheres to the diaphragm and spreads as a film between it and the mercury cathode. It flows radially across the bottom of the cup, up its vertical sides, and overflows at the



Figure 5. Glass catholyte pump for continuous cell

top of the cell. Reduction takes place in the moving film as it passes through the cell.

In addition to the cell itself, a continuous unit requires a feed pot for the catholyte and a pumping system. These must be kept hot to avoid crystallization of phthalic acid and must be free of materials which corrode in dilute sulfuric acid. For these reasons the entire system was made of glass and supported in a metal framework which could be immersed in a thermostated oil bath. A large, rectangular glass battery jar was used for the oil bath, and the frame was arranged to hang from its rim so that it could be lifted out as a unit. The framework was provided with leveling screws, vertical support rods for auxiliary equipment, and legs to facilitate handling when it was outside the bath.

Figure 4 shows the cell assembly. The catholyte feed pot is a graduated vessel of 1500-cc. capacity with a fritted-glass disk sealed in the bottom to act as a filter. To the bottom of the feed pot is sealed the suction line of a glass feed pump. The check valves of this pump are ground-in glass spheres filled with mercury to give them weight. They have glass stems that travel in tubular guides. The flanges of the guides have several small holes to bypass the main flow of the liquid around the valve guides themselves.

The cylinder of the pump is a glass U-tube half filled with mercury as a seal. The U-tube is connected through a water-filled line to an adjustablestroke reciprocating pump from which the valves were removed. The mechanical pump is used to move the mercury up and down in the U-tube like a piston. A three-way stopcock in the pump line is used for filling it. The pump discharges through a surge chamber to the cell proper. A single pump is shown in Figure 4 for simplicity, but in the actual cell assembly a duplex pump (Figure 5) was used to increase the capacity and smooth the flow.



Figure 6. Top and side views of continuous cell

Top and side views of the cell itself are shown in Figure 6. The cell body is a vertical glass cylinder 100 mm. in diameter and 200 mm. high. The cell diaphragm is 80 mm. in diameter and 178 mm. high. It is positioned concentrically with the outer cell wall by a Bakelite cover with a hole in the center and circular gasket grooves on the underside to accommodate the upper rims of the cell and the diaphragm. The buoyancy of the cup in the mercury keeps it firmly seated against the rubber gasket in the cover which, in turn, is held down by wing nuts on bolts fastened to the metal framework. Two vertical tubes are sealed into the bottom of the cathode compartment. One of these is a mercury inlet and is fitted with a thistle-tube top and a capillary constriction to decrease surge from the mercury recycle pump. A heavy iron wire is submerged in the other glass tube to serve as an electrical contact. The catholyte inlet jet ends 3 mm. below the bottom of the cup. The overflow line projects from the side of the cell 25 mm. from the top and extends over the rim of the oil bath. It contains a rubber section to protect it from breakage. It also has a U-trap sealed to its bottom to separate and decant through a separate line the mercury overflowing with the catholyte. The area of that portion of the cup submerged in the mercury is 430 sq. cm.

The anode used with this cell is a closely wound helix of 6.5-mm. lead tubing through which cooling water is run. Cooling is necessary both to prevent boiling of the anolyte and to minimize corrosion of the anode. The submerged area of the anode is about 250 sq. cm. During operation, the anode compartment also contains a thermometer and a level controller of the same type used with the batch cell. In the work done with this cell, mercury was pumped continuously to the cathode compartment at a rate of 500 cc. per hour, decanted through the same caustic scrubber used with the batch cell, and recycled.

The porous porcelain cups used as diaphragms were made by the Coors Porcelain Co. As supplied by the manufacturer, they are too porous for use in a cell of this type because the hydrostatic pressure of the mercury tends to force catholyte through the diaphragm into the anode compartment. Therefore the pores of the cups were sealed by soaking them first in hot dilute water glass and then in hot dilute sulfuric acid. They were conditioned by immersing in dilute sulfuric and passing a current of 20 amperes through them for 0.5 hour. The sealing of the pores raised the electrical resistance of a cup from 0.075 to 0.080 ohm; it reduced the

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Figure 7. Front view of continuous cell assembly

amount of liquid which passed through it under a hydrostatic head to about 1%of its value before treating. The treated cups were kept wet with dilute sulfuric acid at all times.

The behavior of the cell is critically dependent on the surface and the leveling of the porous cup, because these factors control the flow of the catholyte. The rims and bottoms of the cups were slightly irregular and were ground plane and parallel before use. A trial run was then made in the cell by pumping an aqueous solution of a dye in place of the catholyte. The pattern in which the cup was stained showed that the water tended to flow to one side of the cup and travel up its vertical surface in a stream, leaving the rest of the cup dry. The position at which the streaming occurred could be changed by tilting the cell, but no amount of leveling would bring about a uniform flow of catholyte over the whole diaphragm surface.

To promote more even spreading of the catholyte, one of the standard cups was altered by turning a helical gutter in its circumference from about 6.5 mm. above the bottom to the top. The gutter has a square profile, 1.6 mm. deep and 1.6 mm. wide, and is spaced 6.5 mm. between turns. The edges of the grooves chipped slightly during the turning operation. Figure 7 shows a front view of the cell assembly with the threaded cup. When this cup was tested with a solution of dye, the deepest color was in the bottom of the grooves as if they had remained full most of

	Table III.	Capacity	and	Efficiency	of	Continuous	Cel
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Run	Feed Rate.	Applied	Current	Cathode Current Density, Amp./Sq.	Duration,	Av. Voltage	Diene in Product,	Current Efficiency,	KwHr./Kg. Phthalic Acid
No.	Liters/Hour	Amperes	% theory	Dm.	Hour	Drop	%	~ %	Reduced
152	0.75	20	185	4.7	1	4.5	102	54	2.68
153	0.75	15	138	3.5	1	4.1	99	72	1.85
154	0.75	12	110	2.8	1	3,7	104	91	1.32
156	1.5	24	110	5.6	1	4.6	100	91	1.64
159	3.0	48	110	11.2	0.5	6.3	102	91	2.25
164	4.0	61.5	106	14.3	0.5	7.6	103	94	2.60
166	8.0	120	104	27.9	0,5	10.6	100	97	3.55
167	9.0	135	102	31.4	0.5	11.4	96	93	3.98

the time. The lands between the threads had been wetted fairly uniformly, however; and where they had remained dry, the dry area extended between two adjacent grooves only and did not go up the whole side of the cup. Various other diaphragm designs were tried, but none was superior to the threaded cup.

The quantity of catholyte present in the cell at any given flow rate was determined by filling the cell with mercury and measuring the amount that overflowed when the catholyte pump was started. Measured volumes of catholyte are given in Table II for the plain and threaded cups at three different flow rates. Calculated contact times are included. The volumes of catholyte present in the cell are different for the two cups. The threaded cup holds up several times as much as the plain cup, and the holdup is almost independent of flow rate. With the plain cup, the holdup is strongly dependent on flow rate. The calculated total volume of the helical groove in the threaded cup is about 15 cc., which is close to the measured catholyte volumes with this cup. This is consistent with the dyeing experiments, which indicated that most of the solution was contained in the bottom of the groove.

Table II.	Catholyte Volume	and
Contact	Time for Continuous	Cell

Type of Cup	Flow Rate, Liters/Hour	Capacity, Ml.	Contact Time, Seconds
Threaded	2.0	$10.8 \\ 13.2 \\ 13.6 \\ 1.2 \\ 2.0 \\ 4.5$	21
Threaded	4.0		12
Threaded	9.0		5
Plain	2.0		2
Plain	4.0		2
Plain	9.0		2

Procedure. For operation, the cell is assembled, the pump lines are filled, and the bath temperature is adjusted to 85° C. The mercury recycle pump is started, and water is pumped through the cell while the feed rate is set. The water is then replaced with catholyte made up as before. When the cell has been flushed, the current is started through it and adjusted to the desired value. Cooling water is passed through the anode to hold the anolyte temperature at 70° to 80° C. An ice-cooled flask is then placed under the overflow line. Product collected in it is recovered as in the batch runs. When a run is finished, the cell is flushed with distilled water but is not ordinarily disassembled.

Results. The first three runs in Table III (Nos. 152, 153, and 154) were made at the same production rate used in the batch cell, 750 cc. of catholyte per hour. The current was decreased from the 20 amperes used in the batch cell to 12 amperes, with no decrease in the completeness of reduction of the phthalic acid. In the next series of runs (Nos. 156 through 167), the current and feed rate were increased simultaneously while the ratio between them was held approximately constant. This ratio was chosen to give an amperage between 102 and 110% of the theoretical. At 9 liters per hour and 135 amperes, there was some evidence of incomplete reduction. At these higher rates, small droplets of catholyte could be seen escaping from the diaphragm at about the bottom level and running up the glass wall of the cell. It seems likely, therefore, that the maximum capacity of the cell is about 9 liters of catholyte or 403 grams of phthalic acid per hour. Runs at higher rates to check this point could not be made because both the motor-generator and the mechanical feed pump were operating at capacity at the 9-liter rate. The cathode current density at this rate was 31.4 amperes per sq. dm. based on the submerged area of the cup, calculated as a smoothsurfaced cylinder. The production capacity of the continuous cell is about 12 times that of a batch cell built around the same diaphragm.

Calculated values for current efficiency and energy requirements are given in the last two columns of Table III. At rates up to 8 liters per hour, current efficiencies of over 90% were easily achieved with complete reduction. The values for voltage drop across the cell are only approximate because the anolyte increased in concentration during the runs, and its resistance decreased accordingly. The average voltage drop under 20 amperes applied current is about two thirds the average drop in the batch cell. The increased current efficiency and the decreased resistance are both reflected in the energy requirement. The kilowatt-hours required to reduce a kilogram of phthalic acid was about one third that needed in the batch cell at equivalent rates of production; at the maximum throughput, the kilowatt-hours per kilogram was still less than that for the batch unit working at one twelfth the production rate. Although the runs shown in Table III are all short, runs of several hours' duration have been made. No poisoning of the cathode, even with recycle catholyte, was ever observed

The continuous cell has a much larger production capacity and current efficiency than the batch cell. This difference probably results from the fact that the catholyte is forced over the cathode as a flowing film in the continuous cell with no mixing of feed and product. There is, therefore, no need to transport the phthalic acid depolarizer (12) from a large bulk of liquid to the cathode surface by diffusion. Further-

Conditions	Run 173					
Catholyte composition	Component	Grams/ liter				
	Glucose	325				
Food note liter /hour	Na2SO4 NaOH	75 10				
Temperature, °C. Applied current	20)				
Amperes % theory	54 112	1				
Product	nitol (ass	umed)				
Means of identifica- tion or analysis	Fehling analys glucose r	solution is for educed				
% reduced % yield on charge	27					
Remarks	Sodium a: formed i	malgam .n cath-				
References	(7)					

more, there is a gradient in depolarizer concentration from the bottom to the top of the cell. It seems likely that the actual current density in the continuous cell adjusts itself to conform to the concentration gradient so that it is high at the bottom of the cathode where the phthalic acid is most concentrated and decreases along its vertical surface. This situation is analogous to running a batch cell and decreasing the current continuously as the depolarizer is depleted, a procedure that can be used to improve the over-all current efficiency. Unfortunately, it is not possible to determine directly the conditions existing at the cathode surface or in the catholyte

were selected from the extensive literature on electrolytic reduction. Reactions were chosen which would give as much variety as possible without requiring structural changes in the cell. In each case the conditions of temperature and catholyte composition given in the literature were followed as closely as feasible. Excess current was used; in most of the runs about 125% of the amperage theoretically required for complete reduction was applied. The products were analyzed or recovered by standard methods. The conditions and results of representative runs are

Table IV. Comparison of Plain and Threaded Cell Diaphragms

Run No.	Type of Cup	Feed Rate, Liters/Hour	Applied Amperes	Reduced Acid in Product, %	Current Efficiency, %
164	Threaded	4.0	61.5	103	94
168	Plain	4.0	61.5	81	76
158	Threaded	2.0	32	100	91
169	Plain	2.0	32	71	64
170	Plain	2.0	50.5	95	55

film in the continuous cell because any probe that is introduced disrupts the flow of catholyte.

Runs were made to compare the threaded cup with the smooth cup under actual operating conditions. The results in Table IV show that the extent of reduction is much lower with the plain cup. It was improved in run 170 at the expense of current efficiency by raising the amperage. The poorer results with the plain cup are caused by the catholyte streaming up one side of the cup. A large portion of the cathode area under these conditions is doing no useful work.

Other Reductions in Continuous Cell. Runs were made in the continuous cell on several other compounds which given in Table V.

Because only one or two runs were made on each reduction, it was not possible to work out the best conditions. Most of the reductions could probably be improved by careful study of the process variables. However, the runs serve to indicate the versatility of the continuous cell. The only attempted reduction which failed completely was that of benzoic acid, and the literature shows that a mercury cathode is specifically unsuitable for this reaction (23).

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Table V. Reduction of Various Materials in Continuous Cell

Run 253 Run 255		Run 257 Run 256		56	Run 2	58	Run 175				
Component l	ams/ liter	Component	Grams/ liter	Component	Grams/ liter	Component	Grams/ liter	Component	Grams/ liter	Component	Grams/ liter
Maleic anhy- bydride	147	Pyridine	39.5	Caffeine	145.5	p-Nitroanili	ne 67.7	Acetone	87.3	Benzoic acid	47.6
H_2SO_4	52	H_2SO_4	107	H_2SO_4	698	HCl	90	H_2SO_4	107	Alcohol H ₂ SO ₄	416 358
1.0		1.0		1.0	1	1.0		1.0		0.5	
85		72		32		73		30		54	
85		100		100		100		80		25	
106		124		124		127		99		120	
Succinic acid		Piperidine		Deoxycaffe	ine	<i>p</i> -Phenylene mine	edia-	Mostly n alkyls	nercury	None	
Crystallization, melting po neutral equi lent	int, iva-	Steam disti and pH ti	llation itration	Isolation, points of uct, mon and picra	melting f prod- ohydrate, ate	Crystallizati dihydroch and pH ti	on of nloride itration	Heavy oil rated, ca distilled	sepa- atholyte		
79		78		10 (minir	num)	Quantitative	e	Nearly com	plete	Little if any	
79		32		10 (minir	num)	Quantitative	e				
		Byproducts to be d polypiper	appear i- and idyls	Large losses isolation	during	Ser.		Only traces tone or i panol in	of ace- soprop- product	82% of benz recovered changed	oic acid un-
(20, 24)		(11, 14, 2)	1, 30)	(27, 2	9)	(15, 20))	(13, 18, 26,	28, 29)	(16, 23	3)