Electrochemical Oxidation of p-Xylene to Terephthalic Acid

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THIS paper deals with the oxidation of p-xylene to terophthalic acid. As there is no good efficiency with direct oxidation, two stage process for the oxidation has been studied. Chromic acid is used for the chemical oxidation of p-xylene to terephthalic acid. During the oxidation, chromic acid gets reduced to trivalent chromium. The hexavalent chromium is regenerated by electrolytic oxidation at lead dioxide electrode in sulphuric acid medium. Use of blue asbestos fibre instead of a separate cathode chamber has been found to be useful in the regeneration process.

TEREPHTHALIC acid finds extensive application in making polyethylene terephthalate, the polymer used for making fibres and films. The film is used for magnetic tapes, electrical insulation, packaging and photographic applications. Recent reports indicate that polyester moulding materials are being developed. Because of its scartch resistance and luster, it should find application as a moulding material in domestic equipment, hardware and automobiles.

Small amounts of terephthalic acid and dimethyl terephthalate are also used for such miscellaneous applications as an intermediate in herbicide production, adhesive formulations, printing inks, coating and paints. Terepthalic acid is also used in preparing animal feed supplements because its presence in the body increases the level of antibiotics in the blood serum and liver[1,2].

Terephthalic acid and dimethyl terephthalate have been known since the later part of nineteenth century. They were first used for the preparation of poleythylene terephthalate. M/s. I. C. I., England and M/s. Dupont, USA started manufacturing terephthalic acid from p-xylene by dilute nitric acid oxidation process[3]. A number of refinements have improved the process substantially, compared to low yield 80% mole batch operation originally used. There are however three disadvantages still inherent. (1) An auxuliary nitric acid plant is required to utilise the lower oxides of nitrogen produced in the oxidation. (2) Temperature and nitric acid concentration conditions required to give high yields of terephthalic acid make the process prone to explosion[4]. (3) The product terephthalic acid which is produced contains substantial emount of nitrogen impurities which makes it difficult to purify[4].

The latter point is the reason why dimethyl terephthelate becomes the established raw material for polyesters. Manufacture of the dimethyl terephthalate offered ease of purification by conventional processes such as crystallisation and distillation resulting in sufficient purification for polyesterification.

Current commercial processes for technical grade terephthalic acid are es follows :

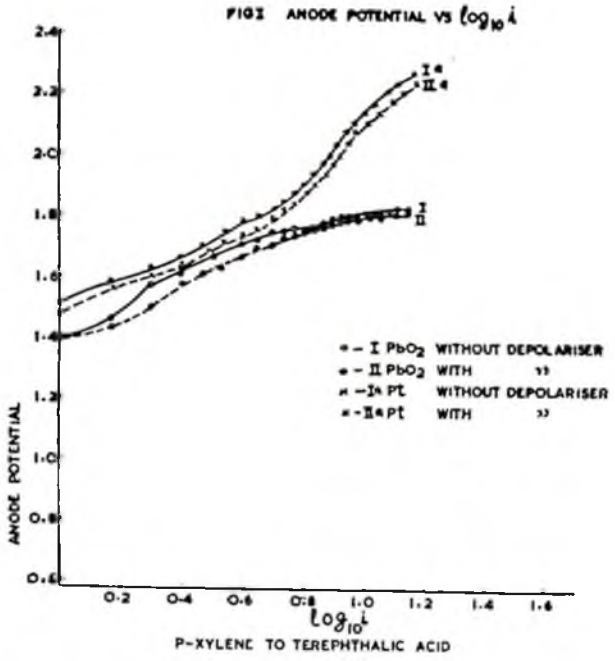
1) *Nitric acid oxidation of p-xylene* : It is a phased process conducted in the range of 300-400 F 125-200 psig in dilute HNO_3 of about 30-40 Wt. % strength[5-7].

2) *Catalytic oxidation* : Catalytic liquid-phase air oxidation of p-xylene is also under practice. Henkel rearrangement of benzoic acid or phthalic anhydride and Grosskiasky process for chloromethylation of toluene[8] are also employed.

The purpose of this study is to investigate the feasibility of an electrochemical process for the preparation of terephthalic acid from p-xylene.

First depolarisation studies were carried out at platinum and lead dioxide electrodes of area 1 cm^2. From the plot of anode potential vs. log i (Fig. 1) it is observed that there is not much depolarisation effect either on lead dioxide electrode or platinum electrode. Indirect processes appear to hold good promise for technical production of some important organic chemicals in particular by oxidation. The use of electrolytically regenerated

manganic and ceric sulphates, periodates[10] and chromic acid [11] need special mention here. Oxidations of organic compounds are carried out by the inorganic oxidants that are regenerated electrochemically. Such "out cell" processes are eminently suited, especially for the controlled oxidation of organic compounds[12,13].



Therefore a two-stage process for the oxidation of p-xylene to terephthalic acid was investigated which consists of the oxidation of chromium sulphate to chromic acid in the cell and reacting the chromic acid obtained with p-xylene outside the cell.

EXPERIMENTAL

The investigation consists of two parts. One is chemical and the other is electrolytic. The apparatus for chemical oxidation is shown in Fig. 2.

Materials : Chromic acid and sulphuric acid are of LR grade. The technical grade p-xylene was distilled and the portion boiling between 137° and 131 °C was collected and employed for investigation.

Cell : The cell employed for the electrolytic regeneration of chromic acid from chromium sulphate is shown in Fig. 3.

Chemical oxidation : 30 ml p-xylene, 93.96g chromic acid and 600 ml of water were placed in a 2 litre three necked flask equipped with a reflux condenser, a mercury sealed mechanical stirrer and a separating funnel. 340g (185 cc) of concentrated sulphuric acid was added dropwise through the separating funnel to the well stirred mixture at

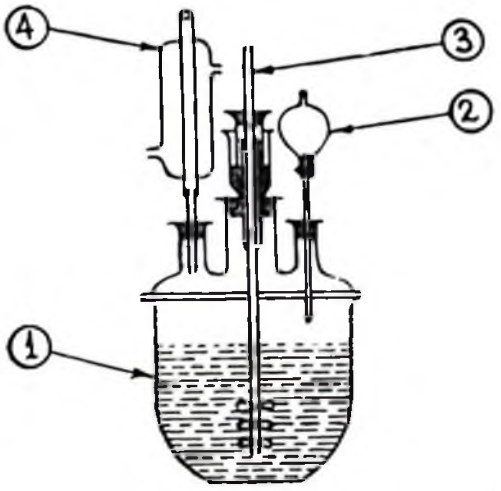


FIG.-II.

1. Reaction Vessel, 2. Separating Funnel, 3. Stirrer
4. Water Condenser

such a rate that the reaction was under control. When all the acid had been introduced and the temperature began to fall, the mixture refluxed gently for half-an-hour. The reaction mixture was

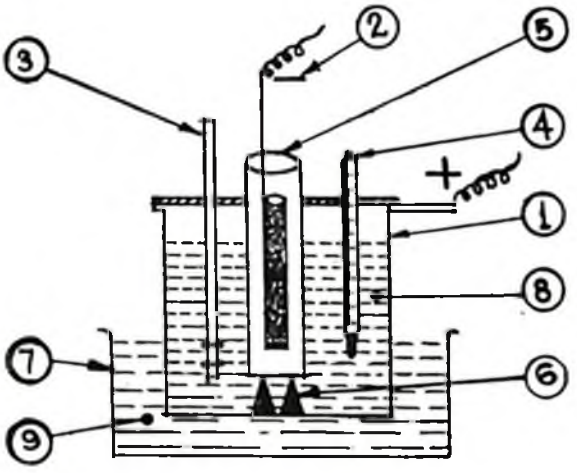


FIG.III.

1. Anode Vessel, 2. Cathode 3. Stirrer, 4. Thermometer
5. Porous Pot, 6. Support for Porous Pot 7. Trough
8. Electrolyte, 9. Water

cooled and poured into about 1 litre of water and allowed to stand for 1 hour. The crude terephthalic was filtered, washed with 25 cc of cold water. The filtrate was collected for the regeneration by electrolytic oxidation. The acid was purified by dissolving in 5% NaOH solution. The solution was filtered from suspended impurities and acidified with dilute sulphuric acid. The precipitated acid was filtered, washed thouroughly with cold

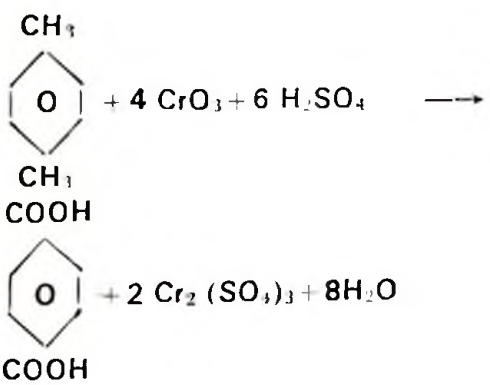
water and dried at 100°C. The chromium sulphate was collected and concentrated before sending to the cell for oxidation to chromic acid.

The second part consists of electrolytic oxidation (Fig. 3). The oxidation of chromium sulphate to chromic acid was carried out.

Electrolytic cell : A lead-lined vessel which itself acts as an anode was employed as a cell. Perforated lead was used as a cathode. The vessels was prepolarised for 30 minutes at an anode current density of 5 A/dm^2 in 5% sulphuric acid. The temperature of the cell was maintained at desired level by keeping in a trough of water which can be heated by means of an immersion heater. An effective glass stirrer was included in the cell for efficient agitation. All the conditions for regeneration are given in Tables.

RESULTS AND DISCUSSIONS

The first step in the chemical reaction of hexavalent chromium with p-xylene which can be represented by equation (1)



$$+ 4\,CrO_3 + 6\,H_2SO_4 \longrightarrow$$

$$+ 2\,Cr_2(SO_4)_3 + 8H_2O \quad \ldots 1$$

The second step consisted of electrolytically oxidising chromium sulphate to chromic acid and may be represented by equation (2)

$$Cr^{3+} \longrightarrow Cr^{6} \quad \ldots (2)$$

On the basis of these two equations, it is possible to arrive at an overall current efficiency for the terephthalic acid formation and upto an yield of 48% could be obtained for the oxidation of p-xylene to terepthalic acid. Detailed investigations on the oxidation of p-xylene with the regenerated chromic acid was then carried out.

The results of the influence of temperature on the oxidation of p-xylene are given in Table 1. The highest yield was obtained at a temperature of 55-60°C. The oxidation was found to be unsatisfactory at lower temperatures and above 70°C, the oxidation was not carried out as it was very difficult to control the reaction.

TABLE 1

Influence of temperature on the oxidation of p-xylene by regenerated chromic acid

Chromic acid, 94 g in 600 ml of water ; p-xylene, 25 g in each case ; Concentrated sulphuric acid 185.0 ml

Temperature °C	Terephthalic acid obtained (g)	Yield efficiency for terephthalic acid (%)
30	....	No oxidation
40	1.22	3
50	10.17	25
60	18.31	45
70	16.28	40

The experiments in Table 2 represent the oxidation of p-xylene by repeated use of the regenerated chromic acid. An average of nearly 47% overall current efficiency was obtained. The results given in Table 2 represent the use of lead strip closely covered with blue asbestos as cathodes. Results given in Table 3 shows the use of a ceramic porous pot diaphragm. A better efficiency is obtained in using a separate cathode chamber, namely, a ceramic porous pot. If porous pots are not available, the cathode covered with blue asbestos can be used advantageously. Table 4. shows the results obtained with regeneration of chromic acid using lead strip covered with blue abestos fibre as cathode and the initial amount of chromic acid in this case was maintained same by adding necessary amount of fresh chromic acid for the oxidation of p-xylene to terephthalic acid. The amount of p-xylene taken was the same for all the experiments in this table. The yield and the current efficiency are fairly high.

Single stage process : Direct oxidation of p-xylene inside the cell using 55% sulphuric acid as electrolyte containing 14 g of chromium sulphate and lead dioxide as anode, gave very low yield and the results are given in Table 5. There is very little formation of terephtalic acid under these

TABLE 2

Results obtained with the cathode covered with blue asbestos

Anode lead dioxide on lead ; Anode area, 0.25 dm^2 ; Anode current density, 2.5 A/dm^2 ; Cathode, lead strip wound with blue asbestos fibre ; Temperature, room temperature (25-30°C) ; Volume of the electrolyte, 600 ml ; p-xylene 25g

Expt. No.	Total current passed (amp-hrs)	Cell voltage (V)	Chromic acid (g)	Current efficiency for chromic acid soln. (%)	Terephthalic acid isolated (g)	Oxidation efficiency for terephthalic acid formed based on chromic acid %	Overall current efficiency for terephthalic acid formation
I Oxidation		...	93.96	....	18.90	48.3	....
II Oxidation (I Regeneration)	80.85	3.4	75.61	75.2	14.96	47.5	35.85
III Oxidation (II Regeneration)	100.5	3.4	68.11	62.4	13.39	47.2	28.85
IV Oxidation (III Regeneration)	105.0	3.4	63.13	48.34	12.15	46.2	22.42
V Oxidation (IV Regeneration)	131.4	3.4	51.95	31.8	9.804	45.3	14.45
VI Oxidation (V Regeneration)	150.1	3.4	37.87	20.3	7.11	45.0	9.117
VII Oxidation (VI Regeneration)	145.6	3.4	27.72	15.3	7.108	44.01	9.458

TABLE 3

Results obtained using porous pot as separate cathode chamber

Anode, lead dioxide on lead ; Anode area, 025 dm^2 ; Anode current density, 2.5 A/dm^2 ; Cathode, lead strip in porous pot ; Catholyte, 55% sulphuric acid ; Temperature, Room temperature (25-30°C) ; Volume of the electrolyte, 600 ml ; p-Xylene 25.0 g

Expt. No.	Total current passed (amp hrs)	Cell voltage (V)	Chromic acid (g)	Curren efficiency for chromic acid soln. (%)	Terephthalic acid isolated (g)	Oxidation efficiency for terephthalic acid formation based on chromic acid (%)	Overall curfent efficiency for terephthalic acid formation (%)
I Oxidation		...	93.96		19.0	48.55	...
II Oxidation (I Regeneration)	81.12	3.4	82.68	82.0	16.26	47.20	38.84
III Oxidation (II Regeneration)	86.14	3.4	75.16	70.0	14.76	47.13	33,21
VI Oxidation (III Regeneration)	113.64	3.4	70.66	50.0	14.16	48.15	34.14
V Oxidation (IV Regeneration)	129.5	3.4	56.37	35.0	11.13	47.35	16.64
VI Oxidation (V Regene.ation)	105.9	3:4	39.50	30.0	7.571	46.0	13.86
VII Oxidation (VI Regeneration)	136.3	3.4	28.18	16.63	5.323	45.32	7.565

TABLE 4

Effect of maintaining the original concentration of chromic acid

Anode, lead dioxide on lead ; Anode area, 0.25 dm^2 ; Anode current density, 2.5 A/dm^2 ; Cathode, lead strip wound with blue asbestos fibre ; Temperature, 30±2° C ; p-Pylene, 25.0 g ; Volume of electrolyte, 600 ml.

Expt. No.	Total current passed (amp-hrs)	Cell voltage (V)	Chromic acid (g)	Chromic acid added (g)	Current efficiency for chromic acid soln. (%)	Terephthalic acid isolated (g)	Oxidation efficiency for terephthalic acid formation based on chromic acid (%)	Overall current efficiency for terephthalic acid formation (%)
I Oxidation			93.96			18.82	48 08	...
II Oxidation	114.0	3.8	79.20	14.77	86.24	18.58	47.31	31.48
III Oxidation	113.4	3.8	78.52	15.44	85.7	18.35	46.87	31.35
IV Oxidation	112.7	3.8	75.43	18.52	85.1	18.21	46.56	31.31
V Oxidation	108.3	3.8	73.50	20.46	79.56	17.17	46 3	30.71
VI Oxidation	106.5	3.8	72.43	21.54	75.2	16.78	45.9	30.42

TABLE 5

Oxidation of p-Xylene by a single stage process

700 ml af 55% sulphuric acid containing 14 g of chromium sulphate ; Anode, lead dioxide on jead ; Anode area, 0.25 dm^2 ; Cathode, two narrow lead strips would with blue asbestos fibre ; Temperature, 55-56°C ; p-Xylene, 25.0 g ; Auxiliary stirrer was included in the cell ; Total current passed, 15 amps

Expt. No.	Current density (A/dm^2)	Current strength (amp)	Cell voltage (V)	Terephthalic acid obtained (G)	Current efrlciency (%)
1	0.5	1.25	1.5	1.2	15.46
2	1.0	2.5	3.0	1.5	19.32
3	2.0	5.0	3.6	1.4	18.03
4	3.0	7.5	4.2	1.65	21.25
5	4.0	10.0	4.4	1.38	17.78
6	5.0	12.5	4.8	1.47	18.93

conditions. Fig. 1 shows the depolarisation studies. Curve I, Ia and curve II, IIa show the behaviour in the presence and in the absence of the depolariser, p-xylene on lead dioxide and platinum electrode respectively. From the curves, it is evident that p-xylene has no good depolarising effect. Hence p-xylene could not be effectively oxidised in a single stage process for the formation of terephthalic acid.

CONCLUSION

It was observed that when oxidation of p-xylene was carried out in an electrolytic cell using chromium sulphate in 55% sulphuric acid, poor current efficiency was obtained for the formation of terephthalic acid.

Good efficiency for the formation of terephthalic acid was obtained, when p xylene was oxidised in a two stage process using electrolytically regenerated chromic acid.

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REFERENCES

1. K. E. Price and E. Zolle, *Jr. Avian Diseases*, 3 (2) (1959) 157.
2. K. E. Price, Z. Zolle and J. H. Hare, *Poultry Sci.*, 38 (1) (1959) 233.
3. D. H. Derbyshire, *Inst. Chem. Eng. (London) Symposium on Chem. Proc. Hazards*, (1960) 37-41.
4. Brit. Pat. 895, 926, May 2, 1962 to Du Pont.
5. Brit. Pat. 655, 674, July 11, 1951 to Du Pont.
6. L. A. Burrows and R. M. Cannanaugh (to Du Pont) *U.S. Pat.*, 2,636, 859, Apr. 28, 1953.
7. P. Boffa, R. Costebella and R. G. Mariorano (to Montecatini) *Fr. Pat.* 1 299,913, July 27 (1962).
8. Search, *Organic Chem. Div.* 4 (1), Item, 46, Jan. 1967.
9. P.F. Lewis, *"Terephthalic acid and dimethyl terephthalate"* in Chem. Eco Hand Book, Stanford Research Institute, Menco Park, Calif. Apr. 1966.
10. H. F. Conway and V. E. Sohns, *Ind. Eng. Chem.*, 51 (1959) 637.
11. S. Chidambaram, M. S. V. Pathy and H. V. K. Udupa, *Indian Pat.*, 95 (1967) 425.
12. S. Chidambaram, M. S. V. Pathy and H. V. K. Udupa- *Indian J. Technol.*, 6, Nos. 12-13 (1968).
13. R. Ramaswamy, M.S.V. Pathy and H.V.K. Udupa, *J. Electrochem. Soc.*, 110 (1965) 202.