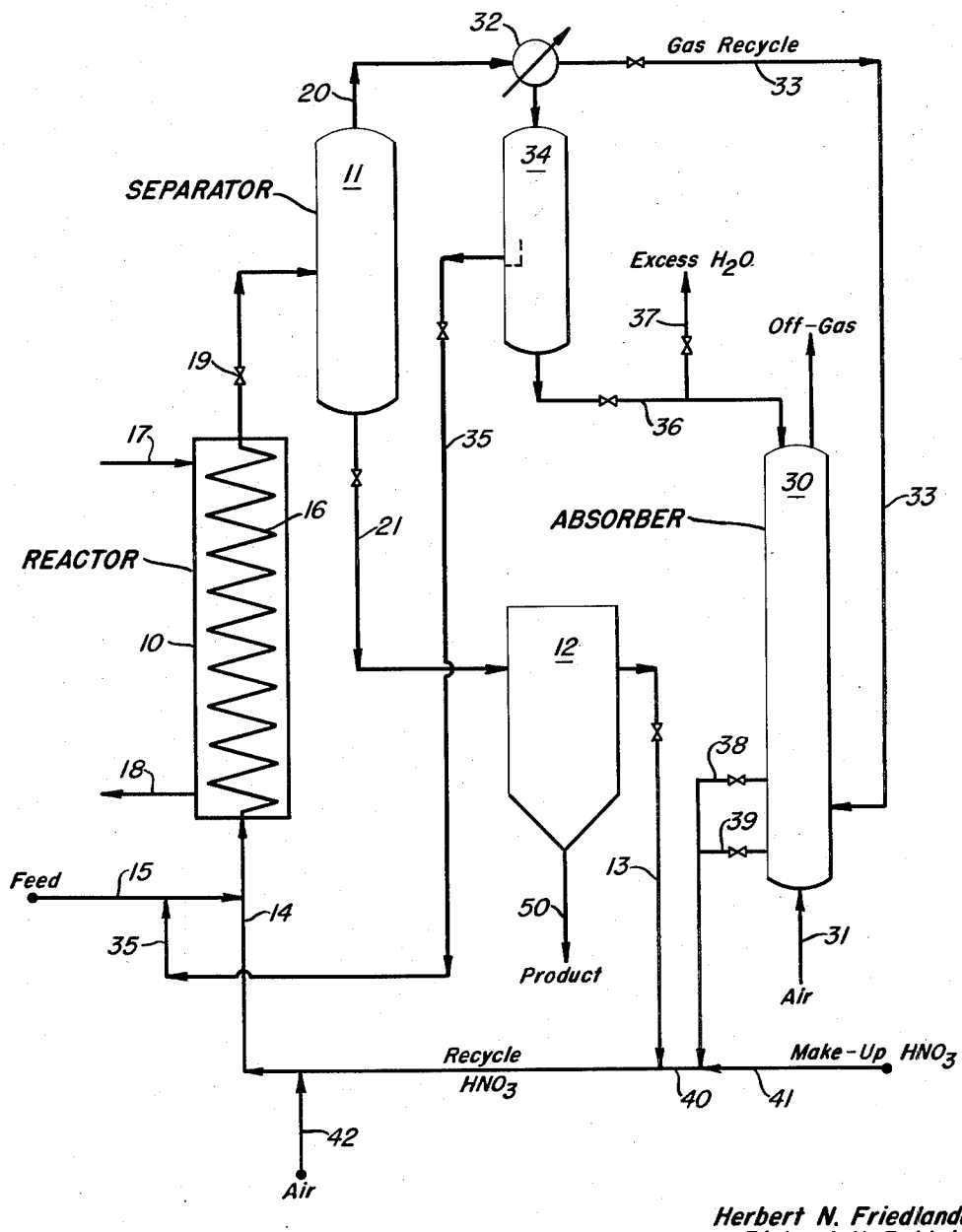
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PRODUCTION OF POLYBASIC AROMATIC ACIDS

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Herbert N. Friedlander
Richard H. Baldwin
INVENTORS.

BY

Arthur G. Gilkes
ATTORNEY

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PRODUCTION OF POLYBASIC AROMATIC ACIDS

Herbert N. Friedlander, Homewood, and Richard H. Baldwin, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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Our invention relates to a process for the production of polybasic aromatic acids by oxidation of alkyl substituted aromatic feed stocks in the liquid phase.

The production of polybasic aromatic acids from alkyl aromatics presents a number of difficult technical problems, chiefly stemming from the difficulty of selectively oxidizing more one alkyl substituent without rupturing the benzene ring. Thus, the first alkyl group is relatively easy to oxidize, but the presence of the resulting carboxyl group makes subsequent groups considerably more difficult to oxidize. Hence, it is difficult to control the oxidation process so as to produce high yields of the selected oxidation product while avoiding production of excessive quantities of undesired by-products associated with under oxidation or over oxidation.

As a consequence, there are a number of competitive processes available including catalytic oxidation with air in both the vapor and liquid phases and chemical oxidation as with nitric or chromic acid. In general, catalytic vapor phase oxidation is satisfactory only with o-xylene, other polyalkyl aromatics undergoing excessive ring rupture under conditions producing polybasic acids; catalytic liquid phase oxidation is satisfactory for production of toluic acids but is unsatisfactory in conversion to polybasic acids requiring two-step operation; and chemical oxidations have appeared non-competitive because of high consumption of the chemical oxidizing agents. In view of these difficulties, the art has adopted the expedient of converting the carboxyl group of the intermediate monobasic alkyl aromatic acids to some other grouping, e.g. an ester, which does not interfere with oxidation of the remaining alkyl groups to the same extent. This, however, means a stepwise process and, for isolation of the free polybasic acids, requires four separate chemical operations.

Nitric acid oxidation is relatively simple and can be operated in a single stage, but it is a high cost process because of high losses of acid through conversion to free nitrogen and nitrous oxide which cannot be economically recovered for recycle. If the process is operated under mild conditions in order to minimize acid losses, under oxidation of the hydrocarbon feed results in the excessive production of intermediate oxidation products, e.g. toluic acids in the case of xylenes oxidation. Also, as conventionally operated, the process is essentially limited to batch processing allowing a prolonged reaction period. Our invention provides a short-time reaction process for the production of polybasic aromatic acids, using nitric acid, under conditions minimizing losses of acid by over reduction while obtaining maximum yields of the desired polybasic acid, which is particularly adapted to continuous processing.

According to the invention, the hydrocarbon charge stock which may comprise, for example, a dialkyl aromatic or mixture thereof such as mixed xylenes is contacted with dilute nitric acid in a reaction zone at a very high molar ratio of acid to feed. The acid to feed ratio is in excess of 50 mols of acid (100% HNO_3 basis) per

mol of feed, assuming complete oxidation of the alkyl groups to carboxyl groups with reduction of the acid to nitric oxide, but preferably is in the range of about 100 to 300 mols of NHO_3 per mol of feed, and may range up to as much as 1000/1 or more. Advantageously, the feed is charged continuously into a flowing stream or body of the acid so that the very high acid ratio is continuously maintained, assuring almost instantaneous oxidation of the feed to the desired organic acid. The contacting procedure therefore is in sharp contrast to conventional nitric acid oxidation which uses acid to feed ratios of about 1 to 10 mols of NHO_3 per mol of feed, and reaction times in the new process have been found to range from the order of several seconds to a few minutes in contrast to conventional nitric acid oxidation requiring prolonged reaction periods of an hour or more.

The acid stream flowing from the reaction zone is treated continuously for separation of polybasic aromatic acid product. In the operating cycle, separation by simple physical techniques is advantageous since the bulk of the acid is being continuously recycled. For example, the nitric acid stream, after degassing, may be centrifuged, filtered or decanted to recover precipitated solid polybasic aromatic acid while maintaining a temperature sufficiently elevated to keep oxidation intermediates in solution. The recovered liquid nitric acid fraction is recycled to the reaction zone.

In operation, the reaction conditions are controlled to maintain an acid concentration of about 5 to 40 weight percent, preferably about 15 to 35 weight percent; a temperature range of about 100 to 300° C., preferably in the range of about 160 to 225° C.; and a pressure in the range of about 100 to 1000 p.s.i.g., preferably in the range of about 150 to 500 p.s.i.g. Because the bulk of the reaction fluid is continuously recirculating through the reaction zone, optimum conditions can be selected for a given charge stock for minimization of over reduction of nitric acid and over oxidation of feed. One hundred percent conversion to polybasic acids is obtained by the internal recycle of oxidation intermediates to extinction.

Advantageously, the off gases separated from the reaction zone effluent, which contain nitrogen oxides, are recovered and charged to an acid regeneration zone with make-up water which may be recovered as a weak acid stream from the reactor off-gases. In the acid regeneration zone, air, or other oxygen containing gas, is introduced in an amount sufficient to reconvert the re-oxidizable nitrogen oxides to nitric acid. The regenerated acid stream is combined with the recycle nitric acid stream for recirculation to the reaction zone.

By conducting the hydrocarbon oxidation in continuous flow under conditions of very high acid to feed ratio, it has been found that losses of nitrogen in the form of nitrous oxide and nitrogen are substantially reduced. The oxygen introduced to the regeneration zone therefore is in effect the oxidizing agent in the over-all process, and the nitric acid functions primarily as a reaction medium and as a catalyst. This again contrasts with conventional nitric acid oxidation in which the ratio of acid to hydrocarbon feed is related to stoichiometric requirements.

The accompanying drawing provides a simplified flow diagram of the new process, and its description will provide an example of operating procedure.

In the cyclic system illustrated in the drawing, the dilute nitric acid inventory is circulated continuously through reactor **10** to gas-liquid separator **11** and thence through product separator **12**. Following product removal, the recovered nitric acid is returned to reactor **10** via lines **13** and **14**.

The feed, for example, paraxylene, is introduced to the system from line 15 by injection into recycle nitric acid line 14. A high ratio of acid to feed is provided at all times by controlling the recycle rate and the rate of feed introduction. For example, a molar ratio of HNO_3 to paraxylene of about 200 to 1 is suitable. The combined stream from line 14 is charged to reactor 10, which advantageously may take the form of a tubular reaction coil 16 surrounded by a heating jacket. A temperature of about 160° to 225° C. is maintained in the reaction zone by circulating superheated steam or other heat transfer medium through the jacket of reactor 10 by means of connections 17 and 18. Back pressure (150 to 425 p.s.i.a.) is maintained on the system by means of pressure control valve 19 in order to maintain the liquid phase, e.g. a pressure of about 300 p.s.i.g. The heat of reaction may be removed downstream as by means of cooler 32.

The effluent from reactor coil 16 is discharged into gas-liquid separator 11. The gas stream taken overhead through line 20 may contain nitrogen, nitrous oxide, oxygen, carbon monoxide, carbon dioxide and water vapor in addition to the recoverable gases, nitric oxide and nitrogen dioxide. The temperature-pressure control of separator 11, at about 120° C. and 100 p.s.i.a., is designed to permit the separation of only the polybasic acid products as solids. A slurry of solid product in nitric acid is withdrawn from separator 11 and is passed via valved line 21 to settler 12 wherein the solid product is separated by filtration or centrifugation. A temperature in separator 12 above about 200–250° F. is advantageously maintained in order to keep intermediate oxidation products in solution. The liquid stream recovered from product separator 12 is continuously returned to reactor 10 via lines 13 and 14. If separation of partial oxidation products should be desired, the acid stream from line 13, or a slip stream thereof may be cooled to ambient temperatures, e.g. 20–30° C., to precipitate such products. After separation of solids, the recovered liquid then would be recirculated directly, or via the acid regeneration zone described below.

The acid regeneration zone comprises a conventional absorption tower 30 of the type used in refortification of weak aqueous nitric acid. Air or oxygen is introduced at the base of tower 30 as by means of connection 31 and passes in countercurrent flow upward through the tower in contact with downflowing weak acid. For heat control, cooling water may be circulated in the usual way through contact trays in tower 30 in order to remove the heat of absorption, thereby maintaining a tower temperature of about 20–30° C. The amount of oxygen introduced through line 31 should be above the molecular requirements for conversion of nitric oxide to nitrogen dioxide, e.g. about 5 to 1. Air is preferred to oxygen or other oxygen containing gas as the oxidizing agent. In the regeneration step, it is necessary to regenerate approximately 8 mols of acid per mole of xylene feed. Higher regeneration ratios are necessary when alkyl aromatics containing alkyl groups higher than methyl are charged to the oxidation step.

In a properly balanced operation, the reactor off-gases recovered through line 20 from separator 11 supply the bulk of the nitrogen oxides required for refortification. The overhead gas stream from line 20, containing substantially all of the nitric oxide produced in the oxidation reaction, is passed through cooler 32 and thence via valved line 33 to tower 30. Liquid knocked out in cooler 32 is collected in drum 34. The oil phase collecting in drum 34 may be recycled through line 35 to reactor 10. The aqueous phase collecting in drum 34 is passed by means of valved line 36 to the top of tower 30. The rate is controlled to provide a stoichiometric amount of make-up water, and excess water is purged from the system through valved line 37. Unrecoverable gases may be vented from the top of tower 30.

Depending upon the operation desired, a refortified acid stream may be drawn from a lower portion of tower 30 through valved connections 38 and 39 and thence via line 40 to recycle line 14. Acid withdrawn by connection 39 will be free of dissolved nitrogen oxides, whereas acid withdrawn at a higher point in the tower as by means of line 38 will contain dissolved nitrogen oxides. Make-up nitric acid is introduced to the system by means of connection 41 as required to supplement the refortification operation in maintaining the desired acid concentration, e.g. about 30%.

If desired, air or oxygen may be introduced in small amounts by means of connection to the recycle nitric acid stream flowing in line 14 to reactor 10. Although the introduction of about 2 to 3 mols of oxygen per mol of xylene has certain theoretical advantages, we have found that higher yields and lower by-product production are obtained without the use of added air or oxygen. The use of oxygen, when this operating alternative is followed, is preferred to air because increased capacity per volume of equipment is attained and losses of nitrogen oxides by the stripping effect of the greater volume of off-gases is reduced.

The invention as described is practicable for the conversion of a variety of aromatic feeds containing alkyl substituent groups. It is applicable however with special advantage to the production of dibasic aromatic acids, e.g. terephthalic, isophthalic or phthalic acid from para-, meta- and ortho-xylenes respectively. The isomers may be charged separately or in admixture. The invention also has value in the production of tribasic, tetrabasic and higher aromatic acids. For example, trimesic, trimellitic and pyromellitic may be produced from polyalkyl aromatic feeds including mesitylene, 1,3,5-ethylxylene, psuedocumene, durene, etc. The invention also has special value in handling partially oxidized polyaromatic feeds. Thus, it is relatively easy and cheap to oxidize xylenes directly with air to the corresponding toluic acids, but there is a need for a process capable of carrying the oxidation reaction to completion on an economically attractive basis. Toluic acids, or mixtures rich in toluic acids (or other oxidation intermediates) can be charged with advantage to the reaction system of the invention. Under the conditions of very high instantaneous ratios of nitric acid to feed, selective oxidation of the unreacted alkyl group is rapid, resulting in high yields of the ultimate polybasic acid products at very low acid consumptions.

We claim:

1. A process for the production of polybasic aromatic acids by oxidation of an alkyl substituted aromatic feed stock which comprises circulating a stream of dilute nitric acid through a reaction zone to a separation zone, injecting the feed stock into the circulating stream in the reaction zone at a controlled rate maintaining a ratio of nitric acid to feed in excess of 50 mols of HNO_3 per mol of feed, maintaining a temperature of about 100° to 300° C. and a pressure of about 100 to 1000 p.s.i.g. in the reaction zone, separating polybasic acid product from the effluent acid stream from the reaction zone, recirculating the separated nitric acid fraction to the reaction zone and maintaining the concentration of the nitric acid recirculating to the reaction zone in the range of about 5 to 40 weight percent.

2. The process of claim 1 in which the feed stock comprises a dialkyl aromatic.

3. The process of claim 2 in which the feed is paraxylene.

4. The process of claim 2 in which the feed is metaxylene.

5. The process of claim 1 in which the feed stock comprises a partially oxidized dialkyl aromatic.

6. The process of claim 5 in which the feed comprises toluic acid.

7. The process of claim 1 in which the molar excess

of nitric acid to feed in the reaction zone is in the range of about 100 to 300 mols of HNO_3 per mol of feed.

8. The process of claim 1 in which the effluent from the reaction zone is separated into a gaseous fraction containing water vapor and substantially all of the nitric oxide produced in the reaction zone and a liquid fraction comprising the bulk of the recirculating nitric acid, the gaseous fraction is charged to a regeneration zone wherein a refortified nitric acid stream is recovered by contacting in an aqueous medium the gaseous fraction with an oxygen containing gas, the refortified nitric acid is recycled from the regeneration zone to the reaction zone, polybasic aromatic acid product is separated as precipitated solid from said liquid fraction and the recovered liquid acid is recirculated to the reaction zone.

9. The process of claim 8 in which the oxygen containing gas introduced to the regeneration zone is air.

10. The process of claim 1 in which the reaction temperature is in the range of about 160 to 225° C., the pressure is in the range of about 150 to 500 p.s.i.g., and the acid concentration is in the range of about 15 to 25% by weight.

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