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POLYHYDRIC ALCOHOL PROCESS

Gerald F. Curtin, Jr., Wilmington, Del., assignor
to E. I. du Pont de Nemours and Company, Wil-
mington, Del., a corporation of Delaware

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1

This invention relates to improvements in the process for production of alcohols, especially polyhydric alcohols, from the mixture of by-products obtained in the oxidation of cyclohexane, cyclohexanol, or cyclohexanone to adipic acid.

Methods for the oxidation of compounds of the nature of cyclohexane, cyclohexanol, and cyclohexanone to adipic acid and other products are well-known. Such oxidations have been described in the Loder Patents 2,223,493 and 2,223,494, the Schrauth Patent 1,921,101, the McCallister Patents 2,193,562, 2,285,601 and 2,286,559, the Cavanaugh Patent 2,291,211, the Cavanaugh et al. Patent 2,343,534, the Ellingboe Patent 2,228,261, the Drossbach Patent 2,285,914, the Amend Patent 2,316,453, and the Hamblet et al. Patent 2,439,513. It is generally preferred to carry out these oxidations at a temperature between 50° and 175° C., preferably between 65° and 175° C., under a pressure of between atmospheric and 500 pounds per square inch or higher. When molecular oxygen is employed as the oxidizing agent the best catalysts are cobalt compounds or manganese compounds dissolved in the oxidation mixture. When the oxidizing agent is nitric acid the best catalysts include dissolved vanadium compounds, or combinations of vanadium compounds with copper compounds. The oxygen absorption in these oxidations is sufficiently high to produce substantial quantities of the relatively highly oxidized products, namely carboxylic acids.

It has been known heretofore that among the various acidic by-products obtained in oxidizing a compound of the class consisting of cyclohexane and cyclohexanone to adipic acid, dibasic acids such as succinic acid and glutaric acid are generally to be found. Numerous other oxidation products (e. g. 2-hydroxycyclohexanone, etc.) also are present with these acidic by-products, and the fact that widely varying types of compounds, which are not readily separated from each other, are present has, in the past, precluded any practical utilization of these products.

An object of this invention is to provide an improved method for the utilization of the by-products obtained in the liquid phase oxidation of compounds of the class consisting of cyclohexane and cyclohexanone to adipic acid. A further object is to prolong catalyst life in the preparation of glycols from the said by-products. Other objects of the invention will appear hereinafter.

It has been discovered in accordance with this

2

invention that upon prolonged continuous hydrogenation of the esterified acidic products of the liquid phase oxidation of compounds of the class consisting of cyclohexane and cyclohexanone, after removal of adipic acid therefrom, a high yield of polyhydric alcohols can be maintained for surprisingly long periods of time if traces of inorganic oxidation catalysts and interfering metals from other sources are eliminated prior to the said hydrogenation. The entire acidic mixture of oxidation products, after removal of cyclohexanol, cyclohexanone, and adipic acid, may be demetalized directly (without a separate esterification step) in accordance with the process of the invention, if desired, but this leads to less satisfactory results; alternatively, an aliphatic alcohol may be present during the demetalization and/or hydrogenation of the mixture. In the latter embodiment, esterification and hydrogenation take place simultaneously.

The present invention provides an improved process for the manufacture of polyhydric alcohols which comprises oxidizing a compound of the class consisting of cyclohexane and cyclohexanone with molecular oxygen, at a temperature between 50° and 175° C., at a pressure sufficient to keep the oxidizable ingredients in the liquid phase (e. g. atmospheric pressure in the case of cyclohexanone and between atmospheric and 500 pounds per square inch in the case of cyclohexane) subjecting the resulting mixture in the presence of water to the action of an ion exchange agent whereby any metal ions therein are removed, and thereafter preparing polyhydric alcohols from the resulting mixture by hydrogenation. In a specific embodiment, adipic acid is preliminarily separated from the oxidation product.

The acidic by-products which may be employed in the practice of this invention include numerous ingredients other than the simple alkanedioic acids. It is, in fact, preferred to employ all of the mixed by-product, after recovering cyclohexane, cyclohexanol, cyclohexanone and adipic acid. Any convenient method for separating adipic acid from the oxidation products obtained by oxidizing a compound of the class consisting of cyclohexane and cyclohexanone in accordance with any of the above-mentioned previously known oxidation processes may be employed. Since adipic acid is the oxidation product which is most readily separated from the mixture by simple crystallization (upon cooling), the removal of adipic acid from the reaction product is not necessarily difficult. The adipic acid may be recovered from the reaction mixture before or

after removal of the volatile ingredients of the oxidation mixture which can be recovered by simple distillation, or steam distillation. Removal of volatiles and adipic acid from the mixture (the mother liquor from aqueous recrystallization of the adipic acid may be added) gives the acidic by-product (hereinafter called the "heel") which may be used in the practice of this invention. It is not essential, of course, that every trace of adipic acid be removed from the oxidation product. In preferred embodiments the acidic by-products may be heated with an alcohol, and after demetalization may be hydrogenated in the presence of a hydrogenation catalyst such as copper, copper chromite, copper-zinc, copper-magnesium chromite, copper-zinc chromite, copper barium chromite, copper-tin chromite, etc. Catalysts containing both copper and zinc (e. g. reduced copper oxide-zinc oxide) give the best results, especially when the hydrogenation is performed continuously, and the catalyst is in the form of a fixed bed. For batch-wise operation finely divided copper chromite is excellent. The hydrogenation may be carried out at a temperature within the range of 175° to 325° C. under a pressure within the range of about 10 to 1500 atmospheres.

This invention is illustrated further by means of the following examples.

Example 1.—A cyclohexanone oxidation product was prepared by passing air through an acetic acid solution of cyclohexanone containing about 30% by weight of cyclohexanone and containing also a catalyst consisting of manganese acetate and barium acetate. The oxidation was continued at a temperature of about 80° C. until about 70% of the cyclohexanone was converted to adipic acid. The volatile ingredients of the oxidation mixture were then removed by distillation, and adipic acid was recovered from the residue by crystallization from water. The mother liquors resulting from the said crystallization of adipic acid were concentrated, and a relatively non-volatile residue was thus obtained. Ninety-nine pounds of this non-volatile oxidation residue was charged to a still and esterified with 81.2 pounds of isobutanol at 175° to 178° C. under atmospheric pressure. Isobutanol was added intermittently to maintain the reaction temperature within the indicated range. Water was removed from the reaction mixture as vapor in admixture with isobutanol vapor. The vapors were fractionated in a distillation column to produce an azeotropic distillate. This distillate was collected and decanted, the lower aqueous layer being withdrawn from the system while the upper organic layer was returned as reflux to the distillation column. When the rate of water removal became negligible, the reaction mixture was cooled and filtered to produce 144.4 pounds of ester and about two pounds of solids containing metallic oxidation catalyst residues. The filtered ester contained 0.3 milliequivalent of free acid and 7.1 milliequivalents of ester per gram while the original oxidation residue contained 10.35 and 2.2 milliequivalents of acid and ester respectively per gram. The filtered ester was hydrogenated by continuously passing the mixture of ester and hydrogen through a catalyst zone containing pills of reduced copper oxide-zinc oxide mixture at a temperature of 250° to 260° C. under a pressure of 300 atmospheres. Conversion of acid and ester amounted to about 99% or better during the initial stages of the hydrogenation, but the conversion decreased as the

hydrogenation progressed, until 91.2% conversion was the maximum which could be achieved employing 22.1 volumes of crude ester per volume of catalyst. Analysis of the ester feed showed 22 p. p. m. iron and about 200 p. p. m. total ash. Examination of the catalyst indicated deposition of a surface coating which was found to be acid soluble and to contain iron and other metals.

To determine the effect of demetalization of the ester upon the hydrogenation reaction the filtered ester mixture was prepared in several large batches under conditions similar to those employed in the test described above except that the ester was subjected to the action of an ion-exchange agent as set forth below. A typical sample contained 0.38 milliequivalent of acid and 6.9 milliequivalents of ester per gram and contained 22 p. p. m. of iron and 152 p. p. m. total ash. This material was demineralized by contacting the ester mixture with a carbonaceous zeolite (Zeokarb H) in the presence of about 1% to 2% of water. Comparative experiments showed that the addition of this small quantity of water increased the rate of ion exchange, and the capacity of the ion exchange material to remove metallic ions. The ion exchange treatment was continued until the iron content of the treated ester was about 2 to 3 p. p. m. and the total ash about 24 p. p. m. The demineralized ester containing 2 to 3 p. p. m. iron was continuously hydrogenated by passing a mixture of ester and hydrogen through a catalyst zone containing reduced copper oxide-zinc oxide at 250° to 260° C. under 300 atmospheres pressure. Initial conversions of 99% were obtained based upon the formation of alcoholic hydroxyl groups from ester and carboxyl groups. Moreover, after processing 92.8 volumes of ester per volume of catalyst the conversion under the same conditions was still very high, namely 97.6%. Removal of metallic catalyst poisons thus resulted in more than a fourfold increase in catalyst life. Distillation of the hydrogenation product gave a mixture of glycols (weight 43.2 pounds) having a boiling temperature of from 117° C. to 137° C. at 10 mm. This glycol fraction contained dihydroxypentane and dihydroxyhexane in about equal quantities. A relatively smaller quantity (10 pounds) of monohydric alcohol (butanol, and higher monohydroxyalkanes) was also collected as a fore-shot, B. P. below 117° at 10 mm.

Example 2.—Example 1 was repeated using the non-volatile residue produced as a by-product in the manufacture of adipic acid by air oxidation of cyclohexane in the presence of a cobalt naphthenate catalyst at about 145° C. under a pressure of about 350 pounds per square inch. The poisoning of the hydrogenation catalyst was inhibited, just as in Example 1.

It is to be understood that the mode of practicing the invention may be varied rather widely and that the invention is not at all restricted to the illustrative examples described above. Measurement of the iron content of the ester provides a convenient method for determining the effectiveness of the demetalization, and it is to be understood that removal of cobalt, manganese, etc. accompanies, and substantially parallels, the removal of iron. If desired, the ion-exchange agent may of course be regenerated after a suitable period of use, e. g., when the iron content of the ester reaches about 6 p. p. m. The regeneration is accomplished by treatment with dilute (4%) aqueous sulfuric acid solution in the known manner. After regeneration and washing with

water the original capacity of the ion-exchanger for demineralizing filtered ester is restored.

In particular embodiments the esterification step need not be carried out in the manner illustrated in the example given above. For instance, the esterification of the acidic residues may be carried out in the presence of added esterification catalysts if desired, but this is not done in the preferred method for carrying out the present invention since these esterification catalysts frequently cause poisoning of the hydrogenation catalyst. At temperatures of 80° to 250° C. no added esterification catalyst is needed. If desired, the alcoholic reactant can be introduced into the acidic mixture at elevated temperatures at such a rate that the mixture always contains an excess of the acidic reactant. In this way relatively high temperatures can be reached while the water is being removed azeotropically by means of an efficient still column. Moreover the catalytic or non-catalytic esterification can be carried out under superatmospheric pressure and the azeotropic removal of water can be accomplished by high pressure distillation. It is generally preferred to separate the alcoholic layer from the distillate obtained from the esterification mixture; this returned alcohol may contain a certain percentage of water, which, if desired, can be removed by any suitable dehydration method if more rapid conversion to ester is desired. The addition of a small amount of hydrocarbon to the distillate decanter reduces the solubility of water in the refluxing alcohol and assists in the removal of water therefrom.

A minor quantity of relatively high-boiling monohydric alcohols is produced in the hydrogenation step as illustrated in Example 1. These alcohols are suitable for use in the esterification step, and accordingly a self-sufficient process with respect to the alcohol reactant is thus provided.

If the acidic by-product which is converted to glycol in accordance with this invention is esterified with methanol (or other lower alcohol) and the resulting mixture of dimethyl succinate, dimethyl glutarate, and dimethyl adipate is distilled from the esterification mixture, and thereafter hydrogenated, a 100% yield would produce only 32 parts of glycol per 100 parts of original heel residue; in contrast with this the actual yields of glycols from the crude undistilled esterification mixture are about 45 to 50 parts per 100 parts of the original residue. Therefore, while separation of the individual esters may be carried out if desired, it is generally preferred to employ the crude esterification mixture since other ingredients thereof evidently also contribute to the production of glycols and serve as intermediates therefor. It is noteworthy that

pure succinate esters degrade under the hydrogenation conditions which give excellent results in the practice of this invention.

The process of this invention is well adapted to continuous operation with recycle of the alcoholic foreshots to the esterification mixture.

The glycols obtained in accordance with this invention are especially useful in the manufacture of polyesters and other valuable products. For example, excellent plasticizers can be prepared by esterifying these glycols with dibasic acids, e. g. the mixed dibasic acids produced by oxidation of cyclohexane, cyclohexanol, or cyclohexanone.

I claim:

In a process for the manufacture of polyhydric alcohols by oxidizing a compound of the class consisting of cyclohexane and cyclohexanone with molecular oxygen in the presence of an oxidation catalyst of the class consisting of compounds of cobalt and compounds of manganese dissolved in the reaction mixture, at a temperature between 50° and 175° C., in the liquid phase, whereby an oxidation product containing adipic acid is obtained, separating volatile products and adipic acid from the resulting mixture, subjecting the other oxidation products to an esterification step by heating these other oxidation products in the presence of a saturated monohydric alcohol in which the hydroxyl group is attached to a hydrocarbon radical containing from 4 to 6 carbon atoms, at a temperature in the range of 80° to 250° C., whereby esterification of the said oxidation products occurs, and subjecting the esterification product to hydrogenation in the presence of a reduced copper-oxide-zinc oxide hydrogenation catalyst at a temperature of 175° to 325° C. under a pressure of 10 to 1500 atmospheres, the step which comprises subjecting the said esterification product prior to hydrogenation to the action of an ion exchange agent in the presence of water, which ion exchange agent is capable of exchanging hydrogen ions for metallic ions.

GERALD F. CURTIN, JR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,040,944	Lazier	May 19, 1936
2,223,493	Loder	Dec. 3, 1940
2,470,500	Lawrence	Aug. 26, 1945
2,415,558	Hesler et al.	Feb. 11, 1947
2,439,513	Hamblet et al.	Apr. 13, 1948
2,463,677	Brandner	Mar. 8, 1949
2,557,281	Hamblet et al.	June 19, 1951