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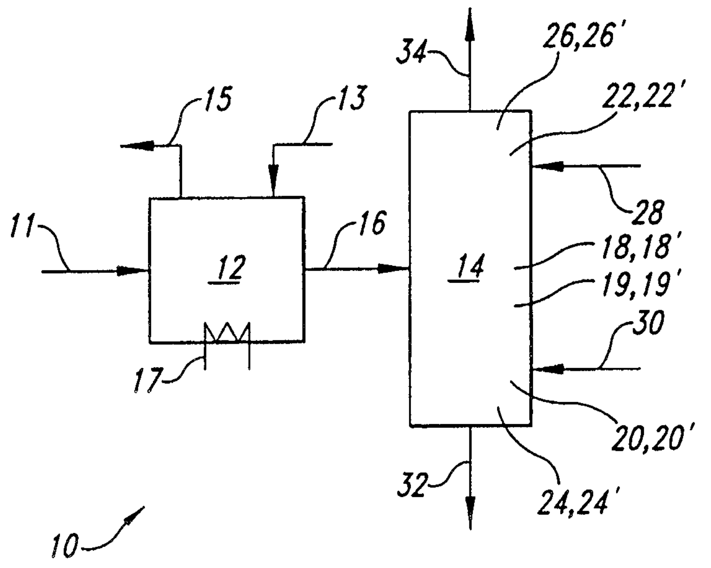
(54) Title: METHODS OF EXTRACTING CATALYST IN SOLUTION IN THE MANUFACTURE OF ADIPIC ACID

(57) Abstract

This invention relates to methods of extracting in solution a metal catalyst from a reaction mixture produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and the metal catalyst. According to this invention, substantially the totality of the cyclohexane is removed, as well as a major part of the adipic acid. A major part of the acetic acid is also removed without precipitating catalyst, thus forming a concentrate in solution. In a preferred embodiment of the instant invention, the concentrate enters a counter-current stream of counter flowing water and cyclohexanone, resulting in an aqueous solution of metal catalyst, which is the extract, and a phase of concentrate solution dissolved in cyclohexanone, which is the raffinate. The two solutions are further treated and/or recycled.



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METHODS OF EXTRACTING CATALYST IN SOLUTION IN THE MANUFACTURE OF ADIPIC ACID

TECHNICAL FIELD

This invention relates to methods of oxidizing cyclohexane to adipic acid and more specifically, how to continuously extract catalyst as a solution, preferably for recycling.

BACKGROUND ART

There is a plethora of references (both patents and literature articles) dealing with the formation of acids, one of the most important being adipic acid, by oxidation of hydrocarbons. Adipic acid is used to produce Nylon 66 fibers and resins, polyesters, polyurethanes, and miscellaneous other compounds.

There are different processes of manufacturing adipic acid. The conventional process involves a first step of oxidizing cyclohexane with oxygen to a mixture of cyclohexanone and cyclohexanol (KA mixture), and then oxidation of the KA mixture with nitric acid to adipic acid. Other processes include, among others, the "Hydroperoxide Process," the "Boric Acid Process," and the "Direct Synthesis Process," which involves direct oxidation of cyclohexane to adipic acid with oxygen in the presence of solvents, catalysts, and promoters.

The Direct Synthesis Process has been given attention for a long time. However, to this date it has found little commercial success. One of the reasons is that although it looks very simple at first glance, it is extremely complex in reality. Due to this complexity, one can find strikingly conflicting results, comments, and views in different references.

It is well known that after a reaction has taken place according to the Direct Synthesis, a mixture of two liquid phases is present at ambient temperature, along with a solid phase mainly consisting of adipic acid. The two liquid phases have been called the "Polar Phase" and the "Non-Polar Phase." However, no attention has been paid so far to the importance of the two phases, except for separating the adipic from the “Polar Phase” and recycling these phases to the reactor partially or totally with or without further treatment.

It is also important to note that most studies on the Direct Synthesis-have been conducted in a batch mode, literally or for all practical purposes.

As aforementioned, there is a plethora of references dealing with oxidation of organic compounds to produce acids, such as, for example, adipic acid and/or intermediate products, such as for example cyclohexanone, cyclohexanol, cyclohexylhydroperoxide, *etc.*

The following references, among others, may be considered as representative of oxidation processes relative to the preparation of diacids and other intermediate oxidation products.

U.S. Patent No. 5,463,119 (Kollar); U.S. Patent No. 5,374,767 (Drinkard et al.); U.S. Patent No. 5,321,157 (Kollar); U.S. Patent No. 3,987,100 (Barnette et al.); U.S. Patent No. 3,957,876 (Rapoport et al.); U.S. Patent No. 3,932,513; (U.S. Patent No. 3,530,185 (Pugi); U.S. Patent No. 3,515,751 (Oberster et al.); U.S. Patent No. 3,361,806 (Lidov et al.); U.S. Patent No. 3,234,271 (Barker et al.); U.S. Patent No. 3,231,608 (Kollar); U.S. Patent No. 3,161,603 (Leyshon et al.); U.S. Patent No. 2,565,087 (Porter et al.); U.S. Patent No. 2,557,282 (Hamblet et al.); U.S. Patent No. 2,439,513 (Hamblet et al.); U.S. Patent No. 2,223,494 (Loder et al.); U.S. Patent No. 2,223,493 (Loder et al.)

German Patent DE 44 26 132 A1 (Kysela et al.) discloses a method of dehydration of process acetic acid from liquid -phase oxidation of cyclohexane with air, in the presence of cobalt salts as a catalyst after separation of the adipic acid after filtration, while simultaneously avoiding cobalt salt precipitates in the dehydration column, characterized in that the acetic acid phase to be returned to the beginning of the process is subjected to azeotropic distillation by the use of added cyclohexane, under distillative removal of the water down to a residual content of less than [sic] 0.3-0.7%.

PCT International Publication WO 96/03365 (Costantini et al.) and U.S. Patent No. 5,756,837 (Costantini et al.) disclose a process for recycling a cobalt-containing catalyst in a direct reaction of oxidation of cyclohexane into adipic acid, characterized by including a step in which the reaction mixture obtained by oxidation into adipic acid is treated by extraction of at least a portion of the glutaric acid and the succinic acid formed during the reaction.

None of the above references, or any other references known to the inventors disclose, suggest or imply, singly or in combination, control of oxidation reactions subject to the intricate and critical controls and requirements of the instant invention as described and claimed.

DISCLOSURE OF THE INVENTION

As aforementioned, this invention relates to methods of oxidizing hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, and more specifically, how continuously to extract catalyst in solution, preferably for recycling. More particularly, this invention pertains a method of extracting in solution a metal catalyst from a reaction mixture produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and the metal catalyst, the method comprising steps of:

(a) removing substantially the totality of the cyclohexane;

(b) removing a major part of the adipic acid;

(c) removing a major part of the acetic acid (up to substantially 100%), but being careful not to exceed a point of acetic acid removal beyond which catalyst may start precipitating, thus forming a concentrate in solution;

(d) introducing the concentrate into a middle region of a counter-current stream, the counter-current stream also having a lower region and an upper region, the lower region having a bottom, and the upper region having a top;

(e) introducing cyclohexanone, which may comprise a minor amount of water, to the lower region of the counter-current stream;

(f) introducing water, which may comprise a minor amount of cyclohexanone, to the upper region of the counter-current stream;

(g) withdrawing a first liquid or raffinate from the top of the upper region, the first liquid comprising the major part of the concentrate, excluding the catalyst; and

(h) withdrawing a second liquid or extract from the bottom of the lower region, the second liquid comprising the major part of the metal catalyst.

The metal catalyst is preferably a cobalt comprising compound. The metal catalyst is substantially the metal itself, preferably in ionic form, regardless of the compound or moiety that it is associated with. Thus, the metal may be associated with one moiety in step (a) and with a different moiety in step (h); for example, it may be predominantly cobalt acetate in step (a), and it may be predominantly cobalt adipate, or cobalt glutarate or cobalt succinate, or any mixture thereof, etc in step (h).

The removal of the cyclohexane may be conducted before, during, or after the removal of the adipic acid, or both before and after the removal of the adipic acid. Before or after means at an earlier or at a later stage of the process, while during means at the same stage. For example, the cyclohexane may be removed by lowering the temperature and allowing formation of two distinct liquid phases, a non-polar phase containing the majority of the cyclohexane and a polar phase containing the majority of the acetic acid, adipic acid and other polar moieties, followed by decantation to remove the non-polar phase, and crystallization to remove the adipic acid. Another alternative is the removal of cyclohexane during flash crystallization of the adipic acid. The cyclohexane may also be removed by distillation.

It is highly preferable that steps (d), (e), (f), (g), and (h) are performed simultaneously. Further, step (c) is preferably conducted by distillation. Small amounts of water may be added continuously or intermittently in step (c).

It is also highly preferable that substantially the totality of the acetic acid is removed in step (c), and that substantially the totality of the metal catalyst is withdrawn in step (h).

In the case that substantially complete removal of the catalyst is required, it is absolutely critical to maintain a high enough temperature in the portions of the counter-current stream, such as the upper portion of the counter-current stream, where only small amounts of catalyst are present, in order to reduce or eliminate a tendency for emulsification.

The temperatures of the upper, middle, and lower portions may be substantially the same; preferably in the range of 50°C to 80°C.

It is more preferable, however, that the upper portion temperature is higher than the middle portion temperature, and the middle portion temperature is higher than the lower portion temperature. Even more preferably, the upper portion temperature is in the range of 50°C to 90°C, the middle portion temperature is in the range of 30°C to 50°C, and the lower portion temperature is in the range of 10°C to 40°.

This invention also pertains a method of extracting in solution a metal catalyst from a reaction mixture produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and the metal catalyst, the method comprising steps of:

(k) removing substantially the totality of the cyclohexane;

(l) removing a major part of the adipic acid;

(m) removing a major part of the acetic acid, without precipitating catalyst, thus forming a concentrate in solution;

(n) introducing the concentrate into a middle stage of a counter-current multi-stage assembly, the middle stage comprising a middle mixing zone and a middle separating zone, the counter-current multi-stage assembly also comprising a front stage and a back stage, the front stage comprising a front mixing zone and a front separating zone, and the back stage comprising a back mixing zone and a back separating zone;

(p) introducing cyclohexanone, which may comprise a minor amount of water, into the front mixing zone;

(q) introducing water, which may comprise a minor amount of cyclohexanone into the back mixing zone;

(r) withdrawing a raffinate from the back separating zone, the raffinate comprising a major part of the concentrate, excluding the catalyst; and

(s) withdrawing an extract from the front separating zone, the extract comprising a major part of the metal catalyst.

It is preferable that step (m) is conducted by distillation, in which case, the method may further comprise a step of adding water in step (m).

At least in the back separation zone, separation may be at least partially conducted by a step of centrifugation.

In one embodiment of this invention, the back stage has a back stage temperature, the middle stage has a middle stage temperature, the front stage has a front stage temperature; and the back stage temperature, the middle stage temperature, and the front stage temperature are substantially the same. Preferably, the substantially same temperature is in the range of 50°C to 80°C.

In a different embodiment, the back stage temperature is higher than the middle stage temperature, and the middle stage temperature is higher than the front stage temperature. Preferably, the back stage temperature is in the range of 50°C to 90°C, the middle stage temperature is in the range of 30°C to 50°C, and the front stage temperature is in the range of 10°C to 40°C.

According to this invention, it is preferable that substantially the totality of the acetic acid is removed in step (m). It is also preferable that substantially the totality of the metal catalyst is withdrawn in step (s).

As aforementioned, the metal catalyst is preferably a cobalt comprising compound. The metal catalyst is substantially the metal itself, preferably in ionic form, regardless of the compound or moiety that it is associated with. Thus, the metal may be associated with one moiety in step (k) and with a different moiety in step (s); for example, it may be predominantly cobalt acetate in step (k), and it may be predominantly cobalt adipate, or cobalt glutarate or cobalt succinate, or any mixture thereof, *etc.*, in step (s).

It is highly preferable that steps (n), (p), (q), (r), and (s) are performed simultaneously. Further, step (m) is preferably conducted by distillation. Small amounts of water may be added continuously or intermittently in step (m) to maintain the solubility of the metal catalyst.

The methods of the present invention may further comprise a step of reacting the adipic acid produced with a reactant selected from a group consisting of a polyol, a polyamine, and a polyamide in a manner to form a polymer of a polyester, or a polyamide, or a (polyimide and/or polyamideimide), respectively, which polymer may further be spun into fibers or mixed with fillers and/or other additives to form composites.

"Major" and "majority" regarding a moiety mean more than 50%, and up to substantially 100%, of said moiety by weight.

"Minor" and "minority" regarding a moiety mean less than 50%, and down to 0%, of said moiety by weight.

"Upper phase" is meant to mean "relatively less polar cyclohexanone phase containing the minority of the catalyst," while "lower phase" is meant to mean "relatively more polar aqueous phase containing the majority of the catalyst." This applies not only in the case that the separator is a decanter, which produces an upper cyclohexanone phase and a lower aqueous phase, but also in the case that the separator is a centrifugal separator, for purposes of simplicity.

"Middle stage" is any stage other than the front stage and the back stage.

BRIEF DESCRIPTION OF THE DRAWING

The reader's understanding of this invention will be enhanced by reference to the following detailed description taken in combination with the drawing figure, wherein:

FIGURE 1 illustrates a block diagram of a preferred embodiment of the present invention, wherein the catalyst extraction is conducted in a counter-current stream.

FIGURE 2 illustrates a block diagram of another preferred embodiment of the present invention, wherein the catalyst extraction is conducted in a multi-stage extraction assembly.

BEST MODE OF CARRYING OUT THE INVENTION

As aforementioned, this invention relates to methods and devices for oxidizing cyclohexane to adipic acid for example, and more specifically, how to extract catalyst in solution after the reaction, preferably for recycling.

Proper catalyst handling in oxidation reactions has always been a considerable problem in the art. According to the present invention, the catalyst is separated in a liquid form dissolved in an aqueous phase, and preferably returned to the reaction chamber with or without any further treatment.

It was found by the inventors that the reaction mixture, after oxidation of the cyclohexane to adipic acid to a desired degree of conversion, and after removal of the majority of the adipic acid, the remaining cyclohexane along with water and at least the majority of the acetic acid, may attain or be maintained in a solids-free, monophasic liquid state before and after addition of critical amounts of cyclohexanone and water. The catalyst may then be extracted with an additional amount of water, or by a temperature decrease, and preferably returned to the reaction chamber with or without any further treatment.

According to this invention, the catalyst separation process is highly improved by using the techniques described hereinbelow:

Referring now to Figure 1, there is depicted a catalyst separation unit 10 comprising an evaporator or still 12, which is connected to the middle region 19 of a complex counter-current extraction column 14 through a transfer line 16. The complex counter-current extraction column 14 encloses a complex extraction region 18. The column 14 has in addition to the middle region 19, a lower region 20, and an upper region 22. The lower region 20 has a bottom 24 and the upper region 22 has a top 26. A water line 28 and a cyclohexanone line 30 are connected to the complex counter-current extraction column 14, which in turn is connected to a catalyst solution line or extract line 32, and a concentrate solution line or raffinate line 34.

The evaporator or still 12 is connected to a vapor line 15, while an optional additive line 13 and a treated reaction mixture line 11 are connected to the evaporator 12. A heater or heat exchanger 17 is part of the evaporator 12.

Apparatuses in front and in back of the catalyst separation unit 10 are not shown in Figure 1, since they are well described in most of our patents and applications, which have been incorporated herein by reference.

In operation of this embodiment, a treated reaction mixture from the oxidation of cyclohexane to adipic acid (as described for example in our patents and pending applications, which have been incorporated herein by reference) enters the evaporator or still 12 through line 11. The treated reaction mixture is the mixture remaining after removing at least a major part of the adipic acid from the reaction mixture, which reaction mixture is produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and a metal catalyst, preferably a cobalt compound. The treated reaction mixture may contain the majority or the minority of the unreacted cyclohexane. The cyclohexane may be removed by separating the reaction mixture into (i) a polar phase containing the majority of the acetic acid, adipic acid, other polar moieties, and catalyst, and (ii) a non-polar phase containing the majority of the cyclohexane. In such a case, the non-polar phase may be recycled, while the majority of the adipic acid may be removed by crystallization from the polar phase. The remainder, after the removal of the adipic acid, constitutes the treated reaction mixture in this case. In a different case, the majority or minority of the cyclohexane may be removed simultaneously with flash crystallization of the adipic acid. The remainder, after the removal of the adipic acid, constitutes the treated reaction mixture in such a case.

It is important to realize that removal of cyclohexane is not necessary, albeit highly desirable, before the treated reaction mixture enters the evaporator or still 12.

The treated reaction mixture entering the evaporator 12 is concentrated to a desired degree by evaporation of the majority of the acetic acid present. It is evident that any cyclohexane present and most of the water evaporate through line 15, even before the acetic acid evaporates, due to their higher volatility. It is very important and critical that the concentrate produced by the evaporation of the majority of the acetic acid leaves through line 16 in the form of a liquid, which even if it is viscous, can still be pumped.

During the process of evaporating the acetic acid, small amounts of water can be added continuously or intermittently through the additive line 13. Addition of water can be critical in minimizing the amount of acetic acid in the concentrate to maintain the concentrate in a solids-free form, depending on conversions, relative levels of compounds in the concentrate, etc.

The concentrate enters the complex extraction region 18 of the complex counter-current extraction column 14, in which region 18 there is present a counter-current stream 18'.

The counter-current stream 18' has a middle region 19', which corresponds to the middle region 19 of the column 14. Similarly, the counter-current stream 18' has a lower region 20' (corresponding to the lower region 20 of the column 14), and an upper region 22' (corresponding to the upper region 22 of the column 14). Further, the lower region 20' of the counter-current stream 18' has a bottom 24' (corresponding to the bottom 24 of the lower region 20 of the column 14). The upper region 22' of the counter-current stream 18' has a top 26' (corresponding to the top 26 of the upper region 22 of the column 14).

As one can see in Figure 1, the counter-current stream 18' is produced by a plurality of secondary streams entering and exiting the column 14.

One of these secondary streams is the concentrate entering a middle region 19' of the counter-current stream 18'. Another secondary stream is a stream of cyclohexanone, which is introduced through the cyclohexanone line 30 at the lower region 20' of the counter-current stream 18'. Still another secondary stream is a stream of water, which is introduced through the water line 28 at the upper region 22' of the counter-current stream 18'.

Since cyclohexanone has a lower specific gravity than water, it moves upwards (in a direction from the lower region 20' toward the upper region 22' of the counter-current stream 18') in the column 14, while the water moves downwards (in a direction from the upper region 22' toward the lower region 20' of the counter-current stream 18') in column 14. As the two secondary streams move in opposite directions, the composition of the counter-current stream 18' changes from place to place, finally resulting in a water phase, containing at least the major part of the metal catalyst, in the vicinity of the bottom 24', and a cyclohexanone phase, containing at least the major part of the concentrate, excluding the catalyst, in the vicinity of the top 26'. The water phase, which is the extract and which contains the majority of the catalyst, is removed via the catalyst solution line or extract line 32, while the cyclohexanone phase is removed via the concentrate solution line or raffinate line 34.

By this technique, a dissolution of the concentrate is achieved with simultaneous extraction of the metal catalyst in solution form by water. The concentrate solution or raffinate and the catalyst solution or extract may be treated further and/or recycled as discussed in our previously mentioned patents and patent applications.

Substantially the totality of the metal catalyst may be extracted and removed through catalyst solution line or extract line 32 by controlling the temperature, and the feed rates through lines 16, 28, and 30.

The water entering the line 28 may contain a minor amount of cyclohexanone, while the cyclohexanone entering through line 30 may contain a minor amount of water. Similarly, the catalyst solution in water or extract exiting through line 32 contains a minor amount of cyclohexanone, while the concentrate solution or raffinate exiting through line 34 contains a minor amount of water.

In regions of the counter-current stream, which have low concentrations of catalyst, such as for example the upper portion 22' of the counter-current stream 18', emulsification of water and cyclohexanone containing the miscellaneous products tends to occur, which allows small amounts of catalyst to become incorporated into the concentrate solution or raffinate line 34. In order to considerably reduce or eliminate such a trend, the temperature in the upper portion 22' has to be above a certain critical temperature, which can be found easily without undue experimentation. Thus, the whole counter-current stream 18' may be maintained at a temperature above said critical temperature, or at least just its upper portion 22'. An easy way to control the temperatures of the lower potion 20', the middle portion 19' and the upper portion 22' of the counter-current stream 18' is by controlling the temperatures of the cyclohexanone stream through line 30, the concentrate stream through line 16, and the water stream through line 28, respectively.

In the case that it is desirable to maintain the whole counter-current stream at about the same temperature, preferable temperatures are in the range of 50°C to 80°C.

More preferably, however, the temperature of the upper portion 22' is maintained in a range of 50°C to 90°C, the middle portion 19' is maintained in a range of 30°C to 50°C, and the lower portion 20' is maintained in a range of 10°C to 40°C. As aforementioned, an easy way to achieve this is by controlling the temperatures of the cyclohexanone stream through line 30, the concentrate stream through line 16, and the water stream through line 28, respectively, without this being necessary, since external or internal heating or cooling, and/or other temperature control means may be used for this purpose.

Referring now to Figure 2, there is depicted a catalyst separation unit 110 comprising an evaporator or still 112, which is connected to the middle stage 119 of a multi-stage counter-current extraction assembly 114 through a transfer line 116. The middle stage 119 comprises a middle separator 118 and a middle mixer 118a. The multi-stage counter-current extraction assembly has in addition to the middle stage 119, a front stage 120, and a back stage 122. The front stage 120 has a front separator 124 and a front mixer 124a. Similarly, the back stage 122 has a back separator 126 and a back mixer 126a. A water line 128 is connected to the back mixer 126a, and a cyclohexanone line 130 is connected to the front mixer 124a. An extract line 132 is connected to the front separator 124, and a raffinate line 134 is connected to the back separator 126.

Intermediate stages 136 and 138, comprising intermediate separators 140 and 142, respectively, and intermediate mixers 140a and 142a, respectively, are also shown in Figure 2. However, the number of stages may be larger or smaller depending on individual circumstances, and degree of completeness of extraction.

The mixers and separators are connected to each other through inlet and outlet lines as clearly exemplified in Figure 2. Certain inlet lines are shown to merge into each other to form single inlet lines leading to the mixers. This, however, is not necessary. The inlet lines may lead individually and directly to the mixers. This direct connection is particularly desirable for cases in which there is potential for solids precipitation. Pumps within lines for moving the miscellaneous streams from a given vessel to another vessel, as well as other accessories, are not shown for purposes of clarity and brevity, but they and their operation are well known in the art.

The separators may be decanters, centrifugal separators, or any other type of separators which are suitable to separate two flowable phases from each other.

The different stages or parts of the stages (including mixers, separators, inlet and outlet lines, *etc.*) may be heated or cooled by any means well known to the art. Heating/cooling means are not shown in Figure 1 for purposes of clarity.

The evaporator or still 112 is connected to a vapor line 115, while an optional additive line 113 and a treated reaction mixture line 111 are connected to the evaporator 112. A heater or heat exchanger 117 is part of the evaporator 112.

Apparatuses in front and in back of the catalyst extraction unit 110 are not shown in Figure 2, since they are well described in most of our patents and applications, which have been incorporated herein by reference.

In operation of this embodiment, a treated reaction mixture from the oxidation of cyclohexane to adipic acid (as described for example in our patents and pending applications, which have been incorporated herein by reference) enters the evaporator or still 112 through line 111. The treated reaction mixture is the mixture remaining after removing at least a major part of the adipic acid from the reaction mixture, which reaction mixture is produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and a metal catalyst, preferably a cobalt compound. The treated reaction mixture may contain the majority or the minority of the unreacted cyclohexane. The cyclohexane may be removed by separating the reaction mixture into (i) a polar phase containing the majority of the acetic acid, adipic acid, other polar moieties, and catalyst, and (ii) a non-polar phase containing the majority of the cyclohexane. In such a case, the non-polar phase may be recycled, while the majority of the adipic acid may be removed by crystallization from the polar phase. The remainder, after the removal of the adipic acid, constitutes the treated reaction mixture in this case. In a different case, the majority or minority of the cyclohexane may be removed simultaneously with flash crystallization of the adipic acid. The remainder, after the removal of the adipic acid, constitutes the treated reaction mixture in such a case.

Of course, the cyclohexane may be removed by evaporation, or any other technique.

It is important to realize that removal of cyclohexane is not necessary, albeit highly desirable, before the treated reaction mixture enters the evaporator or still 112.

The treated reaction mixture entering the evaporator 112 is concentrated to a desired degree by evaporation of the majority of the acetic acid present. It is evident that any cyclohexane present and most of the water evaporate through line 115, even before the acetic acid evaporates, due to their higher volatility. It is very important and critical that the concentrate produced by the evaporation of the majority of the acetic acid leaves through line 116 in the form of a liquid, which even if it is viscous, can still be pumped.

During the process of evaporating the acetic acid, small amounts of water can be added continuously or intermittently through the additive line 113. Addition of water can be critical in minimizing the amount of acetic acid in the concentrate to maintain the concentrate in a solids-free form, depending on conversions, relative levels of compounds in the concentrate, *etc.*

The concentrate enters the middle stage 119 of the multi-stage counter-current assembly 114 through line 116, which merges with a stream in line 140', and later with a stream in line 142", ending at middle mixer 118a. The three streams, from lines 116, 140', and 142", are well mixed in the mixer 18a, and the resulting mixture is transferred to the separator 118 through line 118a', where it is separated into an upper phase, rich in cyclohexanone, and a lower phase, rich in water. The lower phase is directed to the previous mixer (intermediate mixer 140a) through line 118", while the upper phase is directed to the next mixer (intermediate mixer 142a) through line 118'.

Cyclohexanone is fed to the front mixer 124a through line 130, where it is well mixed with a stream coming from the lower phase of the intermediate separator 140, through line 140". The resulting mixture is fed to the front separator 124 through line 124a', where it is separated into a lower phase, which exits the assembly through line 132, and an upper phase, which is directed to the intermediate mixer 140a through line 124'.

The lower phase exiting the assembly 114 through line 132 is an extract comprising the majority of the catalyst in an aqueous solution. It also contains small amounts of cyclohexanone.

At the back stage 122 of the assembly 114, water enters the mixer 126a through line 128, where it is well mixed with a stream coming from the upper phase of the intermediate separator 142 through line 142'. The resulting mixture is directed to the separator 126 through line 126a', where it is separated into a lower phase, and an upper phase. The lower phase is directed to the intermediate mixer 142a through line 126", while the upper phase exits the assembly 114 through line 134.

The upper phase, exiting the assembly 114 through line 134, is a raffinate containing a solution of the majority of the concentrate in cyclohexanone. A small amount of water is also present.

As shown in Figure 2, the operation is based on successive stages of extracting catalyst to form a final aqueous catalyst extract, exiting the assembly 114 through line 132, and leaving behind a concentrate raffinate in cyclohexanone, which exits the assembly 114 through line 134.

As the extracting solvent (water) moves from the back separator 126 toward the front separator 124, it is enriched in catalyst, leaving a continuously more catalyst-depleted raffinate, which finally exits the assembly 114 through line 134.

By this technique, a dissolution of the concentrate entering the multi-stage counter-current assembly through line 116 is achieved with simultaneous extraction of the metal catalyst in solution form by water. The raffinate and the catalyst extract may be treated further and/or recycled as discussed in our previously mentioned patents and patent applications.

Introduction of the concentrate in a middle stage of the multi-stage counter-current assembly or extractor (or in a middle portion of a similar counter-current column) is critical in maximizing the efficiency and effectiveness of the extraction of the catalyst from the concentrate. Introduction of the concentrate in the middle stage 119 of the multi-stage counter-current assembly or extractor 114, and not in the back stage 122, ensures that a considerable amount of catalyst has already been extracted before the final extraction takes place in the final separator 126. Introduction of the concentrate in the front stage 120 of the multi-stage counter-current assembly or extractor 114, would result in considerably higher incorporation of concentrate moieties (other than catalyst) in the catalyst extract exiting through line 132.

Substantially the totality of the metal catalyst may be extracted and removed through the extract line 132 by controlling the temperature at the different stages, the feed rates through lines 128 and 130, and by the number of stages.

The water entering the line 128 may contain a minor amount of cyclohexanone, while the cyclohexanone entering through line 130 may contain a minor amount of water. Similarly, as aforementioned, the catalyst extract exiting through line 132 contains a minor amount of cyclohexanone, while the raffinate exiting through line 134 contains a minor amount of water.

In late stages of the counter-current assembly 114, closer to the back stage 122, which late stages have rather low concentrations of catalyst, emulsification of water and cyclohexanone containing the miscellaneous products tends to occur, which allows small amounts of catalyst to become incorporated into the raffinate, which exits the assembly through line 134. In order to reduce considerably or eliminate such a trend, the temperature at the late stages must be above a certain critical temperature, which can be found easily without undue experimentation. Thus, all stages may be maintained at a temperature above said critical temperature, or just the late stages, or just the back stage 122. One way to achieve this easily, is to control the temperature of the miscellaneous streams by means well known to the art, such as for example heaters, coolers, heat exchangers, *etc.* Of course, the separators or mixers may be also heated or cooled by similar techniques, such as for example by use of external or internal heating or cooling devices, and/or other temperature control means.

In the case that it is desirable to maintain the whole multi-stage counter-current assembly at about the same temperature, preferable temperatures are in the range of 50°C to 80°C.

More preferably, however, the temperature of the back stage 122 should be maintained in a range of 50°C to 90°C, the temperature of the middle stage 119 should be maintained in a range of 30°C to 50°C, and the temperature of the front stage 120 should be maintained in a range of 10°C to 40°C. In the presence of intermediate stages, the intermediate stages should be preferably maintained at temperatures between the temperature of the middle stage the respective end (front or back) stage.

If unacceptable emulsification occurs in the back stage 122, or any other stage, a centrifugal separator such as separator 126, shown in Figure 1, may be used in place of a simple decanter. When a centrifugal separator is used at least in the back stage, maintaining the temperature above the critical points of emulsification is less important.

It should be understood that according to the present invention, any liquids or gases or off-gases may be recycled totally or partially from any section to any other section, if so desired. Further, any combinations of the exemplifying embodiments, in part or in total, or any equivalent arrangements or any combinations of equivalent arrangements may be utilized, and are within the scope of the present invention.

Although miscellaneous functions are preferably controlled by a computerized controller, it is possible, according to this invention, to utilize any other type of controller or even manual controls and/or labor for controlling one or more functions. Preferred computerized controllers include artificially intelligent systems (expert systems, neural networks, and fuzzy logic systems, well known to the art). Of the three types of artificially intelligent systems, the neural network, which is a learning system, collects information from different places of the device (for example pressure, temperature, chemical or other analysis, *etc.*), stores this information along with the result (pressure drop rate, reaction rate, reactivity, and the like, for example), and is programmed to use this information in the future, along with other data if applicable, to make decisions regarding the action to be taken at each instance. The expert systems are programmed based on the expertise of experienced human beings. The fuzzy logic systems are based on intuition rules in addition to expertise rules.

Oxidations according to this invention, are non-destructive oxidations, wherein the oxidation product is different than carbon monoxide, carbon dioxide, and a mixture thereof, such as adipic acid for example. Of course, small amounts of these compounds may be formed along with the oxidation product, which may be one product or a mixture of products.

Regarding adipic acid, the preparation of which is especially suited to the methods of this invention, general information may be found in a plethora of U.S. patents, among other references. These include, but are not limited to:

U.S. Patent Nos. 2,223,493; 2,589,648; 2,285,914; 3,231,608; 3,234,271; 3,361,806; 3,390,174; 3,530,185; 3,649,685; 3,657,334; 3,957,876; 3,987,100; 4,032,569; 4,105,856; 4,158,739 (glutaric acid); 4,263,453; 4,331,608; 4,606,863; 4,902,827; 5,221,800; and 5,321,157.

Diacids (for example adipic acid, phthalic acid, isophthalic acid, terephthalic acid, and the like) or other suitable compounds may be reacted, according to well known techniques to the art, with a third reactant selected from a group consisting of a polyol, a polyamine, and a polyamide in a manner to form a polymer of a polyester, or a polyamide, or a (polyimide and/or polyamideimide), respectively.

Preferably the polyol, the polyamine, and the polyamide are mainly a diol, a diamine, and a diamide, respectively, in order to avoid excessive cross-linking. The polymer resulting from this reaction may be spun by techniques well known to the art to form fibers. The polymer may also be mixed with fillers and/or other additives to form composite materials.

Examples demonstrating the operation of the instant invention have been given for illustration purposes only, and should not be construed as limiting the scope of this invention in any way. In addition it should be stressed that the preferred embodiments discussed in detail hereinabove, as well as any other embodiments encompassed within the limits of the instant invention, may be practiced individually, or in any combination thereof, according to common sense and/or expert opinion. Individual sections of the embodiments may also be practiced individually or in combination with other individual sections of embodiments or embodiments in their totality, according to the present invention. These combinations also lie within the realm of the present invention. Furthermore, any attempted explanations in the discussion are only speculative and are not intended to narrow the limits of this invention.

CLAIMS

What is claimed is:

1. A method of extracting in solution a metal catalyst from a reaction mixture produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and the metal catalyst, the method comprising steps of:

(a) removing substantially the totality of the cyclohexane;

(b) removing a major part of the adipic acid;

(c) removing a major part of the acetic acid, without precipitating catalyst, thus forming a concentrate in solution;

(d) introducing the concentrate into a middle portion of a counter-current stream, the counter-current stream also having a lower portion and an upper portion, the lower portion having a bottom, and the upper portion having a top;

(e) introducing cyclohexanone, which may comprise a minor amount of water, to the lower portion of the counter-current stream;

(f) introducing water, which may comprise a minor amount of cyclohexanone at the upper portion of the counter-current stream;

(g) withdrawing a first liquid or raffinate from the top of the upper portion, the first liquid comprising the major part of the concentrate, excluding the catalyst; and

(h) withdrawing a second liquid or extract from the bottom of the lower portion, the second liquid comprising the major part of the metal catalyst.

2. A method as defined in claim 1, wherein steps (d), (e), (f), (g), and (h) are performed simultaneously.

3. A method as defined in any of claims 1-2, wherein step (c) is conducted by distillation.

4. A method as defined in any of claims 1-3, further comprising a step of adding water in step (c).

5. A method as defined in any of claims 1-4, wherein substantially the totality of the acetic acid is removed in step (c).

6. A method as defined in any of claims 1-5, wherein substantially the totality of the metal catalyst is withdrawn in step (h).

7. A method as defined in any of claims 1-6, wherein the upper portion has an upper portion temperature, the middle portion has a middle portion temperature, the lower portion has a lower portion temperature, and wherein the upper portion temperature, the middle portion temperature, and the lower portion temperature are substantially the same.

8. A method as defined in any of claims 1-6, wherein the upper portion has an upper portion temperature, the middle portion has a middle portion temperature, the lower portion has a lower portion temperature, and wherein the upper portion temperature is higher than the middle portion temperature.

9. A method as defined in claim 8, wherein the middle portion temperature is higher than the lower portion temperature.

10. A method as defined in any of claims 1-9, further comprising a step of reacting the adipic acid with a reactant selected from a group consisting of a polyol, a polyamine, and a polyamide in a manner to form a polymer of a polyester, or a polyamide, or a (polyimide and/or polyamideimide), respectively, which method may further comprise a step of spinning the polymer into fibers or mixing the polymer with fillers and/or other additives to form composites.

11. A method of extracting in solution a metal catalyst from a reaction mixture produced by oxidizing cyclohexane to adipic acid in the presence of acetic acid and the metal catalyst, the method comprising steps of:

(k) removing substantially the totality of the cyclohexane;

(l) removing a major part of the adipic acid;

(m) removing a major part of the acetic acid, without precipitating catalyst, thus forming a concentrate in solution;

(n) introducing the concentrate into a middle stage of a counter-current multi-stage assembly, the middle stage comprising a middle mixing zone and a middle separating zone, the counter-current multi-stage assembly also comprising a front stage and a back stage, the front stage comprising a front mixing zone and a front separating zone, and the back stage comprising a back mixing zone and a back separating zone;

(p) introducing cyclohexanone, which may comprise a minor amount of water, into the front mixing zone;

(q) introducing water, which may comprise a minor amount of cyclohexanone into the back mixing zone;

(r) withdrawing a raffinate from the back separating zone, the raffinate comprising a major part of the concentrate, excluding the catalyst; and

(s) withdrawing an extract from the front separating zone, the extract comprising a major part of the metal catalyst.

12. A method as defined in claim 11, wherein step (m) is conducted by distillation.

13. A method as defined in any of claims 11-12, further comprising a step of adding water in step (m).

14. A method as defined in any of claims 11-13, wherein, at least in the back separating zone, separation is at least partially conducted by a step of centrifugation.

15. A method as defined in any of claims 11-14, wherein the back stage has a back stage temperature, the middle stage has a middle stage temperature, the front stage has a front stage temperature, and wherein the back stage temperature, the middle stage temperature, and the front stage temperature are substantially the same.

16. A method as defined in claim 15, wherein the substantially same

temperature is in the range of 50°C to 80°C.

17. A method as defined in any of claims 1-14, wherein the back stage has a back stage temperature, the middle stage has a middle stage temperature, the front stage has a front stage temperature, and wherein the back stage temperature is higher than the middle stage temperature, and the middle stage temperature is higher than the front stage temperature.

18. A method as defined in claim 17, wherein the back stage temperature is in the range of 50°C to 90°C, the middle stage temperature is in the range of 30°C to 50°C, and the front stage temperature is in the range of 10°C to 40°C.

19. A method as defined in any of claims 1-18, wherein substantially the totality of the acetic acid is removed in step (m).

20. A method as defined in any of claims 1-19, wherein substantially the totality of the metal catalyst is withdrawn in step (s).

21. A method as defined in any of claims 11-20, further comprising a step of reacting the adipic acid with a reactant selected from a group consisting of a polyol, a polyamine, and a polyamide in a manner to form a polymer of a polyester, or a polyamide, or a (polyimide and/or polyamideimide), respectively, which method may further comprise a step of spinning the polymer into fibers or mixing the polymer with fillers and/or other additives to form composites.

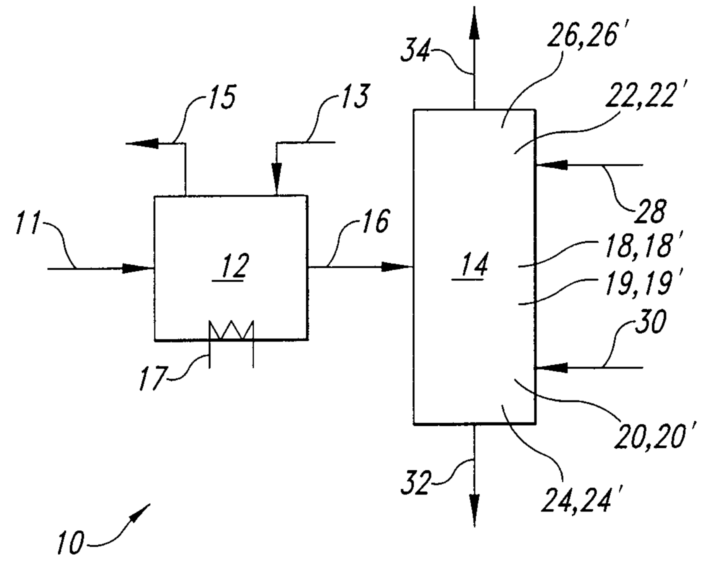

Fig. 1

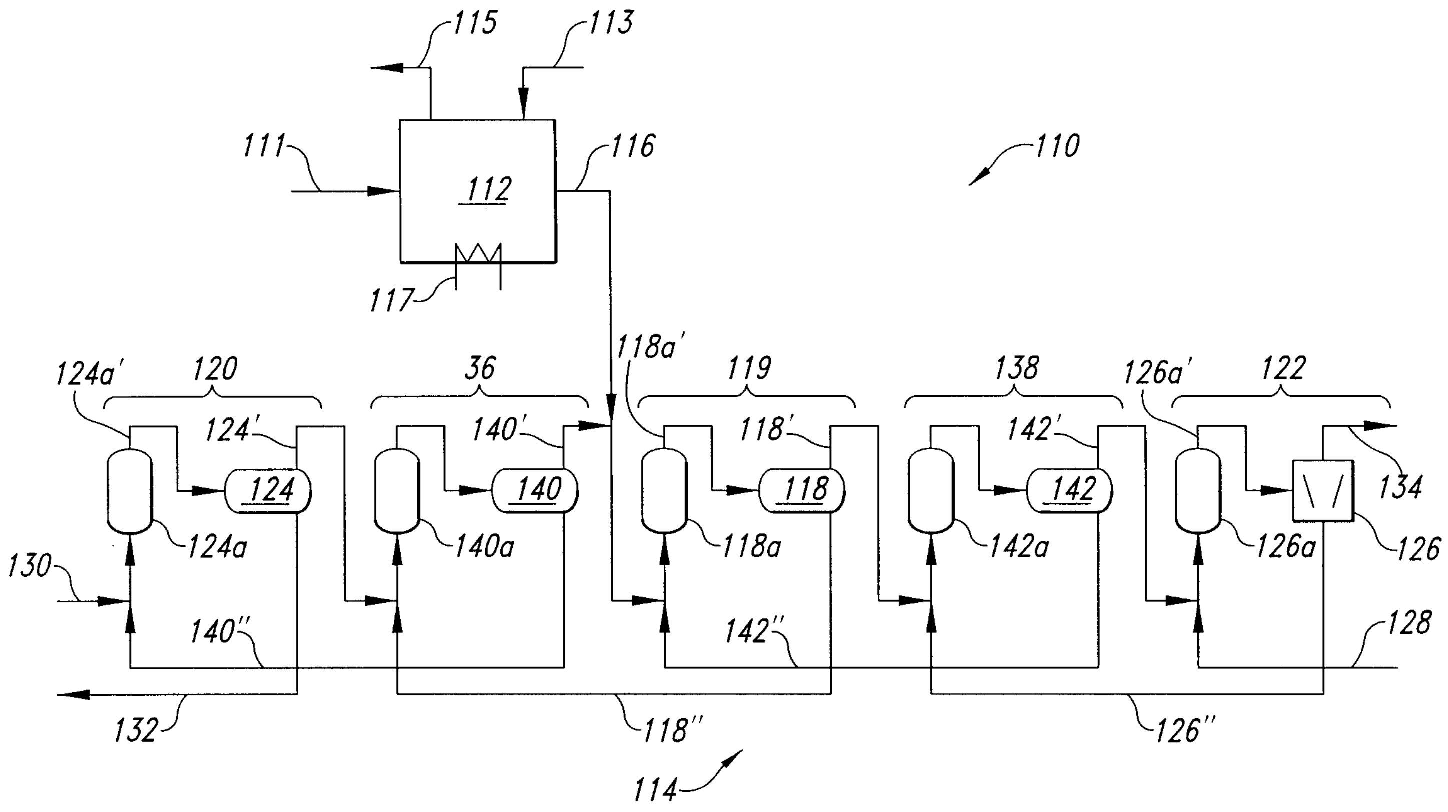
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Fig. 2

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 00/04473

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C51/31 C07C51/48 C07C55/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 44 27 474 A (BAYER) 8 February 1996 (1996-02-08) the whole document ---	1,11
A	DE 44 26 132 A (BAYER) 25 January 1996 (1996-01-25) cited in the application the whole document ---	1,11
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A	US 3 786 096 A (K. KAZUHIKO) 15 January 1974 (1974-01-15) the whole document -----	1,11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2000	13/06/2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/US 00/04473

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