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(54) **PROCEDES DE RECYCLAGE D'UN CATALYSEUR AU COURS
D'OXYDATIONS D'HYDROCARBURES**

(54) **METHODS OF RECYCLING CATALYST IN OXIDATIONS OF
HYDROCARBONS**

(57) Cette invention concerne des procédés de recyclage de catalyseur au cours d'oxydations d'hydrocarbures, tels que le cyclohexane par exemple. Ces procédés sont mis en oeuvre en vue de produire des produits d'oxydation intermédiaires respectifs, tels que de l'acide adipique par exemple, et ce, par processus direct. Le catalyseur reste en solution malgré l'extraction de l'eau contenue dans la composition, puisque l'extraction de l'eau est régulée à des températures et des niveaux d'eau restante qui empêchent le catalyseur de précipiter. L'extraction de l'eau est effectuée de préférence avant l'extraction du produit d'oxydation intermédiaire. Ainsi, certaines, et de préférence, toutes les étapes de ce procédé, sont réalisées dans une seule zone à phase liquide.

(57) This invention relates to methods of recycling catalyst in oxidations of hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, by a direct process. The catalyst remains in solution despite removal of water from the composition, since the water removal is controlled at such temperatures and such remaining water levels that prevent catalyst from precipitating. The water removal is preferably conducted before removal of the intermediate oxidation product. Also, preferably, some, and more preferably all steps of the process are conducted in a single liquid phase region.

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<p>(54) Title: METHODS OF RECYCLING CATALYST IN OXIDATIONS OF HYDROCARBONS</p>		
<p>(57) Abstract</p> <p>This invention relates to methods of recycling catalyst in oxidations of hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, by a direct process. The catalyst remains in solution despite removal of water from the composition, since the water removal is controlled at such temperatures and such remaining water levels that prevent catalyst from precipitating. The water removal is preferably conducted before removal of the intermediate oxidation product. Also, preferably, some, and more preferably all steps of the process are conducted in a single liquid phase region.</p>		

METHODS OF RECYCLING CATALYST IN OXIDATIONS OF HYDROCARBONS

TECHNICAL FIELD

This invention relates to methods of recycling catalyst in oxidations of hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, by a direct process.

BACKGROUND OF THE INVENTION

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

acid 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 Oxidation have been conducted in a batch mode, literally or for all practical purposes.

5 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.

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

 U.S. Patent 5,463,119 (Kollar), U.S. Patent 5,374,767 (Drinkard et al.), U.S. Patent 5,321,157 (Kollar), U.S. Patent 3,987,100 (Barnette et al.), U.S. Patent 3,957,876 (Rapoport et al.), U.S. Patent 3,932,513 (Russell), U.S. Patent 3,530,185
15 (Pugi), U.S. Patent 3,515,751 (Oberster et al.), U.S. Patent 3,361,806 (Lidov et al.), U.S. Patent 3,234,271 (Barker et al.), U.S. Patent 3,231,608 (Kollar), U.S. Patent 3,161,603 (Leyshon et al.), U.S. Patent 2,565,087 (Porter et al.), U.S. Patent 2,557,282 (Hamblet et al.), U.S. Patent 2,439,513 (Hamblet et al.), U.S. Patent 2,223,494 (Loder et al.), U.S. Patent 2,223,493 (Loder et al.), German Patent DE 44 26 132 A1 (Kysela et al.),
20 and PCT International Publication WO 96/03365 (Constantini et al.).

 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.

25 SUMMARY OF THE INVENTION

 As aforementioned, this invention relates to methods of recycling catalyst in oxidations of hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, by a direct process. It relates particularly to a method of maintaining catalyst in solution after water removal,

outside a reaction zone, in a process comprising oxidation of a hydrocarbon by a gaseous oxidant to a respective intermediate oxidation product at an operation temperature in the reaction zone containing a mixture comprising the hydrocarbon, the catalyst, the water, a solvent, and an optional initiator, the method comprising
5 sequential steps of:

(a) changing, outside the reaction zone, the operation temperature of the mixture to a second temperature below a precipitation temperature, at which and over which precipitation temperature, the catalyst in the first mixture would precipitate, at least partially, if the water level in the first mixture had been reduced to or under a
10 precipitation water level;

(b) removing an amount of water from the first mixture, but maintaining the water level in the mixture over the precipitation water level at the second temperature;

(c) removing at least part of the intermediate oxidation product; and

15 (d) re-circulating the remaining mixture to the reaction zone.

It is preferable that all steps are conducted at a substantially single liquid phase region.

Step (b) of the method may comprise a step of lowering the second temperature to a third temperature lower than the second temperature, and step (c) may
20 comprise a step selected from a group consisting of centrifuging, filtering, and a combination thereof. Further, step (a) may comprise a step of atomizing the first mixture.

This invention further pertains a method of maintaining catalyst in solution for recycling after water removal, outside a reaction zone, in a process
25 comprising oxidation of a hydrocarbon by a gaseous oxidant to a respective intermediate oxidation product at an operation temperature in the reaction zone containing a mixture comprising the hydrocarbon, the catalyst, the water, a solvent, and an optional initiator, the method comprising steps of:

(e) precipitating at least partially the intermediate oxidation product,
30 while maintaining a single liquid phase;

(f) removing at least part of the precipitated intermediate oxidation product;

(g) removing part of the water at a temperature below a precipitation temperature, at which and over which precipitation temperature, the catalyst in the mixture would precipitate, at least partially, if the water level in the mixture had been reduced to or under a precipitation water level;

(h) maintaining the water level over the precipitation water level; and

(i) recycling at least part of a mixture created in step (h) back to the reaction zone.

10 This invention is particularly applicable in the case that the intermediate oxidation product comprises adipic acid, the hydrocarbon comprises cyclohexane, the catalyst comprises a cobalt compound, the gaseous oxidant comprises oxygen, the solvent comprises acetic acid, and the optional initiator is selected from a group comprising cyclohexanone, cyclohexylhydroperoxide, acetaldehyde, and a mixture
15 thereof.

Further, the instant invention pertains to a method, wherein the intermediate oxidation product comprises a compound selected from a group consisting of adipic acid, phthalic acid, isophthalic acid, and terephthalic acid, and the method further comprises a step of reacting said intermediate oxidation product with a third
20 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.

The method may further comprise a step of spinning the polymer into fibers.

25 It should be noted that reaction products, by-products, and other compounds in the mixture, influence the catalyst precipitation temperature and the precipitation water level. According to this invention, the catalyst precipitation temperature and the precipitation water level are considered in the presence of such moieties in the mixture.

By the term "steady state" it is meant that the reaction has reached an equilibrium, which equilibrium, however, may be adjusted periodically or continuously in order to achieve a desired result. If for example more water is needed in the reaction zone to avoid catalyst precipitation, the water feed rate to the reaction zone may be increased appropriately, and still the reaction may be considered to be at a "steady state." Similarly, if less water is needed to avoid formation of two phases, the water feed rate to the reaction zone may be decreased appropriately, and still the reaction may be considered to be at a "steady state."

The terms "substantially single-phase liquid" and "substantially single liquid phase" are for all practical purposes synonymous for the purposes of this invention. They both intend to indicate that there is no second liquid phase present, while a solid phase may or may not be present. The terms "second phase formation" or "formation of a second phase" refer to a second liquid phase, and not to a solid phase, unless otherwise specified.

The term "level" of an ingredient (reactant, reaction product, catalyst, water, inert matter, or any other type of matter present) includes both "relative level" and "percentage level." According to the instant invention, both methods and devices may perform by using either one or the other type of "levels." In some occasions it may be easier to use one type rather than the other. "Relative level" of an ingredient denotes the amount of the ingredient present in weight units or in volume units, in a reaction zone or in a cell for example, as compared to 100 units, in weight units or in volume units, respectively, of the rest of the ingredients present, or the rest of the ingredients under consideration. The rest of the ingredients present or the rest of the ingredients under consideration, in this case, have a constant ratio with respect to each other. On the other hand, "percentage level" is the level expressed as a percentage based on total amount of all or of a desired number of specific ingredients. The percentages may be expressed also either by weight or by volume.

A controller, preferably a computerized controller, may handle with ease and accuracy either type of "level." Programming a computerized controller to perform such functions is a routine process, well known to the art. According to this invention,

a controller, based on information received, from a reaction zone for example, controls feed rates, temperatures, pressures, and other parameters in order to achieve the desirable results. The controller may also be programmed, by techniques well known to the art, to include flow sheet simulation, which may account for vapor/liquid
5 equilibrium and energy balance effects.

Analytical techniques known to the art may be used for determination of levels of the different ingredients in the miscellaneous streams and chambers, and provide such information to the controller for further processing and action.

10 BRIEF DESCRIPTION OF THE DRAWINGS

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 is a block diagram illustrating a preferred embodiment of the
15 present invention.

Figure 2 illustrates a block diagram of a preferred distillation column, which may be used in conjunction with the reaction chamber or the de-watering chamber or any other appropriate chamber, or a combination thereof. This column is provided with a re-boiler, and is divided into a lower stripper zone and an upper rectifier
20 zone.

DETAILED DESCRIPTION OF THE INVENTION

As aforementioned, this invention relates to methods of recycling catalyst in oxidations of hydrocarbons, such as cyclohexane for example, to respective intermediate oxidation products, such as adipic acid for example, by a direct process.

25 Proper catalyst handling in oxidation reactions has always been a considerable problem in the art. According to the present invention, the process is controlled in a way that water is removed from the system, while catalyst remains in solution for direct recycling or recycling after any desired treatment. This presents

enormous advantages, because the catalyst may be easily and efficiently recycled for repeated utilization.

As aforementioned, 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 0.3 - 10 0.7%.

The above disclosure does not realize that depending on the level of the catalyst or other ingredients in the composition, these water limits may change drastically, and that it is important to examine in each individual case the water level at which the catalyst precipitates and thus stay above this water level. In addition, the 15 disclosure does not realize that the temperature, at which a mixture containing catalyst is maintained, also drastically changes the water level under which catalyst precipitates.

According to the instant invention, both the temperature of the mixture containing the catalyst, and the water level are controlled in coordination, for a predetermined level of catalyst, so that the catalyst remains in solution, in the presence 20 of other moieties, such as products, by-products, etc. In the case that it is desirable to remove the maximum amount of water from the system, the critical water level, at which catalyst precipitates, is determined at the temperature of the mixture containing the catalyst, and the water level is kept above, but close to the critical level. It is preferable that the water level is maintained in a range of 10% to 100% of the critical 25 value, above the critical value. It is more preferable that the water level is maintained in a range of 20% to 50% of the critical value, above the critical value. For example, if the critical water level value (precipitation water level) at the temperature of the mixture containing the catalyst is 0.6% by weight (based on the total mixture containing the catalyst), it is preferable that the water level is maintained in the range of 0.66% to

1.2% by weight, and more preferably, in the range of 0.72% to 0.9% by weight, based on the total mixture containing the catalyst.

It is important to note that if higher removal of water is desired, the temperature of the mixture containing the catalyst may be lowered, and stripping of water may be conducted at that lower temperature. The lower the temperature of the mixture containing the catalyst, the lower the critical level of water (precipitation water level) at which the catalyst precipitates.

According to the disclosure of the aforementioned patent, removal of the water is conducted after cooling the mixture containing the catalyst, separating the mixture into a polar and non-polar phase, decanting the polar phase containing most of the catalyst and precipitated adipic acid, recycling the non-polar phase back to the reaction chamber, removing the adipic acid from the polar phase, adding cyclohexane to the filtered polar phase, heating the mixture, and stripping off water as an azeotrope with the cyclohexane so that the water level moves to the range of 0.3% to 0.7%.

The disclosed process involves many steps, which may be avoided according to a highly preferred embodiment of the instant invention. According to this highly preferred embodiment, the water removal is conducted before the separation of the intermediate oxidation product, such as adipic acid for example, after determining the appropriate temperature at which the mixture containing the catalyst should be at, and after determining the critical water level at which catalyst precipitates at the temperature of the mixture containing the catalyst. The water level is then maintained at preferable levels as discussed earlier. In a preferred mode of the same embodiment, the intermediate oxidation product, such as adipic acid for example, is precipitated by flash crystallization in one or multiple stages, as discussed later, thus avoiding formation of two liquid phases, need for decantation, etc.

For better clarification of this invention, the examples given below assume that the hydrocarbon is cyclohexane, the intermediate oxidation product is adipic acid, the solvent is acetic acid, and the catalyst is a cobalt compound. It should be understood, however, that the teachings of this invention are applicable to different hydrocarbons, intermediate oxidation products, solvents, and catalysts than the ones

used in the examples. Only minor modifications may be needed to fit each individual case.

Referring now to Figure 1, there is depicted a reactor system or device 10, comprising a reaction chamber 12 containing a reaction zone 14. The reactor system or device 10 is only partially shown for demonstrating the components necessary to exemplify the present invention. Miscellaneous treatment, product or by-product separation, recycling, etc. devices, well known to the art, are not shown for purposes of clarity and brevity.

Feeding means (for raw materials, miscellaneous recycled matter, gaseous oxidant, etc.) connected to the reaction chamber 12 are represented by a single feeding line 16 for purposes of clarity and brevity. However, it should be understood that, in practice, a number of individual lines may be used, including if appropriate, devices such as for example mixing vessels, heaters, coolers, etc.

Preferably a first distillation column 18 may also be utilized. The first distillation column 18 is connected at one end to the reaction chamber 12 through lines 16i and 16ii, while at the other end is connected to a first condenser 20 through line 18i. The first condenser 20 is in turn connected to a first decanter 22 through line 20i. The first decanter 22 has a first vent line 22i, a first cyclohexane (or other hydrocarbon) removal line 22ii, and a first water removal line 22iii. Lines 22i and 22ii are connected to valves 22' and 22", respectively. Line 22ii is also connected to line 18ii for recycling cyclohexane to the first distillation column 18.

The reaction chamber 12 is also connected to the de-watering chamber 26 through line 16iii.

A second distillation column 28 is connected at one end to the de-watering chamber 26 through lines 26i and 26ii, while at the other end is connected to a second condenser 30 through line 28i. The second condenser 30 is in turn connected to a second decanter 32 through line 30i. The second decanter 32 has a second vent line 32i, a second cyclohexane (or other hydrocarbon) removal line 32ii, and a second water removal line 32iii. Lines 32i and 32ii are connected to valves 32' (vent valve) and 32"

(hydrocarbon sampling or removal valve), respectively. Line 32ii is also connected to line 28ii for recycling cyclohexane to the second distillation column 28.

The de-watering chamber 26 is also connected through line 26iii to a cooler 36, which in turn is connected to a crystallizer 38 through line 36i. The crystallizer 38 is preferably a flash crystallizer, which uses a pressure reduction line 38i. The pressure reduction (which may go from the operation pressure to any lower pressure, including sub-atmospheric) in the crystallizer, has as a result a substantially instantaneous drop in temperature, which in turn causes solids (such as adipic acid for example) to crystallize and precipitate. Flashing may be conducted in one or more stages. The crystallizer 38 is connected to a solids separator 40 through line 38ii. The crystallized solids are separated and removed from the solids separator 40 through line 40ii, while the remaining liquids are removed through line 40i, for direct recycling or recycling after further treatment.

In place of the de-watering chamber 26, a re-boiler (not shown) may be used at the bottom of column 28, in which case, line 16iii would be connected at a desired point in column 28. Chamber 26 is useful for containing accidentally precipitated catalyst and prevent plugging of the column.

In operation of this embodiment, miscellaneous raw materials and recyclables, including in this example cyclohexane, acetic acid, cobalt compound catalyst, optional initiator (preferably cyclohexanone or acetaldehyde, or a mixture thereof), optionally water, and a gaseous oxidant, preferably comprising oxygen, enter the reaction zone 14, inside the reaction chamber 12, through the feeding means represented by line 16.

The oxidation is preferably brought to a steady state, and preferably the majority or all the heat of reaction is removed by evaporated condensable matter, which exits the reaction chamber 12 as vapors through line 16i, and at least partially returns to the reaction chamber 12 as condensate through line 16ii. In this example, the majority of vapors exiting the reaction chamber 12 are cyclohexane, acetic acid, and water. The column 18 is designed, by techniques well known to the art, in a manner that, for all practical purposes, substantially all the acetic acid in the vapors exiting through line 16i

is condensed in the first column 18 and returns to the reaction chamber 12 through line 16ii. For all practical purposes, the majority of the cyclohexane and substantially all the water in the vapors exiting the reaction chamber 12, pass through the first column 18, are condensed in the condenser 20, and are separated in the decanter 22. The condensed
5 cyclohexane is returned to the top of the column 18 through line 18ii. As the condensed cyclohexane moves downward, it causes condensation of the acetic acid, and they both return to the reaction chamber 12 through line 16ii. An adequate amount of water is preferably recycled, or fresh water added, to the reaction chamber 12, so that the catalyst remains in solution under the operation conditions. At the same time, the
10 amount of water recycled or added should preferably be low enough, so that substantially a single liquid phase is present in the reaction zone 14 of the reaction chamber 12. Formation or existence of a second liquid phase in the reaction zone 14 reduces considerably the reaction rate and reactivity.

Off-gases are removed from line 22i through valve 22'. The majority of
15 off-gases comprises mainly non-condensable gases, usually nitrogen, oxygen, carbon dioxide, carbon monoxide, etc. for example, with minor amounts of condensable matter, comprising for example such vapors as cyclohexane, acetic acid, water, etc. Recycling of gases (not shown) from line 22i to the reaction chamber 12 is many times desirable in order to improve sparging and mixing, to conserve oxygen, to reduce treatment
20 requirements of the final off-gases, etc.

The valve 22" may be used in order to remove a sample, or part of the cyclohexane, if so desired.

The reaction mixture, having reached a steady state at a predetermined operation temperature, pressure, and desired conversion in the reaction zone 14 of the
25 reaction chamber 12, is preferably continuously being removed from line 16iii as a reaction mixture stream. This stream is directed to de-watering means, such as the de-watering chamber 26, for example.

In the case of adipic acid production for example, if the operation temperature in the reaction zone 14 is 100° C for example, the temperature in the de-
30 watering chamber is brought to a temperature preferably in the range of 70 to 90° C.

The temperature in the de-watering chamber 26 is kept in the desired range by provision of heat to it. For example, heat may be provided to the de-watering chamber 26 by heating coils (not shown), inside or outside the de-watering chamber 26, or by circulating at least part of the contents of the chamber 26 through a heater (not shown),
5 or by any other technique well known to the art.

Adding heat to the contents of the de-watering chamber 26 and maintaining the desired temperature is very important in order to continue evaporating cyclohexane, which azeotropically removes water from the contents of the de-watering chamber 26, as the azeotrope passes through the second distillation column 28 in the
10 same manner as already described for the first distillation column 18. The azeotrope of cyclohexane/water is condensed in the condenser 30, and the cyclohexane is separated from the water in the decanter 32. At least part of the cyclohexane is directed back to the to the top of the distillation column 28, and finally returns to the de-watering chamber 26. Removal of cyclohexane, through line 32ii for example, helps in attaining
15 a lower water level in the de-watering chamber 26, at a given temperature, without catalyst precipitation.

More than one de-watering chambers with respective distillation columns, and respective or common condensers and decanters may be used, preferably in series for greater removal of water.

20 A stream containing an amount of water above the critical water level as explained above (and also see comments below) moves through line 26iii to an optional cooler 36. The stream may be cooled down either by the cooler 36, or more preferably by flash crystallization in the crystallizer 38, or both. Flash crystallization is conducted by pressure reduction through line 38i in one or more stages. During the pressure
25 reduction, cyclohexane and/or acetic acid is evaporated from the mixture, causing drastic temperature drop, so that the intermediate oxidation product, adipic acid in this example, precipitates and forms a slurry, which slurry is transferred, preferably continuously, to the solids separator 40. The adipic acid is removed through line 40ii, while the filtrate is removed through line 40i for recycling. The cyclohexane which is
30 removed from line 38i may be condensed, and preferably also be recycled to the

reaction chamber 12 through feeding line 16, with or without pretreatment. The cooler 36 may be used by itself for cooling the mixture or it may be used in conjunction with the flash crystallization process. The cooler 36 may also be part of the crystallizer 38 for further cooling the contents of the crystallizer. Liquid cyclohexane may be introduced to line 36i for cooling in the flash crystallizer 38.

Due to the low content of water in the mixture entering the crystallizer 38, and the removal of cyclohexane in the crystallizer, a second liquid phase is not formed under normal circumstances.

It should be pointed out that some water also evaporates along with the cyclohexane due to the reduced pressure in the crystallizer. The amount of water leaving the system may be found experimentally very easily from the vapor stream in line 38i, or the condensate of the vapors at a later stage, for example. This amount of water, at the operating temperature of the crystallizer 38, has to be taken into account in determining the amount of water to be removed by the second distillation column 28, so that no catalyst precipitates in the crystallizer 38.

In a different embodiment of the instant invention, the intermediate oxidation product, such as adipic acid for example, may be removed before the removal of water. The operation of this embodiment is very similar to the one discussed above. Preferably, the precipitation of the intermediate oxidation product is conducted in a manner that a single liquid phase is maintained, by flash crystallization for example.

In the practice of this invention, on many occasions, it is preferable to use one or more distillation columns of the type shown in Figure 2, which may replace column 18 and/or 28, shown in Figure 1. The distillation columns of this type are well known to the art. They have a stripper zone S and a rectifier zone R, above the stripper zone, as well as a re-boiler section 52, as shown in Figure 5. They are characterized by better separation of the constituents entering the column, although they use more energy due to the additional re-boiler.

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.

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 are artificially intelligent systems (expert systems, neural networks, and fuzzy logic systems, well known to the art). Of the three types of the 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 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 gases may be formed along with the oxidation product, which may be one product or a mixture of products.

Examples include, but of course, are not limited to preparation of $C_5 - C_8$ aliphatic dibasic acids from the corresponding saturated cycloaliphatic hydrocarbons, such as for example preparation of adipic acid from cyclohexane. Examples of aromatic carboxylic acids are benzoic acid, phthalic acid, isophthalic, and acid terephthalic acid, among others.

Regarding adipic acid, the preparation of which is especially suited to the methods and apparatuses 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. Patents 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 to the art techniques, 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
5 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 well known to the art techniques to form fibers.

10 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,
15 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
20 discussion are only speculative and are not intended to narrow the limits of this invention.

CLAIMS

1. A method of maintaining catalyst in solution after water removal, outside a reaction zone, by coordinating temperature with water level, in a process comprising oxidation of a hydrocarbon by a gaseous oxidant to a respective intermediate oxidation product at an operation temperature in the reaction zone containing a mixture comprising the hydrocarbon, the catalyst, the water, a solvent, and an optional initiator, the method characterized by:

either the sequential steps of

(a) changing, outside the reaction zone, the operation temperature of the mixture to a second temperature below a precipitation temperature, at which and over which precipitation temperature, the catalyst in the first mixture precipitates, at least partially, if the water level in the first mixture is reduced to or under a critical precipitation water level;

(b) removing an amount of water from the first mixture, but maintaining the water level in the mixture over the critical precipitation water level at the second temperature;

(c) removing at least part of the intermediate oxidation product;

and

(d) re-circulating the remaining mixture to the reaction zone;

or the steps of

(e) precipitating at least partially the intermediate oxidation product, while maintaining a single liquid phase;

(f) removing at least part of the precipitated intermediate oxidation product;

(g) removing part of the water at a temperature below a precipitation temperature, at which and over which precipitation temperature, the catalyst in the mixture precipitates, at least partially, if the water level in the mixture is reduced to or under a critical precipitation water level;

(h) maintaining the water level over the critical precipitation water level; and

(i) recycling at least part of a mixture created in step (h) back to the reaction zone;

wherein all steps are conducted at a substantially single phase region.

~~2. A method as defined in claim 1, wherein all steps are conducted at a substantially single liquid phase region.~~

2~~2~~. A method as defined in claim 1 ~~or 2~~, wherein step (b) comprises a step of lowering the second temperature to a third temperature lower than the second temperature.

3~~4~~. A method as defined in claim 1~~3~~^{or 2}, wherein step (c) comprises a step selected from a group consisting of centrifuging, filtering, and a combination thereof.

4~~5~~. A method as defined in claim 1-~~4~~³, wherein step (a) comprises a step of atomizing the first mixture.

5~~6~~. A method as defined in claim 1-~~5~~⁴, wherein the intermediate oxidation product comprises adipic acid, the hydrocarbon comprises cyclohexane, the catalyst comprises a cobalt compound, the gaseous oxidant comprises oxygen, the solvent comprises acetic acid, and the optional initiator is selected from a group comprising cyclohexanone, cyclohexylhydroperoxide, acetaldehyde, and a mixture thereof.

6~~7~~. A method as defined in claim ~~6~~⁵, further comprising a step of reacting said 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.

7~~8~~. A method as defined in claim ~~7~~⁶, further comprising a step of spinning the polymer into fibers.

~~8~~⁸. A method as defined in claim 1-~~4~~⁴, wherein the intermediate oxidation product comprises a compound selected from a group consisting of adipic acid, phthalic acid, isophthalic acid, and terephthalic acid, and the method further comprises a step of reacting said intermediate oxidation product 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.

~~9~~⁹~~10~~. A method as defined in claim ~~8~~⁸, further comprising a step of spinning the polymer into fibers.

~~10~~¹⁰~~11~~. A method as defined in claim 1-~~10~~⁹, wherein the water level is maintained in a range of 10% to 100% by weight of the critical precipitation value, above the critical precipitation value at the second temperature.

~~11~~¹¹~~12~~. A method as defined in claim ~~11~~¹⁰, wherein the water level is maintained in a range of 20% to 50% by weight of the critical precipitation value, above the critical precipitation value at the second temperature.

~~12~~¹²~~13~~. A method as defined in claim 1-~~12~~¹¹, wherein the critical precipitation water level is determined at the second temperature before conducting step (b) and/or (h).

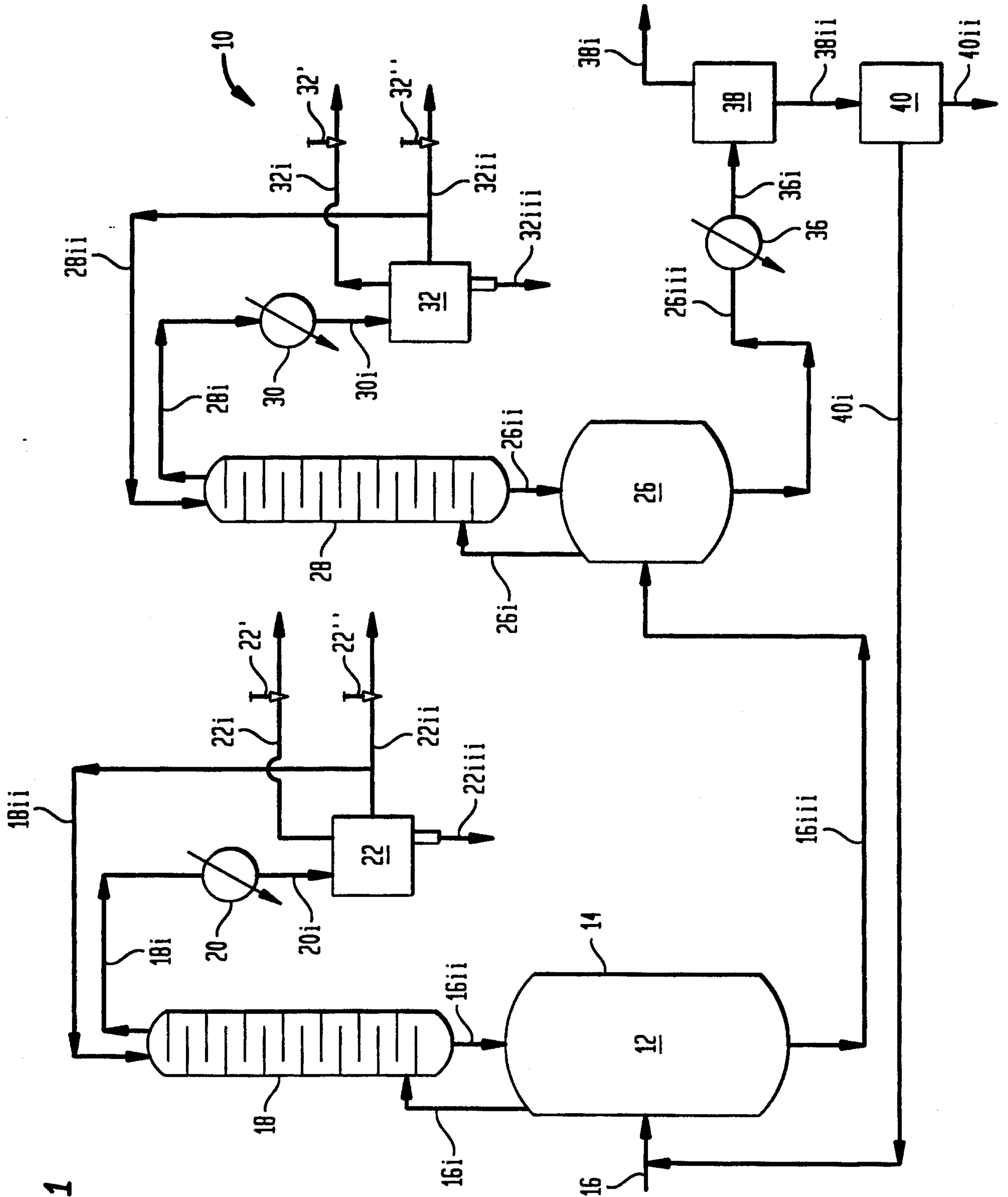


FIG. 1

FIG. 2

