

OXIDATION OF HYDROCARBONS TO ACIDS IN THE PRESENCE OF FLUORO COMPOUNDS

TECHNICAL FIELD

5 This invention relates to methods of making intermediate oxidation products, and especially dibasic acids, by oxidizing a compound selected from group consisting of cyclohexane, o-xylene, m-xylene, p-xylene, and a mixture thereof, under controlled conditions in the presence of a small critical amount of a fluorocompound co-solvent.

10 BACKGROUND OF THE INVENTION

 There is a plethora of references (both patents and literature articles) dealing with the formation of intermediate oxidation products, such as dibasic 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
15 miscellaneous other compounds. Examples of other intermediate oxidation products include, but are not limited to cyclohexanol, cyclohexanone, cyclohexylhydroperoxide, benzoic acid, terephthalic acid, isophthalic acid, phthalic acid, etc.

 There are different processes of manufacturing adipic acid. The conventional process involves a first step of oxidizing cyclohexane with oxygen to a
20 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 initiators or promoters.

25 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

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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.

There are many 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 the plethora of others, may be considered as representative of oxidation processes relative to the preparation of diacids and 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 (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), and PCT International Publication WO 96/03365 (Costantini et al).

The following patents or publications disclose use of fluorocarbons.

WO 9631455 (Costantini et al) discloses the use of strong acids in heterogeneous catalysis of oxidizing hydrocarbons, alcohols, and ketones, leading to acids. Among the solvents, Costantini et al. mention perfluoroalkylcarboxylic acids,

such as trifluoroacetic acid. They also disclose the use of mineral or organic acids, the pKa of which is less than or equal to 3. They further disclose that the addition of a strong acid has the effect of improving kinetics of the reaction and generally its carboxylic acid selectivity. The disclosed content of strong acid in the reaction mixture
5 is in the range of 0-20%.

U.S. Patent 5,585,515 (Camaioni et al.) discloses a method and pathway for selectively oxidizing hydrocarbon compounds, especially in the presence of copper compounds. Camaioni et al. further disclose fully fluorine substituted carboxylic acids, such as trifluoroacetic acid. Other acids may be used such as sulphuric acid,
10 trifluoromethane sulfonic acid, acetic acid, halogenated carboxylic acids, and mixtures thereof.

French Patent FR 2541993 (Costantini et al.) discloses a method for the preparation of adipic acid from cyclohexanone or a mixture of cyclohexanone and cyclohexanol in the presence of Manganese as catalyst at 65 ° C, and in the presence of
15 strong acids, such as for example hydrochloric, hydrobromic, hydroiodic, orthophosphoric, sulfuric, perchloric, iodic, periodic, phosphorous, dichloroacetic, trichloroacetic, trifluoroacetic, difluoroacetic, methane sulfonic, trifluoromethanesulfonic, methylsulfonylacetic, and paratoluenesulfonic acids.

European Publication EP 341163 B1 (Blanchard et al.) discloses a
20 process for the preparation of cyclohexanol by reaction of cyclohexene with water in the presence of a zeolite and a carboxylic acid. Acids suitable for the process are formic, acetic, trifluoroacetic, monochloroacetic, butyric, isobutyric, succinic, glutaric, dodecanedioic, and benzoic. Formic, acetic, and trifluoroacetic are particularly suitable.

French Publication 2744719 (Costantini et al.) discloses decomposition
25 of organic hydroperoxides, such as cyclohexylhydroperoxide, in the presence of heterogeneous catalysts consisting of molecular sieves. Cyclohexylhydroperoxide in decomposition leads to formation of cyclohexanone and cyclohexanol, which in turn may be oxidized to adipic acid. A mobilizing agent, such as hydroxide, fluoride, or amine is especially suitable.

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

5 Our U.S. Patents 5,801,282; 5,580,531; 5,654,475; 5,558,842; and 5,502,245; our co-pending U.S. Patent application Serial No. 08/587,967 (filed 01/17/96), and PCT International publication WO 96/07056, all of which are incorporated herein by reference, describe methods and apparatuses relative to controlling reactions in atomized liquids.

10 Our U.S. Patents 5,824,819; 5,817,868; and 5,801,273; and our co-pending U.S. Patent application Serial Nos. 08/812,847 filed on March 6, 1997; Serial No. 08/824,992, filed on March 27, 1997; 08/861,180, filed on May 21, 1997; 08/861,281, filed on May 21, 1997; 08/861,210, filed on May 21, 1997; 08/876,692, filed on June 16, 1997; 08/900,323, filed on July 25, 1997; 08/931,035, filed on
15 September 16, 1997; 08/932,875, filed on September 18, 1997; 08/934,253, filed on September 19, 1997; 08/989,910, filed on December 12, 1997; 08/986,505 filed December 8, 1997; 60/074,068 filed February 9, 1998; 60/075,257 filed February 19, 1998; 60/086,159 filed May 20, 1998; 60/086,118 filed May 20, 1998; 60/101,918 filed September 24, 1998; 60/086,119 filed May 20, 1998; 60/091,483 filed July 2, 1998;
20 60/093,256 filed July 17, 1998; 60/091,796 filed July 6, 1998; 60/105,048 filed October 20, 1998; 60/111,848 filed December 11, 1998; 60/110,206 filed November 30, 1998; as well as concurrently filed "Methods and Devices for Separating Catalyst from Oxidation Mixtures", (Attorney Docket No. 900105.424, Express Mail No. EM067732648US) and "Methods and Devices for Treating Cobalt Catalyst in
25 Oxidation Mixtures Resulting from Oxidation of Hydrocarbons to Dibasic Acids", (Attorney Docket No. 900105.423, Express Mail No. EM067732722US) are all also incorporated herein by reference.

Each of our following PCT patent applications are also incorporated herein by reference: PCT/US97/10830 filed on June 23, 1997 (WO 97/49485);
30 PCT/US97/12944 filed on July 23, 1997 (WO 98/07677); PCT/US96/07056 filed May

17, 1996 (WO 96/40610); PCT/US97/17684 filed September 30, 1997 (WO 98/19789);
PCT/US97/17812 filed October 2, 1997 (WO 98/27029); PCT/US97/17883 filed
October 3, 1997 (WO 98/20966); PCT/US98/25105 filed December 1, 1998;
PCT/US98/19111 filed September 14, 1998; PCT/US98/14506 filed July 13, 1998;
5 PCT/US98/19099 filed September 16, 1998; and PCT/US98/19057 filed September 14,
1998.

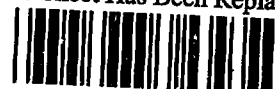
SUMMARY OF THE INVENTION

As aforementioned, the present invention relates to methods and devices
of oxidizing a hydrocarbon, such as cyclohexane for example, to an acid, such as adipic
10 acid for example. More particularly this invention pertains a method of oxidizing a
hydrocarbon selected from a group consisting of cyclohexane, o-xylene, m-xylene, p-
xylene, and a mixture of two or more of o-xylene, m-xylene, and p-xylene, to a
respective acid, in a mixture comprising a solvent and a cobalt catalyst, the method
comprising a step of adding to the mixture an effective amount of a fluorocompound
15 resulting in a rate of increase of reaction rate, preferably at least 5%, as compared to a
rate of increase of reaction rate in the absence of the fluorocompound, without changing
relative oxygen consumption to become lower than 75% of a relative oxygen
consumption observed in the absence of the fluorocompound.

The rate of increase in reaction rate and the relative oxygen consumption
20 are determined as described under the Detailed Description of the Invention

Preferably, the fluorocompound is a perfluorinated compound. More
preferably, the fluorocompound is selected from a group consisting essentially of
fluoroacid, fluoroketone, fluoroalcohol, fluorinated hydrocarbon, and a mixture thereof.
Still more preferably, the fluorocompound is a fluoroacid comprising 2 to 22 carbon
25 atoms. Even more preferably, the fluorocompound is a perfluoroacid comprising 2 to
22 carbon atoms. Examples of such perfluoroacids are perfluoroacetic acid,
perfluoropropionic acid, perfluorobutyric acid, perfluoropentanoic acid,
perfluorohexanoic acid, perfluoroheptanoic acid, etc.

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It is preferable that the perfluoroacid is perfluoroacetic acid, and it is added to the single-phase liquid mixture in an in a level within the range of 0.1 to 4% by weight.

The perfluoroacid may also be selected from a group consisting essentially of perfluorobutyric acid, perfluorooctanoic acid, and a mixture thereof. Perfluorobutyric acid may be preferable from a downstream processing point of view.

Preferably, perfluoroacids having more than two carbon atoms are introduced at a level of 1 to 5% by weight.

This invention is particularly applicable in the case that the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

The reaction mixture may also contain an initiator, which preferably is cyclohexanone or acetaldehyde. Other initiators may also be used, including ketones, such as methylethylketone for example, peroxides, etc.

The respective acid, in other examples of the present invention, may comprise a compound selected from a group consisting of adipic acid, phthalic acid, isophthalic acid, and terephthalic acid, and the method may further comprise a step of reacting said respective acid 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. The method may further comprise a step of spinning the polymer into fibers or making composites.

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".

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The terms "substantially single-phase liquid", "substantially single liquid phase", "single liquid phase", and "single phase" are for all practical purposes synonymous for the purposes of this invention. They all 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 or gaseous phase, unless otherwise specified.

The term "level" of an ingredient (reactant, reaction product, inert matter, solvent, or any other type of matter present) is given as a percentage by weight.

Selectivity to an acid is the mole percent of the acid in a mixture of other major acids. For example, the selectivity to adipic acid in the direct oxidation of cyclohexane is the mole percent level of adipic acid in the total moles of adipic acid, plus moles of glutaric acid, plus moles of succinic acid.

Reaction rate of hydrocarbon is defined as the rate of moles of hydrocarbon oxidized per unit of time. Similarly, reaction rate of oxidant is defined as the rate of moles of oxidant reacted per unit of time. For all practical purposes, the two reaction rates may be assumed to be proportional to each other, and also proportional to the pressure drop in a closed reactor in which no matter is entering or exiting.

Reactivity is defined as the reaction rate divided by the volume of the reaction mixture.

Rate of increase of the reaction rate is measured by the tangent at the ascending portion of a curve having dP/dt as the Y-axis and time as the X-axis. Therefore it is $dP/(dt)^2$, and can be expressed as psig/min^2 . An example of such a tangent is tangent 53.1 in Figure 1.

A controller, preferably a computerized controller, may handle with ease and accuracy the operation of this invention. 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 desired results. The controller may also be pre-programmed, by well known to the art techniques, to include flow sheet simulation, which may account for



vapor/liquid equilibrium and energy balance effects. A preferable type of controller is a computerized controller; and more preferably a "learning computer" or a "neuro-computer", the functionality of which is known to the art, and which collects information from different places of the device (for example pressure, temperature, chemical or other analysis, etc.), stores this information along with the result (reaction rate, 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.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIGURE 1 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, wherein the curve is characterized by an ascending portion, a tangent to the ascending portion, the inclination (psig/min^2) of which represents the rate of increase of the reaction rate, and a maximum followed by a descending portion.

FIGURE 2 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, with and without adding different amounts of perfluoroacetic acid into the reaction mixture.

FIGURE 3 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, with and without adding different smaller amounts of perfluoroacetic acid than in the case of Figure 2.

FIGURE 4 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, with and without adding perfluorooctanoic acid into the reaction mixture.

FIGURE 5 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, with and without adding different amounts of perfluorobutyric acid into the reaction mixture.



FIGURE 6 illustrates a curve of pressure change vs. time in a batch reactor during oxidation of cyclohexane to adipic acid, with and without adding perfluorononane or perfluoroacetophenone in the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

5 As mentioned earlier, this invention relates to methods of making dibasic acids, by oxidizing a hydrocarbon with a gas containing an oxidant, preferably oxygen.

It was found by the inventors that addition of critical amounts of fluorocompounds in the reaction mixture during the oxidation of hydrocarbons, such as cyclohexane and xylenes, in the presence of cobalt catalyst to form the respective
10 dibasic acids, may increase the reaction rate without hurting selectivity, yield, and/or control of the reaction.

Although only continuous systems are of practical importance for the production of dibasic acids, as compared to batch reactors, it was found by the inventors that a mini-reactor may be used to determine the limits within which a fluorocompound
15 may be utilized beneficially in a continuous system which is run under steady conditions.

Two critical parameters are related to the above mentioned limits, and are determined with the mini-reactor described below. The first parameter is the rate at which the initial reaction rate increases after initiation of the reaction and before it
20 reaches a maximum value. The second parameter is the consumption of oxidant; oxygen in this case.

It is evident that in a continuous reactor system under steady conditions, these two parameters cannot be measured. However, it was found that the two critical parameters may be determined easily, using the mini-reactor described below, and
25 utilized to efficiently and effectively run any continuous reactor system under steady state conditions.

A tubular rocking mini-reactor containing steel balls is used for the determinations. The steel balls are added to provide highly enhanced surface factor by means of distributing a thin film on the surface of the steel balls. Surface factor is



defined in this case as the ratio of the surface of the liquid/gas interface per unit volume of the liquid. The mini-reactor comprises a tubular stainless steel body having an inside diameter of $23/32$ ", an outside diameter of $2\frac{1}{4}$ ", an outside length of about $11\frac{1}{2}$ ", and an inside length of about $9\frac{1}{2}$ ". The total capacity of the mini-reactor is 75 cc. 890

5 stainless steel balls having a diameter of $1/8$ " are used in the mini-reactor as agitation and mixing means, along with a rocking action of ± 33 degrees from horizontal at a frequency of 10 cycles per minute. The mini-reactor has a screw cap top, a number of thermocouples inside and outside for measuring and controlling the temperature. It is surrounded by heating tape, and insulated by glass fiber. It has ports for feeding gases

10 and liquids. It is also provided with a pressure transducer. Both temperature and pressure are recorded and controlled through a computer using supervisory control software.

For the operation of the mini-reactor, the following procedure is followed. The system is initially purged with nitrogen, and the feed (6-6.5 grams) is

15 added through a port in the top of the mini-reactor which is in an upright position. The mini-reactor is then capped and purged again with nitrogen to a pressure of about 50 psig, the temperature is raised to 100°C , the pressure is brought to 100 psig with nitrogen, and the oxygen is introduced to a pressure of an additional 100 psig, thus bringing the total pressure to substantially 200 psig. The pressure (P) and the rate of

20 pressure drop (dP/dt), among other variables are then recorded. Since dP/dt follows a parallel path to the path of the reaction rate, dP/dt represents the reaction rate for all practical purposes. Unless no substantial reaction takes place, the dP/dt follows a curve from substantially zero rate to a maximum through an ascending portion of the curve, and then it drops off again to substantially zero rate on a descending portion of the

25 curve. Oxygen is incrementally added during the period of the ascending portion of the curve, and oxygen feeding is stopped soon after the maximum on the curve has been passed. The increments of oxygen are then added. An initial sharp peak preceding the ascending portion of the curve is disregarded, as it is believed to correspond to a fast oxidation of the initiator, such as acetaldehyde for example. In the case that

30 cyclohexanone is used as initiator, such a preceding peak is not as sharp or pronounced.



Although the terms "promoter" and "initiator" are many times used in the literature and in this work interchangeably to mean "initiator", the more strict meaning of the term "initiator" should be used for a substance which decreases the reaction initiation period, such as acetaldehyde or cyclohexanone, or methylethylketone, for example, and the term "promoter" should be used for a substance that promotes the reaction, such as bromide ions in the case of producing terephthalic acid from p-xylene, for example.

The mini-reactor was used to run a series of experiments for determining the two important parameters mentioned above, and for demonstrating the instant invention. The procedures presented above were followed. The feed solutions for the mini-reactor in the miscellaneous cases are shown in Tables 1 to 13. The increments of oxygen additions and oxygen consumption are shown in Tables 1A to 13A.

Referring now to Figure 1, there is depicted a curve 10 produced by an oxidation as described above. The feed solution in this case is given in Table 1, and the oxygen additions and consumption are given in Table 1A. Curve 10 is a plot of oxidation rate in terms of dP/dt (psig/min) versus time that the reaction takes place.

The initial sharp peak 52.1 is due to an abrupt oxidation of the initiator, acetaldehyde. The Curve 10 has an ascending portion 54.1, a maximum 55.1, and a descending portion 56.1. The tangent 53.1 to the ascending portion 54.1, given in this case in psig/min^2 , is a measure of the rate of increase of the reaction rate observed within the ascending portion 54.1, in a batch reactor. In other words it is the tangent of the angle formed by the line 53.1 and the Time axis. The value of the tangent 53.1, as measured in the batch system, provides the potential for an increased or decreased steady state reaction rate in the case of a respective continuous reactor. The higher the value of the tangent, as measured in the batch reactor, the higher the reaction rate at a steady state in a continuous reactor, and vice versa. Also the higher the maximum 55.1, the higher the reaction rate at a steady state in a continuous reactor, and vice versa.

In addition to the above requirement, it is critical that the rate of increase of the reaction rate by the addition of the fluorocompound, and preferably



perfluoroacid, is preferably at least 5% higher than the one observed in the absence of the fluorocompound. At increases less than 5%, any benefits received are small.

The curve of Figure 1 was used as a control to be compared to respective curves obtained with addition of additives, and in order to evaluate different compositions containing fluorocompounds, and especially perfluoroacids.

Although the present state of the art claims that strong acids in general improve the kinetics of an oxidation, the inventors have found no appreciable benefit, except for the case of perfluoroacids, which are strong acids. Not only that, but it was found by the inventors that the perfluoroacids have to be at a critical range of levels in order to provide substantial benefits. Outside this range, the reaction control suffers when compared to the composition, that does not contain the additive.

In the case of the curve 10 in Figure 1, the relative oxygen consumption (measured as total psig drop) during the reaction was 267 psig (see Table 1A). Further, the curve 10 has a gradual and smooth transition from the ascending portion 54.1 to the maximum 55.1, to the descending portion 56.1, and then to its substantially zero value 58.1. The maximum was 4 psig/min. The selectivity to adipic acid was 84%.

Curve 12 in Figure 2 (see also Tables 2 and 2A) represents a composition containing 7% perfluoroacetic acid. This curve is characterized by a high initiator peak 52.2 and an excessively fast rate increase of the reaction rate at the ascending portion 54.2 of curve 12. This condition fulfills the requirement of the present invention regarding the rate increase of the reaction rate. However, the relative oxygen consumption in this case was 140 psig, which is considerably lower than 200 psig (75% of 267 psig of curve 10, which represents the same composition of the reaction mixture in the absence of the fluorocompound). This shows that the level of perfluoroacetic acid of at least 7% does not fall within the beneficial range of the present invention, despite the fact that the selectivity to adipic acid was 82%. Control of the reaction would suffer substantially in a continuous system under steady state conditions. Suffering of control of the reaction is also indicated by the excessively fast rate increase of the reaction rate at the ascending portion 54.2 of curve 12. It should be noted that the perfluoroacetic acid was injected into the reactor after the initiation had



started. In all other cases, discussed hereinbelow, the fluorocompound was in the feed itself.

Curve 14 in Figure 2 (see also Tables 3 and 3A) represents a composition containing 3.2% perfluoroacetic acid. This curve is also characterized by a high initiator peak 52.3 and a very fast reaction rate at the ascending portion 54.3 of curve 14. It has a very long initiation (about 1.5 hours). It should be noted that there was no incremental addition of oxygen during the reaction, so that oxygen depletion took over and minimized the conversion to 92 psig. One can also see that if oxygen had been added as in the other cases, the curve would have a higher maximum 55.3, and certainly considerably higher relative oxygen consumption. The selectivity to adipic acid was 76%. This low value is probably due to the long initiation period (about 1.5 hours). It might also be due to low conversion after the initiation period due to oxygen depletion, which might have prevented intermediates from oxidizing completely to adipic acid.

Curve 16 in Figure 3 (see also Tables 4 and 4A) represents a composition containing 1.3% perfluoroacetic acid. This curve is also characterized by a very fast reaction rate 53.4 (as compared to 53.1) at the ascending portion 54.4 of curve 16. It had a very short initiation period. It has a considerably higher maximum 55.4 (6 vs. 4 psig/min of the control). The relative oxygen consumption was 262.8 psig, well within the limits of the instant invention. The selectivity to adipic acid was 84%.

Curve 18 in Figure 3 (see also Tables 5 and 5A) represents a composition containing 0.3% perfluoroacetic acid. This curve is also characterized by a fast reaction rate 53.5 (as compared to 53.1) at the ascending portion 54.5 of curve 18. It had a very short initiation period. It has a higher reaction rate maximum 55.5 (4.7 vs. 4 psig/min of the control). The relative oxygen consumption was 275.2 psig, well within the limits of the instant invention.. The selectivity to adipic acid was 84%.

The conclusion after the comparison of the control with the same composition at different levels of added perfluoroacetic acid is that there is a critical region between 0.1 and 4% by weight within which the perfluoroacetic acid provides an overall beneficial effect without sacrificing the selectivity. Further, in the case of levels



of perfluoroacetic acid higher than 4, and even more higher than 7, the control of the reaction becomes difficult due to the very steep ascending and descending portions. It takes only minute changes to activate the destructive consequences of a high tendency for formation of a second liquid phase.

5 Curve 20 in Figure 4 (see also Tables 6 and 6A) represents a composition containing 2.5% perfluorooctanoic acid. Again the inclination of the tangent 53.6 of the ascending portion 54.6 is considerably higher than the control's inclination of the tangent 53.1 of the ascending portion 54.1. In addition, the maximum 55.6 of the curve 20 is considerably higher than the maximum 55.1 of the control curve
10 10 (7 versus 4 psig of the control). The relative oxygen consumption was 302 psig, as compared to 266 psig in the case of the control, and therefore well within the limits of the present invention. The selectivity to adipic acid was 83%.

 Curve 20' in Figure 4 (see also Tables 7 and 7A) represents a composition containing 6.4% perfluorooctanoic acid, run at 90° C. The inclination of
15 the curve 20' has started deteriorating, mainly because of the lower temperature at which the reaction was conducted. This indicates that the temperature should be certainly higher than 80° C, and preferably higher than 90° C. Generally, temperatures between 95° C and 105° C, are most preferable in the oxidation of cyclohexane to adipic acid, although temperatures as high as 120-150° C may also be used in certain
20 occasions. The total oxygen consumed was 268 psig, as compared to 266 psig in the case of the control. The selectivity to adipic acid was 84%.

 Curves 22, 24, and 26 in Figure 5 (see also Tables 8, 8A; 9, 9A; and 10, 10A) correspond to compositions containing 4.05%, 3.13%, and 2.35% perfluorobutyric acid, respectively. One can observe that all three curves have rate increases of reaction
25 rates, as well as maxima considerably higher than those of the control. Curve 24 has the highest maximum. It is worth noting that the level (3-13%) of perfluorobutyric acid in the composition corresponding to curve 34 is between the levels (4.05% and 2.35%) of the compositions corresponding to the other two curves 22 and 26. The selectivity to adipic acid was 82%, 84%, and 84% for the compositions corresponding to curves 22,
30 24, and 26, respectively. The oxygen consumption was 218, 215 and 243, respectively.

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The above data place these levels of perfluorobutyric acid well within the requirements of the present invention. It is believed by the inventors that a level in the range of 1.2% to 1.7% perfluorobutyric acid in the composition would bring the maximum closer to that of the control, with a lower rate of increase of the reaction rate, and an increase of
5 the amount of relative oxygen consumption.

Curves 28 and 30 in Figure 6 (see also Tables 11, 11A; and 12, 12A) correspond to compositions containing 4.94% perfluorononane and 6.03% perfluoroacetophenone, respectively. Both have maxima and rate of increase of the reaction rate moderately higher than that of the control. However, the relative oxygen
10 consumption was considerably higher than that of the control (347 psig and 359 psig, respectively, as compared with 267 psig in the case of the control). The selectivity to adipic acid was in both cases 82%. The above data place these levels of perfluorononane and perfluoroacetophenone well within the requirements of the present invention.

15 The addition of the fluorocompound at the desired levels may be done by direct feeding to the reactor, or through recycled streams, or a combination thereof.



TABLE 1.

Control containing no fluorocompound (Curve 10 in Figures 1-6)

Feed Solution	wt %	g	millimoles
Cyclohexane	40.45%	2.427	28.841
Acetaldehyde	0.35%	0.021	0.471
Acetic Acid	54.98%	3.300	54.948
Cobalt Acetate Tetrahydrate	3.98%	0.239	0.960
Water	0.24%	0.014	0.791

5

TABLE 1A.

Oxygen charges and consumption in composition of Table 1 (Curve 10 in Figures 1-6)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.3	201.2			100.9
1st oxygen addition	180.1	205.5		21.1	25.4
2nd oxygen addition	185.3	213.4		20.2	28.1
3rd oxygen addition	189.9	215.3		23.5	25.4
4th oxygen addition	195.0	217.8		20.3	22.8
5th oxygen addition	199.6	226.9		18.2	27.3
6th oxygen addition	204.1	230.4		22.8	26.3
7th oxygen addition	206.8	238.6		23.6	31.8
8th oxygen addition	215.1	242.0		15.3	26.9
9th oxygen addition	220.8	246.8		17.8	26.0
Final oxygen reading	154.8			83.8	
Total oxygen added and consumed (psig):				266.6	340.9
Total oxygen added and consumed (millimoles):				32.695	41.783

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TABLE 2.

Composition containing 7% trifluoroacetic acid (Curve 12 in Figure 2)

Feed Solution	wt %	g	millimoles
Cyclohexane	37.55%	2.439	28.982
Acetaldehyde	0.32%	0.021	0.473
Acetic Acid	51.22%	3.327	55.397
Cobalt Acetate Tetrahydrate	3.71%	0.241	0.968
Water	0.22%	0.014	0.797
Perfluoroacetic Acid	6.98%	0.453	3.974
Total In	100.00%	6.495	90.592

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TABLE 2A.

Oxygen charges and consumption in composition of Table 2 (Curve 12 in Figure 2)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	101.7	201.3			99.6
1st oxygen addition	175.2	211.5		26.1	36.3
perfluoroacetic acid addition	194.9	210.5		16.6	
2nd oxygen addition	190.1	229.3		20.4	39.2
3rd oxygen addition	200.3	241.8		29.0	41.5
4th oxygen addition	210.1	250.5		31.7	40.4
Final oxygen reading	234.5			16.0	
Total oxygen added and consumed (psig):				139.8	257.0
Total oxygen added and consumed (millimoles):				17.015	31.279

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TABLE 3.

Composition containing 3.2% perfluoroacetic acid (Curve 14 in Figure 2)

Feed Solution	wt %	g	millimoles
Cyclohexane	38.82%	2.399	28.499
Acetaldehyde	0.33%	0.020	0.465
Acetic Acid	53.52%	3.307	55.072
Cobalt Acetate Tetrahydrate	3.88%	0.240	0.962
Water	0.23%	0.014	0.792
Perfluoroacetic Acid	3.22%	0.199	1.745
<i>Total In</i>	100.00%	6.179	87.537

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TABLE 3A.

Oxygen charges and consumption in composition of Table 3 (Curve 14 in Figure 2)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂	O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.4	199.9		99.5
1st oxygen addition	117.5	226.6	82.4	109.1
Final oxygen reading	216.9		9.7	
Total oxygen added and consumed (psig):			92.1	208.6
Total oxygen added and consumed (millimoles):			11.267	25.519

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TABLE 4.

Composition containing 1.3% perfluoroacetic acid (Curve 16 in Figure 3)

Feed Solution	wt %	g	millimoles
Cyclohexane	39.87%	2.443	29.029
Acetaldehyde	0.34%	0.021	0.474
Acetic Acid	54.35%	3.330	55.459
Cobalt Acetate Tetrahydrate	3.94%	0.241	0.969
Water	0.23%	0.014	0.798
Perfluoroacetic Acid	1.27%	0.078	0.684
Total In	100.00%	6.128	87.413

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TABLE 4A.

Oxygen charges and consumption in composition of Table 4 (Curve 16 in Figure 3)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.6	201.6			101.0
1st oxygen addition	180.2	206.4		21.4	26.2
2nd oxygen addition	185.3	211.4		21.1	26.1
3rd oxygen addition	189.8	217.0		21.6	27.2
4th oxygen addition	194.9	223.5		22.1	28.6
5th oxygen addition	195.7	229.7		27.8	34.0
6th oxygen addition	196.0	233.2		33.8	37.3
7th oxygen addition	204.8	242.8		28.4	38.0
Final oxygen reading	156.2			86.6	
Total oxygen added and consumed (psig):				262.8	318.4
Total oxygen added and consumed (millimoles):				44.567	42.434

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TABLE 5.

Composition containing 0.3% perfluoroacetic acid (Curve 18 in Figure 3)

Feed Solution	wt %	g	millimoles
Cyclohexane	40.04%	2.424	40.371
Acetaldehyde	0.34%	0.021	0.246
Acetic Acid	55.05%	3.332	75.652
Cobalt Acetate Tetrahydrate	3.99%	0.241	0.970
Water	0.24%	0.014	0.799
Perfluoroacetic Acid	0.34%	0.021	0.181
Total In	100.00%	6.054	118.219

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TABLE 5A.

Oxygen charges and consumption in composition of Table 5 (Curve 18 in Figure 3)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.8	199.9			99.1
1st oxygen addition	180.3	206.0		19.6	25.7
2nd oxygen addition	185.4	218.0		20.6	32.6
3rd oxygen addition	195.2	215.8		22.8	20.6
4th oxygen addition	200.3	225.2		15.5	24.9
5th oxygen addition	205.1	231.0		20.1	25.9
6th oxygen addition	210.4	236.5		20.6	26.1
7th oxygen addition	215.4	242.6		21.1	27.2
8th oxygen addition	218.6	247.8		24.0	29.2
9th oxygen addition	225.5	251.8		22.3	26.3
Final oxygen reading	154.0			88.6	
Total oxygen added and consumed (psig):				275.2	337.6
Total oxygen added and consumed (millimoles):				33.701	41.342

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TABLE 6.

Composition containing 2.5% perfluorooctanoic acid (Curve 20 in Figure 4)

Feed Solution	wt %	g	millimoles
Cyclohexane	39.72%	2.445	29.053
Acetaldehyde	0.34%	0.021	0.474
Acetic Acid	53.37%	3.286	54.717
Cobalt Acetate Tetrahydrate	3.87%	0.238	0.956
Water	0.23%	0.014	0.787
Perfluorooctanoic Acid	2.47%	0.152	0.367

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TABLE 6A.

Oxygen charges and consumption in composition of Table 6 (Curve 20 in Figure 4)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.7	200.8			100.1
1st oxygen addition	177.1	231.8		23.7	54.7
2nd oxygen addition	190.2	215.5		41.6	25.3
3rd oxygen addition	193.2	222.3		22.3	29.1
4th oxygen addition	195.3	232.8		27.0	37.5
5th oxygen addition	202.3	231.8		30.5	29.5
6th oxygen addition	210.8	245.5		21.0	34.7
7th oxygen addition	220.5	244.3		25.0	23.8
8th oxygen addition	225.2	251.1		19.1	25.9
Final oxygen reading	159.5			91.6	
Total oxygen added and consumed (psig):				301.8	360.6
Total oxygen added and consumed (millimoles):				36.913	44.093

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TABLE 7.

Composition containing 6.4% perfluorooctanoic acid, run at 90° C

(Curve 20' in Figure 4)

Feed Solution	wt %	g	millimoles
Cyclohexane	36.52%	2.321	27.579
Acetaldehyde	1.75%	0.111	2.520
Acetic Acid	51.38%	3.265	54.379
Cobalt Acetate Tetrahydrate	3.72%	0.237	0.950
Water	0.22%	0.014	0.782
Perfluorooctanoic Acid	6.42%	0.408	0.985
Total In	100.00%	6.356	86.210

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TABLE 7A.

Oxygen charges and consumption in composition of Table 7 (Curve 20' in Figure 4)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	102.0	202.7			100.7
1st oxygen addition	180.7	209.7		22.0	29.0
2nd oxygen addition	185.5	210.0		24.2	24.5
3rd oxygen addition	191.0	215.9		19.0	24.9
4th oxygen addition	192.2	221.5		23.7	29.3
5th oxygen addition	199.4	233.6		22.1	34.2
6th oxygen addition	210.8	237.4		22.8	26.6
7th oxygen addition	216.2	240.6		21.2	24.4
8th oxygen addition	220.9	246.4		19.7	25.5
Final oxygen reading	152.4			94.0	
Total oxygen added and consumed (psig):				268.7	319.1
Total oxygen added and consumed (millimoles):				33.683	39.960

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TABLE 8.

Composition containing 4.05% perfluorobutyric acid (Curve 22 in Figure 5)

Feed Solution	wt %	g	millimoles
Cyclohexane	37.22%	2.359	28.032
Acetaldehyde	1.78%	0.113	2.561
Acetic Acid	52.89%	3.353	55.830
Cobalt Acetate Tetrahydrate	3.83%	0.243	0.975
Water	0.23%	0.014	0.803
Perfluorobutyric Acid	4.05%	0.257	1.201
Total In	100.00%	6.339	88.202

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TABLE 8A.

Oxygen charges and consumption in composition of Table 8 (Curve 22 in Figure 5)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	101.5	202.1			100.6
1st oxygen addition	180.4	209.8		21.7	29.4
2nd oxygen addition	185.1	212.5		24.7	27.4
3rd oxygen addition	190.3	216.8		22.2	26.5
4th oxygen addition	195.2	223.2		21.6	28.0
5th oxygen addition	199.4	229.6		23.8	30.2
6th oxygen addition	205.4	231.8		24.2	26.4
Final oxygen reading	152.4			79.4	
Total oxygen added and consumed (psig):				217.6	268.5
Total oxygen added and consumed (millimoles):				26.544	32.753

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TABLE 9.

Composition containing 3.13% perfluorobutyric acid (Curve 24 in Figure 5)

Feed Solution	wt %	g	millimoles
Cyclohexane	38.14%	2.378	28.259
Acetaldehyde	1.82%	0.114	2.582
Acetic Acid	52.85%	3.295	54.871
Cobalt Acetate Tetrahydrate	3.83%	0.239	0.959
Water	0.23%	0.014	0.790
Perfluorobutyric Acid	3.13%	0.195	0.911
Total In	100.00%	6.235	87.460

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TABLE 9A.

Oxygen charges and consumption in composition of Table 9 (Curve 24 in Figure 5)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.9	202.4			101.5
1st oxygen addition	180.6	206.4		21.8	25.8
2nd oxygen addition	183.7	211.7		22.7	28.0
3rd oxygen addition	190.3	216.5		21.4	26.2
4th oxygen addition	193.5	220.1		23.0	26.6
5th oxygen addition	200.6	228.6		19.5	28.0
6th oxygen addition	205.4	231.3		23.2	25.9
Final oxygen reading	147.6			83.7	
Total oxygen added and consumed (psig):				215.3	262.0
Total oxygen added and consumed (millimoles):				26.303	32.009

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TABLE 10.

Composition containing 2.35% perfluorobutyric acid (Curve 26 in Figure 5)

Feed Solution	wt %	g	millimoles
Cyclohexane	38.01%	2.356	27.998
Acetaldehyde	1.82%	0.113	2.558
Acetic Acid	53.70%	3.329	55.443
Cobalt Acetate Tetrahydrate	3.89%	0.241	0.969
Water	0.23%	0.014	0.798
Heptafluoro Butyric Acid	2.35%	0.146	0.682
Total In	100.00%	6.200	87.766

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TABLE 10A.

Oxygen charges and consumption in composition of Table 10 (Curve 26 in Figure 5)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	100.1	202.8			102.7
1st oxygen addition	180.1	209.7		22.7	29.6
2nd oxygen addition	185.9	211.0		23.8	25.1
3rd oxygen addition	187.4	217.0		23.6	29.6
4th oxygen addition	193.4	232.5		23.6	39.1
5th oxygen addition	198.1	236.8		34.4	38.7
6th oxygen addition	209.9	237.8		26.9	27.9
Final oxygen reading	149.8			88.0	
Total oxygen added and consumed (psig):				243.0	292.7
Total oxygen added and consumed (millimoles):				29.687	35.758

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TABLE 11.

Composition containing 4.9% perfluorononane (Curve 28 in Figure 6)

Feed Solution	wt %	g	millimoles
Cyclohexane	37.39%	2.395	28.452
Acetaldehyde	0.32%	0.020	0.465
Acetic Acid	53.27%	3.412	56.818
Cobalt Acetate Tetrahydrate	3.86%	0.247	0.993
Water	0.23%	0.015	0.818
Perfluoro Nonane	4.94%	0.316	0.648
Total In	100.00%	6.405	87.545

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TABLE 11A.

Oxygen charges and consumption in composition of Table 11 (Curve 28 in Figure 6)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	99.0	198.9			99.9
1st oxygen addition	181.0	225.4		17.9	44.4
2nd oxygen addition	191.0	231.8		34.4	40.8
3rd oxygen addition	196.2	235.3		35.6	39.1
4th oxygen addition	203.0	231.5		32.3	28.5
5th oxygen addition	211.0	249.9		20.5	38.9
6th oxygen addition	221.0	254.9		28.9	33.9
7th oxygen addition	224.4	251.2		30.5	26.8
8th oxygen addition	228.1	254.2		23.1	26.1
9th oxygen addition	230.2	270.8		24.0	40.6
Final oxygen reading	171.3			99.5	
Total oxygen added and consumed (psig):				346.7	419.0
Total oxygen added and consumed (millimoles):				42.222	51.067

TABLE 12.

Composition containing 6.0% perfluoroacetophenone (Curve 30 in Figure 6)

Feed Solution	wt %	g	millimoles
Cyclohexane	37.85%	2.422	28.782
Acetaldehyde	0.32%	0.021	0.470
Acetic Acid	51.82%	3.316	55.227
Cobalt Acetate Tetrahydrate	3.76%	0.240	0.965
Water	0.22%	0.014	0.795
Perfluoroacetophenone	6.03%	0.386	1.462
Total In	100.00%	6.400	86.238

TABLE 12A.

5 Oxygen charges and consumption in composition of Table 12 (Curve 30 in Figure 6)

Oxygen Charges & Consumption Profiles (psig)	Before O ₂	After O ₂		O ₂ Consumed	O ₂ Added
Initial oxygen charge	99.5	200.4			100.9
1st oxygen addition	180.3	207.3		20.1	27.0
2nd oxygen addition	185.4	210.5		21.9	25.1
3rd oxygen addition	190.2	214.4		20.3	24.2
4th oxygen addition	142.4	240.4		72.0	98.0
5th oxygen addition	220.3	249.3		20.1	29.0
6th oxygen addition	224.9	251.0		24.4	26.1
7th oxygen addition	230.5	258.7		20.5	28.2
8th oxygen addition	238.7	261.8		20.0	23.1
9th oxygen addition	240.4	260.7		21.4	20.3
10th oxygen addition	244.8	270.9		15.9	26.1
Final oxygen reading	170.0			100.9	
Total oxygen added and consumed (psig):				357.5	428.0
Total oxygen added and consumed (millimoles):				43.557	52.157

Analysis of the products of reaction was conducted by HPLC, GC, MS, all being well known techniques to the art.

Although the 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 for controlling one or more functions.

Oxidations according to this invention, are non-destructive oxidations, wherein the oxidation product is different than carbon monoxide, carbon dioxide, and a mixture thereof. 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.

Examples include, but of course, are not limited to preparation of $C_3 - C_8$ aliphatic dibasic acids from the corresponding saturated cycloaliphatic hydrocarbons, such as for example preparation of adipic acid from cyclohexane. Other examples include, but are not limited to formation of benzoic acid, phthalic acid, isophthalic acid, and terephthalic acid from toluene, ortho-xylene, meta-xylene, and para-xylene, respectively.

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 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. Also, the polymer may be combined with other polymers, fillers, extenders, etc., well known to the art for making miscellaneous composites.

Regarding adipic acid, the preparation of which is especially suited to the methods and devices 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.

Examples demonstrating the operation of the instant invention have been
5 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. Furthermore, any attempted explanations in the
10 discussion are only speculative and are not intended to narrow the limits of the claims
of this invention.

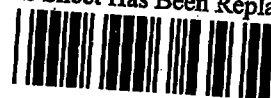


CLAIMS

What is claimed is:

1. A method of oxidizing a hydrocarbon selected from a group consisting of cyclohexane, o-xylene, m-xylene, p-xylene, and a mixture of two or more of o-xylene, m-xylene, and p-xylene, to a respective acid, in a mixture comprising a solvent and a cobalt catalyst, the method comprising a step of adding to the mixture an effective amount of a fluorocompound to increase reaction rate as compared to a reaction rate in the absence of the fluorocompound, without changing relative oxygen consumption to become lower than 75% of a relative oxygen consumption observed in the absence of the fluorocompound.
2. A method as defined in claim 1, wherein the fluorocompound is a perfluorinated compound.
3. A method as defined in claim 1, wherein the fluorocompound is selected from a group consisting essentially of fluoroacid, fluoroketone, fluoroalcohol, fluorinated hydrocarbon, and a mixture thereof.
4. A method as defined in claim 2, wherein the perfluorinated compound is selected from a group consisting essentially of perfluoroacid, perfluoroketone, perfluoroalcohol, perfluorinated hydrocarbon, and a mixture thereof.
5. A method as defined in claim 1, wherein the fluorocompound is a fluoroacid comprising 2 to 22 carbon atoms.
6. A method as defined in claim 3, wherein the fluorocompound is a perfluoroacid comprising 2 to 22 carbon atoms.

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7. A method as defined in claim 2, wherein the perfluorinated compound is a perfluoroacid comprising 2 to 22 carbon atoms.

8. A method as defined in claim 4, wherein the perfluorinated compound is a perfluoroacid comprising 2 to 22 carbon atoms.

9. A method as defined in claim 5, wherein the perfluoroacid is perfluoroacetic acid.

10. A method as defined in claim 6, wherein the perfluoroacid is perfluoroacetic acid.

11. A method as defined in claim 7, wherein the perfluoroacid is perfluoroacetic acid.

12. A method as defined in claim 8, wherein the perfluoroacid is perfluoroacetic acid.

13. A method as defined in claim 9, wherein the amount of the perfluoroacetic acid in the single-phase liquid mixture is in the range of 0.1 to 4% by weight.

14. A method as defined in claim 10, wherein the amount of the perfluoroacetic acid in the single-phase liquid mixture is in the range of 0.1 to 4% by weight.

15. A method as defined in claim 11, wherein the amount of the perfluoroacetic acid in the single-phase liquid mixture is in the range of 0.1 to 4% by weight.

16. A method as defined in claim 12, wherein the amount of the perfluoroacetic acid in the single-phase liquid mixture is in the range of 0.1 to 4% by weight.

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17. A method as defined in claim 5, wherein the perfluoroacid is selected from a group consisting essentially of perfluorobutyric acid, perfluorooctanoic acid, and a mixture thereof.

18. A method as defined in claim 6, wherein the acid is selected from a group consisting essentially of perfluorobutyric acid, perfluorooctanoic acid, and a mixture thereof.

19. A method as defined in claim 7, wherein the acid is selected from a group consisting essentially of perfluorobutyric acid, perfluorooctanoic acid, and a mixture thereof.

20. A method as defined in claim 7, wherein the acid is selected from a group consisting essentially of perfluorobutyric acid, perfluorooctanoic acid, and a mixture thereof.

21. A method as defined in claim 1, wherein the solvent comprises acetic acid, and the respective acid comprises adipic acid.

22. A method as defined in claim 2, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

23. A method as defined in claim 3, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid..

24. A method as defined in claim 4, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.



25. A method as defined in claim 7, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

26. A method as defined in claim 11, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

27. A method as defined in claim 13, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

28. A method as defined in claim 14, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

29. A method as defined in claim 15, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

30. A method as defined in claim 16, wherein the hydrocarbon comprises cyclohexane, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid..

31. A method as defined in claim 1, wherein the respective acid 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 respective acid 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.



32. A method as defined in claim 31, further comprising a step of spinning the polymer into fibers or making a composite.

33. A method as defined in claim 2, wherein the respective acid 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 respective acid 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.

34. A method as defined in claim 33, further comprising a step of spinning the polymer into fibers or making a composite.

35. A method as defined in claim 3, wherein the respective acid 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 respective acid 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.

36. A method as defined in claim 35, further comprising a step of spinning the polymer into fibers or making a composite.

37. A method as defined in claim 4, wherein the respective acid 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 respective acid 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.



38. A method as defined in claim 37, further comprising a step of spinning the polymer into fibers or making a composite.

39. A method as defined in claim 7, wherein the respective acid 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 respective acid 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.

40. A method as defined in claim 39, further comprising a step of spinning the polymer into fibers or making a composite.

41. A method as defined in claim 11, wherein the respective acid 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 respective acid 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.

42. A method as defined in claim 41, further comprising a step of spinning the polymer into fibers or making a composite.

43. A method as defined in claim 13, wherein the respective acid 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 respective acid 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.



44. A method as defined in claim 43, further comprising a step of spinning the polymer into fibers or making a composite.

45. A method as defined in claim 14, wherein the respective acid 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 respective acid 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.

46. A method as defined in claim 45, further comprising a step of spinning the polymer into fibers or making a composite.

47. A method as defined in claim 15, wherein the respective acid 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 respective acid 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.

48. A method as defined in claim 47, further comprising a step of spinning the polymer into fibers or making a composite.

49. A method as defined in claim 16, wherein the respective acid 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 respective acid 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.



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50. A method as defined in claim 49, further comprising a step of spinning the polymer into fibers or making a composite.

51. A method of oxidizing a hydrocarbon selected from a group consisting of cyclohexane, o-xylene, m-xylene, p-xylene, and a mixture of at least two of o-xylene, m-xylene, and p-xylene, to a respective acid, in a mixture comprising of a solvent, an initiator, and a cobalt catalyst, the method comprising a step of adding perfluoroacetic acid at a level of 0.1 to 4% by weight, based on total liquid mixture, and maintaining such level during oxidizing.

52. A method as defined in claim 51, wherein the respective acid 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 respective acid 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.

53. A method as defined in claim 52, further comprising a step of spinning the polymer into fibers or making a composite.

54. A method as defined in claim 51, wherein the hydrocarbon comprises cyclohexane, the initiator comprises cyclohexanone or acetaldehyde, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

55. A method as defined in claim 54, wherein the method further comprises a step of reacting the adipic acid 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.



56. A method as defined in claim 55, further comprising a step of spinning the polymer into fibers or making a composites

57. A method of oxidizing a hydrocarbon selected from a group consisting of cyclohexane, o-xylene, m-xylene, p-xylene, and a combination of at least two of o-xylene, m-xylene, and p-xylene, to a respective acid, in a mixture comprising of a solvent, an initiator, and a cobalt catalyst, the method comprising a step of perfluoroacid having more than two carbon atoms at a level of 1 to 5% by weight, based on total liquid mixture, and maintaining such level during oxidizing.

58. A method as defined in claim 57, wherein the respective acid 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 respective acid 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.

59. A method as defined in claim 58, further comprising a step of spinning the polymer into fibers or making a composite,

60. A method as defined in claim 57, wherein the hydrocarbon comprises cyclohexane, the initiator comprises cyclohexanone or acetaldehyde, the solvent comprises acetic acid or a mixture of acetic acid and propionic acid, and the respective acid comprises adipic acid.

61. A method as defined in claim 60, wherein the method further comprises a step of reacting said respective acid 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.



62. A method as defined in claim 61, further comprising a step of spinning the polymer into fibers or making a composite.