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H. HARDUNG-HARDUNG ET AL  
OF MAKING CYCLOHEXANOL AND CYCLOH  
BY OXIDATION OF CYCLOHEXANE

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2 Sheets-Sheet 1

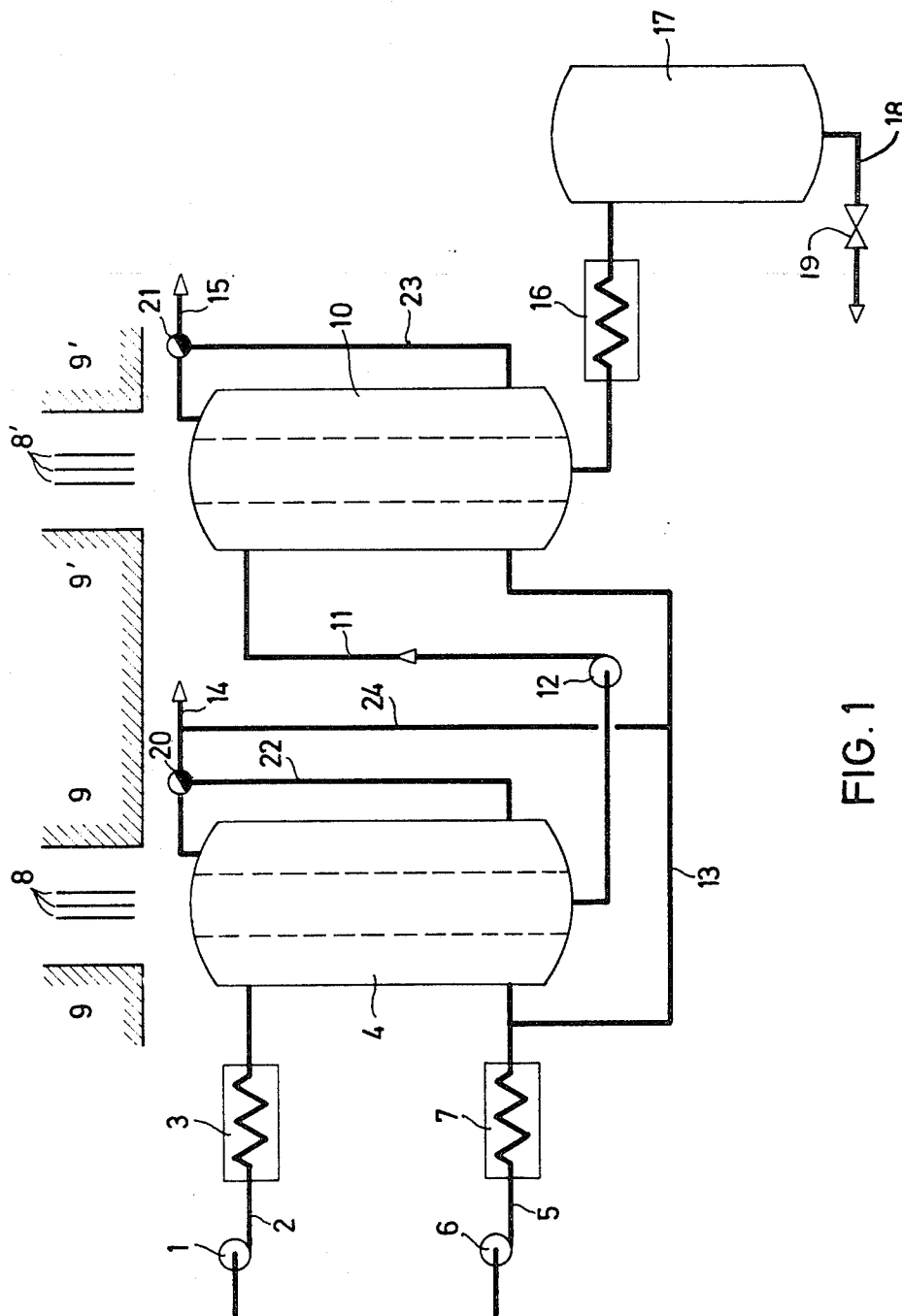


FIG. 1

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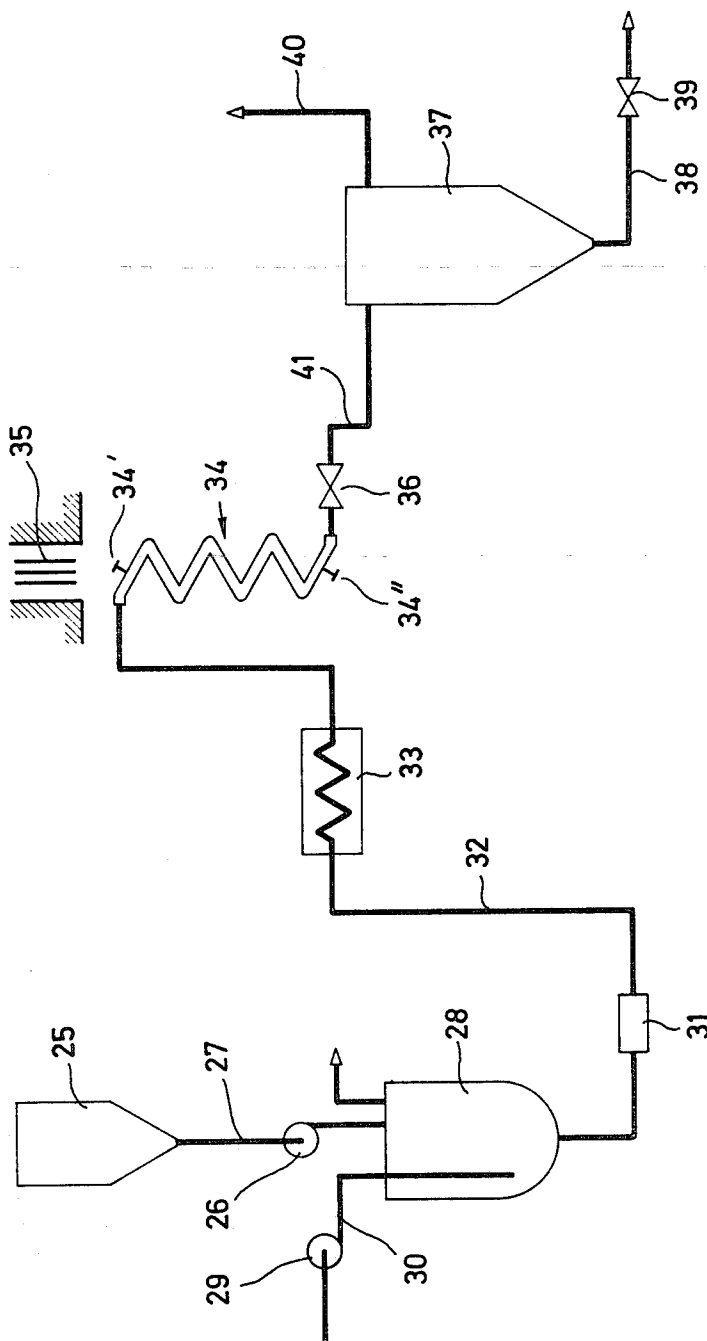


FIG. 2

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## METHOD OF MAKING CYCLOHEXANOL AND CYCLOHEXANONE BY OXIDATION OF CYCLOHEXANE

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14 Claims

### ABSTRACT OF THE DISCLOSURE

Process for the oxidation of cyclohexane to cyclohexanol and cyclohexanone wherein the oxidation reaction takes place in liquid phase in the presence of ionizing rays below about 170° C. and at elevated pressure. Improved yields of 86–88% in a conversion range of 5 to 9% are obtained.

### BACKGROUND OF THE INVENTION

This invention relates to a process for the production of cyclohexanol and cyclohexanone by oxidation of cyclohexane in liquid or gaseous phase with oxygen or oxygen-containing gases, which may be carried out in the presence of oxidation catalysts.

It is a known practice to obtain cyclohexanol and cyclohexanone by way of the oxidation of cyclohexane. The recovery is carried out as a rule under pressure at reaction temperatures between 170° and 220° C. with the use of catalysts. Besides cyclohexanol and cyclohexanone there arises in the process a considerable amount of by-products. Moreover, there exists a relation between the degree of conversion of cyclohexane and the yield in cyclohexanol and cyclohexanone. A lower conversion of cyclohexane results in a higher yield of cyclohexanol and cyclohexanone and vice versa. The conversion of cyclohexane, accordingly, is to be kept as low as possible if there is to be achieved a good yield of cyclohexanol and cyclohexanone. Excessively low degrees of conversion, for example below 4%, however, render the process uneconomical through the large amount of cyclohexane to be circulated. The optimum lies at present at a degree of conversion of 5% to 9% with a yield of about 65% to 78% of cyclohexanol and cyclohexanone.

What is disturbing in the known process is, above all, the secondary attack of the oxygen on the cyclohexanol already formed. For the economy of the cyclohexanol and cyclohexanone production, therefore, it is important to reduce to a minimum the constituent of the sequence and side reactions—especially by the oxygen. This is accomplished mainly by maintaining a brief residence time of the cyclohexane at the continuously operating oxidation reactor and by maintenance of a relatively low degree of conversion by corresponding dosing of the oxygen. The oxidized products are to be removed as rapidly as possible from the hot reaction zone and to be withdrawn from the further attack of the oxygen. High degrees of conversion, just like the long staying times, bring about an increasing amount of by-products to the disfavor of the cyclohexanol and cyclohexanone yield. However, the maintenance of a short staying time is technically achievable only with great difficulty. Furthermore, at low degrees of conversion, as already indicated above, the economy of the process is jeopardized.

It is, accordingly, an object of the present invention to provide a novel process for the production of cyclo-

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hexanol and cyclohexanone by the oxidation of cyclohexane.

It is another object of the invention to provide an economical process for the production of cyclohexanol and cyclohexanone.

These and other objects of the invention can be gathered from the following detailed description.

### SUMMARY OF THE INVENTION

It has now been found that the oxidation of cyclohexane to cyclohexanol and cyclohexanone is feasible with high yield in an extremely short time, if, according to the invention, the oxidation takes place in the presence of ionizing rays.

### BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 shows a schematic view of an installation for the two-stage two-phase oxidation in accordance with the invention;

FIG. 2 shows a schematic view of an installation for the single-stage single-phase oxidation in accordance with the invention.

The drawings will be further described in detail below in connection with the description of the preferred embodiments of the invention.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

As indicated above, the present invention provides a process for the oxidation of cyclohexane to cyclohexanol and cyclohexanone under ionizing rays. As the source for the radiation or ionizing rays, there is preferably used a cobalt 60 gamma-installation. Although the applicants do not wish to be bound by any theory explaining the process of the invention, it is believed that the oxidation induced by radiation-chemical means is a radical reaction—i.e., through the irradiation there takes place first of all the formation of free alkyl radicals, which then react further with the oxygen molecules. Under the supposition that such a chain reaction mechanization is present, it can be further believed that the gamma rays, having a low ionization density, yield longer chains, and are therefore more effective than other rays with high ionization density. This, however, does not exclude the possibility that other energy-rich rays can be used.

The oxidation is carried out at a temperature of about from 50° to 170° C., preferably at 80° to 160°, and elevated pressure. The preferred temperature range lies below the temperature range which was hitherto used for the purely thermal oxidation. It is possible, to be sure, to carry out the thermal reaction at temperatures that lie below 170° C. However, the reaction then takes place only very slowly, which renders its practical utilization in commercial installations unfeasible. Through the use of elevated pressure, the speed of the reaction is increased. In order to accelerate the reaction, it is possible at the beginning of the oxidation to add to the cyclohexane a catalyst, especially a cobalt, manganese or copper compound which is soluble in hydrocarbons. Through the catalyst there is achieved an additional improvement of the reaction. It has been found that with the extremely low reaction temperatures the hydroperoxide arising as a by-product is very stable. Through the catalyst there is achieved a more rapid disintegration of the hydroperoxide, even at low temperatures. An addition of, in particular, cobalt naphthenate, with conditions otherwise the same, yields an increase in the conversion by a factor of three.

Advantageously, the reaction components are preheated, before introduction into the reactor, to a temperature which lies 15° to 90° C. below the reaction temperature. Also it is favorable to carry out the oxidation in more than

one stage, preferably in two stages. Through the two-stage oxidation, there is achieved a further increase of the yield. The two-stage oxidation can take place in successively engaged reactors or in a reactor subdivided in cascade manner.

An especially high yield with most economical utilization of the radiation source can be achieved if the dose power of the radiation source is adapted to the course of the oxygen concentration in the reactor—i.e., if at the places in the reactor in which a higher oxygen concentration is present there is also present a higher dose power of the radiation source. The higher oxygen concentration is present at the entry of the oxygen into the reactor. The oxygen concentration falls off forward of the oxygen outlet. A corresponding adaptation of the dose power is to be provided in order to achieve the most economical utilization of the radiation source. The oxygen concentration is generally chosen in such a way that it is sufficient for a conversion of 5% to 9%. Care should be taken that both at the beginning and at the end of the reaction, sufficient oxygen is present. The oxidation is to be carried out in such a way that the oxygen is not completely consumed. In this manner, the undesired recombinations of cycloalkyl radicals, formed by radiation chemical means, are avoided.

The process of the invention can be used in the two-phase oxidation, known per se, of cyclohexane, in which the liquid cyclohexane and the gaseous oxygen are introduced into the reactor in diluted form. It is also possible to dissolve the oxygen in the cyclohexane, which preferably takes place in a solution container under elevated pressure, and to carry out the oxidation at a pressure at which the reaction components present a homogeneous phase. The pressure supplied to the solution container is chosen according to the desired oxygen concentration in the cyclohexane or according to the cyclohexane conversion to be obtained.

According to a further feature of the invention, the reaction mixture is given subsequent treatment after the oxidation at a temperature of 120° to 200° C. over a period of about from 5 to 30 minutes in a reactor following the oxidation reactor.

For the explanation of the reaction mechanism it can be stated that, as is well known, the purely thermal oxidation is a chain reaction in which the chain-starting radicals are thermally generated. A temperature elevation accelerates both the radical formation and the chain reaction thereby triggered.

Through the irradiation, it is believed that radicals are formed which, like the thermally generated radicals, react further into the various oxidation products. The formation speed of the radicals is proportional to the beamed-in dose power. A temperature elevation has no influence on the number of radicals generated by the rays, but accelerates their subsequent reaction. With a predetermined dose power and correspondingly chosen temperature, therefore, there is achieved a considerable increase of the conversion over the conversion attainable in purely thermal oxidation. This increase in the conversion is comparatively greater at lower oxidation temperatures, since with falling oxidation temperature the purely thermal radical formation declines strongly and the radical formation takes place predominantly through the irradiation. From this, it follows that with irradiation and low temperature there can be achieved the same conversion as without irradiation but with high temperature. The lower reaction temperature and the lower pressure generally associated with it in the reactor yield very substantial technical advantages in the execution of the oxidation installation. Furthermore, at the lower temperatures, a number of side reactions either do not take place or are much reduced; and the selectivity, the yield in cyclohexanol and cyclohexanone, as well as product purity, rise.

The higher the beam dose is, the higher is the conver-

sion at the same reaction temperature. In order to achieve a given conversion, therefore, it is possible to oxidize at a lower temperature under radiation with a higher absorbed dose.

We have found that with irradiation with the same process conditions, the oxidation of the liquid phase leads to higher conversions than the oxidation of the gaseous phase. With the use of liquid cyclohexane the oxidation begins at lower temperatures under irradiation than with the use of gaseous cyclohexane. It has also been ascertained that the conversions rise exponentially with the temperature.

The invention will now be further explained in detail in connection with the drawings.

The embodiment represented in FIG. 1 illustrates the two-stage oxidation of cyclohexane in accordance with the invention. The cyclohexane is introduced with the aid of the pump 1 through the line 2 and the preheater 3 into the reactor 4. The reactor 4 is at an elevated pressure. Over a further conduit 5, by means of the compressor 6, air is injected into the reactor 4. The air is preheated in the same manner as the cyclohexane in a preheater 7 and has an oxygen concentration of from 5 to 21%, preferably about 10%. The reactor 4 is provided in its interior with a cylindrical hollow space, shown in broken lines, into which the radiation source can be introduced. For the irradiation, there is used a cobalt 60 gamma source.

The radiation source consists of three tubes comprehended in bundle form, which reach to the lower end of the interior space of the reactor 4. Into the tubes there can be driven the active cobalt 60 gamma rods 8 from a shielding contained 9 situated above the reactor. In their end position, the rods 8 extend approximately over the entire length of the reactor 4. The total dose and dose power can be varied by the number of the bars 8 driven in as well as by their introduction depth. Hereby, there can also be carried out an adaption of the dose power to the oxygen concentration present in the reactor 4. In view of the fact that in the present design of the reactor 4 the oxygen concentration will be greatest at the lower end of the reactor 4, it is necessary to increase the dose power at the lower end of the reactor 4. This can be achieved by the means that one or more of the rods 8 are provided with radioactive material only at their lower end.

Clearly, it is possible to provide a large number of bars 8 with the same or differing power, so that any desired dose power can be achieved.

From the lower end of the reactor 4, the already partially oxidized cyclohexane is removed and supplied to the reactor 10 over the conduit 11 and the pump 12. In the same manner as in the case of reactor 4, preheated air is injected into the reactor 10. For this there serves the conduit 13. The form of the reactor 10 as well as that of the rods 8' and of the shielding container 9' of the radiation source is in correspondence to the reactor 4 and the radiation source used there. The exhaust gases escaping from the reactors 4 and 10 over the gas exhaust lines 14 and 15 still contain small amounts of oxygen, so that no impoverishment in oxygen has occurred in any part of the reactors. The cyclohexane-anolone mixture is taken from the reactor 10, conducted through a heater 16 and maintained in an after-reactor 17 for several minutes at a temperature of 120° to 200° C. The run-off line 18 of the after-reactor 17 is provided with a pressure reducing valve 19. The waste-gas lines 14 and 15 are provided with coolers 20 and 21, in which the product particles in the waste gas are precipitated and conducted over pipe lines 22 and 23 back to the reactors 4 and 10. It is also possible to connect to the waste-gas line 14 a conduit 24 which issues into the conduit 13, so that, in case of need, there can be achieved a thinning of the air conducted in the conduit 13 by waste-gases poor in oxygen.

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In FIG. 2 there is represented another embodiment for the production of cyclohexanone and cyclohexanol. The cyclohexane is filled from a supply container 25 over a conduit 27 provided with a pump 26 into the dissolving container 28 and enriched with oxygen. The oxygen is injected by means of the pump 29 through the conduit 30 into the solution so that there results a saturated solution. A dosing piston pump 31 conveys the solution saturated with oxygen through the conduit 32 and the preheater 33 into the oxidation reactor 34. The reactor 34 consists of a jacketed pipe wound in coil form. In the jacketing, there is conducted a heating medium for the heating of the cyclohexane to the reaction temperature. The heating of the reactor 34 and of the preheater 33 is accomplished over separate heating devices with liquid circulations. The heating of the reactor 34 is required only up to the start of the reaction. After this, there is necessary a cooling of the reactor 34. For this there can be used the same circulation which is provided for the heating. With 34' and 34'' there are designated the connecting pieces for the liquid circulation of the reactor 34. Into the interior of the reactor 34 there can be driven the radioactive rods 35. The rods 35 are comprehended into a bundle and extend when driven in to the lower end of the reactor 34. In the embodiment shown, there is achieved a favorable radiation field when the rods 35 are introduced only half way into the reactor 34. The dose powder is then advantageously adapted to the oxygen concentration.

The product leaves the reactor 34 at its lower end and is relieved of pressure by way of an expansion valve 36

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C., and pass, with a staying time of 9 minutes, through the after reactor. The reaction products are worked up in a known manner. With a total cyclohexane conversion of 7.6%, the reaction mixture has the following composition:

	Percent
Cyclohexanol	4.3
Cyclohexanone	2.8
Peroxide <sup>1</sup>	0.2

The yield in mol. percent amounts to 88.3.

<sup>1</sup> Prepared as cyclohexyl hydroperoxide.

#### EXAMPLES 2-5

In an apparatus according to FIG. 2 there were pumped, in one series of experiments, 215 parts per hour of cyclohexane initially at 60 atmospheres excess pressure and 20° C. and saturated with oxygen, at a pressure of 100 atmospheres excess pressure over the preheater maintained at a temperature of 90° C. into the reactor. Examples 2 and 3 involved no catalysts while Examples 4 and 5 were carried out with catalysts, as shown by the table below. The reaction temperature amounted in each case to 145° C. and the staying time in each case amounted to about 45 minutes.

After a test-period without influence of rays, the oxidation reactor was irradiated with a cobalt-60- $\gamma$ -radiation source of 1500 Curie. The reaction products separately collected in each case after achieving steady state were analyzed and yielded the following composition of the most important substances.

TABLE

Test No.	$\gamma$ -Rays	Catalyst	Percent of--				
			Cyclohexanol	Cyclohexanone	Peroxide <sup>1</sup>	Conversion	Yield in mo.
2	—	—	0.27	0.47	0.33	1.28	65
3	+	—	0.63	0.85	0.34	2.06	76
4	—	5 p.p.m. Co.	2.30	1.12	0.02	4.13	79.1
5	+	do.	3.32	1.77	0.08	6.10	86.4

<sup>1</sup> Prepared as cyclohexyl hydroperoxide.

to atmospheric pressure and then collected in a collecting tank 37. The collecting tank 37 is provided with a removal conduit 38 with valve 39, and a ventilating line 40. It serves simultaneously as an after-treatment tank, in which the mixture is subjected for a certain period of time to an elevated temperature. The pipe line 41 from the reactor 34 to the collecting tank 37 is conducted in such a way that there is always present a slight gradient and a separation of the aqueous phase is avoided. In deviation to the gasification process described for FIG. 1, in this installation the cyclohexane oxidation takes place in a homogeneous solution.

#### EXAMPLE 1

In a plant according to FIG. 1, there are fed to the first reactor 235 parts by weight per hour of cyclohexane preheated to 100° C. with 7.5 p.p.m. of cobalt in the form of cobalt naphthenate, at a pressure of 12 atmospheres excess pressure, and a reaction temperature of 142° C. In counterflow to this there are supplied 21,000 normal volume parts per hour of air in fine distribution. In central arrangement there is in each reactor a cobalt 60- $\gamma$ -radiation source, which is started at the commencement of the operation and decreases in intensity from the bottom upward. The reaction product from the first reactor, with about 4.7% cyclohexane conversion, passes into the second reactor and is there gasified at a pressure of 10.5 atmospheres excess pressure under the influence of the ionizing rays at 135° C. again with 11,000 normal volume parts of finely distributed air. The waste was still contains between 0.3 to 1.5 vol. percent of oxygen. The reaction products flowing off from the second reactor are heated, under expulsion of the rays, and of air, to 165°

The experiments show quite clearly the effect of the ionizing rays and the influence of the catalyst. The latter has, in the partial oxidation by radiation chemical means, no influence on the induction period of the oxidation in contrast to the thermal partial oxidation.

Surprisingly, it has now been found that the catalyst, for example, cobalt, catalyzes the decomposition of the primarily formed cyclohexyl hydroperoxide even in the temperature range at and under 145° C. sufficiently so that there result well usable, economical reaction speeds. From the catalytic effect and the influence of the ionizing rays as well as the increase in conversion and selectivity thereby brought about there is yielded a quite particularly advantageous process for the obtaining of the extremely important products cyclohexanol and cyclohexanone.

The invention has been described in detail with reference to particular and preferred embodiments thereof, but it will be understood that variations and modifications can be made within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What is claimed is:

1. Process for the production of cyclohexanone and cyclohexanol by the oxidation of cyclohexane which comprises the steps of:

(a) mixing an oxygen containing gas with a liquid cyclohexane feed,

the amount of oxygen provided by said gas in excess of stoichiometric to convert said cyclohexane to cyclohexanone and cyclohexanol,

(b) exposing said mixture to a source of ionizing rays from a radioactive source to initiate radical formation, and

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- (c) maintaining said mixture in liquid phase at elevated pressure and temperature below about 170° C. to form a partially oxidized product mixture, thereby converting said cyclohexane in said product mixture to cyclohexanone and cyclohexanol with improved yield.
2. Process according to claim 1 wherein said mixture is exposed to ionizing rays supplied by a cobalt 60 gamma-source.
3. Process according to claim 1 wherein said mixture is maintained in a temperature range of about 50° to 170° C.
4. Process according to claim 3 wherein said mixture is maintained in a temperature range of about 80° to 160° C. and said elevated pressure is in the range of from 12 to 100 atmospheres.
5. Process according to claim 1 wherein said mixture is exposed to said radiation in the presence of a catalyst.
6. Process according to claim 5 wherein said catalyst is one selected from a cobalt, manganese or copper compound which is soluble in hydrocarbons.
7. Process according to claim 3 which includes the added step of preheating the mixture to a temperature about 15° to 90° C. below the reaction temperature prior to exposing said mixture to said source of ionizing rays.
8. Process according to claim 1 wherein the steps of exposing and maintaining are carried out in 2 stages.
9. Process according to claim 1 which includes the added step of controlling the strength of the ionizing rays reaching said mixture in proportion to the oxygen concentrated therein.

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10. Process as in claim 1 wherein said oxygen containing gas and cyclohexane are continuously fed into exposure with said ionizing rays source.

11. Process according to claim 1 wherein the oxygen is mixed with the cyclohexane simultaneously with exposure of said mixture to said source of ionizing rays.

12. Process according to claim 1 wherein the oxygen is dissolved in the cyclohexane under elevated pressure.

13. Process according to claim 1 wherein said pressure is controlled to maintain said oxygen-cyclohexane mixture in a homogeneous phase.

14. Process according to claim 1 which includes the added steps of:

(a) removing said product mixture from exposure to said ionizing rays, and

(b) maintaining said product mixture at a temperature in the range of about 120° to 200° C. for a period of about 2 to 30 minutes,

thereby to accelerate the conversion after initiation by said ionizing rays.

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