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(54) Title: PROCESS FOR THE PRODUCTION OF A MIXTURE COMPRISING CYCLOHEXANOL AND CYCLOHEXAN-ONE

(57) Abstract: A continuous process for the preparation of a mixture of cyclohexanone and cyclohexanol, said process comprising: a) oxidizing cyclohexane, in an oxidation section, without a transition metal-containing catalyst, in the presence of an oxygen-containing gas to form an oxidized reaction mixture; b) cooling the oxidized reaction mixture, in a cooling section, c) decomposing the oxidized reaction mixture, in a decomposition section, at a temperature below 130 °C in the presence of a transition metal-containing catalyst and an aqueous caustic solution, to form a decomposed reaction mixture; and d) recovering cyclohexane, in a recovery section, from the decomposed reaction mixture; characterized in that b) comprises i) evaporating cyclohexane in one or more fractionation columns operated at a pressure lower than the pressure of the oxidation section, without external heat input, and returning a portion of the cyclohexane so evaporated to the oxidation section; and ii) cooling the reaction mixture in one or more indirect heat exchangers; and apparatus for carrying out the same.


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PROCESS FOR THE PRODUCTION OF A MIXTURE
COMPRISING CYCLOHEXANOL AND CYCLOHEXANONE

The invention is directed to a process for preparing a mixture comprising cyclohexanol and cyclohexanone.

Cyclohexanol and cyclohexanone can be commercially produced from cyclohexane in a two-step process. The first step is oxidation of cyclohexane by an oxygen-containing gas to produce a mixture comprising cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide. Conventionally, in this first step cyclohexane is oxidized in the liquid phase with air. On an industrial scale, this oxidation is normally conducted either uncatalysed or catalysed with a soluble cobalt catalyst, in one or more reactors at temperatures in the range of 130-200 °C. The vapourised cyclohexane and other products in the gaseous effluent are condensed and recovered, and the off-gases leave the system. The product mixture is recovered from the liquid effluent from the reactor or reactors, and the unreacted cyclohexane is recycled (Kirk-Othmer, Encyclopedia of Chemical Technology, John Wiley & Sons, New York, 1979, 3rd Edition, Vol. 7, pp. 410-416 and Ullmanns, Encyklopädie der Technischen Chemie, Verlag Chemie, Weinheim, 1975, 4th Edition, Vol. 9, pp. 689-698).

In known processes, typically the first step (oxidation) occurs in an oxidation section, wherein the reaction (I) occurs. The produced oxidized reaction mixture consists of cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide, unreacted cyclohexane and some minor by-products. In the second step, this oxidized reaction mixture is decomposed in the presence of a hydroxide ion-containing phase and a cobalt catalyst, according to reaction (II) in a decomposition section to form a decomposed reaction mixture. The hydroxide ions also act to neutralize acid by-products (not depicted). For simplicity the reactions (I) and (II) are depicted here as unbalanced equations. The by-products produced in reaction (I) and in reaction (II) are in general different regarding composition, concentrations and quantities.

(I) \( C_6H_{12} + O_2 \rightarrow C_6H_{10}O + C_6H_{11}OH + C_6HnOOH + \text{by-products} \)

(II) \( C_6H^\cdot OOHH_{\text{OH}^+ + \text{Co}} \rightarrow C_6H_{10}O + C_6H^\cdot OH + \text{by-products} \)
The decomposed reaction mixture is then passed to a distillation section, and cyclohexane is distilled therefrom. Further processing steps yield a mixture of cyclohexanone and cyclohexanol.

EP0579323 describes such a process, wherein the oxidized reaction mixture leaving the oxidation section is cooled by at least 10 °C, preferably at least 30 °C, before allowing the cyclohexyl hydroperoxide to decompose. Cyclohexyl hydroperoxide decomposition is effected after cooling, under the influence of a transition metal-containing catalyst. Cooling can be effected by means of heat exchangers or by expansion.

In such a system, there exists a problem that, when cooling is applied to the oxidized reaction mixture, for example by water cooling, energy is removed from the reaction mixture. Further, energy must be applied to the reaction mixture later in the process to recover cyclohexane from the reaction mixture to yield the desired product of a mixture of cyclohexanone and cyclohexanol.

US2931834 describes a process wherein a flash distillation unit equipped with a reboiler is located between an oxidation reactor and a decomposition reactor. Low boiling acids, water, and most (about 90%) of the unreacted cyclohexane are removed by distilling from the oxidized reaction mixture. The cyclohexane is recycled to the oxidation reactor. The concentrated oxidized products are passed to a decomposition reactor. Oxidation and decomposition are carried out in the absence of catalysts. In the Examples, concentration of the oxygenated products from 14.6 to 16.8 wt% is shown to give a higher yield of product than the Comparative Example where concentration to 28.7 wt% is described.

One problem with such a system is that the volume of cyclohexane in the concentrated oxidized reaction mixture is reduced. Therefore heat generated in the exothermic decomposition reaction causes the decomposition reaction to occur at higher temperature than it would in a more dilute reaction mixture. Such a high temperature means the reaction is less selective for the production of cyclohexanone and cyclohexanol.

One possible solution to this is to cool the concentrated oxidized reaction mixture to a lower temperature, for example 35-40 °C, rather than approximately 60 °C, before it enters the decomposition section. However, cooling to such a temperature can lead to precipitation of organic acids, for example adipic acid, in the oxidized reaction mixture as the temperature drops below the solubility
temperature of these compounds. Such precipitates foul, and can ultimately block the pipes, leading to maintenance shutdown of the chemical plant.

Accordingly it is an object of the present invention to provide an improved process for the production of a mixture of cyclohexanone and cyclohexanol. More specifically to provide a process wherein, following partial flash evaporation of cyclohexane from the oxidized reaction mixture, cyclohexyl hydroperoxide may be decomposed efficiently without precipitating organic acids and without reducing yields of cyclohexanol or cyclohexanone.

The present inventors have realized a process for keeping the decomposition reaction at a temperature below which cyclohexanone and cyclohexanol are produced in a good yield from the decomposition of cyclohexyl hydroperoxide; and wherein organic acids do not precipitate in the oxidized reaction mixture. Accordingly, the present invention provides a continuous process for the preparation of a mixture of cyclohexanone and cyclohexanol, said process comprising:

1) oxidizing cyclohexane, in an oxidation section, without a transition metal-containing catalyst, in the presence of an oxygen-containing gas to form an oxidized reaction mixture;
2) cooling the oxidized reaction mixture, in a cooling section;
3) decomposing the oxidized reaction mixture, in a decomposition section, at a temperature below 130 °C in the presence of a transition metal-containing catalyst and an aqueous caustic solution, to form a decomposed reaction mixture; and
4) recovering cyclohexane, in a recovery section, from the decomposed reaction mixture;

characterized in that b) comprises
i) evaporating cyclohexane in one or more fractionation columns operated at a pressure lower than the pressure of the oxidation section, without external heat input, and returning a portion of the cyclohexane so evaporated to the oxidation section; and
ii) cooling the reaction mixture in one or more indirect heat exchangers.

The present invention further comprises apparatus suitable for carrying out the process above, said apparatus comprising:

a) an oxidation section;
b) a cooling section;
c) a decomposition section; and
d) a cyclohexane recovery section;
characterized in that the cooling section comprises i) one or more fractionation columns without external heat input; and ii) one or more indirect heat exchangers.

Lowering the temperature of the oxidized reaction mixture before decomposition is desired in order to improve the selectivity of the cyclohexyl hydroperoxide decomposition reaction. Typically a cooling section is employed in a cyclohexanone plant for this purpose. The advantages of a system of recycling cyclohexane by means of a partial flash evaporation unit from the oxidized reaction mixture to the oxidation section are not fully recognized in US2931834. The main advantage is to use the energy released on lowering the pressure of the oxidized reaction mixture to remove some cyclohexane and return it to the oxidation section.

This leads to the following downstream advantages:

1. Removal of a significant proportion of cyclohexane occurs earlier than in prior art processes, i.e. before the cyclohexane recovery section, thereby saving energy in the cyclohexane recovery section. Such energy is typically expressed as the quantity of steam required for distilling cyclohexane.
2. Less cyclohexane than in the prior art processes passes through all process steps downstream of the cooling section. Therefore the capacity of the downstream plant equipment is effectively increased, with respect to the amount of cyclohexanol and cyclohexanone handled.
3. Less by-product formation, for example organic acids which may form by oxidation of cyclohexanone and cyclohexanol being oxidized in the oxidation section. This is due to a decrease of cyclohexanone and cyclohexanol recycle being passed though the oxidation section from the cyclohexane recovery section (further oxidation). This may also be due to operating the oxidation reaction at lower conversion and thus higher selectivity without additional energy costs. This in turn leads to an increased yield of cyclohexanone and cyclohexanol from cyclohexane oxidation. It also leads to lower consumption of caustic solution for the neutralization of organic acids in the decomposition section. This latter improvement is particularly beneficial for the environment.

The present inventors have realized that there is yet a further advantage to evaporate cyclohexane at this point in the process, rather than in the cyclohexane recovery section. That is because cyclohexyl hydroperoxide is significantly less volatile than either cyclohexanone or cyclohexanol. Accordingly, it requires less energy to separate cyclohexane from cyclohexyl hydroperoxide (the main
oxidation product), than it does to separate cyclohexane from a mixture of
cyclohexanone and cyclohexanol. Therefore recovery of cyclohexane before
decomposition, according to the present invention, reduces energy consumption of the
chemical plant compared with recovery of cyclohexane after decomposition, according
to prior art processes.

Evaporating cyclohexane in one or more fractionation columns in the
cooling section and recycling said cyclohexane to the oxidation section, according to
the present invention has the further advantage in that it leads to more options for
improving the operation of a chemical plant. For example, one option is to operate the
oxidation reaction at higher cyclohexane circulation rates i.e. lower conversion. This
increases the selectivity of the reaction for cyclohexyl hydroperoxide. The fractionation
column-containing cooling section counteracts the increase in flow out of the oxidation
section.

As used herein, the term oxidized reaction mixture refers to the
reaction mixture that has been oxidized in the oxidation section, but not yet
decomposed in the decomposition section. By oxidized is meant the reaction (I)
described above has occurred. It will be understood that this term does not mean that
the reaction mixture is completely oxidized.

The oxidation section is typically a system of reactors arranged in
series or in a pipe-reactor with compartments. Usually oxygen or oxygen containing
gases are supplied to each reactor or reactor part. Oxidation is carried out in the
absence of a transition metal-containing catalyst. This may be referred to as
uncatalysed oxidation.

As oxygen-containing gas, oxygen as such; air, rich or poor in
oxygen; or oxygen mixed with nitrogen or another inert gas may be chosen. Air is
preferred, but the air can be mixed with extra inert gas to eliminate the risk of
explosions. In such a case usually so much oxygen containing gas is fed to the
reactors, in such a way, that the oxygen concentration of the off-gas remains below the
explosive limit.

As used herein, the term "without a transition metal-containing
catalyst" means without an effective amount of such catalyst. Trace amounts of
transition metal-containing catalyst could be present in the reaction mixture and have
no appreciable effect. Therefore an amount of transition metal-containing catalyst
which has substantially no effect on the cyclohexyl hydroperoxide fraction may be
present.
The decomposition section comprises one or more decomposition units arranged in series. A decomposition unit is a reactor in which the reaction (II) above is carried out. As used herein, the term decomposed reaction mixture refers to the reaction mixture that has been decomposed in the decomposition section. By decomposed is meant the reaction (II) described above has occurred. It will be understood that this term does not mean that the reaction mixture is completely decomposed. By definition the decomposed reaction mixture has already undergone oxidation as described above.

The temperature in each decomposition unit is below 130 °C. This reduces the formation of by-products. Typically it is between 20 and 120 °C; preferably between 50 and 100 °C. Cyclohexyl hydroperoxide decomposition is effected using a transition metal-containing catalyst, for example cobalt or chromium or a mixture thereof. Aqueous caustic solution is also present and acts to catalyse decomposition. For efficiency decomposition is typically effected at a lower temperature than oxidation. This is carried out preferably as described in EP-A-004105 or EP-A-092867.

The decomposition section may include one or more washing units. The decomposition section may include one or more heat exchangers. One embodiment of the decomposition section comprises a wash unit followed by a heat exchanger followed by a wash unit.

Cyclohexane may be recovered from the decomposed reaction mixture by techniques known to the person of skill in the art. Typically cyclohexane is distilled from the reaction mixture in a distillation section. The distillation section typically comprises a number of distillation columns arranged in series. The distillation section may be preceded by partial flash evaporation of cyclohexane from the reaction mixture. The presence of partial flash operation has the advantage of removal of a fraction of low boiling components, including inerts, which hamper heat transfer in condensers/reboilers. This is especially important in case various distillation columns are operated in series. The impact of the presence of partial flash evaporation on the heat required to be input to the decomposed reaction mixture to distil off cyclohexane can be rather limited.

A heat exchanger is a device for transferring heat from one fluid stream to another. A heat exchanger may be direct (wherein the fluid streams are mixed) or indirect (wherein the fluid streams remain separated by a dividing wall). Indirect heat exchangers are well-known to the person of skill in the art. Examples of indirect heat exchangers suitable for the present invention are shell & tube, plate, and
tubular. Typically the indirect heat exchanger comprises a shell & tube indirect heat 
exchanger. A shell & tube indirect heat exchanger is preferred, because it is capable of 
handling a large flow of reaction mixtures.

The fractionation column is operated at a pressure lower than the 
pressure of the oxidation section. As the pressure drops, a portion of cyclohexane is 
evaporated, which cools the remaining oxidized reaction mixture. The fractionation 
column does not use an external heat input, since the main purpose is to lower the 
temperature of the oxidized reaction mixture. The fractionation column is equipped with 
a condenser to condensate the majority of the overhead. The liquid obtained in the 
condenser is partially used as reflux in the fractionation column in order to recover 
cyclohexane with high purity.

It is important that recycled cyclohexane is of high purity. If 
cyclohexanone and/or cyclohexanol and/or cyclohexyl hydroperoxide are also recycled 
to the oxidation section, they will be further oxidized to form organic acids, meaning not 
only a loss of product but an increased consumption of caustic. Typically, in step b) i) 
the portion of cyclohexane returned to the oxidation section comprises at most 2 wt% 
of compounds other than cyclohexane. Preferably, the portion comprises at most 1 
wt% of compounds other than cyclohexane. More preferably it comprises at most 0.5 
wt%; most preferably at most 0.25 wt%.

The quantity of cyclohexane removed in the cooling section is 
important because it determines the concentration of the oxidized reaction mixture to 
be decomposed. As mentioned above, there are many advantages to this being a large 
quantity. However, if this is too high, the temperature rise in the decomposition reaction 
can become too high resulting in product losses. Accordingly, typically the portion of 
cyclohexane returned to the oxidation section is from 10 to 40 wt% of the cyclohexane 
present in the oxidized reaction mixture.

Typically the oxidation section is operated at a pressure of from 0.8 to 
1.5 MPa.

Typically, in the cooling section, the one or more fractionation 
columns are operated at a pressure of from 0 to 0.6MPa. Preferably, the one or more 
fractionation columns are operated at a pressure of from 0.03 to 0.2 MPa. More 
preferably, the one or more fractionation columns are operated at a pressure of from 
0.05 to 0.15 MPa.

A method of improving the purity of cyclohexane returned to the 
oxidation section is to utilise trays or packing or a combination thereof in the
fractionation column. This can be expressed as the number of theoretical trays. Generally the higher the number of theoretical trays, the higher the purity of cyclohexane leaving the fractionation column will be. Typically at least one fractionation column has at least 2 theoretical trays. Preferably all fractionation columns have at least 2 theoretical trays. More preferably at least one fractionation column has at least 3 theoretical trays. Yet more preferably all fractionation columns have at least 3 theoretical trays.

Optionally, a portion of the decomposed reaction mixture leaving the decomposition section is recycled to one or more indirect heat exchanger(s) in the cooling section. The advantage of this is to increase the volume of reaction mixture passing through the decomposition section and therefore increase the volume in which absorption of heat generated in the decomposition reaction occurs. This in turn prevents the temperature of the decomposition reaction from rising to a point where by-product formation is excessively increased.

The size of the portion of the decomposed reaction mixture leaving the decomposition section recycled to one or more indirect heat exchanger(s) in the cooling section is determined with reference to the temperature and concentration of the reaction mixture leaving the fractionation column.

The cyclohexane evaporated in step b) may be supplied directly to an oxidation reactor, or alternatively may be heated prior to being supplied to an oxidation reactor. Preferably, the portion of cyclohexane returned to the oxidation section is, before being returned to the oxidation section, first passed through a heat exchanger being supplied with off-gas from the oxidation section. The advantage of this is of course to use heat from off-gas that would otherwise be wasted, or need to be transported to another part of the plant for utilisation. The heat from the recycled cyclohexane can also be used to control the temperature of oxidation reactors.

A further option for improving energy efficiency of the plant by heat transfer, according to the present invention is to introduce an in-process heat exchanger between the oxidation section and decomposition section. Therefore, preferably, the oxidized reaction mixture is used to heat the decomposed reaction mixture by means of an in-process heat exchanger. An in-process heat exchanger is an indirect heat exchanger wherein a process fluid from one part of the process transfers heat to a process fluid in another part of the process.

In the apparatus of the present invention, optionally the decomposition section further comprises a recycle loop configured to recycle
decomposed reaction mixture leaving the decomposition section back to the one or more indirect heat exchanger(s) in the cooling section.

Preferably, the cooling section comprises at least one fractionation column without external heat input and having at least two theoretical trays; followed by one or more indirect heat exchangers.

Preferably, the cyclohexane recovery section comprises a series of distillation columns which are integrated such that the overhead stream of a first distillation column is used as heat source of a second distillation column.

Figure 1 represents an embodiment of a prior art process, in which the present invention has not been implemented. Fresh cyclohexane is provided through feed (11) into oxidation section (A) containing one or more oxidation reactors. Oxygen-containing gas is fed into (A) through feed (12). The oxidized reaction mixture comprising cyclohexanone, cyclohexanol, cyclohexyl hydroperoxide, by-products and unreacted cyclohexane passes through feed (1) into cooling unit (D) which comprises one or more indirect heat exchangers. The cooled oxidized reaction mixture is then passed through feed (4) into decomposition section (E) which comprises one or more decomposition reactors and one or more liquid/liquid phase separators. Aqueous caustic solution containing a transition metal-containing catalyst is passed into the decomposition section (E) through feed (13); separated aqueous phase is removed through feed (14). The decomposed reaction mixture is passed through feed (5) into cyclohexane recovery section (G) comprising one or more distillation columns. Removed cyclohexane is passed through feed (16) into oxidation section (A). A mixture comprising mainly cyclohexanone, cyclohexanol and cyclohexane exits through feed (15).

Figure 2 represents an embodiment of the process according to the present invention. Fresh cyclohexane is provided through feed (11) into oxidation section (A) containing one or more oxidation reactors. Oxygen-containing gas is fed into (A) through feed (12). The oxidized reaction mixture comprising cyclohexanone, cyclohexanol, cyclohexyl hydroperoxide, by-products and unreacted cyclohexane passes through feed (1) into in-process heat exchange unit (B), which comprises one or more in-process heat exchangers, where it is cooled. The cooled oxidized reaction mixture then passes through feed (2) into fractionation column-containing section (C), where a portion of cyclohexane is removed by evaporation and returned via feed (17) to (A). As a result of this flash evaporation the remaining oxidized reaction mixture is cooled and concentrated. The remaining oxidized reaction mixture then passes through
feed (3) into cooling unit (D), which comprises one or more indirect heat exchangers, where it is further cooled. The further cooled oxidized reaction mixture is passed through feed (4) into decomposition section (E) which comprises one or more decomposition reactors and one or more liquid/liquid phase separators. Aqueous caustic solution containing a transition metal-containing catalyst is passed through feed (13) into the decomposition section (E); separated aqueous phase is removed through feed (14). The decomposed reaction mixture is passed through feed (5) into in-process heat exchange unit (B) where it is heated. The heated decomposed reaction mixture is passed through feed (6) into partial flash evaporation section (F), which comprises one or more flash evaporators, where a portion of low boiling components is removed by flash evaporation. The decomposed flashed reaction mixture is then passed through feed (7) into cyclohexane recovery section (G) comprising one or more distillation columns. Removed cyclohexane is passed through feed (16) into oxidation section (A). Optionally, partial flash evaporation section (F) is by-passed and the heated decomposed reaction mixture is passed through feed (6) directly into cyclohexane recovery section (G) (Not shown in Figure 2). A mixture comprising mainly cyclohexanone, cyclohexanol and cyclohexane exits through feed (15).

Figure 3 represents an embodiment of the process according to the present invention analogous to Figure 2, but without in-process heat exchange unit (B) and partial flash evaporation section (F) and feeds (2), (6) and (7). Fresh cyclohexane is provided through feed (11) into oxidation section (A) containing one or more oxidation reactors. Oxygen-containing gas is fed into (A) through feed (12). The oxidized reaction mixture comprising cyclohexanone, cyclohexanol, cyclohexyl hydroperoxide, by-products and unreacted cyclohexane passes through feed (1) into fractionation column-containing section (C), where a portion of cyclohexane is removed by evaporation and returned via feed (17) to (A). As a result of this flash evaporation the remaining oxidized reaction mixture is cooled and concentrated. The remaining oxidized reaction mixture then passes through feed (3) into cooling unit (D), which comprises one or more indirect heat exchangers, where it is further cooled. The further cooled oxidized reaction mixture is passed through feed (4) into decomposition section (E) which comprises one or more decomposition reactors and one or more liquid/liquid phase separators. Aqueous caustic solution containing a transition metal-containing catalyst is passed through feed (13) into the decomposition section (E); separated aqueous phase is removed through feed (14). The decomposed reaction mixture is passed through feed (5) into cyclohexane recovery section (G) comprising one or more
distillation columns. Removed cyclohexane is passed through feed (16) into oxidation section (A). A mixture comprising mainly cyclohexanone, cyclohexanol and cyclohexane exits through feed (15).

The present invention is illustrated by but not necessarily limited to the following examples.

EXAMPLES

The Examples were carried out in an operating cyclohexanone plant. For convenience of comparison the data presented in the Examples according to the invention were scaled to the same capacity as the plant described in the Comparative Example. For the Examples according to the invention, results are presented which were obtained by simulating a plant according to the invention as described below.

Comparative Example

A cyclohexanone plant, consisting of an uncatalysed cyclohexane oxidation reaction section, a cooling unit, a decomposition section and a cyclohexane recovery section, as described above with reference to Figure 1, directly after cleaning of the whole plant including the reboiler of the first distillation column in the cyclohexane recovery section, is operated at an hourly mass flow of the decomposed reaction mixture leaving the decomposition section of 500 metric tons. The sum of weight fractions of cyclohexanol and cyclohexanone in the organic flow obtained after decomposition is maintained at 3.4 per cent. In this Comparative Example, the oxidation section consists of five oxidation reactors in-series with air as oxygen source. The cooling section consists of a series of 6 shell-and-tube type indirect heat exchangers. The oxidized reaction mixture leaving the uncatalysed cyclohexane oxidation reaction section has a temperature of about 165 °C and a pressure of about 1.2 MPa and flows through the inside of the tubes of the heat exchangers. Water is used as coolant and flows on the outside of the tubes of the heat exchangers of the cooling section. The cooled down oxidized reaction mixture leaving the cooling section is fed to the decomposition section.

The decomposition section consists of a pre-neutralization section and a biphasic decomposition section. In the pre-neutralization section the incoming oxidized reaction mixture is washed with aqueous spent caustic recovered from the decomposition section. In the biphasic decomposition section the washed organic
phase is decomposed with an aqueous caustic solution in the presence of a Co-containing homogeneous catalyst, followed by phase separation of the obtained organic phase and aqueous spent caustic. The aqueous caustic flow recovered after the washing in the pre-neutralization is disposed of. In the decomposition section the temperature of the organic phase increases due to the release of reaction heat of neutralization reactions and decomposition of cyclohexyl hydroperoxide. The temperature of the organic flow, the decomposed reaction mixture, leaving the decomposition section is maintained constant by adjusting the water flow in the cooling section. The decomposed reaction mixture is fed to the cyclohexane recovery section.

The cyclohexane recovery section consists of 3 distillation columns that are operated-in-effect. In other words the vapours of the first distillation column are used to heat the second distillation column, and the vapours of the second distillation column are used to heat the third distillation column. The decomposed reaction mixture is fed to the first cyclohexane distillation column, which is equipped with a steam driven reboiler. The head pressures of these three distillation columns are about 0.5 MPa, 0.3 MPa, and 0.1 MPa, respectively. All these distillation columns are operated with reflux in order to recover overheads, mainly cyclohexane, with low concentrations of cyclohexanone and cyclohexanol. The recovered overheads are re-used in the oxidation section. The bottom flow of the last distillation column contains about 66% by weight cyclohexane, while the remainder mainly being cyclohexanone, cyclohexanol, lights and heavies. The bottom flow of the last distillation column is sent to the cyclohexanone purification section for further purification and for converting cyclohexanol into cyclohexanone.

Under these conditions, the following performance of the cyclohexanone plant is observed:

<table>
<thead>
<tr>
<th>Total duty coolers in cooling section</th>
<th>8.1 GJ/ton cyclohexanone**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duty reboiler of first distillation column in cyclohexane recovery section</td>
<td>7.6 GJ/ton cyclohexanone**</td>
</tr>
<tr>
<td>Amount of cyclohexanol and cyclohexanone in recovered overheads in cyclohexane recovery section</td>
<td>74 kg/ton cyclohexanone**</td>
</tr>
<tr>
<td>Overall selectivity of the cyclohexanone plant</td>
<td>83.0 %</td>
</tr>
</tbody>
</table>

** based on cyclohexanone in outlet of cyclohexanone plant
Example 1

A cyclohexanone plant, consisting of an uncatalysed cyclohexane oxidation reaction section, a fractionation column-containing section, a cooling section, a decomposition section, and a cyclohexane recovery section, as described above with reference to Figure 3, was operated at an hourly mass flow of the decomposed reaction mixture fed to the cyclohexane recovery section of about 357 metric tons. The sum of weight fractions of cyclohexanol and cyclohexanone in the organic flow obtained after decomposition was maintained at 4.8 per cent. The oxidation section consisted of five oxidation reactors in-series with air as oxygen source. The oxidized reaction mixture leaving the uncatalysed cyclohexane oxidation reaction section had a temperature of around 165 °C and a pressure of about 1.2 MPa and was fed to the fractionation column-containing section.

The fractionation column-containing section contained a fractionation column, a water cooled condenser and a reflux vessel. The fractionation column contained 8 trays with an assumed Murphree efficiency of 65% and was not equipped with an external heat source. This fractionation column was operated with reflux in order to recover overheads, mainly cyclohexane, with low concentrations of cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. The sum of weight fractions of cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide in the obtained overhead flow was maintained at approximately 0.10 wt%. The recovered overheads were re-used without additional purification in the oxidation section. The top pressure of the fractionation column was maintained at approximately 0.20 MPa. In this section about 29% of the amount of cyclohexane being present in the feed was recovered as overhead product of the fractionation column. The bottom flow of the fractionation column-containing section was, after being re-pressurized, fed to the cooling section.

The cooling section consisted of a series of 3 shell-and-tube type indirect heat exchangers. The oxidized reaction mixture leaving the fractionation column-containing section flowed through the inside of the tubes of the heat exchangers. Water was used as coolant and flowed on the outside of the tubes of the heat exchangers of the cooling section. The cooled oxidized reaction mixture leaving the cooling section was fed to the decomposition section. The decomposition section consisted of a pre-neutralization section in which the incoming oxidized reaction mixture was washed with aqueous spent caustic recovered from the decomposition section; and a biphasic decomposition section in which the washed organic phase was
decomposed with an aqueous caustic solution in the presence of a Co-containing homogeneous catalyst, followed by phase separation of the obtained organic phase and aqueous spent caustic. The aqueous caustic flow recovered after the washing in the pre-neutralization was disposed of. In the decomposition section the temperature of the organic phase increased due to the release of reaction heat of neutralization reactions and decomposition of cyclohexyl hydroperoxide. The temperature of the decomposed reaction mixture leaving the decomposition section was maintained constant at the same temperature as in the Comparative Example by adjusting the water flow in the cooling section. The decomposed reaction mixture was fed to the cyclohexane recovery section. In order to prevent precipitation of adipic acid in the cooling section, about 30 ton per hour of the decomposed reaction mixture leaving the decomposition section is recycled to the stream leaving the fractionating column (not depicted in Figure 3).

The cyclohexane recovery section consisted of 3 distillation columns that were operated in-effect. In other words the vapors of the first distillation column were used to heat the second distillation column, and the vapors of the second distillation column were used to heat the third distillation column. The decomposed reaction mixture obtained in the decomposition section, having a pressure of about 1.2 MPa, was fed to the first cyclohexane distillation column, which was equipped with a steam driven reboiler. The head pressures of these three distillation columns were about 0.5 MPa, 0.3 MPa, and 0.1 MPa, respectively. All these distillation columns were operated with reflux in order to recover overheads, mainly cyclohexane, with low concentrations of cyclohexanone and cyclohexanol. The recovered overheads were re-used in the oxidation section. The bottom flow of the last distillation column contained about 66% by weight cyclohexane, the remainder mainly being cyclohexanone, cyclohexanol, lights and heavies. The bottom flow of the last distillation column was sent to the cyclohexanone purification section for further purification and for converting cyclohexanol into cyclohexanone.
Under these conditions, the following performance of the cyclohexanone plant was observed:

<table>
<thead>
<tr>
<th>Table 1: Performance of the Cyclohexanone Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total duty coolers in cooling section</td>
</tr>
<tr>
<td>Duty reboiler of first distillation column in cyclohexane recovery section</td>
</tr>
<tr>
<td>Total amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads in fractionation column-containing section and in cyclohexane recovery section</td>
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<td>Overall selectivity of the cyclohexanone plant</td>
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** based on cyclohexanone in outlet of cyclohexanone plant

The sum of the duties of the condenser of the fractionation column-containing section and the condensers in the cyclohexane distillation section is almost equal to the duty of the condensers in the cyclohexane distillation section as described in the Comparative Example.

This example clearly shows that the total cooling duty needed in the cooling section can be reduced to a large extent by introducing the fractionation column-containing section. In addition it is shown that the duty of the reboiler of the first distillation column in the cyclohexane recovery section can be reduced by about 28%. And it is shown that due to a reduced amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads the overall selectivity of the cyclohexanone plant is increased by about 0.2 per cent.

**Example 2**

A cyclohexanone plant, consisting of an uncatalysed cyclohexane oxidation reaction section, a fractionation column-containing section, a cooling section, a decomposition section, and a cyclohexane recovery section, as described above with reference to Figure 2, was operated at an hourly mass flow of the decomposed reaction mixture fed to the indirect heat exchanger of about 359 metric tons. The sum of weight fractions of cyclohexanol and cyclohexanone in the organic flow obtained after decomposition was maintained at 4.7 per cent. The oxidation section consisted of five oxidation reactors in-series with air as oxygen source. The oxidized reaction
mixture leaving the uncatalysed cyclohexane oxidation reaction section had a
temperature of around 165 °C and a pressure of about 1.2 MPa and was fed to the in-
process heat exchanger section.

In the in-process heat exchange section the oxidized reaction mixture
originating from the uncatalysed cyclohexane oxidation reaction was cooled, while
heating up counter currently the decomposed reaction mixture originating from the
decomposition section. The in-process heat exchange section consisted of a series of
3 shell-and-tube type indirect heat exchangers. The oxidized reaction mixture
originating from the uncatalysed cyclohexane oxidation reaction flowed on the outside
of the tubes of the heat exchangers. The decomposed reaction mixture originating from
the decomposition section flowed through the inside of the tubes of the heat
exchangers and was heated to about 155 °C before being fed to the cyclohexane
recovery section. The cooled oxidized reaction mixture was fed to the fractionation
column-containing section.

The fractionation column-containing section contained a fractionation
column, a water cooled condenser and a reflux vessel. The fractionation column
contained 8 trays with an assumed Murphree efficiency of 65% and was not equipped
with an external heat source. This fractionation column was operated with reflux in
order to recover overheads, mainly cyclohexane, with low concentrations of
cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. The sum of weight
fractions of cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide in the obtained
overhead flow was maintained at approximately 0.10 wt%. The recovered overheads
were re-used without additional purification in the oxidation section. The top pressure of
the fractionation column was maintained at approximately 0.070 MPa. In this section
about 28% of the amount of cyclohexane being present in the feed was recovered as
overhead product of the fractionation column. The bottom flow of the fractionation
column-containing section was, after being re-pressurized, fed to the cooling section.

The cooling section consisted of a series of 3 shell-and-tube type
indirect heat exchangers. The oxidized reaction mixture leaving the fractionation
column-containing section flowed through the inside of the tubes of the heat
exchangers. Water was used as coolant and flowed on the outside of the tubes of the
heat exchangers of the cooling section. The cooled oxidized reaction mixture leaving
the cooling section was fed to the decomposition section. The decomposition section
consisted of a pre-neutralization section in which the incoming oxidized reaction
mixture was washed with aqueous spent caustic recovered from the decomposition
section; and a biphasic decomposition section in which the washed organic phase was decomposed with an aqueous caustic solution in the presence of a Co-containing homogeneous catalyst, followed by phase separation of the obtained organic phase and aqueous spent caustic. The aqueous caustic flow recovered after the washing in the pre-neutralization was disposed of. In the decomposition section the temperature of the organic phase increased due to the release of reaction heat of neutralization reactions and decomposition of cyclohexyl hydroperoxide. The temperature of the decomposed reaction mixture leaving the decomposition section was maintained constant at the same temperature as in the Comparative Example by adjusting the water flow in the cooling section. The decomposed reaction mixture was fed to the cyclohexane recovery section. In order to prevent precipitation of adipic acid in the cooling section, about 30 tons per hour of the decomposed reaction mixture leaving the decomposition section is recycled to the stream leaving the fractionating column (not depicted in Figure 2).

After being heated in the in-process heat exchange section the decomposed reaction mixture, having a pressure of 1.2 MPa was fed to a 1-stage partial flash evaporation vessel in order to remove low boiling components. The 1-stage partial flash evaporation vessel was operated at a pressure of 0.80 MPa.

The cyclohexane recovery section consisted of 3 distillation columns that were operated in-effect. In other words the vapors of the first distillation column were used to heat the second distillation column, and the vapors of the second distillation column were used to heat the third distillation column. The bottom flow of the 1-stage partial flash evaporation vessel was fed to the first cyclohexane distillation column, which is equipped with a steam driven reboiler. The head pressures of these three distillation columns were about 0.5 MPa, 0.3 MPa, and 0.1 MPa, respectively. All these distillation columns were operated with reflux in order to recover overheads, mainly cyclohexane, with low concentrations of cyclohexanone and cyclohexanol. The recovered overheads were re-used in the oxidation section. The bottom flow of the last distillation column contained about 66% by weight cyclohexane, the remainder mainly being cyclohexanone, cyclohexanol, lights and heavies. The bottom flow of the last distillation column was sent to the cyclohexanone purification section for further purification and for converting cyclohexanone into cyclohexanone.
Under these conditions, the following performance of the cyclohexanone plant was observed:

| Total duty coolers in cooling section | 1.4 GJ/ton cyclohexanone
| Duty reboiler of first distillation column in cyclohexane recovery section | 2.1 GJ/ton cyclohexanone
| Total amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads in fractionation column-containing section and in cyclohexane recovery section | 54 kg/ton cyclohexanone
| Overall selectivity of the cyclohexanone plant | 83.2 %

*based on cyclohexanone in outlet of cyclohexanone plant

The sum of the duties of the condenser of the fractionation column-containing section and the condensers in the cyclohexane distillation section was almost equal to the duty of the condensers in the cyclohexane distillation section as described in the Comparative Example.

This example clearly shows that the total cooling duty needed in the cooling section can be reduced to a large extent by introducing the fractionation column-containing section in combination with the in-process heat exchange section. In addition it is shown that the duty of the reboiler of the first distillation column in the cyclohexane recovery section can be reduced by about 72%. And it is shown that due to a reduced amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads the overall selectivity of the cyclohexanone plant is increased by about 0.2 per cent.

**Example 3**

Example 2 was repeated, except that the top pressure of the fractionation column-containing section was maintained at about 0.10 MPa. As consequences, about 20% of the amount of cyclohexane present in the feed was recovered as overhead product of the fractionation column-containing section and the hourly mass flow of the decomposed reaction mixture leaving the decomposition section was approximately 400 metric tons. No precipitation of adipic acid is expected in the cooling section.
Under these conditions, the following performance of the cyclohexanone plant is observed:

<table>
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<tr>
<th>Description</th>
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<td>Total duty coolers in cooling section</td>
<td>1.8 GJ/ton cyclohexanone”</td>
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<td>Duty reboiler of first distillation column in cyclohexane recovery section</td>
<td>2.4 GJ/ton cyclohexanone”</td>
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<tr>
<td>Total amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads in fractionation column-containing section and in cyclohexane recovery section</td>
<td>59 kg/ton cyclohexanone”</td>
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<td>Overall selectivity of the cyclohexanone plant</td>
<td>83.2 %</td>
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” based on cyclohexanone in outlet of cyclohexanone plant

The sum of the duties of the condenser of the fractionation column-containing section and the condensers in the cyclohexane distillation section was almost equal to the duty of the condensers in the cyclohexane distillation section as described in the Comparative Example.

This example clearly shows that the total cooling duty needed in the cooling section can be reduced to a large extent by introducing the fractionation column-containing section in combination with the in-process heat exchange section. In addition it is shown that the duty of the reboiler of the first distillation column in the cyclohexane recovery section can be reduced by about 69%. And it is shown that due to a reduced amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads the overall selectivity of the cyclohexanone plant is increased by about 0.2 per cent.

Example 4

Example 2 was repeated, except that the hourly mass flow of the decomposed reaction mixture leaving the decomposition section was about 500 metric tons and the sum of weight fractions of cyclohexanol and cyclohexanone in this flow was maintained at about 3.4 per cent by lowering the conversion in the oxidation section. No precipitation of adipic acid is expected in the cooling section.
Under these conditions, the following performance of the cyclohexanone plant was observed:

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<tr>
<td>Total duty coolers in cooling section</td>
<td>0.7 GJ/ton cyclohexanone”</td>
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<tr>
<td>Duty reboiler of first distillation column in cyclohexane recovery section</td>
<td>2.8 GJ/ton cyclohexanone”</td>
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<tr>
<td>Total amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads in fractionation column-containing section and in cyclohexane recovery section</td>
<td>64 kg/ton cyclohexanone”</td>
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<td>Overall selectivity of the cyclohexanone plant</td>
<td>86.0 %</td>
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" based on cyclohexanone in outlet of cyclohexanone plant

In this case the sum of the duties of the condenser of the fractionation column-containing section and the condensers in the cyclohexane distillation section were about 18 GJ per ton of produced cyclohexanone. This is about 60 per cent more than the duty of the condensers in the cyclohexane distillation section as described in the Comparative Example.

This example clearly shows that the total cooling duty needed in the cooling section can be reduced to a large extent by introducing the fractionation column-containing section in combination with the in-process heat exchange section. In addition it is shown that the duty of the reboiler of the first distillation column in the cyclohexane recovery section can be reduced by about 63%. And it is shown that due to a reduced amount of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in recovered overheads and mainly due to the lower conversion in the oxidation section the overall selectivity of the cyclohexanone plant is increased by about 3.0 per cent.
CLAMS

1. A continuous process for the preparation of a mixture of cyclohexanone and cyclohexanol, said process comprising:
   a) oxidizing cyclohexane, in an oxidation section, without a transition metal-containing catalyst, in the presence of an oxygen-containing gas to form an oxidized reaction mixture;
   b) cooling the oxidized reaction mixture, in a cooling section,
   c) decomposing the oxidized reaction mixture, in a decomposition section, at a temperature below 130 °C in the presence of a transition metal-containing catalyst and an aqueous caustic solution, to form a decomposed reaction mixture; and
   d) recovering cyclohexane, in a recovery section, from the decomposed reaction mixture;
characterized in that b) comprises
   i) evaporating cyclohexane in one or more fractionation columns operated at a pressure lower than the pressure of the oxidation section, without external heat input, and returning a portion of the cyclohexane so evaporated to the oxidation section; and
   ii) cooling the reaction mixture in one or more indirect heat exchangers.

2. A process according to claim 1, wherein in step b) i) the portion of cyclohexane returned to the oxidation section comprises at most 2 wt% of compounds other than cyclohexane.

3. A process according to claim 1 or claim 2, wherein the portion of cyclohexane returned to the oxidation section is from 10 to 40 wt% of the cyclohexane present in the oxidized reaction mixture.

4. A process according to any one of claims 1 to 3, wherein the oxidation section is operated at a pressure of from 0.8 to 1.5 MPa

5. A process according to any one of claims 1 to 4, wherein the one or more fractionation columns are operated at a pressure of from 0 to 0.6 MPa.

6. A process according to claim 5, wherein the one or more fractionation columns are operated at a pressure of from 0.03 to 0.2 MPa.

7. A process according to claim 5 or claim 6, wherein the one or more fractionation columns are operated at a pressure of from 0.05 to 0.15 MPa.
8. A process according to any one of claims 1 to 7, wherein at least one fractionation column has at least 2 theoretical trays.

9. A process according to any one of claims 1 to 8, wherein a portion of the decomposed reaction mixture leaving the decomposition section is recycled to the indirect heat exchanger(s) in the cooling section.

10. A process according to any one of claims 1 to 9, wherein the portion of cyclohexane returned to the oxidation section is, before being returned to the oxidation section, first passed through a heat exchanger being supplied with off-gas from the oxidation section.

11. A process according to any one of claims 1 to 10, wherein the oxidized reaction mixture is used to heat the decomposed reaction mixture by means of an in-process heat exchanger.

12. Apparatus suitable for carrying out the process of any one of claims 1 to 10, said apparatus comprising:
   a) an oxidation section;
   b) a cooling section;
   c) a decomposition section; and
   d) a cyclohexane recovery section;
   characterized in that the cooling section comprises i) one or more fractionation columns without external heat input; and ii) one or more indirect heat exchangers.

13. Apparatus according to claim 12, wherein the decomposition section further comprises a recycle loop configured to recycle decomposed reaction mixture leaving the decomposition section back to the indirect heat exchangers in the cooling section.

14. Apparatus according to claim 12 or claim 13, wherein the cooling section comprises at least one fractionation column without external heat input and having at least two theoretical trays; followed by one or more indirect heat exchangers.

15. Apparatus according to any one of claims 11 to 14, wherein the cyclohexane recovery section comprises a series of distillation columns which are integrated such that the overhead stream of a first distillation column is used as heat source of a second distillation column.
FIGURE 2

[Diagram showing a flowchart with nodes labeled A, B, C, D, E, F, and G, and numbered connections 1 to 17.]
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/EP2012/074216

### A. CLASSIFICATION OF SUBJECT MATTER

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

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):

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

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

**EPO-Internal**

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 0 579 323 AI (DSM NV [NL]) 19 January 1994 (1994-01-19) cited in the application on claim 1 page 4, column 6, line 34 - line 39 page 4, column 6, line 54 - line 58</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
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**Date of the actual completion of the international search**

1 March 2013

**Date of mailing of the international search report**

12/03/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Panday, Narendra

Form PCT/ISA/210 (second sheet) (April 2005)
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