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(54) PROCESS AND APPARATUS FOR OXIDISING
 CYCLOALKANES

(71) We, STAMICARBON B.V., a Netherlands Limited Liability Company of P.O. Box 10, Geleen, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process and 10 apparatus for use in a process for oxidizing cycloalkanes in the liquid phase and at elevated temperature and pressure to the corresponding cycloalkanones and/or cycloalkanols by means of a gas containing 15 molecular oxygen and in the presence of a dissolved metal salt serving as a catalyst but in the absence of a boric acid derivative.

This type of oxidation is used on an industrial scale using mainly cyclohexane and cyclododecane. Normally the gas containing 20 molecular oxygen is not pure oxygen, but a mixture of oxygen and inert gas, for example air, or air of increased or reduced oxygen content, and using as catalyst a cobalt salt that is soluble in the reaction mixture, such as 25 cobalt naphthenate, although salts of other metals especially of transition metals like chromium, vanadium, manganese, iron or nickel, may also be employed.

During the oxidation of cyclohexane on an industrial scale the degree of conversion of 30 the cyclohexane is normally kept low, for example between 2 and 12%, preferably between 3 and 7%. In practice this involves that after termination of the oxidation reaction a large quantity of unconverted cyclohexane has to be evaporated from the reaction mixture for subsequent recycle. During 35 the oxidation the heat of reaction is carried away with the offgas, which apart from unconverted oxygen substantially consists of inert gas, cyclohexane vapour and water vapour. Said offgas is subsequently cooled yielding a condensate which splits up into a 40 separate organic phase and a separate aque-

ous phase. The aqueous phase is removed, while the organic phase, which is saturated with water vapour, is recycled to the oxidation reactor. With this known process however fouling of the reactor vessels is liable to occur. This is a serious drawback because the necessary periodic cleaning of the vessels involves considerable loss of production and expense. It is a further feature in the known process that the degree of oxidation is difficult to control at unpredictable times, resulting in an increased oxygen content of the reactor offgas, so-called oxygen breakthrough. Since too high an oxygen content of the offgas may constitute an explosion hazard, it is common practice to shut down the reactor when the oxygen content in the offgas reaches a predetermined maximum by the actuation of a protective device. This also gives rise to serious loss of production. The invention aims at mitigating such difficulties and provides a process for oxidizing a cycloalkane in the liquid phase and at elevated temperature and pressure in an oxidation reactor to the corresponding cycloalkanone and/or cycloalkanol by means of a gas containing molecular oxygen and in the presence of a dissolved metal salt serving as a catalyst, but in the absence of a boric acid derivative, with subsequent removal of unconverted cycloalkane from the reaction mixture and recycle of the separated cycloalkane to the oxidation stage; wherein the water content of the cycloalkane to be oxidised is reduced before being supplied to the oxidation reactor.

In the following description the term "dissolved water" includes not only water dissolved in a continuous aqueous phase, but also water that is distributed in the organic phase as a fine dispersion which cannot be removed in the customary separators.

It is a surprising feature of the present invention that removal of such dissolved water inhibits fouling of the reactor vessels and also the onset of oxygen breakthrough as

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hereinbefore referred to. This is in contradiction to previously held views that it is desirable to add water to the cycloalkane to be oxidised (see for example British Patent specification 1,172,655).
 Removal of dissolved water from the cycloalkane oxidation treatment is occasionally applied during oxidation of a cycloalkane in the presence of a boric acid derivative. However said operation serves quite a different purpose, namely converting a fully hydrated boric acid derivative, for example orthoboric acid, into a less hydrated derivative, for example metaboric acid, in order to promote the esterification of the boric acid derivative with cycloalkanol formed during the oxidation reaction. The present application does not claim protective rights regarding oxidation in the presence of a boric acid derivative.

The cycloalkane to be oxidized preferably contains from 5 to 12 carbon atoms per molecule. Of particular importance in industrial processes are cyclohexane and cyclododecane and to a lesser extent cyclopentane and cyclooctane. The cycloalkane may contain one or several substitutes which have no impeding effect on the process, for example alkyl substituents, e.g. C₁–C₄ alkyl, particularly methyl groups.

The temperature and pressure used in the process of the invention are those used conventionally and for example are between 120° and 220°C, particularly between 140° and 180°C, and between 5 and 100 kg/cm², particularly between 7 and 15 kg/cm², respectively.

The gas containing molecular oxygen may for example be pure oxygen, or air of increased or decreased oxygen content. Air of decreased oxygen content is preferably obtained by mixing freshly supplied air with recycled off gas from the oxidation reaction.

The catalyst is a dissolved metal salt, (including metal containing esters), which may be salts of transition metals e.g. cobalt, nickel, manganese and copper, with organic acids. Examples of suitable salt other than the customary cobalt naphtenate are cobalt octoate, t-butyl chromate, chromium acetyl acetonate and manganese naphtenate. The catalyst concentration is preferably between 1 and 100 ppm.

The degree of conversion of the cycloalkane is conventional and for example may be between 2 and 12%, preferably from 3 to 7%.

Reducing the water concentration in the cycloalkane to be subjected to the oxidation treatment can be effected in various ways. Use may be made for example of a chemical or physical water absorption agent, preferably a molecular sieve. A preferred possibility is to remove the water by distillation in the form of an azeotrope with the cycloalkane, wherein preferably a stripping gas is used, for example nitrogen or air, preferably off gas from the oxidation reaction.

The invention is hereinafter particularly described and illustrated by the accompanying drawings, of which.

Figure 1 is a schematic representation of a previously-known process, and

Figure 2 is a schematic representation of one embodiment of a process according to the present invention.

Referring to Figure 1 oxidation of cyclohexane to cyclohexanone and/or cyclohexanol (and corresponding oxidative treatments of other cycloalkanes) is effected in series-connected oxidation reactors 1, 2, 3, 4 to which the cyclohexane feed is supplied through line 5 and a gas containing molecular oxygen through lines 6, 7, 8 and 9. Cobalt naphtenate is fed to one or several reactors through lines not shown in Figure 1. The liquid reaction product passes through line 10 to distillation column 11 where unconverted cyclohexane is distilled off. The cyclohexanone/cyclohexanol mixture, which may still contain cyclohexane, leaves column 11 through line 12 to be processed in customary manner.

Distilled cyclohexane is withdrawn from column 11 through line 13 and a condenser (not shown) and after being mixed with fresh cyclohexane supplied through 14, is introduced into cooling scrubber 15, to be contacted there with off gas withdrawn from oxidation reactors 1, 2, 3 and 4 through lines 16, 17, 18 and 19 and supplied to cooling scrubber through line 20.

Cyclohexane vapour and water vapour condense in the cooling scrubber. Non-condensed gases are carried away through line 21. Inside cooling scrubber 15 a mixture of two liquid phases is formed, namely an organic phase and an aqueous phase. The mixture flows through line 22 to separator 23, where it is separated into the individual phases. The aqueous phase is carried away through line 24 and the organic phase is fed to the oxidation reactors through line 5, to serve as cyclohexane feed.

All of the water formed during the oxidation reaction, including any water present in the fresh cyclohexane supplied through line 14, is delivered into cooling scrubber 15. At least part of the reaction water in the form of cyclohexane/water azeotrope, is fed to the cooling scrubber 15 through lines 16–20. Water not evaporated in the reactors is evaporated as cyclohexane/water azeotrope in column 11, and fed to cooling scrubber 15 through line 13. It will be clear that the cyclohexane feed supplied to the reactors along line 5 is saturated with dissolved water (at the prevailing temperature), and may moreover still contain some finely dispersed water which cannot be removed in the customary separators, and thus comes under the definition of "off gas".

tion of 'dissolved water'.

It is this water which is responsible for the difficulties and disadvantages hereinbefore referred to.

5 Referring to Figure 2, reference numbers 1-24 have the same meaning as those used in Figure 1. However the organic phase withdrawn from separator 23 is now not directly supplied to the oxidation reactors, but flows 10 through line 25 into a stripping column 26 where it is contacted with reactor off gas from line 20. The non-condensed gases from stripping column 26 are carried to scrubber 15 through line 27. The major advantage of 15 this arrangement is that stripping with the off gas removes water from the organic phase that is saturated with dissolved water, so that the objective of the invention is achieved.

20 According to a particularly convenient mode of realizing the process of the invention, the vapour formed in distillation column 11 and discharged through line 13 is not, or not entirely, supplied to cooling scrubber 15 through line 13a and the condensor (not shown) but is at least partly also used as stripping vapour, and for that purpose fed to stripping column 26 through line 25. This ensures an even more effective removal of water from the cyclohexane feed 25 to the reactors.

30 Since the distillation of the liquid reaction product is usually carried out at a lower pressure than the oxidation reaction, with the consequence that the vapour from column 11 usually has a lower temperature than the reactor offgas, it is preferred to arrange the outlet of line 13b into stripping column 26 above the outlet of line 20.

35 It is also possible to include a condenser (not shown) in line 13b to condense the cyclohexane vapour in the said condenser, and feed the condensed cyclohexane in liquid form to stripping column 26. The water content of the vapour produced in distillation column 11, and hence also the water vapour of the condensate, will usually be low compared with that of the liquid in stripper 26, which in a later stage is to serve as cyclohexane feed to the oxidation reactor, from which it is evident that also by dilution the water concentration in the cyclohexane feed can be reduced.

40 Thus the invention also provides apparatus for effecting oxidation of cycloalkane comprising an oxidation reactor for effecting oxidation of cycloalkane in the liquid phase, a feed line for introducing cyclohexane to the said reactor, and a distillation column for distilling the oxidised product whereby unconverted cyclohexane is 45 separated from the liquid reaction product and recycled to the said oxidation reactor; wherein a stripping column is provided for reducing the water content of cyclohexane introduced to the said reactor.

The following practical Example of the invention is provided.

50 In a continuously conducted process, 1000 parts by weight of liquid cyclohexane feed was supplied to an oxidation reactor per unit time. The oxidation temperature was 155-160°C. and the oxidation pressure 9-10 kg/cm². A mixture of molecular oxygen and nitrogen was fed to the oxidation reactor in such a quantity as is needed to achieve a 3-3.5% degree of conversion of the cyclohexane.

55 The cyclohexane feed contained 0.04% wt. of water, obtained by bringing 690 parts by weight of cyclohexane to be oxidized and containing 0.5% wt. of water into contact with the reactor offgas in a stripping column, the said cyclohexane of 0.5% wt. water content in turn having been obtained by condensing the condensable vapours from the stripper offgas, separating the resulting system of two liquid phases and removing the aqueous phase. The oxidation mixture contained from 1 to 3 ppm of a soluble cobalt catalyst.

60 After 350 days continuous operation, the oxidation reactor had still not become fouled to such a degree that cleaning was necessary. Breakthrough of oxygen did not occur.

Comparative Experiment

65 Unless otherwise indicated the run was carried out in an analogous way to the above example. However the cyclohexane feed consisted of the liquid obtained by condensing the condensable vapours from the reactor offgas, separating the resulting system of two liquid phases and removing the aqueous phase. The water content of this cyclohexane feed was 0.5% wt.

70 After 60 days of continuous operation, the oxidation reactor became fouled up to such a degree that cleaning was necessary.

WHAT WE CLAIM IS:-

75 1. A process for oxidizing cycloalkanes in the liquid phase and at elevated temperature and pressure in an oxidation reactor to the corresponding cycloalkanones and/or cycloalkanols by means of a gas containing molecular oxygen and in the presence of a dissolved metal salt serving as a catalyst, but in the absence of a boric acid derivative, with subsequent removal of unconverted cycloalkane from the reaction mixture and recycle of the separated cycloalkane to the oxidation stage; wherein the water content of the cycloalkane to be oxidized is reduced before being supplied to the oxidation reactor.

80 2. A process according to Claim 1, wherein the water concentration is reduced using a physical or chemical water absorption agent.

85 3. A process according to Claim 1, wherein the water concentration is reduced by evaporating the water as an azeotrope with cycloalkane.

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4. A process according to Claim 3, wherein the cycloalkane to be oxidized is stripped with a stripping gas.

5. A process according to Claim 4, wherein off gas from the oxidation reaction is used as the stripping gas.

10 6. A process according to Claim 4 or 5, wherein cycloalkane evaporated from the liquid oxidation product is used as the stripping gas.

15 7. A process according to Claim 1, wherein the water concentration is reduced by diluting the cycloalkane to be oxidized with relatively dry liquid cycloalkane obtained by condensation of the cycloalkane vapour evaporated from the liquid oxidation product.

20 8. A process for oxidizing a cycloalkane according to Claim 1, substantially as described with particular reference to Figure 2 of the accompanying drawings or to the Example.

25 9. A cycloalkanone and/or a cycloalkanol when obtained by a process according to any of Claims 1 to 8.

30 10. Apparatus when used in the process according to Claim 1, comprising an oxidation reactor for effecting oxidation of cycloalkane in the liquid phase, a feed line for introducing cyclohexane to the said reactor, and a distillation column for distilling the oxidized product whereby unconverted cyclohexane is separated from the liquid reaction product and recycled to the said oxidation reactor; wherein a stripping column is provided for reducing the water content of cyclohexane introduced to the said reactor.

35 11. Apparatus according to Claim 10, wherein at least a portion of the unconverted cyclohexane obtained from the said distillation column is recycled directly to the said stripping column.

40 12. Apparatus for oxidizing a cyclohexanol as claimed in Claim 10, substantially as hereinbefore described with particular reference to Figure 2 of the accompanying drawings.

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2. **Partial or global** and **non-parallel**.

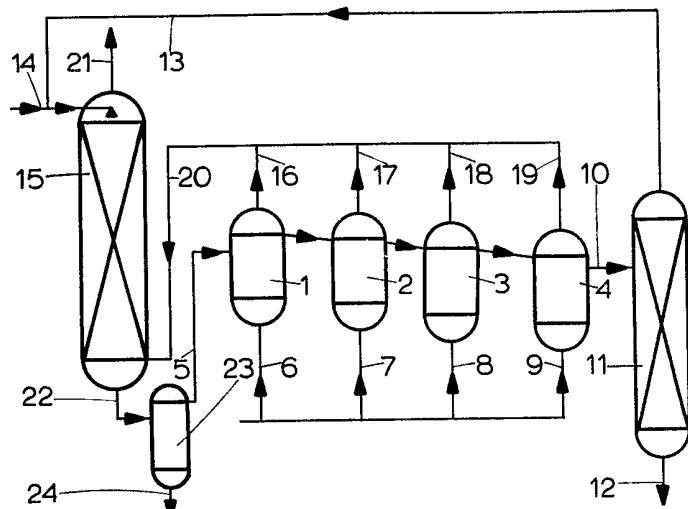
¹⁰ See, for example, the discussion of the 1992 Constitutional Convention in the *Constitutional Convention of 1992: The Final Report* (1993).

1. *What is the primary purpose of the study?* (e.g., to evaluate the effectiveness of a new treatment, to describe a population, to compare two groups).

1. *What is the relationship between the two variables?*

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17. *Georgi Dzhagava. The First Step to the Second Step* (1989).



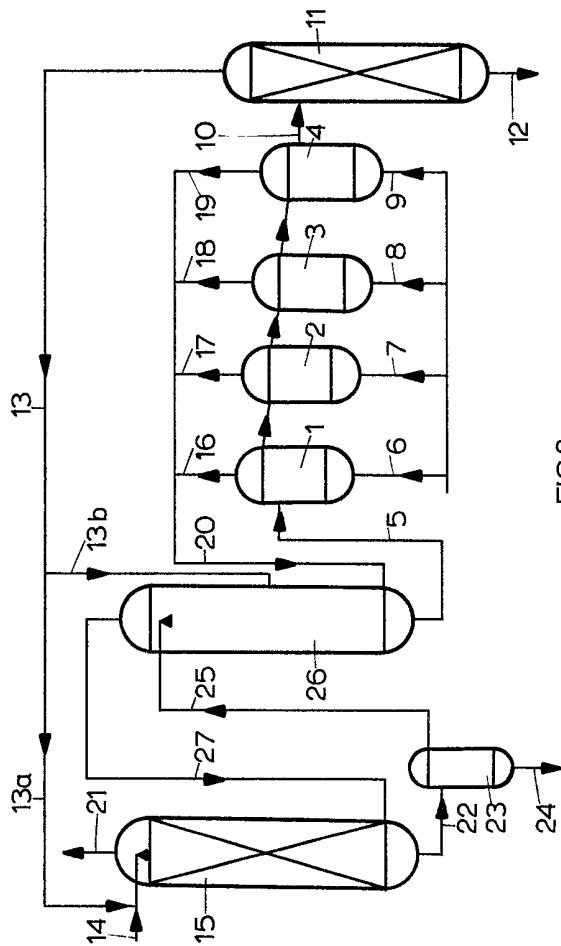


FIG2