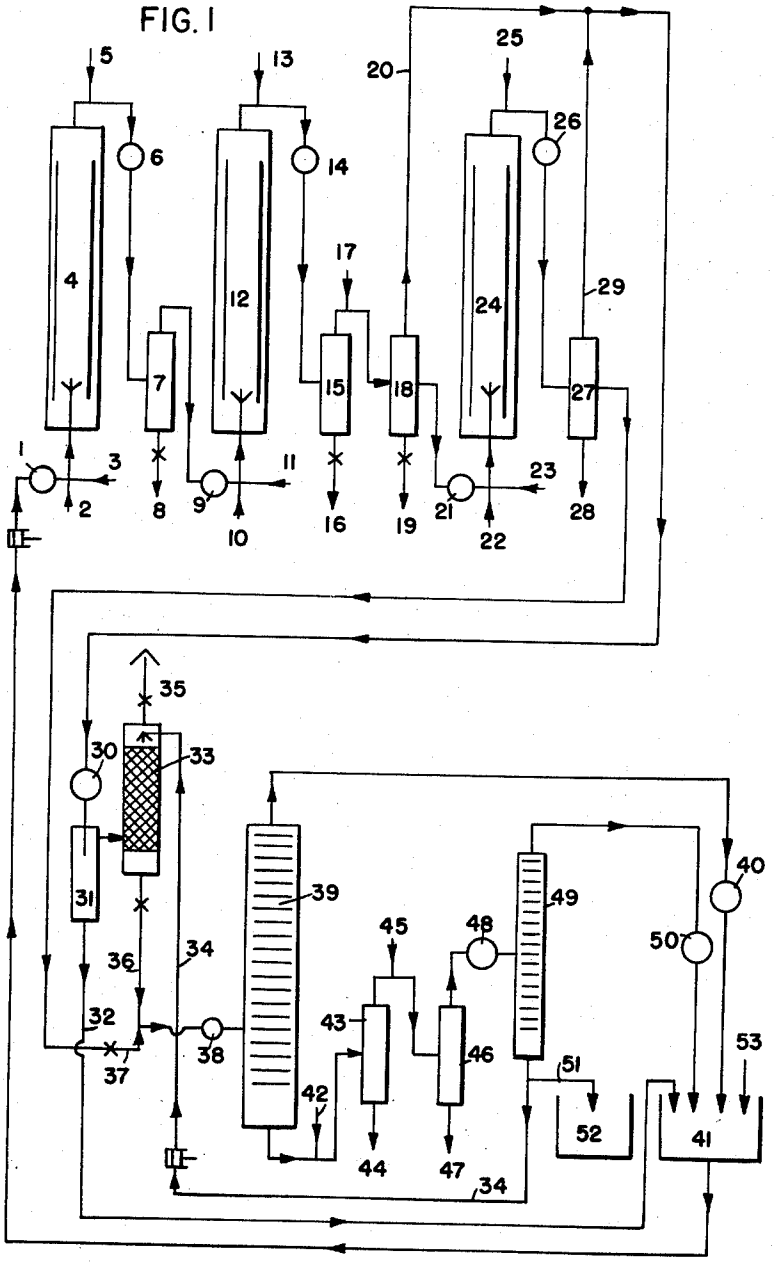
May 31, 1960 W. SIMON ET AL 2,938,924

PRODUCTION OF ALCOHOLS AND KETONES BY THE OXIDATION OF CYCLOALIPHATIC OR ARALIPHATIC HYDROCARBONS

Filed June 13, 1956 4 Sheets-Sheet 1

FIG. 1





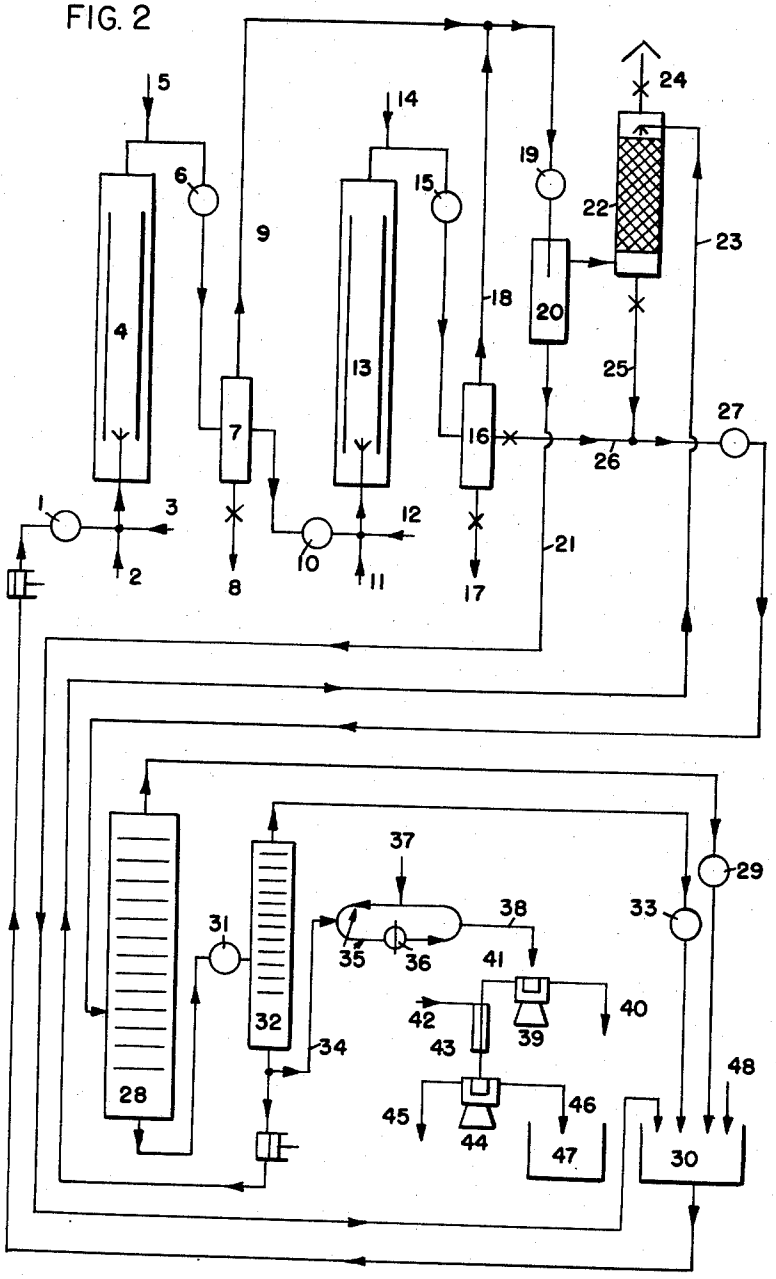
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Filed June 13, 1956 4 Sheets-Sheet 2

FIG. 2




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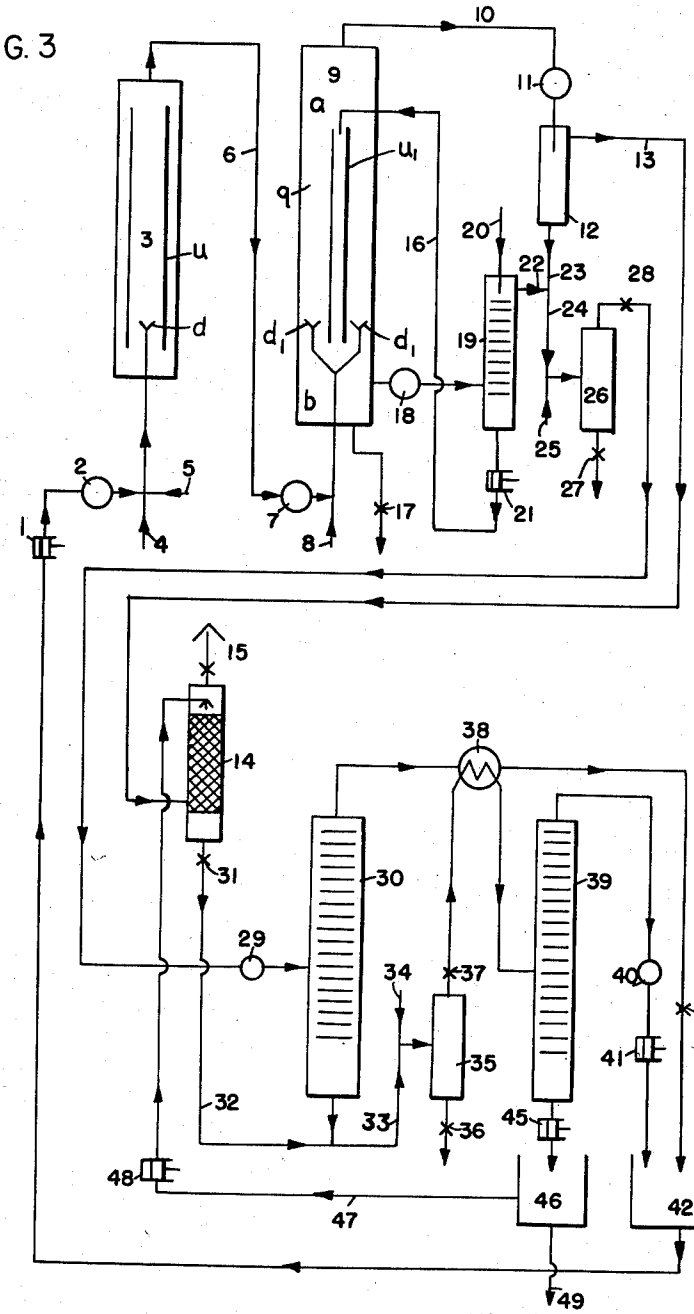
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Filed June 13, 1956 4 Sheets-Sheet 3

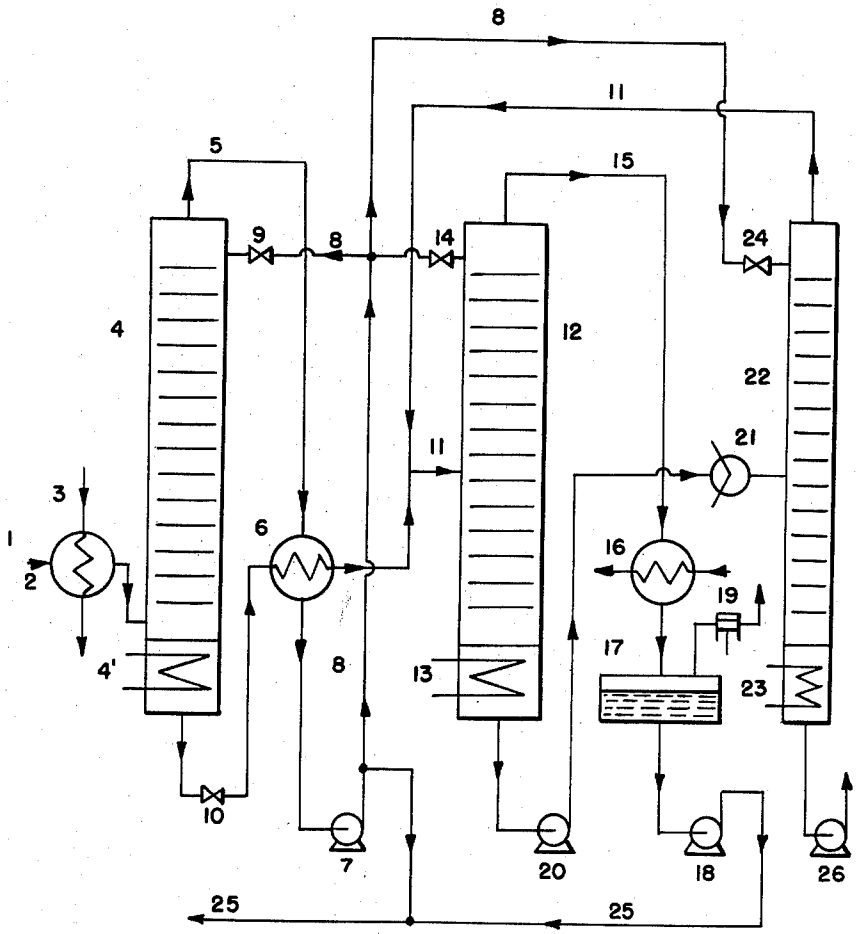
FIG. 3




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FIG. 4




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United States Patent Office 2,938,924
Patented May 31, 1960



2,938,924

# PRODUCTION OF ALCOHOLS AND KETONES BY THE OXIDATION OF CYCLOALIPHATIC OR ARALIPHATIC HYDROCARBONS

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10 Claims. (Cl. 260—586)

This invention relates to an improved process for the production of alcohols and ketones by oxidation of cycloaliphatic or araliphatic hydrocarbons. In particular it relates to the production of cyclohexanol and cyclohexanone, or of cyclo-octanol and cyclo-octanone, by the oxidation of cyclohexane or cyclo-octane by means of oxygen, air or other oxygen-containing gases, and, if necessary, while using any conventional oxidation catalysts.

The conversion of cycloaliphatic or araliphatic hydrocarbons to alcohols and ketones by treatment with oxygen or oxygen-containing gases is known in the art. In the practice of the prior art processes, however, acid products were obtained in varying amounts as by-products and this, as a result, not only reduced the yield of the oxidation products sought, but also further reduced the yields of alcohols by ester formation between the acid products and the alcohols. The separation of the oxidation mixture is also rendered considerably more difficult because of the presence of the esters.

In a known method, these shortcomings, in particular the formation of esters, are avoided by carrying out the oxidation of the hydrocarbons in the presence of added water, the amount of water added being between about 10 and 30% by weight with reference to the amount of hydrocarbon (U.S. Patent No. 2,565,087). This processing technique not only has the disadvantage that with the same space-time yields of oxidation products, such as alcohols and ketones, the capacity of the oxidation vessel must be considerably increased, but also the added water acts as an inhibitor by removing from the reaction zone substances which accelerate the reaction. Moreover when catalysts are used, their action is reduced.

In the method described in U.S. Patent No. 2,557,281, not only is feed of water to the oxidation vessel avoided, but even the water arising from the oxidation is removed immediately after its formation and stripped in separators from the hydrocarbons, which are returned to the oxidation zone. This method has the shortcoming that deposits of the acids, otherwise solid at room temperature, will occur in the connection lines causing clogging of the lines with consequent interruptions in the operation.

The primary object of this invention is to provide a simple method, capable of being carried out on an industrial scale, for the oxidation of cycloaliphatic or araliphatic hydrocarbons in the liquid phase with oxygen, air or other oxygen-containing gases which makes it possible to work in continuous operation without trouble and in which ester formation is substantially suppressed.

A further object of the invention is the oxidation of cycloaliphatic or araliphatic hydrocarbons in a plurality of successive oxidation zones and the maintenance of the content of acids, which are by themselves very valuable by-products, in the oxidation vessels and in the distillation processing of the oxidation mixture within such limits that they do not separate.



Another object is to minimize the formation of esters by the removal of the major proportion of the acidic oxidation products in the oxidation mixture emerging from at least one oxidation zone.

A still further object of the invention is the removal from the oxidation mixture of the acid components, as far as their presence interferes with carrying out the process in the individual oxidation stages, by washing with water the oxidation mixture resulting from at least one oxidation zone, to obtain an oxidation product of a composition which lends itself especially advantageously to further processing and from which the desired alcohols and ketones are separated readily in good yields and good purity.

A still further object of the invention is to provide higher efficiency in the distillation processing of the reaction mixture into its components, the distillation being rendered extremely cheap and economic by an extensive utilization of the energy, in particular the heat, available.

Still another object of the invention lies in the use of a definite type of reaction vessel for the practice of the oxidation. Other objects of the invention will appear from the following description.

We have found that the oxidation of cycloaliphatic or araliphatic hydrocarbons in the liquid phase to form the alcohols and ketones can be carried out with special efficiency and without the disadvantages hereinbefore described by passing the hydrocarbons at elevated temperature, if desired with the addition of oxidation catalysts, through a plurality of successive reaction vessels while introducing into said vessels a gaseous oxidizing agent, such as a gas containing oxygen. The oxidation products are washed with water at least once during the processing advantageously after they emerge from the last reaction vessel and the oxidation products are separated by distillation from the unreacted initial hydrocarbons. Another step in the process of our invention involves at least one treatment of the water washed oxidation mixture with aqueous solutions of basic-reacting alkali compounds, such as alkali metal hydroxides or carbonates.

As gases containing oxygen in accordance with the invention there can be employed air, air enriched with or deprived of oxygen and oxygen itself.

Preferred alkali metal hydroxides or carbonates for use in the practice of our invention are the hydroxides and carbonates of sodium and potassium metal. It is advantageous to use them in a concentration of 5 to 35%, advantageously 10 to 25% by weight.

Suitable cycloaliphatic or araliphatic hydrocarbons are in particular cycloparaffins, as for example cyclohexane or cyclo-octane, and also ethylbenzene and other alkylbenzenes having two or more, in particular 2 to 6, carbon atoms in the side chain.

The oxidation is carried out at elevated temperatures, as for example between about 120° and 170° C. The optimum temperatures differ with the particular hydrocarbon reactant used. In the case of cycloparaffins they lie below 150° C., for example at 135° to 145° C. for cyclohexane. The reaction is carried out at atmospheric or superatmospheric pressure, as for example at 2 to 50 atmospheres.

The preferred type of reaction vessels are those having a tubular insertion, in which the inner tube is positioned either on center or off center of the reaction vessel. The inner tube has a cross-section of 20 to 70% of the overall cross-section of the vessel and is positioned in the inner space of the vessel to provide a free space at both ends. The tube can be secured to the inner wall of the vessel at different places. The initial material and oxygen-containing gas, such as air, are introduced into the inner tube. A part of the liquid reaction product,

consisting of unreacted feed stock and oxidation product, is withdrawn together with the oxygen-containing gas at the opposite end of the reaction vessel. If the gas is removed at the opposite end, the liquid reaction mixture can also be removed from circulation at the inlet side. The other part of the reaction mixture flows back into the intermediate space between the tube and vessel wall and again enters the interior of the tube so that a circulation is produced. The initial material and the oxygen-containing gas can also be introduced into the intermediate space with the aid of one or more nozzles so that a part of the reaction mixture flows back through the interior of the tube and then passes again into the intermediate space. In general the volume circulated per hour in such vessels amounts to more than ten times, often 20 to 50 times, the total volume contained in the vessel.

To prevent the reaction temperature rising beyond a permissible degree cooling may be necessary, for example by providing cooling aggregates in the circulation system or by withdrawing part of the circulated reactants and products, passing them through a cooler outside the vessel and then returning them to the vessel. The circulation of the reactants and products in the vessel can also be intensified by pumping them through a recycle pipe situated outside the vessel. On the other hand vessels without the tubular insertion may be used—the circulation provided by one or more external pipes with circulatory pumps therein.

Suitable catalysts for use in the oxidation are the conventional type oxidation catalysts, as for example metals, in particular cobalt and also cerium, nickel, iron, lead, titanium, vanadium, chromium, molybdenum, uranium, manganese, platinum, silver, tin, calcium or magnesium. Oil-soluble salts of these metals are especially suitable, as for example naphthenic acid or mono- or dicarboxylic acid salts. Inorganic compounds of metals, as for example oxides or halides, sulfates, phosphates, vanadates, molybdates, tungstates and chromates can also be used. The catalysts can also be applied to carriers, such as bleaching earths, synthetically-made silicates, active aluminas, magnesia or zinc oxide. Further substances which accelerate oxidation, such as peroxides, can be co-employed. The catalysts are added to the hydrocarbons to be oxidized or to the oxidation mixture in amounts of 0.1 to 200 grams of metal to 1,000 kilograms of hydrocarbon or oxidation mixture. It is advantageous to work with 0.3 to 40 grams of metal to 1,000 kilograms of hydrocarbon or oxidation mixture.

In the practice of our invention the initial material as a feed stock, preferably in preheated condition, is charged in the first reaction vessel, with oxygen or oxygen-containing gas being simultaneously fed in in fine dispersion, for example by spraying at room temperature or a temperature ranging between 20° and 100° C. When needed, oxidation catalysts may also be fed in in a finely divided form, e.g. by spraying. The feed stock is preferably preheated to a temperature which lies about 10° to 50° C. below the oxidation temperature. About 20 to 70 cubic metres of air, for example, are introduced into the vessel for each 1,000 kilograms of hydrocarbon or of liquid oxidation mixture.

The reaction mixture is withdrawn for example at a point opposite to the point of entry, and introduced into the second reaction vessel, if necessary with further supply of oxygen or oxygen-containing gases and of catalysts. After passing through this vessel it is led in the same way through any further vessel, for example through five reaction vessels. The residence time in the entire reaction zone preferably amounts to at least 15 minutes, advantageously 40 minutes and more, as for example 1 to 3 hours and more. At least after passage through one stage, advantageously at least after the last oxidation stage, and preferably after each stage, water is fed in in an amount of 0.3 to 5% by weight, in particular 0.5 to 3% by weight with reference to the reaction mixture. It is advantageous thereafter to cool the water-containing mixture, if desired without decompression, in a cooler or heat exchanger to a temperature which lies about 20° to 70° C. below the oxidation temperature. The heat set free by the cooling of the mixture is preferably utilized by heat exchange to preheat the hydrocarbon mixture before the first reaction stage, and also may be employed to evaporate extensively the oxidation mixture after decompression on the way to the first distillation column.

The aqueous layer is stripped in a separator, it contains the major part, for example 50 to 90%, of the undesired acid oxidation products formed. The non-aqueous layer is led into the next oxidation vessel or to a distillation column, as the case may be, after a short washing with an aqueous solution of a basic-reacting alkali metal compound, such as a metal hydroxide or alkali metal carbonate, and separation from the aqueous washing phase.

The water can be introduced in an amount of 0.3 to 5%, in particular 0.5 to 3%, also into the last part of the reaction vessel in which oxidation no longer takes place. In this case the vessels having inbuilt tubes described above have proved especially suitable. The water is resupplied at various points to the recycle or the oxygen-containing gas. The aqueous layer is withdrawn at the lower part of the vessel. Above the aqueous layer, part of the liquid reaction mixture can be withdrawn in so far as it has not already been withdrawn overhead with the gas. Special regard should be had to the fact that no larger amounts of water are used because otherwise the course of the reaction is retarded and the yield lowered.

The alkaline washing solutions preferably used are from 5 to 30% aqueous solutions of sodium or potassium metal hydroxide or carbonate. The amount of solution used may be from about one quarter to about four times the amount of the oxidation product to be treated. The washing is carried out at elevated temperature, advantageously above 60° C., for example at 65° to 105° C. It is of advantage to follow each washing with alkali by a washing with water. Preferably in each separator, but at least in the last separator, the gases also are stripped. The gases are cooled, for example to room temperature, and treated with washing solutions. As washing solutions in the gas strippers, the oxidation product or fractions thereof, as for example cyclohexanone or cyclohexanol or the residue left after distilling off the cyclohexanone-cyclohexanol fraction, are especially suitable. It is preferable to use about 0.2 to 4 kilograms of solvent for each cubic metre of gas for the washing of the gases.

The non-aqueous portion of the oxidation mixture is then separated by distillation. This can be effected by a short residence time in vaporizers or preferably by longer residence times in a plurality of successive distillation columns at rising temperatures. In the latter case it is preferable to separate in the first column the bulk of the non-oxidized hydrocarbon. The temperature in the sump of this column lies at about 20° to 50° C. above the boiling temperature of the hydrocarbon, i.e., at about 100° to 130° C. in the case of cyclohexane.

The residue is then freed from the remaining fraction of the unconverted hydrocarbon in the second column at a higher temperature, for example at about the boiling temperature of the oxidation product of lowest boiling point, as for example cyclohexanone, and if desired split up into its alcoholic and ketonic components in further distillation columns. If the distillation is carried out in stages, the alkaline treatment can be carried out after the first distillation column. This treatment is carried out for example with an oxidation mixture which still contains at least 20% of non-oxidized hydrocarbons. The alkaline treatment can however be carried out in the same way after the practically complete separation of the non-oxidized hydrocarbons.

A specially preferred separation of the oxidation mixture, and one which is especially advantageous from the point of view of economy in heat, may be achieved by carrying out the distillation in stages, the pressure in the first stage being so much higher than in the second stage that the vapors leaving the first stage of the distillation provide by indirect heat exchange the heat of vaporization wholly or for the most part, and preferably also at least a part of the reflux heat, for the second stage.

Since considerable amounts, as for example up to 95%, of hydrocarbons of low boiling point are contained in the mixture leaving the last oxidation stage, and a high reflux ratio is needed for their separation at the necessary sharpness of separation, the utilization of the heat energy of the vapors leaving the first distillation stage is of great economical advantage. An embodiment of this distillative method of processing is shown by way of example in Figure 4 of the accompanying drawings and will now be described in greater detail.

The reaction mixture consisting of hydrocarbons and oxidation products, especially alcohols and ketones, enters the distillation apparatus at **1**. In a preheater **2**, which is heated with low pressure steam by a coiled tube **3**, the oxidation product is preheated to a temperature of about 95° C. and the mixture of vapor and liquid introduced at the bottom into the distillation column **4** which is kept under a pressure of 1.5 atmospheres. The constituents of highest volatility, i.e. the hydrocarbons, leave at the top of column **4** through a pipe **5**. The vapors are condsensed in a heat exchanger **6** and led with the aid of a pump **7** through a pipe **25** to a reservoir (not shown). Part of the hydrocarbons is branched off through a pipe **8** and returned as a reflux into the upper part of the column **4** through a valve **9**. The fraction of the oxidation product vaporized at the same time from the up-rising hydrocarbon vapors is driven back by rectification into the residue. In the sump of the column **4** such an amount of heat is supplied by a heating coil **4'** that the reflux is wholly or partly vaporized.

The mixture occurring in the sump of the distillation column **4**, which contains, in addition to the oxidation products, in particular alcohols and ketones, also hydrocarbons in amounts of from 85 to 90%, with reference to the mixture contained in the sump, is decompressed to about 0.3 atmosphere through a valve **10**. In this way a part, for example 10%, of the mixture, in particular low boiling hydrocarbon components, is vaporized. A further major part of the hydrocarbons which still remain liquid and a part of the oxidation product evaporate in the exchanger **6** by indirect heat exchange with the vapors leaving the column **4** through pipe **5**, which are condensed. The mixture of vapors and fractions of the mixture withdrawn through pipe **10** which have not yet vaporized is introduced into a column **12** which is additionally heated by sump heating **13**. The column **12** operates under a reduced pressure of about 0.2 to 0.25 atmosphere, the diminished pressure being maintained by a vacuum apparatus, for example a vacuum pump. The distillate escapes at the upper part of the column **12** through a pipe **15** and is condensed in a cooler **16** cooled with water and pumped through a collecting vessel **17** and pump **18** through a pipe **25** to a reservoir (not shown). In order that in the column **12** the up-rising vapors be fractionated and the oxidation products held back from the escaping hydrocarbon vapors, a part of the hydrocarbons is introduced as reflux into the upper part of the column through a valve **14**. By heating means **13**, such an amount of heat is supplied to the column **12** that the reflux is wholly or partly vaporized. Further heat of vaporization can also be supplied by the heating means **13**. In the latter case not only does the reflux vaporize completely, but also additional, partially liquid parts of the initial product introduced into the column **12** are vaporized. The residue collecting at the bottom of the column **13** is forced by pump **20** through a preheater **21**, which is heated with high pressure steam of 20 excess atmospheres, into distillation column **22**. Column **22** works at about the pressure of column **12**. In the preheater **21** as well as in the sump heating **23** of the column **22**, the residual fractions of the hydrocarbon, which are still mixed with the oxidation product withdrawn at the bottom of the column **12**, are vaporized. Fractions of the oxidation product vaporized therewith are fractionated out and held back for the most part by the introduction of hydrocarbons from the pipe **8** through valve **24** into the upper part of column **22**. The vapors leaving at the top of the column **22**, which contain mainly hydrocarbons with also slight traces of oxidation products, are supplied again to the column **12** through pipe **11**. The oxidation product free from hydrocarbons is withdrawn at the bottom of column **22** and conveyed by a pump **26**.



The rectification can also be carried out entirely in the last stage by condensing the hydrocarbons leaving at the top of column **22** in a special condenser. In this case the column **22** can be kept under any pressure, as for example atmospheric pressure.

For the first vaporization of the hydrocarbons in the preheater **2** there may preferably be utilized the heat inherent in the mixture to be worked up from the preceding oxidation of the hydrocarbons, which must be withdrawn between the reaction vessels.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

*Example 1*

5 cubic metres of cyclohexane which has been heated to 100° C. in a preheater **1** are fed per hour at a pressure of 30 atmospheres into a reaction vessel **4** (see Figure 1 of the accompanying drawings) having a capacity of 1.55 cubic metres from a container **41** by means of a pump. At the same time 100 cubic metres of air per hour are fed in through a pipe **2**, while 15 grams per hour of cobalt are sprayed in through pipe **3** in the form of an aqueous solution of cobalt acetate. The temperature in the reaction vessel is about 140° C. and is kept constant by the air introduced cold and the preheated cyclohexane.

The hot oxidation mixture which leaves the reaction vessel **4** together with exhausted air at a rate of 5 cubic metres per hour at a temperature of 140° C. is mixed continually with 30 kilograms of water per hour through the pipe **5**, cooled to about 90° C. in the cooler **6** and freed in separator **7** from the aqueous layer which is run off through pipe **8**. The oxidation mixture substantially freed from acid components, as well as the exhausted air are sprayed into the reaction vessel **12** after having passed the intermediate preheater **9**. The mixture of liquid and air is mixed when introduced in reaction vessel **12** with 100 cubic metres of air at room temperature per hour through the pipe **10** and 15 grams of cobalt in the form of an aqueous solution of cobalt acetate through pipe **11**. The temperature in the vessel **12** also amounts to 140° C. and is maintained in the same way as in the vessel **4** in spite of the heat of reaction set free by the added cold air and the reaction mixture entering at about 100° to 110° C.

From the reaction vessel **12**, the mixture leaving at a temperature of 140° C., which has been further oxidized up to about 3.5% with reference to the amount of cyclohexane supplied to vessel **4** per hour, is led through a cooler **14** where it is cooled to about 90° C. after 30 kilograms per hour of water have been continuously added to it through pipe **13**. From the separator **15** the aqueous phase is withdrawn through pipe **16**. To the non-aqueous phase 75 kilograms per hour of a 25% aqueous sodium hydroxide solution are added through a pipe **17**. From the separator **18**, the liquor containing the neutralized acid components is withdrawn through pipe

19, while through pipe 20 the exhausted air escapes and the oxidation mixture is withdrawn at about the middle of the separator. This is then led to a reaction vessel 24 after passing the preheater 21. At the same time 100 cubic metres of air are led per hour through pipe 22 and 235 grams of cobalt in the form of the catalyst solution already mentioned are introduced. The oxidation temperature in the reaction vessel 24 also amounts to 140° C. The oxidation mixture and the exhausted air, which leave the reaction vessel 24 at the top are mixed with 30 kilograms of water through pipe 25, the water being added continuously. The mixture is cooled to 90° to 100° C. in a cooler 26 and then brought into the separator 27. The aqueous phase is run off through pipe 28 while the air escapes through pipe 29. It is united with the waste air flowing out through the pipe 20 and cooled to 20° C. in the cooler 30. The condensate, which consists mainly of cyclohexane, is passed through separator 31 and pipe 32 to the container 41.

The uncondensed cold gases flow from the separator 31 into the washer 33, in which they are washed with oxidation product free from cyclohexane which is supplied through pipe 34 from the colum 49, and allowed to escape through pipe 35. 200 kilograms of washing liquor are thus introduced into the washer per hour.

The washing liquor laden with cyclohexane withdrawn from the sump of the washer 33 is united through pipe 36 with the product supplied from the separator 27 through pipe 37 and passed through vaporizer 38 to a distillation column 39. The coolers 6, 14, 26 and 30 may be in heat exchange with the vaporizer 38 and preheaters 1, 9 and 21.

In the column 39 there distills over at about 100° C. sump temperature the bulk of the unconverted cyclohexane. It is liquefied in the condenser 40 and supplied to the container 41.

The residue of the distillation column 39, which still contains about 60% of cyclohexane, is withdrawn from the bottom of the column, mixed per hour with 65 kilograms of a 12% aqueous caustic soda solution supplied through pipe 42 and passed into separator 43. The aqueous alkaline liquor is separated through pipe 44. The non-aqueous layer flows into separator 46 after 50 kilograms per hour of water have been added thereto through pipe 45. The water is run off from the separator 46 through pipe 47 and can be used for the preparation of the caustic soda solution. The washed product from the separator 46 is led through a preheater 48 into a distillation column 49 where the remaining cyclohexane is distilled off at a sump temperature of about 160° C. The cyclohexane is condensed in a cooler 50 and then passed to the container 41. The residue from the distillation column 49 consists of 40% of cyclohexanone, about 52% of cyclohexanol and about 8% of components of higher boiling point. A part thereof, amounting to about 180 kilograms per hour, is run off into a collecting vessel 52 while the remaining part is supplied through pipe 34 to a washer 53.

Through pipe 53, fresh cyclohexane is supplied from a container (not shown) to the container 41 at the rate at which it is used up by the oxidation.

The oxidation mixture freed from acid components and unreacted hydrocarbons which collects in the collecting vessel 52 may if desired be further separated into cyclohexanol and cyclohexanone by a conventional fractional distillation under reduced pressure, for example at 10 to 100 torr.

From the washing liquor run off through pipes 8, 16 and 28 there are obtained per hour as by-product about 15 kilograms of adipic acid by distilling off 10 to 20% of the water together with dissolved hydrocarbons, cooling, crystallizing out and filtering off. About twice the amount can be recovered by working up the alkaline washing water.

*Example 2*

From a container 30 (see Figure 2 of the accompanying drawings) 8 cubic metres per hour of cyclohexane are led under a pressure of 40 atmospheres through a preheater 1 into a reaction vessel 4 which is heated to 105° C. and which has a capacity of 3.2 cubic metres. At the same time 300 cubic metres per hour of air at room temperature are led through a pipe 2 and 20 grams of cobalt in the form of a solution of cobalt naphthenate in cyclohexane through a pipe 3. Through the common inlet pipe, cyclohexane, air and catalyst solution are mixed with reaction mixture circulating in the reaction vessel at 140° C. and the reaction temperature of 140° C. thereby kept constant.

75 kilograms of water per hour are mixed through a pipe 5 with the oxidation mixture which leaves the reaction vessel with the exhausted air. The mixture is cooled to 95° C. in a cooler 6 and separted into its phases in a separator 7. The aqueous phase with the dissolved acids is run off from the separator 7 through a pipe 8, while the exhausted air, laden with cyclohexane vapor, is allowed to escape through a pipe 9. The oxidation mixture, still containing a small amount of acid (about 0.2% by weight) is brought to a temperature of 110° C. by a preheater 10 and led into a reaction vessel 13 of 3.2 cubic metres capacity, there being mixed with the mixture per hour 250 cubic metres of cold air through a pipe 11 and 10 grams of cobalt in the form of a cobalt naphthenate solution in cyclohexane through a pipe 12.

The further oxidized mixture leaves the reaction vessel 13 with the exhausted air at 140° C. 90 kilograms per hour of water, supplied through a pipe 14, are added, the whole cooled in a cooler 15 to 90° C. and separated in a separator 16. The water laden with acid components is run off through a pipe 17 and the exhausted air through a pipe 18.

The air flowing from the pipes 9 and 18 is cooled to 20° C. in a cooler 19, freed in a separator 20 from condensed cyclohexane (which is withdrawn through a pipe 21 and returned to the container 30) and led to a washer 22 filled with filler bodies. In this the gas is washed free from cyclohexane with 200 kilograms per hour of oxidation product fed in through pipe 23. The oxidation product with the absorbed cyclohexane is decompressed through a pipe 25. It is united with the oxidation mixture free from water and gas which is decompressed through a pipe 26 from the separator 16, and led through a preheater 27 into a column 28. The gases washed out in the washer 22 are allowed to escape through a pipe 24.

In the column 28, the bulk of the unreacted cyclohexane (about 90° by weight) is distilled off, condensed in a cooler 29 and collected in the container 30. The sump of the column, with a content of 25% of cyclohexane, is led through a preheater 31 into a column 32. The cyclohexane distilled off from the top of the column is condensed in a cooler 33 and also collected in the container 30. As a sump there remains in the column 32 an oxidation product completely freed from hydrocarbon.

The oxidation product free from cyclohexane (of which 600 kilograms per hours are obtained and which still has an acid number of 60 and an ester number of 50) is withdrawn from the sump of the column 32 and supplied through a pipe 34 to treatment with alkali solution. Part of the product is branched off through a pipe 34 and supplied through the pipe 23 to the washer 22 in the amount already described.

The treatment with alkali solution takes place in the circulation pipe 35 in which 400 kilograms of oxidation product from the pipe 34 and 175 kilograms of a 20% aqueous caustic soda solution from the pipe 37 per hour are stirred up by a pump 36. The treated mixture is supplied from the cycled mixture through a pipe 38 to a centrifuge 39. The aqueous phase flows through a pipe

40, while the product separated from the alkali solution flows through a pipe 41. The product withdrawn through the pipe 41 in an amount of 350 kilograms per hour has 80 kilograms of water added to it through a pipe 42 and after mixing in a mixer 43 is led into a centrifuge 44. This separates the water through a pipe 45. The product free from water and acid (335 kilograms per hour) flows off through a pipe 46 into a container 47. The cyclohexane used up for the oxidation is replaced by fresh cyclohexane which is supplied through a pipe 48 to the container 30. Cyclooctane can be oxidized in an analogous manner, cyclooctanone and cyclooctanol being obtained as the main products. In addition suberic acid and low molecular acids are obtained.

*Example 3*

From a cyclohexane reservoir 42 (see Figure 3 of the accompanying drawings) 6.5 cubic metres per hour of cyclohexane are conveyed by means of a pump 1 under a pressure of 50 atmospheres through a heater 2 to a reaction vessel 3, the temperature of the cyclohexane thus being raised to 100° to 110° C. 200 cubic metres per hour of air are admixed through a pipe 4 and 5 grams per hours of manganese in the form of an alcoholic solution of manganese chloride through a pipe 5. The mixture is sprayed through a nozzle *d* into the inner central circulation tube *u* of the reaction vessel 3. The reaction vessel has a capacity of about 2 cubic metres. The mixture circulating in the reaction vessel, which is further heated by the heat of oxidation set free, is kept at a temperature of 145° C. The oxidation mixture (6.5 cubic metres per hour) from the reaction vessel 3 (which contains about 2.5% of oxidation products—mainly cyclohexanol and cyclohexanone, besides acids and esters) is led together with the exhausted air through a pipe 6 and through a cooler 7 and thus cooled to about 80° C. Through a pipe 8, a further 200 cubic metres per hour of air at room temperature are admixed and supplied to the reaction vessel 9. The reaction vessel 9 has a capacity of about 4 cubic metres and a central circulation tube $u_1$. This is of such length and so arranged that below and above the circulation there are separating chambers *a* and *b* each occupying about one fifth of the total space in the reaction vessel. The mixture supplied to the reaction vessel 9 is introduced through nozzles $d_1$ into the annular space between the inner circulation tube and the jacket of the reaction vessel. The temperature of the circulating mixture is kept at 140° C. The exhausted air is separated in the upper separating chamber while maintaining a liquid level. The air drawn off through a pipe 10 is cooled to 25° C. in a cooler 11 and led through a separator 12 and a pipe 13 to a washer 14 and therein washed with the oxidation product from container 46. The cold outgoing air, washed free from cyclohexane, is released from pressure and allowed to escape through a valve 15.

The fraction of hydrocarbons condensed in the cooler 11 is run off from the separator 12 through a pipe 23.

In the reaction vessel 9 about 110 kilograms per hour of aqueous solution from the pipe 16 are added through the central circulation tube $u_1$ through which the oxidation mixture, practically free from air, flows back. In the lower separation chamber *b* of the reaction vessel 9, the aqueous solution is separated and decompressed and allowed to escape through a valve 17. This solution contains about 70% of the acids and acid esters formed in the oxidation reation vessels 3 and 9 as well as other oxidation products and has a concentration of about 40% by weight of these organic substances.

Above the aqueous phase in the reaction vessel 9, the oxidation mixture, after a total of about 5% of the cyclohexane has been oxidized, is withdrawn, cooled to about 90° C. in a cooler 18 and washed countercurrently in a washer 19 with 100 kilograms of water per hour introduced through a pipe 20. During the washing the water absorbs the acid compounds still present in the oxidation mixture. From the lower end of the washer 19 the wash water is supplied by means of a pump 21 through the pipe 16 to the reaction vessel 9.

The washed oxidation mixture, which now contains about 4% of the oxidation product in the cyclohexane, is united through a pipe 22 with the condensate from the separator 12 conveyed through a pipe 23; 70 kilograms per hour of a 20% by weight aqueous caustic soda solution from a pipe 25 are added in pipe 24 and introduced into a separator 26. The alkali solution neutralizes and absorbs the free acids left and at the same time saponifies the bulk of the ester, the acids being absorbed. The aqueous solution is then decompressed through valve 27.

The oxidation mixture which is now neutral is decompressed down to about 1.5 atmospheres through a valve 28 and through a vaporizer 29 into a distillation column 30. The heater 2 and vaporizer 29 may be in heat exchange relation with the coolers 7, 11 and 18. About two-thirds of cyclohexane is distilled off in the distillation column 30 under a pressure of 1.5 atmospheres. The enriched oxidation mixture occurring in the sump of the column 30 is united with the washing oil laden with cyclohexane and coming from the washer 14 through valve 31 and pipe 32, and mixed in a pipe 33 with 20 litres per hour of a 10% by weight aqueous caustic soda solution. The caustic soda solution, which is introduced through a pipe 34, is separated again in a separator 35 and run off through a valve 36. The enriched oxidation mixture is decompressed through a valve 37 to a pressure of 0.5 atmosphere and extensively vaporized in a heat exchanger 38 with the aid of condensing vapors coming from the column 30. In a subsequent column 39, the cyclohexane is completely distilled off, condensed in a cooler 40 and conveyed by a pump 41 to a cyclohexane container 42. The cyclohexane condensed in the heat exchanger 38 and coming from the distillation column 30 is also collected in the container 42 through a valve 43. The amount of cyclohexane used up is replenished through a pipe 44. The amount of cyclohexane supplied per hour through the pipe 44 amounts to about 250 kilograms.

The oxidation product free from cyclohexane occurring in the sump of the column 39 (consisting per hour of 150 kilograms of cyclohexanone, 220 kilograms of cyclohexanol and 20 kilograms of products of higher boiling point) is conveyed by means of a pump 45 to a reservoir 46. From this 200 kilograms per hour are conveyed through a pipe 47 and a pump 48 to the gas washer 14. 190 kilograms of the oxidation product collected in the container 39 are withdrawn per hour through a pipe 49 to be separated by distillation.

The saving in energy in the separation of the non-oxidized hydrocarbons from the oxidation product by distillation, which is obtained by carrying out the distillation in a plurality of stages, the pressure in the first stage being so much higher than that of the second stage that the vapors leaving the first stage wholly or mainly supply the heat of evaporation and if desired also part of the reflux heat for the second stage, is illustrated by the following example.

*Example 4*

For the separation by distillation of an oxidation mixture which has been obtained, as described in the foregoing examples, by oxidation of cyclohexane and accumulates in an hourly amount of 10,000 kilograms of unreacted cyclohexane (95%) and 500 kilograms of oxidation product (5%), it would be necessary for the recovery of pure cyclohexane by conventional distillation to add about 30% of the amount of the distillate, i.e. 3,000 kilograms per hour of reflux liquid to the head of the rectification column. Thus 13,000 kilograms per

hour of cyclohexane would have to be vaporized with a heat expenditure of about 1,000,000 Kcal./hour.

By working according to Figure 4, about 4,000 kilograms of cyclohexane per hour are vaporized in vaporizer 2 by means of low pressure steam at a pressure of 6 atmospheres. The vapors are dephlegmated in column 4 with 1,200 kilograms per hour of cyclohexane at a pressure of 1.5 atmospheres and at about 90° C. The heat for the vaporization of the reflux is provided by a heating coil situated in the column through which low pressure steam of about 6 atmospheres flows.

5,200 kilograms of cyclohexane vapor flow at 90° C. into the heat exchanger 6 and are condensed therein. The heat of condensation serves further to vaporize the mixture coming from valve 10 which has been decompressed down to a pressure of 0.2 atmosphere, and in fact about the equivalent amount of cyclohexane, namely 5,200 kilograms per hour, is evaporated so that 5,200 kilograms of vaporous cyclohexane enter column 12 together with vaporized portions of the oxidation product and a mixture of only 800 kilograms of liquid cyclohexane and the bulk of the oxidation product. The vaporization temperature of this mixture with about 60% of cyclohexane amounts to about 60° C. at 0.2 atmosphere so that a heat interval of about 30° C. is present in the heat exchanger 6.

Into the column 12 there must be introduced again 30% of 5,200 kilograms, i.e. about 1,500 kilograms, of reflux for rectification. The heat necessary for this is produced in the heating means 13. The remaining 800 kilograms of cyclohexane are vaporized in the preheater 21. In the sump heating means 23, the heat necessary for vaporization of 30%=240 kilogram of reflux is produced.

In all therefore the following amounts of cyclohexane are vaporized by external supply of energy:

| | Kilograms/hour |
|---|---|
| Preheater 2 | 4,000 |
| Sump heating 4 | 1,200 |
| Sump heating 13 | 1,500 |
| Preheater 21 | 800 |
| Sump heating 23 | 240 |
| Total | 7,740 |

As compared with the vaporization of 13,000 kilograms per hour this represents a saving of heat of 41%.

If in this process the utilizable reaction heat arising in the oxidation (400,000 Kcal.%hour) is used in the heat exchanger 2 for the vaporization, about 5,000 kilograms of cyclohexane can be vaporized in the preheater 2. In this case the amounts of cyclohexane to be vaporized by external supply of heat are only as follows:

| | Kilograms/hour |
|---|---|
| Sump heating 4' | 200 |
| Sump heating 13 | 1,500 |
| Pheheater 21 | 800 |
| Sump heating 23 | 240 |
| Total | 2,740 |

As compared with the vaporization of 13,000 kilograms per hour, this represents a saving of heat of 79%.

What we claim is:

1. A process for production of alcohols and ketones by oxidation of cyclic hydrocarbons from the group consisting of cyclohexane, cyclo-octane, and alkyl benzenes having from 2 to 6 carbon atoms in their alkyl chain by passing the cyclic hydrocarbons in the liquid phase through successive oxidation zones and therein contacting the cyclic hydrocarbons with gases containing oxygen at temperatures from about 120–170° C. and pressures from atmospheric up to 50 atmospheres, separating the unreacted hydrocarbons from the cyclic hydrocarbon partial oxidation products containing alcohols and ketones, and, prior to separation of the unreacted hydrocarbons from the partial oxidation products, washing the oxidation mixture of partially oxidized products and unreacted hydrocarbons at least once with water to remove water-soluble carboxylic acids resulting from the partial oxidation and thereafter washing the oxidation mixture of the partially oxidized products and unreacted hydrocarbons at least once with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of alkali metal hydroxides and alkali metal carbonates.

2. The process according to claim 1 wherein, after the washing steps in accordance with the process of claim 1, the bulk of the unreacted hydrocarbons are distilled from the oxidation mixture, the residual oxidation mixture of the distillation step is washed with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of alkali metal hydroxides and alkali metal carbonates, the aqueous solution of alkali metal alkaline compound is separated from the washed, residual mixture, and the unreacted hydrocarbon remaining in the residual mixture is then distilled off from the partial oxidation products consisting essentially of alcohols and ketones.

3. A process according to claim 1 wherein, after the washing steps in accordance with the process of claim 1, the unreacted hydrocarbons are substantially completely separated from the oxidation mixture of partial oxidation products and unreacted hydrocarbons, the separated partial oxidation products are washed with an aqueous solution alkali metal alkaline compound, selected from the group consisting of alkali metal hydroxides and alkali metal carbonates, and the aqueous washing solution is separated from the washed partial oxidation products.

4. A process for production of alcohols and ketones by oxidation of cyclic hydrocarbons from the group consisting of cyclohexane, cyclo-octane, and alkyl benzenes having from 2 to 6 carbon atoms in their alkyl chain by passing cyclic hydrocarbons in the liquid phase through successive oxidation zones and therein contacting the cyclic hydrocarbons with gases containing oxygen at temperatures from about 120–170° C. at pressures from atmospheric up to 50 atmospheres, and, prior to separation of the unreacted hydrocarbons from the partial oxidation products, which contain the alcohols and ketones, washing with water the hot mixture of partial oxidation products and unreacted hydrocarbons exiting from at least one of the oxidation zones, cooling the water-organic mixture resulting from the water-washing step, separating the washing water from the cooled water-organic mixture, and thereafter washing the water-washed oxidation mixture of partially oxidized products and unreacted hydrocarbons at least once with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of alkali metal hydroxides and alkali metal carbonates.

5. The process according to claim 4 wherein the water-washing step is carried out between two successive oxidation zones, the water-organic mixture is cooled to a temperature 20° C.–70° C. below the oxidation temperature, and the water-washed organic mixture, after separation of the water phase therefrom, is again heated to an oxidation temperature in the range of 120–170° C. before it is conducted to the next oxidation zone.

6. A process for production of alcohols and ketones by oxidation of cyclic hydrocarbons from the group consisting of cyclohexane, cyclo-octane, and alkyl benzenes having from 2 to 6 carbon atoms in their alkyl chain by passing the cyclic hydrocarbons in the liquid phase through at least two successive oxidation zones and therein contacting the cyclic hydrocarbons with gases containing oxygen at temperatures from about 120–170° C. and pressures from atmospheric up to 50 atmospheres, washing with water the oxidation mixture of partially oxidized products and unreacted hydrocarbons exiting from each zone, and, at least after the last water-washing of the oxidation mixture, further washing the oxidation

mixture of partially oxidized products and unreacted hydrocarbons at least once with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of alkali metal hydroxides and alkali metal carbonates.

7. The process according to claim 6 wherein the water-washing after each oxidation zone is carried out by mixing the water with the hot oxidation mixture exiting from each oxidation zone, the water-organic mixture is cooled to about 20°–70° C. below the oxidation temperature, and the wash water phase is separated from the cooled water-organic mixture.

8. The process according to claim 6 wherein the number of water-washing steps in one less than the number of oxidation zones employed in the process of claim 6.

9. A process for the production of alcohols and ketones by the oxidation of cyclic hydrocarbons from the group consisting of cyclohexane, cyclo-octane, and alkyl benzenes having from 2 to 6 carbon atoms in their alkyl chain by passing the cyclic hydrocarbons in the liquid phase through successive oxidation zones and therein contacting the cyclic hydrocarbons with gases containing oxygen at temperatures from about 120–170° C. and pressures from atmospheric up to 50 atmospheres, washing the oxidation mixture of partially oxidized products and unreacted hydrocarbons at least once with water to remove water-soluble carboxylic acids resulting from the partial oxidation, thereafter distilling off from the oxidation mixture the bulk of the unreacted hydrocarbons, washing the resulting residual oxidation mixture of the distillation step with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of alkali



metal hydroxides and alkali metal carbonates, separating the aqueous solution of the alkali metal alkaline compound from the washed, residual mixture and thereafter distilling off the unreacted hydrocarbon remaining in the residual mixture from the partial oxidation products consisting esesntially of alcohols and ketones.

10. A process for production of alcohols and ketones by oxidation of cyclohexane by passing cyclohexane in the liquid phase through successive oxidation zones and therein contacting the cyclohexane with gases containing oxygen at temperatures from about 120–170° C. and pressures from atmospheric up to 50 atmospheres, separating the unreacted hydrocarbon from the cyclohexane partial oxidation products containing alcohols and ketones, and, prior to separation of the unreacted hydrocarbons from the partial oxidation products, washing the oxidation mixture of partially oxidized products and unreacted hydrocarbons at least once with water to remove water-soluble carboxylic acids resulting from the partial oxidation and thereafter washing the oxidation mixture of the partially oxidized products and unreacted hydrocarbon at least once with an aqueous solution of an alkali metal alkaline compound selected from the group consisting of sodium hydroxide, sodium carbonate, potassium hydroxide, and potassium carbonate.

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UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 2,938,924 May 31, 1960

Walter Simon et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 19, for "separted" read -- separated --; line 62, for "hours" read -- hour --; column 9, line 68, for "reation" read -- reaction --; column 11, line 40, for "heating 4" read -- heating 4′ --; line 49, for "Kcal.%hour" read -- Kcal./hour --; column 13, line 14, for "in one" read -- is one --.

Signed and sealed this 29th day of November 1960.

(SEAL)

Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents