

Process for separating off organic acids from aqueous solutions

The present invention relates to a process for separating off organic acids
5 from aqueous solutions.

In particular, the invention relates to a process for cleaning up the process
water in aldolization reactions.

In many base-catalyzed condensation reactions of organic compounds, in
particular in the reaction of aldehydes, carboxylic acids, which neutralise
10 some of the catalyst, are formed as byproduct. A process of great industrial
importance is, for example, the condensation of n-butyraldehyde to form 2-
ethylhex-2-enal and water. In this process, the reaction mixture is usually
worked up as follows: in the first step, the product-containing organic phase
is separated from the aqueous phase (catalyst solution and reaction water)
15 in a settling tank. Owing to the polarity of the organic acids formed in the side
reactions and the base used as catalyst, these two components are principal-
ly present in the aqueous phase. Direct feeding of this aqueous phase to the
effluent treatment plant is therefore usually undesirable, owing to the high
loading with bases and organic constituents. In addition, on account of the
20 injection of the base with the aqueous phase from the process, to ensure a
constant catalyst concentration, fresh base must constantly be fed to the
process, which is cost-intensive and contradicts the actual meaning of the
term catalyst.

WO 92/07648 discloses a process for the recovery of sodium hydroxide
25 solution from process waters of the abovementioned type. In this process,
the object of which is to treat the aqueous phases arising in the aldol
condensation, cation-exchange membranes are used. The aqueous phase in
this process, in addition to the basic catalyst, also comprises the metal salts

of the organic acid and alcohol formed as byproducts. This solution is conducted through the anode chamber into a two-chamber membrane electrolysis cell. When an electric field is applied, the metal cations migrate into the cathode chamber and react with the hydroxide ions formed at the cathode to give the metal hydroxide. In the anode circuit, an aqueous solution remains which comprises predominantly only the organic acids and alcohol. Disposal of this solution is complex, since the organic constituents are only present at low concentrations and the solution cannot thus be fed directly to thermal waste disposal. Recovery of the organic acids present in low concentrations is also not worthwhile.

DE 196 04 903 discloses a similar process for separating off alkali solution from the product arising in the aldol condensation, which process operates according to the principle of three-chamber electrolysis or three-chamber electrodialysis. In this process, the product-containing phase, after removal of an aqueous phase, is conducted through the central chamber of the electrolysis cell which is bounded by an anion-exchange membrane and a cation-exchange membrane. In the electric field, in the case of sodium hydroxide solution as catalyst, the Na^+ ions migrate through the cation-exchange membrane and form, in the cathode chamber, with the OH^- ions produced at the cathode, sodium hydroxide solution. The OH^- ions present in the central chamber migrate through the anion-exchange membrane into the anode chamber and react with the H^+ ions produced at the anode to form water. In this process for separating off alkali solution, the base is removed from the product, but the basic and organic constituents present in the aqueous phase are not worked up.

In both of the abovementioned processes, the phase to be treated, during the course of the electrolysis or electrodialysis, is depleted in dissolved metal hydroxide, and the conductivity of the solution decreases with advancing electrolysis or electrodialysis. This means that an ever increasing power input is necessary to separate off constituents still present in the phase to be treated.

A further known possible method for treating aqueous solutions comprising organic constituents is acidifying the aqueous solution until phase separation results. However, in this case only the high boilers are removed from the solution, the organic acids remain in the aqueous phase. In addition, there is
5 further salting of the mass stream of the aqueous solution, which makes disposal still more difficult.

The object therefore underlying the invention is to provide a simple process for separating off organic acids from aqueous solutions which, in particular, facilitates the workup of aqueous phases separated off from aldolization
10 reactions.

Surprisingly, it has been found that separating off organic acids from aqueous solutions is considerably simplified by the use of electrochemical processes.

The present invention therefore relates to a process for separating off
15 organic acids from aqueous solutions, which comprises separating off the organic acids from the solution to be treated by electrochemical processes.

Using the process according to the invention, all aqueous solutions of organic acids can be treated independently of their origin, but in particular those which are produced in aldolization reactions.

20 In these base-catalyzed aldol condensations carried out in a known manner, on account of the reaction mechanism, 1 mol of water is formed per 2 mol of aldehyde or ketone used. In addition, the base is added to the reaction as an aqueous solution. After the reaction, an organic phase and an aqueous phase are present. To separate off the wanted product, use is generally
25 made of phase separation using a phase separator. The organic phase principally comprises the wanted product, whereas the aqueous phase comprises the catalyst used and organic constituents which frequently arise in side reactions of the aldol condensation. In particular the disproportiona-

tion reaction of the aldehydes or ketones, which is also known as the Cannizarro reaction, is to be mentioned here. In this reaction, two molecules of aldehyde or ketone produce one molecule of carboxylic acid and one molecule of alcohol, whose carbon chain length depends on that of the aldehyde or ketone used. The organic acids are readily water-soluble up to a chain length of 4 to 5 carbon atoms, so that they principally remain in the aqueous phase in the phase separation.

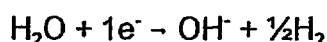
The organic acids are separated from aqueous solutions by two variants of the electrochemical process according to the invention, electrolysis and electrodialysis. In the two variants, preferably, before the electrochemical process according to the invention is carried out, some of the water is taken off from the mass stream by generally known processes, preferably by a flash evaporation. This water is virtually free of inorganic and organic pollutants and can thus be fed directly to further use or disposal. However, a partial stream of the aqueous phase can also be withdrawn and treated directly.

In the electrolytic variant, the separation is achieved by introducing the aqueous solution to be treated into the cathode chamber of an electrolysis module. This is equipped according to the invention with at least one commercial anion-exchange membrane, such as the AHA-2 from Tokuyama Soda Ltd., which separates the cathode chamber from the anode chamber.

The cathode chamber is preferably incorporated into a reservoir circuit into which the solution to be treated is introduced. The anode chamber, into which the organic acid, preferably the acid already present in the solution to be treated, is introduced, is preferably likewise connected into a circuit containing at least one reservoir. Flow passes through the cathode chamber cocurrently or countercurrently, preferably cocurrently, with the anode chamber. However, flow can pass through the cathode chamber and anode chamber without, in each case, recirculation of the solution to be treated or the acid solution introduced.

In the anode chamber and the cathode chamber there is at least one electrode in each case, that is to say one anode and one cathode. The cathode consists of a material known to be used for electrolyses, preferably steel. The anode preferably consists according to the invention of steel,
5 platinum black, platinum, graphite, mixed oxide, or it consists of a combination of these constituents, pure or applied to, or incorporated in, a support material, preferably titanium.

Applying an electrical voltage produces an electric field between the electrodes. According to the invention, under the influence of the field, the
10 cations, in the case of, for example, base-catalyzed preparation of octenyl from butanal using sodium hydroxide solution as base, sodium ions, migrate toward the cathode, and the anions, preferably organic acid radicals, but also OH^- ions, migrate through the anion-exchange membrane toward the anode. At the cathode in the cathode chamber, the sodium ions react with the
15 hydroxide ions produced at the electrode in accordance with the formula



to form sodium hydroxide solution. At the anode, the negatively charged acid radicals which have migrated into the anode chamber react with the H^+ ions produced at the electrode in accordance with the formula



to form the acid. By means of the abovementioned processes, the organic acids are separated off in the cathode chamber from the solution to be treated comprising the organic acids and these organic acids accumulate in the anode chamber. The process is therefore outstandingly suitable for
25 separating off organic acids from aqueous solutions. In the case of base-catalyzed aldolization processes, the aqueous solution in the cathode chamber to be treated also comprises bases, in addition to organic acids. This solution can not only be depleted in the cathode chamber in organic

acids by the abovementioned process, but also be enriched with base, and thus can be reused directly in the process as catalyst, without needing to be disposed of.

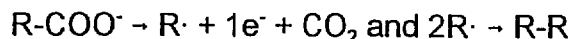
If the solution to be treated originates from aldolization processes and if it thus contains, in addition to organic acids, the basic catalyst, the ratio of acid to base in the aqueous solution to be treated is preferably varied to optimize the separation efficiency. By neutralizing the base in the aqueous solution by increasing the acid concentration, preferably the organic acids which are already present in the solution to be treated, the proportion of acid anions in comparison with hydroxide anions increases. As a result, the organic acid can be transported through the anion-exchange membrane with higher selectivity, i.e. higher current efficiency. The electric current is therefore principally transported by the acid anions.

Likewise, to optimize the separation efficiency and to decrease the energy input necessary, a strong mineral acid, such as sulfuric acid, or a base, preferably - if present - the base already present in the solution to be treated, can be added to the organic acids introduced into the anode chamber in order to increase the conductivity in this chamber. This is advisable, since the conductivity of the solution in the anode chamber is dependent on the ionic concentration. This is only very low when the pure acid solution is introduced, since the ionic concentration is dependent on the dissociation constants of the organic acids introduced. By adding base which is present in dissociated form in water and thus increases the ionic concentration of the solution in the anode chamber, the conductivity in the anode chamber can be matched to that in the cathode chamber and as a result the energy input can be reduced.

By setting a current density at from 100 to 1000 A/m² according to the invention, two additional treatment effects can be achieved.

Firstly, the Kolbe reaction at the anode can be exploited to split organic acids

electrochemically into water-insoluble hydrocarbons, in accordance with the formulae



(R is any organic radical) by elimination of CO_2 . Since the resulting hydrocarbons are mainly water-insoluble, these can be separated off from the anode liquid, for example, by a phase separator downstream of the anode chamber and fed to disposal or further processing. By choosing the voltage applied, in this process there is therefore the possibility, depending on which organic acids are formed in the aldolization process, of deciding whether principally the acid or some of the acid is to be further processed as hydrocarbon which can be synthesized according to the formula given above.

The second effect which the process according to the invention can make use of, depending on the way it is carried out, is apparently based on induced convection flow in the membranes. Surprisingly, even neutral organic compounds are separated off during the electrolysis from the aqueous solution to be treated. These compounds frequently occur as byproducts in aldolization reactions in the aqueous phase in addition to bases and organic acids. Owing to the effect, the neutral organic compounds migrate with the anions through the anion-exchange membrane from the cathode chamber which comprises the aqueous solution to be treated into the anode chamber, where they likewise can be separated off by phase separation. The neutral organic compounds thus obtained can again be fed to disposal or further processing.

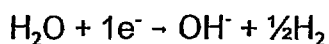
The second variant of the process according to the invention is electrodialysis, which is preferably used when relatively large volumes of solutions are to be treated or organic acids are to be separated off from aqueous solutions in a relatively short time. For this purpose, the number of chambers in the electrolysis module is increased in such a manner, that between the outer chambers which receive the electrodes, which correspond to those in

the electrolytic variant of the process according to the invention, anion-exchange membranes and bipolar membranes are used alternately. Commercial membranes can be used. As anion-exchange membrane, use can be made of, for example, the AHA-2 membrane from Tokuyama Soda Ltd., and,
5 as bipolar membrane, use can be made, for example, of the bipolar membrane from Aqualytics.

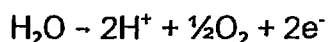
The cathode chamber and the chambers receiving the solution to be treated are jointly or separately, preferably jointly, preferably again incorporated into a reservoir circuit into which the solution to be treated is introduced. Flow
10 passes through the cathode chamber countercurrently or cocurrently, preferably cocurrently, to the stream of the chambers receiving the acid, the acid chambers. Flow likewise passes through the solution-containing chambers countercurrently or cocurrently, preferably cocurrently, to the stream in the chambers bearing the acid. The anode chamber and the other
15 chambers receiving the acid are jointly or separately, preferably jointly, preferably likewise incorporated into a reservoir circuit into which acid is introduced. Flow passes through the anode chamber countercurrently or cocurrently, preferably cocurrently, to the stream in the chamber bearing the solution to be treated. Flow likewise passes through the acid chambers
20 countercurrently or cocurrently, preferably cocurrently, to the stream in the chambers bearing the solution to be treated. As was the case earlier in the electrolysis, incorporating the chambers into circuits is not compulsory.

Applying an electrical voltage produces an electric field between the electrodes. According to the invention, under the effect of the field, the
25 cations - in the case of, for example, base-catalyzed preparation of octenal from butanal using sodium hydroxide solution as base, the sodium ions - migrate toward the cathode to the cathode or a bipolar membrane, and the anions, preferably organic acid radicals, but also OH^- ions, migrate through the anion-exchange membrane toward the anode or toward a bipolar
30 membrane. At the cathode in the cathode chamber, and at the bipolar membranes, in the solution circuit, the sodium ions, together with the

hydroxide ions produced at the electrode in accordance with the formula



or at the bipolar membranes by splitting water into OH^- and H^+ ions, form sodium hydroxide solution. At the anode or the bipolar membranes, the negatively charged acid radicals which have migrated into the anode chamber or the acid chambers, together with the H^+ ions produced at the electrode in accordance with the formula



or at the bipolar membranes by splitting water into OH^- and H^+ ions, form acid. By means of the abovementioned processes, the organic acids are separated off from the organic-acid-containing solution and these organic acids accumulate in the anode chamber and the acid chambers. The process is therefore outstandingly suitable for treating relatively large volumes of organic-acid-containing aqueous solutions. In the case of base-catalyzed aldolization processes, the aqueous solution to be treated in the cathode chamber or in the chambers bearing the solution to be treated also comprises bases, in addition to organic acids. This solution can be depleted in organic acids and enriched in base by the abovementioned processes in the cathode chamber or in the chambers bearing the solution to be treated, and thus can be directly reused in the process as catalyst.

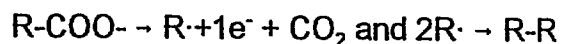
If the solution to be treated originates from aldolization processes and if it thus comprises, in addition to organic acids, the basic catalyst as well, preferably, to optimize the separation efficiency, the ratio of acid to base in the aqueous solution to be treated is varied. By neutralization of the base in the aqueous solution by increasing the acid concentration, preferably the organic acids which are already present in the solution to be treated, the proportion of acid anions compared with the hydroxide anions increases. As a result, the organic acid can be transported through the anion-exchange

membrane with higher selectivity, i.e. higher current efficiency. The electrical current is therefore principally transported by the acid anions.

Likewise, to optimize the separation efficiency and to decrease the energy input required, a base, preferably - if present - the base already present in the solution to be treated, can be added to the acid introduced to increase the conductivity in the chambers in which acid is introduced. This is advisable, since the conductivity of the solution in the anode chamber and in the acid chambers is dependent on the ionic concentration. When the pure acid solution is introduced, this is only very low, since the ionic concentration is dependent on the dissociation constant of the organic acid introduced. By adding the base which is present in dissociated form in water and thus increases the ionic concentration of the solution in the anode chamber, the conductivity in the anode chamber or the acid chambers can be matched with that in the cathode chamber or in the chambers comprising the solution to be treated and as a result the energy input can be reduced.

By setting a current density of from 100 to 1000 A/m² according to the invention, two additional treatment effects can be achieved.

Firstly, the Kolbe reaction at the anode can be utilized to split the organic acids electrochemically into water-insoluble hydrocarbons in accordance with the formulae



(R is any organic radical) by eliminating CO₂. Since the resulting hydrocarbons are chiefly water-insoluble, these can be separated off from the anode liquid, for example, in a phase separator downstream of the anode chamber and fed to disposal or further processing. By the choice of the applied voltage, there is thus in this process the possibility of deciding, depending on which organic acids are produced in the aldolization process, whether the acid or some of the acid is to be further processed as hydrocarbon which can

be synthesized in accordance with the formula specified above. Since the Kolbe reaction only takes place directly at the anode, in the electrodialytic variant of the process according to the invention, only a small portion of the acid can be transformed into a hydrocarbon.

5 The second effect which the process according to the invention can make use of, depending on the variant, is apparently based on an induced convection flow in the membranes. Surprisingly, even neutral organic compounds are separated off from the aqueous solution to be treated during the electrolysis. These compounds frequently occur as byproducts in
10 aldolization reactions in the aqueous phase in addition to bases and organic acids. Owing to this effect, the neutral organic compounds migrate together with the anions through the anion-exchange membrane from the chamber which comprises the aqueous solution to be treated into the anode or acid chambers. The neutral organic compounds can likewise be separated off by
15 phase separation from the anode circuit or acid circuits. The neutral organic compounds thus obtained are again fed to disposal or further processing.

Preferably, the aqueous solution treated according to the invention is fed to an effluent treatment plant or to further processing. The organic constituents in the acid circuit which have been separated off from the aqueous solution
20 to be treated are concentrated and either fed directly to thermal disposal or further processed, e.g. separated into water-soluble and water-insoluble compounds by means of a phase separator and disposed of or further processed individually.

The processes according to the invention are preferably carried out at
25 atmospheric pressure and preferably at temperatures between 20°C and 90°C, particularly preferably from 30°C to 60°C.

The processes according to the invention can be carried out continuously or batchwise by an electrolysis or electrodialysis method. The strength of the electric field applied is dependent, inter alia, on apparatus conditions and on

the material pairs present in the solution to be treated and should be of a level such that the effects according to the invention are achieved. Preferably, a current density of from 50 to 1000 A/m² is set.

Figures 1 and 2 show by way of example two variants of the process according to the invention, without the process being restricted to these.

Figure 1 shows an electrolytic variant of the process according to the invention. The electrolysis module is divided by an anion-exchange membrane A into the two chambers 1 and 2. The anode chamber 1, in which the anode marked with + is disposed, is here charged, for example, with a solution comprising butyric acid HBs. The aqueous solution to be treated, in this example a wastewater stream which comprises NaOH and the sodium salt of butyric acid NaBs, flows through the cathode chamber 2 in which is disposed the cathode marked by -. In the electric field, the Na⁺ ions migrate to the cathode and there, together with the OH⁻ ions formed, form sodium hydroxide solution. The H⁺ ions produced at the anode (+) react with the anions OH⁻ and Bs which have migrated through the anion-exchange membrane A to form butyric acid and water.

An electrodialysis variant of the process according to the invention is shown in Figure 2. The electrolysis module is divided by four anion-exchange membranes A and three bipolar membranes BM into a cathode chamber 2, an anode chamber 1, three chambers 3 bearing the solution to be treated and three acid chambers 4. A butyric acid (HBs)-containing solution, which is introduced from reservoir V1, flows in this example in the circuit cocurrently through the anode chamber 1 which is marked by +. The acid chambers 4 are likewise charged cocurrently with the solution introduced in the reservoir V1. The solutions of the anode chamber and the acid chambers combine after flowing through the electrolysis module and are collected in a reservoir V1. From this reservoir, the solution is fed to the chambers, the solution being divided among chambers 1 and 4. The cathode chamber 2, in which the cathode marked by - is disposed, is charged cocurrently by the

solution to be treated, which comprises, in this case, NaOH and NaBs, which is introduced from the reservoir V2. The chambers 3 comprising the solution to be treated are likewise charged concurrently with the solution introduced in the reservoir V2. The solutions of the cathode chamber 2 and the chambers
5 3 bearing the solutions to be treated are combined after flowing through the electro dialysis module and are collected in the reservoir V2. In the electric field, the Na^+ ions in chambers 2 and 3 migrate to the cathode or to the bipolar membranes BM and there, with the OH^- ions formed at the cathode (-) or the bipolar membrane BM, form sodium hydroxide solution. The H^+ ions
10 formed at the anode (+) or at the bipolar membranes BM, react with the OH^- and Bs^- anions which have migrated through the anion-exchange membrane A from the chambers 2 or 3 into chamber 1 or the chambers 4, to form organic acid and water.

The process according to the invention is described in more detail by the
15 following examples, without being restricted thereto. In the examples, the process is illustrated on the basis of electrolysis, since this is also the basis of the electro dialysis variant and other variants.

Examples

Example 1: Cleaning up the reaction water from a methylbutanal aldolization

20 In a two-chamber electrolysis module, whose chambers are separated by an anion-exchange membrane of AHA-2 from Tokuyama Soda Ltd., an electrolysis was carried out at a current density of 350 A/m^2 using an anode of titanium with mixed oxide having a surface area of 100 cm^2 , and a cathode of expanded stainless steel metal having a surface area of 100 cm^2 . The
25 distance of the electrodes from the membrane was 2.5 mm and the membrane area was 100 cm^2 . In the anode circuit, a preconcentrated methylbutyric acid solution, to which 1% by weight of the sodium hydroxide solution had been added to increase conductivity, was introduced; in the cathode circuit, the reaction water from a methylbutanal aldolization, which comprises

sodium hydroxide solution and methylbutyric acid, was introduced. The conductivities of these solutions in all chambers were determined permanently using a measuring apparatus from WTW during the entire electrodialysis operation.

- 5 In the course of electrolysis, the conductivity in the reaction water circuit increased to a maximum value of 13 mS/cm. In the anode circuit, the conductivity remains virtually constant. Figure 3 shows the time course of conductivity in the anode chamber, and Figure 4 shows the time course of conductivity in the cathode chamber.

10 Example 2: Cleaning up the reaction water from an octenal preparation

- In a two-chamber electrolysis module as specified in Example 1, with the same equipment, three further electrolyses were carried out. Instead of methylbutyric acid, the reaction water used, which arose in octenal preparation, comprised butyric acid. In these experiments, in addition, the ratio of
15 initial butyric acid concentration to hydroxide concentration was varied. For this purpose, in the second and third electrolysis, the concentration of butyric acid in the reaction water was increased by 0.3 or 0.6 mols/l by adding butyric acid. The conductivities of these solutions in all chambers were determined permanently using a measuring apparatus from WTW during the
20 entire electrodialysis procedure.

- At relatively high butyric acid concentrations, the conductivity decreases, since the sodium hydroxide solution present in the reaction water is neutralized by the butyric acid. By neutralizing the base in the aqueous solution by increasing the acid concentration, preferably the organic acids which are
25 already present in the solution to be treated, the proportion of acid anions increases in comparison with the hydroxide anions. As a result, the organic acid can be transported through the ion-exchange membrane with higher selectivity, i.e. with higher current efficiency. The electric current is therefore principally transported by the acid anions. As a result, the current efficiency

increases with greater addition of butyric acid to the reaction water circuit. In Figure 5, the current efficiency is plotted against butyric acid concentration.



Patent Claims:

1. A process for separating off organic acids from aqueous solutions, which comprises carrying out the separation by an electrochemical process.
2. The process as claimed in claim 1, wherein the organic acids are
5 separated off by electrolysis.
3. The process as claimed in claim 1, wherein the organic acids are separated off by electrodialysis.
4. The process as claimed in claim 2, wherein the solution to be treated is introduced into the cathode chamber 2, the cathode chamber 2
10 being separated from the anode chamber 1 by at least one anion-exchange membrane A.
5. The process as claimed in claim 3, wherein, in the electrodialysis, the acid chambers 4 are separated from the adjacently disposed chambers 3 and 2, which comprise the aqueous solution to be treated, on the side
15 facing the cathode by at least one anion-exchange membrane A and on the side facing the anode by at least one bipolar membrane BM.
6. The process as claimed in at least one of the preceding claims, wherein base is added to the acid, which was charged for the uptake of anions, in chambers 1 or 4 or 1 and 4.
- 20 7. The process as claimed in at least one of the preceding claims, wherein neutral organic compounds are separated off.
8. The process as claimed in at least one of the preceding claims, wherein use is made of at least one electrode of steel, platinum black, graphite, mixed oxide, pure platinum or of a combination of these
25 constituents in pure form or applied to or incorporated in a support material.
9. The process as claimed in at least one of the preceding claims, wherein the separation process is carried out at from 20 to 140°C.
10. The process as claimed in claim 9, wherein the separation process is carried out at from 30 to 60°C.
- 30 11. The process as claimed in at least one of the preceding claims, wherein the process is carried out continuously.
12. The process as claimed in at least one of claims 1 to 10, wherein



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the process is carried out batchwise.

13. The process as claimed in at least one of the preceding claims.
wherein organic compounds are split electrochemically at the anode.

14. The process as claimed in at least one of the preceding claims.
5 wherein the solution to be treated comprises base, and organic acid is added
to this aqueous solution.

15. The process as claimed in claim 14, wherein preferably an acid
which is already present in the solution to be treated is added.

16. The process as claimed in at least one of the preceding claims 1
10 to 15 for separating off organic acids from the process water which arises in
aldolization reactions.

This Sheet Has Been Replaced

