



PROCESS FOR THE SEPARATION OF ALIPHATIC DIACIDS FROM THEIR MIXTURES WITH ADIPIC ACID

The present invention relates to a process for the separation of one or more aliphatic diacids, from mixtures comprising adipic acid.

Adipic acid is one of the two starting materials on which polyamides-66 are based.

Various processes exist for the preparation of adipic acid, some of which are industrial and others of which are at the research or development stage.

One process which forms the subject of various patent applications comprises hydroxycarbonylating butadiene in order to form pentenoic acids, and then hydroxycarbonylating the latter acids in order to form adipic acid. During the second hydroxycarbonylation reaction, methylglutaric acid, ethylsuccinic acid and dimethylsuccinic acid are also formed, in amounts which vary depending on the conditions under which the process is carried out.

These various branched saturated aliphatic diacids may be upgradable to a greater or lesser extent, but it is important in all cases to separate them as much as possible from the adipic acid, which remains, qualitatively and quantitatively, the most important compound.

It is possible to use processes for fractionating the mixtures, for example by crystallization, in order to separate the branched diacids from the adipic acid. However, this technique does not allow a suitable, easy separation of the adipic acid isomers due to the very close physical properties of all these diacids.

The present invention provides a process for the separation of at least some of one or more branched, saturated aliphatic diacids having 6 carbon atoms, from a mixture comprising said diacid or diacids and adipic acid, which comprises at least partly converting said diacid or at least some of said diacids into the corresponding anhydride or anhydrides.

In the present text, the diacid mixtures to which



the invention applies encompasses both mixtures of a single one of these diacids with adipic acid and mixtures of several of them with adipic acid, and may, obviously, comprise other compounds. When the term "diacids" is used it is intended at the same time to cover a single diacid. Similarly, this term "diacids" will not, except where otherwise mentioned, encompass adipic acid. Finally, the operation for the conversion of the diacids into corresponding anhydrides will also be referred to as "anhydridization".

The saturated aliphatic diacids used in the process of the invention are, for example, 2-methylglutaric acid and/or 2-ethylsuccinic acid and/or dimethylsuccinic acid.

Anhydridization of the saturated aliphatic diacids may, for example, be performed by heating the mixture comprising them to a temperature equal to or above 60°C.

In order to facilitate the dehydration of the diacids, it is generally preferable to separate, especially by distillation or crystallization, the anhydrides formed or the water formed, during the anhydridization or after it. However, this is not essential and the anhydrides formed may also remain in the reaction mixture and may be separated from the adipic acid and from the other compounds present by a known means such as, for example, a distillation or a crystallization, only during a subsequent operation.

Since the heating and the possible distillation may be carried out at a pressure equal to, above or below atmospheric pressure, the temperature at which the anhydridization will be performed may vary as a function of this pressure, and as a function of the composition of the mixture to be treated.

However, as a guide, the process will generally be carried out at a temperature of 80°C to 350°C.

The process may advantageously be performed in the presence of a homogeneous acid catalyst, that is to say one which is soluble in the reaction medium, having a pKa below or equal to 5 such as, for example, sulphuric acid, hydriodic acid, para-toluenesulphonic acid, trifluoroacetic acid, or trifluoromethanesulphonic acid, or a heterogeneous acid catalyst such as, for example, boron phosphate, zirconia or

sulphonated resins such as those marketed under the trade name Nafion or alternatively acidic clays such as, in particular, smectites such as, for example, montmorillonites, beidellites, nontronites, hectorites, stevensites and saponites.

The amount of homogeneous or heterogeneous acid catalyst may vary very widely since the presence of such an acid is not essential. It may thus be such that there is an acid:diacids to be anhydridized molar ratio of 0:1 to 10:1. The homogeneous or heterogeneous acid catalyst will preferably be used in an amount such that the acid:diacids to be anhydridized molar ratio is from 0.0005:1 to 1:1. When a sulphonated acidic resin is used, the molar ratio will be considered between the sulphonic acid functions of said resin and the diacids to be anhydridized. When an acidic clay is used, an acidic clay/diacids to be anhydridized weight proportion of at least 5% may be used, but it is obvious that this proportion may be very variable, depending on the way in which the process is performed. In particular, when a continuous mode is used, the idea of weight ratio no longer has meaning and is replaced by that of contact time.

Another advantageous variant of the invention consists in working in the presence in the reaction medium of at least one anhydride of an acid, such as the anhydride of a monocarboxylic or polycarboxylic aliphatic acid, it being necessary for the boiling point of these acids to be less than that of adipic acid (that is to say about 265°C at 13.3 kPa) in order for said acids formed from the anhydrides thereof to be separable by distillation. The anhydrides used are especially the anhydrides of monocarboxylic or polycarboxylic acids having from 2 to 8 carbon atoms, such as, for example, the anhydrides of acetic acid, propionic acid, succinic acid, valeric acid, 2-ethylsuccinic acid, dimethylsuccinic acid, methylbutanoic acids, methylbutenoic acids or pentenoic acids, as well as the possible mixed anhydrides of these acids.

It is obvious that the choice of 2-ethylsuccinic anhydride and dimethylsuccinic anhydride is not justified if the diacids to be separated from adipic acid are not



2-ethylsuccinic acid and dimethylsuccinic acid respectively.

As for the above variant, the amount of anhydride optionally added to the reaction medium in order to facilitate anhydridization of the diacids may vary within a very wide range since the presence of such a compound is not essential, even though this constitutes a preferred variant of the invention. The amount of anhydride may thus be such that there is an anhydride:diacids to be anhydridized molar ratio of 0:1 to 10:1. The anhydride:diacids to be anhydridized molar ratio is preferably from 0.5:1 to 2:1, and even more preferably from 1:1 to 1.5:1.

As indicated above, the diacid mixtures used in the process of the invention may be mixtures coming from any origin; they may in particular come from the recovery of the diacids in recrystallization waters of adipic acid or alternatively from the diacid distillation residues, or they may consist of more or less pure fractions derived from crystallization, refining or distillation operations performed in the context of the preparation of adipic acid.

They may also be derived directly from processes for the synthesis of adipic acid. This is especially the case for the mixtures of adipic acid with 2-methylglutaric acid and/or 2-ethylsuccinic acid and/or dimethylsuccinic acid, which are obtained during the hydroxycarbonylation of the pentenoic acids or, where appropriate, even during the hydroxycarbonylation of butadiene or derivatives thereof. These mixtures may also contain, depending on the development of the steps in the synthetic process, larger or smaller amounts of the catalyst used, such as, for example, iridium or iridium compounds, rhodium or rhodium compounds and palladium or palladium compounds, this last family of catalysts being used more particularly for the hydroxycarbonylation of butadiene or derivatives thereof. They may also include compounds used such as pentenoic acids, possible solvents, and cocatalysts, as well as compounds formed during the synthesis of adipic acid such as, in particular, valeric acid, methylbutanoic acids, methylbutenoic acids and gamma-valerolactone.

The presence of a catalyst, in particular of iridium

or iridium compounds, rhodium or rhodium compounds and palladium or palladium compounds, as well as the respective cocatalysts or promoters of these catalysts, may play a beneficial role in the anhydridization of the diacids. Whether they come from the reaction mixtures derived from processes for the hydroxycarbonylation of the pentenoic acids or of butadiene, or whether they are optionally added before the anhydridization process is carried out, the catalyst generally represents, in moles of metal relative to the moles of diacids to be treated, from 0% to 20%, preferably from 0% to 10% and even more preferably from 0% to 5%.

The amounts of the various compounds indicated above in the reaction mixtures derived from the hydroxycarbonylation of the pentenoic acids or of butadiene or derivatives thereof are not critical. Illustrations of the amounts which may be obtained may be found in the various patents describing these processes for the synthesis of adipic acid, such as in EP-A-0,477,112, EP-A-0,478,472, EP-A-0,493,273, EP-A-0,511,126 and EP-A-0,536,064.

In the context of the anhydridization process of the invention, it is also possible to add a solvent to the mixture of diacids to be treated. This solvent may be one of the compounds mentioned above or may be different from the compounds present in the reaction mixture derived from the process for the synthesis of adipic acid and the diacids to be anhydridized.

These solvents may be chosen in particular from aliphatic or cycloaliphatic hydrocarbons, halogenated, in particular chlorinated, aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons, halogenated, in particular chlorinated, aromatic hydrocarbons, aliphatic or aromatic or mixed ethers, carboxylic acids, in particular aliphatic carboxylic acids, and halogenated carboxylic acids.

Example of such solvents are benzene, toluene, xylenes, n-hexane, dichloromethane, 1,2-dichloroethane, cyclohexane, chlorobenzene, diphenyl ether, dibutyl ether, pentenoic acids, valeric acid, gamma-valerolactone, acetic acid, propionic acid and trifluoroacetic acid.

These solvents are added for the aim of diluting the

diacids and promoting their anhydridization. They may also be chosen in order to allow the azeotropic distillation of the water formed during the anhydridization.

The amount of solvent may, for example, represent from 0% to 95% of the total weight of the mixture containing the diacids.

The diacids to be anhydridized generally represent from 10% to 90% by weight, relative to the diacids/adipic acid total weight ratio in the mixture to be treated.

The conversion of the diacids into their anhydrides makes it possible to be able to separate them more readily from the adipic acid, in particular by distillation, on account of the much lower boiling points of the anhydrides relative to their respective diacids.

The Examples which follow further illustrate the invention.

EXAMPLE 1

A mixture containing 50 millimol (mmol) of 2-methylglutaric acid, 25 mmol of adipic acid and 50 mmol of pentenoic acid (serving as solvent) is loaded into a 50 ml glass round-bottomed flask, to which are added 2 mmol of concentrated sulphuric acid.

The mixture is stirred, heated to 130°C and maintained at this temperature for 30 minutes.

On distillation under reduced pressure (about 1000 Pa), 80% of corresponding anhydride is obtained relative to the 2-methylglutaric acid charged.

EXAMPLE 2

Example 1 is repeated under the same operating conditions, but the 2-methylglutaric acid is replaced by the same molar amount of 2-ethylsuccinic acid. On distillation, 100% of corresponding anhydride is obtained relative to the 2-ethylsuccinic acid charged.

EXAMPLE 3

A mixture containing 34 mmol of 2-methylglutaric acid, 39 mmol of 2-ethylsuccinic anhydride and 25 mmol of adipic acid is loaded into a 50 ml glass round-bottomed flask.

The mixture is stirred, heated to 120°C and

maintained at this temperature for one hour. On distillation as in Example 1, 2 mmol of anhydride corresponding to 2-methylglutaric acid are obtained.

EXAMPLE 4

Example 1 is repeated under the same operating conditions, but the sulphuric acid is replaced by 2.5 mmol of boron phosphate. On distillation as in Example 1, 9 mmol of anhydride corresponding to 2-methylglutaric acid are obtained.

EXAMPLE 5

The following are successively loaded into a 125 ml autoclave:

- 0.8 mmol of RhCl(cod)
{cod = 1,5-cyclooctadiene}
- 8 mmol of HI (at a concentration of 57% in water)
- 45 mmol of water (provided by the HI solution)
- 20 mmol of adipic acid
- 39 mmol of 2-ethylsuccinic acid
- 45 ml of acetic acid.

The mixture is maintained at 230°C and at 50 bar of CO (total pressure at this temperature) for 5h, with stirring.

On distillation as in Example 1, 3 mmol of anhydride corresponding to 2-ethylsuccinic acid are obtained.

EXAMPLE 6

The following are successively loaded into a 125 ml autoclave:

- 0.8 mmol of IrCl(cod),
- 1.6 mmol of HI (at a concentration of 57% in water)
- 9 mmol of water (provided by the HI solution)
- 20 mmol of adipic acid
- 39 mmol of 2-methylglutaric acid
- 45 ml of acetic acid.

The mixture is maintained at 230°C and at 50 bar of CO (total pressure at this temperature) for 5h, with stirring.

On distillation as in Example 1, 3 mmol of anhydride

corresponding to 2-ethylsuccinic acid are obtained (via an isomerization of the 2-methylglutaric acid into 2-ethylsuccinic acid).

EXAMPLE 7

50 mmol of 2-methylglutaric acid and 11.6 g of a solution from a trial hydroxycarbonylation of 3-pentenoic acid and containing:

- 0.0386 mmol of Ir in soluble form
- 0.0907 mmol of HI
- 3.6 mmol of gamma-valerolactone
- 67 mmol of pentenoic acid
- 23.6 mmol of adipic acid
- 6 mmol of 2-methylglutaric acid
- 1.8 mmol of 2-ethylsuccinic acid.

are successively loaded into a 50 ml glass round-bottomed flask.

The mixture is maintained at 130°C for 30 minutes and then at 200°C for 2 h, with stirring.

On distillation as in Example 1, 4.5 mmol of anhydride corresponding to 2-methylglutaric acid and 1.8 mmol of anhydride corresponding to 2-ethylsuccinic acid are obtained.

EXAMPLE 8

10 g of a solution containing:

- 0.016 mmol of Ir in soluble form
- 28 mmol of pentenoic acid
- 8.2 mmol of adipic acid
- 37.7 mmol of 2-methylglutaric acid
- 3.4 mmol of 2-ethylsuccinic acid

are loaded into a 50 ml glass round-bottomed flask.

The mixture is heated at 220°C for 90 min, under reduced pressure (430 Pa).

On assaying, it is observed that 23% of the 2-methylglutaric acid and 100% of the 2-ethylsuccinic acid used were converted into their respective anhydrides, a considerable part of which was distilled off during the anhydridization reaction.

EXAMPLE 9

10 g of a solution containing:

- 0.026 mmol of Ir in soluble form
- 41 mmol of pentenoic acid
- 17.1 mmol of adipic acid
- 19.2 mmol of 2-methylglutaric acid
- 4.1 mmol of 2-ethylsuccinic acid
- 24 mmol of acetic anhydride

are loaded into a 50 ml glass round-bottomed flask.

The mixture is heated at reflux (about 120°C) for 60 min, followed by distillation at 1300 Pa, up to a temperature of 220°C in the reaction mixture.

On assaying, it is found that 99% of the 2-methylglutaric acid and 99% of the 2-ethylsuccinic acid used were converted and distilled off.

EXAMPLE 10

The following are loaded into a 500 ml glass round-bottomed flask:

- 200 mmol of adipic acid
- 200 mmol of 2-methylglutaric acid
- 250 ml of meta-xylene
- 10 mmol of sulphuric acid.

The mixture is heated, with stirring, at the reflux temperature of the xylene for 4 h and the water formed is distilled off in an azeotropic column (100% of the theoretical amount).

The distillation carried out on the dehydrated mixture made it possible to separate out the 2-methylglutaric anhydride formed (90 mol% relative to the 2-methylglutaric acid charged).

EXAMPLE 11

A mixture containing 15 g (103 mmol) of 2-methylglutaric acid, 2 g (13.7 mmol) of 2-ethylsuccinic acid and 10 g (68.5 mmol) of adipic acid is loaded into a 50 ml glass round-bottomed flask.

The mixture is stirred, heated at 120°C and maintained at this temperature for 2 hours. It is then maintained at 160°C under reduced pressure (1400 Pa) for 6 hours.

On assaying the distillate obtained, it is observed that 2.2% of the 2-methylglutaric acid and 93% of the

2-ethylsuccinic acid used were distilled off in the form of their respective corresponding anhydrides.

EXAMPLE 12

A mixture containing 15 g (103 mmol) of 2-methylglutaric acid, 2 g (13.7 mmol) of 2-ethylsuccinic acid and 10 g (68.5 mmol) of adipic acid, as well as 3 g of sulphonated resin of trade name Nafion NR 50 (10-35 mesh) is loaded into a 50 ml glass round-bottomed flask.

The mixture is stirred, heated at 120°C and maintained at this temperature for 2 hours. It is then maintained at 160°C under reduced pressure (1400 Pa) for 6 hours.

On assaying the distillate obtained, it is observed that 4% of the 2-methylglutaric acid and 99% of the 2-ethylsuccinic acid used were distilled off in the form of their respective corresponding anhydrides.

EXAMPLE 13

A mixture containing 15 g (103 mmol) of 2-methylglutaric acid, 2 g (13.7 mmol) of 2-ethylsuccinic acid and 10 g (68.5 mmol) of adipic acid, as well as 3 g of KSF montmorillonite acidic clay, is loaded into a 50 ml glass round-bottomed flask.

The mixture is stirred, heated at 120°C and maintained at this temperature for 2 hours. It is then maintained at 160°C under reduced pressure (1400 Pa) for 6 hours.

On assaying the distillate obtained, it is observed that 24% of the 2-methylglutaric acid and 92% of the 2-ethylsuccinic acid used were distilled off in the form of their respective corresponding anhydrides.

EXAMPLE 14

The following are successively charged into a 125 ml autoclave:

- 0.9 mmol of PdCl₂
- 7 mmol of chlorobutene
- 92.5 mmol of water
- 92.5 mmol of butadiene
- 10 mmol of 3-pentenoic acid
- 34 mmol of adipic acid

- 68.5 mmol of 2-methylglutaric acid.

The mixture is maintained at 100°C under 200 bar of CO (total pressure at this temperature) for 5h 30, with stirring.

On distillation as in Example 1, 13 mmol of anhydride corresponding to 2-methylglutaric acid and 1 mmol of anhydride corresponding to 2-ethylsuccinic acid are obtained.

CLAIMS

1. A process for the separation of at least some of one or more branched, saturated aliphatic diacids having 6 carbon atoms, from a mixture comprising said diacid or diacids and adipic acid, which comprises at least partly converting said diacid or at least some of said diacids into the corresponding anhydride or anhydrides.
2. A process according to Claim 1 wherein the diacid or diacids used are 2-methylglutaric acid and/or ethylsuccinic acid and/or dimethylsuccinic acid.
3. A process according to Claim 1 and 2 wherein the anhydridization is performed by heating the mixture to a temperature equal to or above 60°C.
4. A process according to Claims 3 which is performed at a temperature of 80°C to 350°C.
5. A process according to any one of Claims 1 to 4 wherein the anhydride or anhydrides or water formed are separated from the mixture either during or after the anhydridization.
6. A process according to Claim 5 wherein the anhydride or anhydrides or water are separated by distillation or crystallization.
7. A process according to any one of Claims 1 to 6 which is performed in the presence of a homogeneous acid catalyst which is soluble in the reaction medium, having a pKa below or equal to 5, or in the presence of a heterogeneous acid catalyst.
8. A process according to Claim 7 wherein the homogeneous acid catalyst is sulphuric acid, hydriodic acid, para-toluenesulphonic acid, trifluoroacetic acid or trifluoromethanesulphonic acid, or the heterogeneous acid catalyst is a phosphate, zirconia or sulphonated resin, or an acidic clay.
9. A process according to Claim 8 wherein the acidic clay is a smectite.
10. A process according to Claim 9 wherein the smectite is a montmorillonite, beidellite, nontronite,



hectorite, stevensite or saponite.

11. A process according to any one of Claims 7 to 10 wherein the amount of the homogeneous or heterogeneous acid catalyst is such that there is an acid:diacid to be anhydridized molar ratio of 0:1 to 10:1 or an acidic clay/diacid to be anhydridized weight proportion of at least 5%.

12. A process according to Claim 11 wherein the acid:diacid molar ratio is 0.0005:1 to 1:1.

13. A process according to any one of Claims 1 to 6 which is performed in the presence in the reaction medium of at least one anhydride of an acid, said acid having a boiling point which is less than that of adipic acid.

14. A process according to Claim 13 wherein the anhydride is of a monocarboxylic or polycarboxylic aliphatic acid or is a mixed anhydride thereof.

15. A process according to Claim 14, wherein the anhydride is an anhydride of a monocarboxylic or polycarboxylic acid having from 2 to 8 carbon atoms or is a mixed anhydride thereof.

16. A process according to Claim 15 wherein the anhydride is an anhydride of acetic acid, propionic acid, succinic acid, valeric acid, 2-ethylsuccinic acid, dimethylsuccinic acid, a methylbutanoic acid, a methylbutenoic acid or a pentenoic acid or is a mixed anhydride thereof.

17. A process according to any one of Claims 13 to 16 wherein the amount of the anhydride used is such that there is an anhydride:diacids to be anhydridized molar ratio of 0:1 to 10:1.

18. A process according to Claim 17 wherein the anhydride:diacids molar ratio is 0.5:1 to 2:1.

19. A process according to claim 18 wherein the anhydride:diacids molar ratio is 1:1 to 1.5:1.

20. A process according to any one of Claims 1 to 19 wherein the mixture used is a mixture coming from the recovery of the diacids in recrystallization waters of adipic acid, a mixture coming from the diacid distillation residues, or a mixture comprising a more or less pure fraction derived





from crystallization, refining or distillation operations performed in the context of the preparation of adipic acid.

21. A process according to Claim 20 wherein the mixture used is a mixture derived from a processes for the synthesis of adipic acid.

22. A process according to Claim 21 wherein the mixture used is a mixture of adipic acid with 2-methylglutaric acid and/or 2-ethylsuccinic acid and/or dimethylsuccinic acid, which is obtained during the hydroxycarbonylation of at least one pentenoic acid or the hydroxycarbonylation of butadiene or a derivative thereof.

23. A process according to any one of Claims 1 to 13 wherein a solvent is added to the mixture of diacids to be treated.

24. A process according to Claim 23 wherein the solvent is an aliphatic or cycloaliphatic hydrocarbon, halogenated, aliphatic or cycloaliphatic hydrocarbon, an aromatic hydrocarbon, a halogenated aromatic hydrocarbon, an aliphatic or aromatic or mixed ether or a carboxylic acid.

25. A process according to Claim 24 wherein the solvent is a chlorinated aliphatic or cycloaliphatic hydrocarbon, a chlorinated aromatic hydrocarbon or an aliphatic or halogenated carboxylic acid.

26. A process according to any one of Claims 23 to 25 wherein the solvent is benzene, toluene, a xylene, n-hexane, dichloromethane, 1,2-dichloroethane, cyclohexane, chlorobenzene, diphenyl ether, dibutyl ether, a pentenoic acid, valeric acid, gamma-valerolactone, acetic acid, propionic acid or trifluoroacetic acid.

27. Adipic acid wherever obtained by a process as defined in any one of Claims 1 to 26.

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