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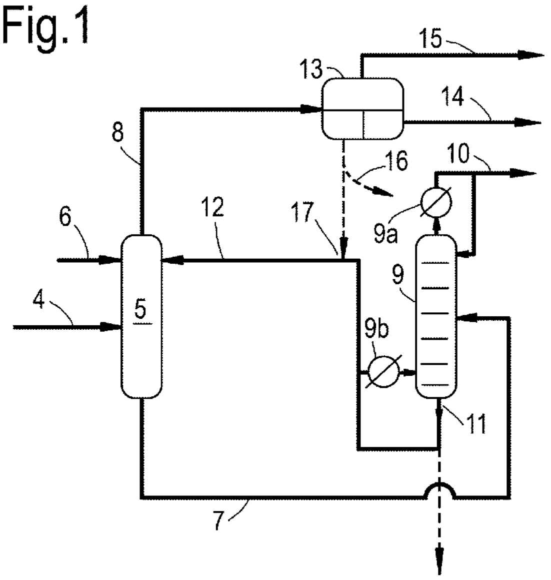
[Continued on next page]

(54) Title: CARBOXYLIC ACID ABSORPTION FROM VAPOROUS AQUEOUS STREAMS

Fig.1



(57) Abstract: The invention provides a process for the recovery of C_3-C_6 carboxylic acid from a vaporous aqueous stream, comprising providing a vaporous aqueous stream comprising C_3-C_6 carboxylic acid, contacting said vaporous aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water vapour, feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent, and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit, wherein the absorbing solvent is an oxygen-containing organic compound having (i) a Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid as determined at 25°C of 15 $\text{MPa}^{1/2}$ or less, preferably 12 $\text{MPa}^{1/2}$ or less, more preferably 10 $\text{MPa}^{1/2}$ or less; (ii) a 1-octanol/water partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, preferably at least 0.5, more preferably at least 1.0, even more preferably at least 1.5, yet even more preferably at least 2.0, most preferably at least 3.0; and (iii) a boiling point at atmospheric pressure that is at least 5 °C higher, preferably at least 10 °C higher, more preferably at least 20 °C higher than the boiling point of the C_3-C_6 carboxylic acid.

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CARBOXYLIC ACID ABSORPTION FROM VAPOROUS AQUEOUS STREAMS

Field of the invention

The present invention relates to a process of recovering C_3-C_6 carboxylic acids from vaporous aqueous streams by means of absorption.

Background of the invention

Several oxidative chemical conversion processes known in the art produce aqueous streams comprising carboxylic acids as a side product. For example, it is known to oxidatively dehydrogenate alkanes having 3 to 6 carbon atoms ("C_3-C_6 alkanes") such as propane or butane resulting in propylene and butylene, respectively, in an oxidative dehydrogenation (oxydehydrogenation; ODH) process. The dehydrogenated equivalent of the alkane may be further oxidized under the same conditions into the corresponding carboxylic acid, which may or may not contain one or more unsaturated double carbon-carbon bonds, such as acrylic acid and methacrylic acid. Other examples include the dehydrogenation of alcohols, the oxidation of aldehydes and the conversion (fermentation, pyrolysis, liquefaction) of biomass.

In the above process as well as in other oxidative conversion process, the carboxylic acids thus produced are generally considered as waste products. Although they could be condensed together with water from the reactor effluent as an aqueous carboxylic acid (ca. 10 wt%) stream, the low relative volatility of carboxylic acids to water renders ordinary distillative separation of carboxylic acid and water troublesome, as this would require very large condensate recycle and/or separation trains.

However, C_3–C_6 carboxylic acids are valuable ingredients and building blocks for use in the chemical industry. For example, the global demand for acrylic acid is around 5 million tonnes per year (Mt/a), with applications as superabsorbent in e.g. incontinence and personal care products, in surface coatings, adhesives and sealants, in textiles, in the water treatment industry, in mineral processing and numerous other applications in the form of acrylate esters.

It is an objective of the present invention to provide a technically advantageous, efficient and affordable process for recovering C_3–C_6 carboxylic acids from vaporous aqueous streams.

Summary of the invention

It was surprisingly found that the above-mentioned objective can be attained by means of an absorption process for recovering C_3–C_6 carboxylic acid from a mixture of C_3–C_6 carboxylic acid and water, wherein the absorbing solvent is characterized by a small Hansen solubility parameter distance R_a with respect to the one or more C_3–C_6 carboxylic acids to be recovered, a relatively high 1-octanol/water partition coefficient $\log P_{OW}$ and a boiling point exceeding that of the C_3–C_6 carboxylic acids to be recovered.

Accordingly, in a first aspect the present invention pertains to a process for the recovery of C_3–C_6 carboxylic acid from an aqueous stream, comprising

providing a vaporous aqueous stream comprising C_3–C_6 carboxylic acid,

contacting said vaporous aqueous stream comprising C_3–C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water vapour,

feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent,

and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit,

wherein the absorbing solvent is an oxygen-containing organic compound having

(i) a Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid as determined at 25 °C of 15 $MPa^{1/2}$ or less, preferably 12 $MPa^{1/2}$ or less, more preferably 10 $MPa^{1/2}$ or less;

(ii) a 1-octanol/water partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, preferably at least 0.5, more preferably at least 1.0, even more preferably at least 1.5, yet even more preferably at least 2.0, most preferably at least 3.0; and

(iii) a boiling point at atmospheric pressure that is at least 5 °C higher, preferably at least 10 °C higher, more preferably at least 20 °C higher than the boiling point of the C_3-C_6 carboxylic acid to be recovered.

The invention further relates to a process for the recovery of C_3-C_6 carboxylic acid from a vaporous aqueous stream, comprising

providing a vaporous aqueous stream comprising C_3-C_6 carboxylic acid,

contacting said aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water vapour,

feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent,

and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit,

wherein the absorbing solvent is a cyclic or aromatic alcohol having 6 to 20 carbon atoms, a linear aliphatic alcohol having 6 to 14 carbon atoms or a branched aliphatic alcohol having 5 to 14 carbon atoms.

In another aspect, the invention relates to the use of an oxygen-containing organic compound having

(i) a Hansen solubility parameter distance R_a with respect to the C_3-C_6 carboxylic acid as determined at 25 °C of 15 $MPa^{1/2}$ or less, preferably 12 $MPa^{1/2}$ or less, more preferably 10 $MPa^{1/2}$ or less;

(ii) a 1-octanol/water partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, preferably at least 0.5, more preferably at least 1.0, even more preferably at least 1.5, yet even more preferably at least 2.0, most preferably at least 3.0; and

(iii) a boiling point of at least 125 °C, preferably at least 140 °C, more preferably at least 160 °C, even more preferably at least 180 °C, most preferably at least 200 °C at atmospheric pressure

as a solvent for absorbing C_3-C_6 carboxylic acid from a water-containing vapour stream.

Brief description of the drawings

Figure 1 shows an embodiment of the present invention, wherein an aqueous vapour stream comprising C_3-C_6 carboxylic acid is contacted with an absorbing solvent in an absorption unit, to produce a top stream comprising water vapour and a bottom stream comprising absorbing solvent and C_3-C_6 carboxylic acid, and wherein said bottom stream comprising absorbing solvent and C_3-C_6 carboxylic acid is fed to a solvent recovery unit to produce a top stream comprising C_3-C_6 carboxylic acid and a bottom stream comprising absorbing solvent.

Detailed description of the invention

While the process of the present invention and the streams used in said process are described in terms of "comprising", "containing" or "including" one or more various described steps and components, respectively, they can also "consist essentially of" or "consist of" said one or more various described steps and components, respectively.

The aqueous stream comprising C_3-C_6 carboxylic acid used as feed stream for the absorption process may be any stream comprising at least 0.1, or at least 1 wt%, more preferably at least 3 wt%, even more preferably at least 5 wt%, yet even more preferably at least 10 wt% or 15 wt%, most preferably at least 20 wt% wt% of C_3-C_6 carboxylic acid. Herein, unless specified otherwise, the term "C_3-C_6 carboxylic acid" and any amounts or concentrations specified in connection therewith refers to the sum of all saturated and unsaturated carboxylic acids having 3, 4, 5 and 6 carbon atoms that are present. Typically, said aqueous stream comprising one or more C_3-C_6 carboxylic acid originates from an oxidative chemical conversion process of C_3-C_6 alkanes and/or C_3-C_6 alkenes, wherein the C_3-C_6 carboxylic acid is obtained as a side product. It is preferred that the aqueous feed stream of the absorption process comprises C_3-C_6 carboxylic acid in a concentration of at least 1 wt%, more preferably at least 3 wt%, even more preferably at least 5 wt%, yet even more preferably at least 10 wt%, most preferably at least 20 wt%.

In one embodiment, the aqueous stream comprising carboxylic acid originates from the oxidative dehydrogenation (“ODH”) of an alkane containing 3 to 6 carbon atoms, preferably propane or butane. This oxidative alkane dehydrogenation process typically produces a product stream comprising the corresponding alkene and carbon dioxide, as well as water and carboxylic acid. In case of propane, the product of said alkane oxidative dehydrogenation process may comprise propylene and acrylic acid. Further, in case of butane, the product of said alkane oxidative dehydrogenation process may comprise butylene, butadiene, vinylacetic acid, crotonic acid and/or methacrylic acid.

In another embodiment, the aqueous stream comprising carboxylic acid originates from the oxidation of an alkene containing 3 to 6 carbon atoms, preferably propylene, in the presence of water to produce a product stream comprising the corresponding carboxylic acids. Said carboxylic acid may or may not contain one or more unsaturated double carbon-carbon bonds. As mentioned above, it is preferred that the alkene containing 3 to 6 carbon atoms is propylene, butylene or butadiene. In case of propylene, the product of said alkene oxidation process may comprise acrylic acid. Further, in case of butylene and/or butadiene, the product of said alkene oxidation process may comprise vinylacetic acid, crotonic acid and/or methacrylic acid.

In a preferred embodiment, the C_3-C_6 carboxylic acid is a C_3 or a C_4 carboxylic acid, or a combination thereof. Preferably, the carboxylic acid to be recovered is acrylic acid, propionic acid, vinylacetic acid, iso-crotonic acid, n-crotonic acid, iso-butyric acid, n-butyric acid, methacrylic acid, or a combination thereof. In a particularly preferred embodiment, the carboxylic acid to be recovered is methacrylic acid and/or acrylic acid, most preferably acrylic acid.

A concentration step, for example of a dilute aqueous gaseous process effluent comprising C_3-C_6 carboxylic acid, may be applied prior to contacting the C_3-C_6 carboxylic acid with the absorbing solvent in the absorption unit. Such concentration step may comprise any suitable method for removing excess water from an aqueous C_3-C_6 carboxylic acid stream, including reverse osmosis or carboxylic acid-selective pervaporation, liquid-liquid (L/L) extraction or adsorption on a solid adsorbant.

In one embodiment of the invention, a vaporous effluent comprising C_3-C_6 carboxylic acid is treated using carboxylic acid-selective pervaporation to produce a concentrated C_3-C_6 carboxylic acid/water vapour stream, which is subsequently separated using an absorption process as described herein. In another embodiment, a vaporous effluent comprising C_3-C_6 carboxylic acid is concentrated by condensation followed by L/L extraction with a high-boiling solvent and distillation of the more concentrated C_3-C_6 carboxylic acid/water vapour stream from the high boiling solvent and, finally, separation using absorption from the vapour phase as described herein. In another embodiment, a vaporous effluent comprising C_3-C_6 carboxylic acid is concentrated by adsorption onto a solid, followed by desorption of a more concentrated C_3-C_6 carboxylic acid/water vapour stream subsequently separated using absorption from the vapour phase as described herein.

Typically, such a concentration step yields an aqueous feed stream comprising C_3-C_6 carboxylic acid in a concentration of at least 5 wt%, more preferably at least 10 wt%, even more preferably at least 15 wt%, most preferably at least 20 wt%.

The vaporous phase stream comprising water and C_3-C_6 carboxylic acid may be the effluent stream from a gas-phase (oxidative) conversion process of C_3-C_6 alkane and/or C_3-C_6 alkene. By directly subjecting the vaporous effluent comprising C_3-C_6 carboxylic acid and water of such process to the absorption step, capital and operating expenditure on excessive condensation and reheating steps can be avoided.

In the absorption process of the invention, the gaseous aqueous stream comprising C_3-C_6 carboxylic acid is contacted with an absorbing solvent in a suitable absorption unit in order to separate the carbocyclic acid from water. Several absorption methods for vaporous streams are available in the art. For example, absorption may suitably be performed in an absorption column, typically a multi-stage countercurrent packed or tray absorption column having inlets for receiving a vaporous feed stream and for absorbing solvent, wherein absorbing solvent is continuously fed at an upper stage of the absorption column, and wherein the C_3-C_6 carboxylic acid is absorbed by the solvent via direct contact of the rising vapour stream and the falling solvent.

Generally, choice of absorbing solvent is of high importance in the absorption process, since suitable absorbing solvents can decrease the solvent ratio and/or the liquid load of the absorption unit, thus rendering an easy and more economical implementation of the absorption set-up, such as an absorption column, in a process line-up.

The present inventors have now surprisingly found that certain oxygen-containing solvents being characterized by (i) a short Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid, (ii) a partition $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, and (iii) a boiling point at atmospheric pressure that is at least 5 °C higher, preferably at least 10 °C higher, more preferably at least 20 °C higher than the boiling point of C_3-C_6 carboxylic acid, are excellent absorbing solvents for use in a process for recovering C_3-C_6 carboxylic acid from aqueous vapour streams comprising C_3-C_6 carboxylic acid.

Hansen solubility parameters (HSP) can be used as a means for predicting the likeliness of one compound (solvent) dissolving in another. More specifically, each compound is characterized by three Hansen parameters, each generally expressed in $MPa^{0.5}$: δ_d, denoting the energy from dispersion forces between molecules; δ_p, denoting the energy from dipolar intermolecular forces between molecules; and δ_h, denoting the energy from hydrogen bonds between molecules. The affinity between compounds can be described using a multidimensional vector that quantifies these solvent atomic and molecular interactions, as a Hansen solubility parameters (HSP) distance R_a which is defined in Equation (1):

$$R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \qquad (1)$$

wherein

R_a = distance in HSP space between compound 1 and compound 2 ($MPa^{0.5}$)

δ_{d1}, δ_{p1}, δ_{h1} = Hansen (or equivalent) parameter for compound 1 (in $MPa^{0.5}$)

δ_{d2}, δ_{p2}, δ_{h2} = Hansen (or equivalent) parameter for compound 2 (in $MPa^{0.5}$)

Thus, in the context of the present invention, the smaller the value for R_a for a given solvent calculated with respect to the C_3-C_6 carboxylic acid to be recovered (i.e., the C_3-C_6

carboxylic acid being compound 1 and the solvent being compound 2, or vice versa), the higher the affinity of this solvent for the C_3-C_6 carboxylic acid to be recovered will be.

Hansen solubility parameters for numerous solvents can be found in, among others, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters, Second Edition* by Allan F.M. Barton, CRC press 1991; *Hansen Solubility Parameters: A User's Handbook* by Charles M. Hansen, CRC press 2007. It is also explained in these handbooks how analogous, equivalent solubility parameters have been derived by alternative methods to the original Hansen method, resulting in similarly useful parameters such as Hoy's cohesion parameters for liquids.

It is preferred that the Hansen solubility parameter distance R_a with respect to the one or more C_3-C_6 carboxylic acids to be recovered as determined at 25 °C is 12 $MPa^{1/2}$ or less, preferably 10 $MPa^{1/2}$ or less, more preferably 8 $MPa^{1/2}$ or less, most preferably 5 $MPa^{1/2}$ or less.

It was further found by the present inventors that selective recovery of C_3-C_6 carboxylic acid from aqueous streams is obtained when the 1-octanol/water partition coefficient of the absorbing solvent is relatively high. The 1-octanol/water partition coefficient, commonly expressed as its logarithmic value $\log P_{OW}$, represents the relative concentrations of a compound when dissolved in a mixture of 1-octanol and water at equilibrium, according to the following expression:

$$\log P_{OW} = {}^{10}\log[C_{octanol}/C_{water}] \qquad (2)$$

wherein

$C_{octanol}$ = concentration of the compound in 1-octanol

$C_{octanol}$ = concentration of the compound in water

As such, in the context of the present invention, the partition coefficient is a measure for the hydrophobicity of an absorbing solvent. Without wishing to be bound by theory, it is the inventors' belief that solvents having a suitably high partition coefficient are effective in minimizing the absorption of water from the C_3-C_6 carboxylic acid-water mixture.

Suitable absorbing solvents for use as described herein have a partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0. Typically, the absorbing solvent for use as described herein has a $\log P_{OW}$ of at least 0.5, preferably at least 1.0, more preferably at least 1.5, even more preferably at least 2.0, most preferably at least 3.0.

Experimentally determined 1-octanol/water partition coefficients for several organic solvent classes are listed in, for example, James Sangster, *Octanol-Water Partition Coefficients of Simple Organic Compounds*, J. Phys. Chem. Ref. Data, Vol.18, No. 3, 1989. Where experimentally determined partition coefficients are not accessible, several established reliable methods for calculating $\log P_{OW}$ values are available; these include the proprietary methods ClogP (Bio-Loom; BioByte Corp./Pomona College) and miLogP (Molinspiration Cheminformatics) (see also Mannhold, M. et al. *Calculation of Molecular Lipophilicity: State-of-the-Art and Comparison of Log P Methods on more than 96,000 compounds*. J. Pharm. Sci. 2009, 98, 861-893).

In order to realize cost-effective separation (recovery) of the absorbing solvent from C_3-C_6 carboxylic acid by e.g. distillation, advantageously the absorbing solvent has a boiling point at atmospheric pressure that is at least 5 °C higher, preferably at least 10 °C higher, more preferably at least 20 °C higher than the boiling point of the C_3-C_6 carboxylic acid(s).

For example, for the recovery of acrylic (C_3) acid, which has a boiling point of ca. 140 °C at atmospheric pressure, it is preferred that the absorbing solvent has a boiling point of at least 145 °C. Preferably, it has a boiling point of at least 150 °C, more preferably at least 160 °C, even more preferably at least 170 °C.

For the recovery of methacrylic (C_4) acid, which has a boiling point of ca. 160 °C at atmospheric pressure, it is preferred that the absorbing solvent has a boiling point of at least 165 °C. Preferably, it has a boiling point of at least 170 °C, more preferably at least 180 °C, even more preferably at least 200 °C.

From an economic perspective, it is preferred that the absorbing solvent has a boiling point that does not exceed 300 °C, more preferably not exceeds 280 °C, even more preferably not exceeds 250 °C, most preferably not exceeds 225 °C, at atmospheric pressure, in order to avoid excessive heating expenditure and eventual thermal degradation of the solvent.

Suitable oxygen-containing compounds having a Hansen solubility parameter distance R_a, partition coefficient and boiling point ranges as defined herein can be found in the classes of carboxylic acids, esters of carboxylic acids, ethers, aldehydes, ketones, alcohols and organic phosphates. These oxygen-containing component may be linear, branched or cyclic, saturated or unsaturated, and may be aliphatic or contain aromatic rings. Examples of such compounds include organic phosphates such as triethyl phosphate and tributyl phosphate, heterocyclic hydrocarbons such as benzofuran, carboxylic esters such as methyl benzoate, n-butyl butyrate, n-butyl acrylate, 2-ethylhexyl acetate, diethyl phthalate, isopropyl acetate, octyl acetate and cyclohexyl acetate, ketones such as acetophenone, dipropyl ketone and 5-ethyl-2-nonanone, high-boiling functionalized ethers such as anisole, diethylene glycol ethyl ether, diethylene glycol monobutyl ether, propylene glycol phenyl ether, 2-butoxy ethanol, 2-phenoxy ethanol and butyl diglycol acetate and, depending on the carboxylic acid to be recovered, higher-boiling carboxylic acids such as pentanoic acid, hexanoic acid, heptanoic acid and octanoic acid. Based on the criteria as provided herein for the Hansen solubility parameter distance R_a, partition coefficient and boiling point, and taking into account the boiling point of the carboxylic acid to be recovered, the skilled person will be capable of selecting suitable absorbing solvents from each of these classes of oxygen-containing organic compounds.

Particularly preferred oxygen-containing compounds having a Hansen solubility parameter distance R_a, partition coefficient and boiling point as defined herein are selected from the class of protic oxygenates, i.e. containing hydroxyl (-OH) group such as acids and alcohols and more preferably organic alcohols. Herein, organic alcohols are understood to organic compounds wherein one or more hydroxyl functional groups (-OH) are bound to a carbon atom. This includes linear, branched and cyclic alcohols, saturated and unsaturated alcohols, primary, secondary or tertiary alcohols, and aromatic as well as aliphatic alcohols. The alcohol may contain one hydroxyl group, or may contain two (diol) or more (triol, etc.) hydroxyl groups, provided that any surplus of hydroxyl groups does not result in an undesirably high affinity for water. The alcohols for use according to the invention may further contain other functional groups, such as oxygen-containing groups such as carbonyl, acid-, ether- or ester functional groups.

Preferred alcohols for use according to the invention are cyclic or aromatic alcohols having 6 to 20 carbon atoms, linear aliphatic alcohols having 6 to 14 carbon atoms and branched aliphatic alcohols having 5 to 14 carbon atoms.

In one aspect, the invention relates to process for the recovery of C_3-C_6 carboxylic acid from a vaporous aqueous stream, comprising

providing a vaporous aqueous stream comprising C_3-C_6 carboxylic acid,

contacting said aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water,

feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent,

and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit,

wherein the absorbing solvent is a cyclic or aromatic alcohol having 6 to 20 carbon atoms, a linear aliphatic alcohol having 6 to 14 carbon atoms or a branched aliphatic alcohol having 5 to 14 carbon atoms.

Examples of cyclic alcohols include unsubstituted and alkyl-substituted cyclohexanols and cyclopentanols, such as cyclohexanol, methyl cyclohexanol, methyl cyclopentanol, trimethyl cyclohexanols and (4-methylcyclohexyl)methanol; examples of aromatic alcohols include phenol, benzyl alcohol, 1- phenyl ethanol, 2-phenyl ethanol, cumyl alcohol (2-phenyl-2-propanol), xylenols (such as 2,6-xylen-1-ol), guaiacol (2-methoxyfenol), creosol, cresols such as m-cresol, phenoxy ethanol and naphthol; examples of suitable linear alcohols include those having the general formula $C_nH_{n+1}OH$, wherein n is in the range of 6 to 14, preferably in the range of from 8 to 12, such as 1-hexanol, 2-hexanol, 3-hexanol, 1-octanol and 2-octanol, 1-decanol, 2-decanol, 1-dodecanol and 2-dodecanol; examples of suitable branched alcohols include those having in the range of 5 to 14, preferably in the range of 6 to 12 carbon atoms, such as 2-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 2-methyl-1-pentanol, 2,3-dimethyl-1-butanol, 2,2-dimethyl-1-butanol, 2,3-dimethyl-2-butanol, 3,3-dimethyl-2-butanol, 4-methyl-1-pentanol (iso-hexanol), 4-methyl-2-pentanol, 2-ethyl-1-butanol, 5-methyl-2-hexanol, 3-methyl-2-hexanol, 2,2-dimethyl-1-pentanol, 4,4-dimethyl-1-pentanol, 2-ethyl-1-hexanol (iso-octanol), di-isobutyl carbinol (2,6-dimetyl-4-heptanol), 2-propyl heptanol, 3-methyl-1-butanol (isopentyl alcohol), 2-methyl-1-butanol, 2-benzyloxy-ethanol, 2-phenoxy ethanol and 2-butoxy-ethanol.

Examples of alcohols containing other functional groups, such as oxygen-containing groups like aldehyde, ether- or ester groups, are diacetone alcohol and methyl salicylate. Other suitable alcohols include terpene-based alcohols such as pinacol, citronellol, menthol, and isoborneol.

Particularly preferred absorbing solvents for use according to the invention are 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 2-ethyl-hexanol, diisobutyl carbinol, cresols, xylenols, anisole, butyl butyrate and 2-ethyl-hexyl-acetate.

An overview of suitable absorbing solvents for use according to the invention, including their Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid, 1-octanol/water partition coefficient and boiling point is provided in Table 1.

Table 1. Values for Hansen solubility parameter distance Ra with respect to acrylic acid at 25 °C, 1-octanol/water partition coefficient at 25 °C and pH 7, and boiling point at atmospheric pressure. Values for Hansen solubility parameter distance R_a have been calculated from the known values of δ_d, δ_p, and δ_h for acrylic acid acid (δ_d = 17.7; δ_p =6.4; δ_h = 14.9; all in $MPa^{0.5}$), and of the solvent using Equation (1) as provided above. Hansen solubility parameters are taken from *CRC Handbook of Solubility Parameters and Other Cohesion Parameters, Second Edition* by Allan F.M. Barton, CRC press 1991; *Hansen Solubility Parameters: A User's Handbook* by Charles M. Hansen, CRC press 2007. $LogP_{OW}$ values are taken from James Sangster, *Octanol-Water Partition Coefficients of Simple Organic Compounds*, J. Phys. Chem. Ref. Data, Vol.18, No. 3, 1989, from technical data sheets supplied by solvent manufacturers or calculated using miLogP software (Molinspiration Cheminformatics).

Solvent	**R_a ($MPa^{0.5}$) w.r.t. acrylic acid**	**$LogP_{OW}$**	**bp (°C)**
acrylic acid	*0*	*0.28*	*138*
n-butyl acrylate	11	2.39	145
2-butyl 1-octanol	7	5.05	145
5-methyl-2-hexanol	7	1.97	148
iso-hexanol (4-methyl-1-pentanol)	4	1.6	152
anisole	9	2.11	153
cyclohexanone	10	0.81	155

cyclo-hexanol	3	1.32	161
furfural	13	0.41	162
n-butyl butyrate	11	2.83	165
2-butoxy-ethanol	4	0.8	171
cyclohexyl acetate	9	2.29	173
benzofuran	10	2.67	174
di-isobutyl carbinol	8	3.31	178
2-octanol	6	2.90	179
iso-octanol (2-ethyl hexanol)	5	2.72	180
phenol	1	1.46	181
pentanoic acid	7	1.39	185
1-octanol	5	3.05	195
methyl benzoate	11	2.2	199
2-ethylhexyl acetate	11	3.71	200
2,6-xylenol	6	2.4	201
acetophenone	12	1.58	202
cresol (m)	2	1.94	203
octyl acetate	11	3.84 (calc)	203
guaiacol	4	1.34	205
benzyl alcohol	2	1.1	205
hexanoic acid	4	1.84	206
triethyl phosphate	8	1.08	215
isophorone	8	2.07	215
2-propyl heptanol	8	4.4	218
iso-decanol	8	3.62 (calc)	220
1-decanol	6	4.2 (calc)	220
isopropyl acetate	9	1.28	220
2-undecanol	9	4.4	229

octanoic acid	9	3.32 (calc)	237
butyl diglycol acetate	8	1.1	238
propylene glycol phenyl ether	4	1.41	241
1-undecanol	6	4.66 (calc)	243
1-phenoxy ethanol	3	1.1	245
2-phenoxy ethanol	1	1.2	247
2-dodecanol	10	5.02 (calc)	257
1-dodecanol	6	5.13	259
2-benzyloxy ethanol	3	1.17 (calc)	265
tributyl phosphate	11	2.5	289

The oxygen-containing solvents as defined herein are characterized by having very good selectivity, as compared to water, for C_3-C_6 carboxylic acid. Furthermore, these solvents have relatively high boiling points and low volatility, thus minimizing their loss as vapour in the top stream of an absorption unit and allowing efficient separation from C_3-C_6 carboxylic acid as the bottom stream using in a subsequent distillation (solvent recovery) step.

It is possible to combine the absorbing solvent with one or more other solvents. In one embodiment, a mixture of two or more absorbing solvents as defined herein are used. In another embodiment, an absorbing solvent as defined herein is combined with one or more solvents selected from carboxylic esters, ethers, aldehydes or ketones. When one or more absorbing solvents as defined herein are used in admixture with another solvent not according to the invention, it is preferred that the one or more absorbing solvents with Hansen solubility parameter distance R_a, partition coefficient and boiling point as defined herein are present in a concentration of at least 40 wt%, more preferably at least 50 wt%, even more preferably at least 70 wt%, most preferably at least 80 wt% or 90 wt% based on total weight of the solvent mixture. In one embodiment, the solvent mixture contains less than 40 wt%, preferably less than 30 wt%, more preferably less than 20 wt%, even more preferably less than 10 wt% of amine. In one embodiment, the one or more absorbing solvents as defined herein are used in the absence of amine compounds. In one embodiment, the absorbing solvent is employed in the absence of any other solvent not according to the invention. In order to avoid loss of solvent with C_3-C_6 carboxylic acid, it is further preferred that if a mixture of solvents is used, that such mixture contains less than 20 wt%, more preferably less than 10 wt%, even more preferably less than 5 wt%, most preferably less than 2 wt%, based on total weight of the solvent mixture, of a solvent having a boiling that is less than 5 °C higher than the boiling point of C_3-C_6 carboxylic acid.

In one embodiment, the solvent mixture may comprise one or more organic alcohols as defined herein and additionally one or more of the corresponding acetate esters, which may form during absorption and/or regeneration of the absorbing alcohol solvent. If this is undesirable, these esters may at least partially be hydrolyzed, for example by feeding steam to the bottom of the column in the absorption or solvent regeneration (desorption) step.

The invention further relates to the use of an oxygen-containing organic compound as fully defined above as a solvent for absorbing C_3-C_6 carboxylic acid from a water-containing vapour stream.

Depending on, among others, the concentration of C_3-C_6 carboxylic acid in the aqueous feed stream, the amount of absorbing solvent employed in the absorption process may vary within wide ranges, for example in a ratio (wt/wt) of absorbing solvent to C_3-C_6 carboxylic acid supplied to the absorption unit in the range of from 100:1 to 0.1:1, preferably in the range of from 50:1 to 0.25:1, more preferably in the range of from 40:1 to 0.5:1.

The temperature in the absorption step may vary within wide ranges due to the selection of different mixtures of acid and solvents and operation pressures. It is within the ability of one skilled in the art to select appropriate operating temperature for a given mixture at a given pressure.

Typically, the temperature in the absorption unit as described herein is in the range of of from 80 to 300 °C, more preferably 90 to 260 °C, most preferably 100 to 250 °C. The pressure in the absorption unit may also vary within wide ranges. Typically, the pressure in the absorption unit is in the range of of from 0.1 to 20 bar, more preferably 1 to 10 bar, most preferably 2 to 6 bar.

In one embodiment, the temperature is at most 50 °C, preferably at most 20 °C, more preferably at most 10 °C, most preferably at most 5 °C higher than the condensation temperature of the C_3-C_6 carboxylic acid(s) to be recovered at operating pressure. In one embodiment, the temperature is at least 0 °C, preferably at least 10 °C, more preferably at least 20 °C, most preferably at least 30 °C above the condensation temperature of water at operating pressure.

In one embodiment, the pressure is at least 50 %, preferably at least 80 %, more preferably at least 100 %, most preferably at least 120 % of the condensation pressure of the C_3-C_6 carboxylic acid(s) to be recovered at operating temperature. Furthermore, the pressure is typically at most 99 %, preferably at most 90 %, more preferably at most 80 %, even more preferably at most 70 %, most preferably at most 50 % of the condensation pressure of water at operating temperature.

Advantageously, substantially all of the C_3-C_6 carboxylic acid present in the vaporous aqueous feed stream of the absorption unit exits said absorption unit in the absorbing solvent stream. Typically, at least 90 wt%, preferably at least 95 wt%, more preferably at least 99 wt%, even more preferably at least 99.5 wt%, yet even more preferably at least 99.8 wt%, most preferably at least 99.9 wt% of C_3-C_6 carboxylic acid present in the feed stream of the absorption unit is recovered in the absorbing solvent stream of said absorption unit. Furthermore, in order to avoid the need for any further water removal steps, it is preferred that the absorbing solvent entrains substantially none of the water present in the gaseous aqueous feed stream of the absorption unit. Preferably, the absorbing solvent effluent stream of the absorption unit comprises water and C_3-C_6 carboxylic acid in a weight ratio of less than 1:1, more preferably less than 0.5:1, even more preferably less than 0.1:1, yet even more preferably less than 0.05:1, most preferably less than 0.01:1 or about zero.

In the solvent recovery unit, C_3-C_6 carboxylic acid is removed (desorbed) from the absorbing solvent resulting in a product stream comprising C_3-C_6 carboxylic acid and another stream comprising the absorbing solvent now depleted of C_3-C_6 carboxylic acid.

In the solvent recovery unit, recovery of the absorbing solvent, and of optional other solvents present, is typically effectuated by distilling the effluent stream of the absorption unit comprising C_3-C_6 carboxylic acid and absorbing solvent, resulting in a top stream comprising C_3-C_6 carboxylic acid and a bottom stream comprising the absorbing solvent. Distillation may be carried out in any distillation unit known to the skilled that is suitable for separating absorbing solvent from C_3-C_6 carboxylic acid, and it is within the ability of one skilled in the art to select appropriate operating conditions for obtaining a desired degree of product purity and/or solvent recovery. Typically, the temperature in the solvent recovery unit would vary depending on the solvent/mixture of solvents selected and is in the range of of from 80 to 300 °C, more preferably 100 to 250 °C, most preferably 110 to 200 °C. The pressure in the solvent recovery unit is suitably in the range of of from 0.1 to 10 bar, more preferably 0.5 to 5 bar, most preferably 1 to 3 bar.

In one embodiment, the temperature in the solvent recovery unit is at least 0 °C, preferably at least 10 °C, more preferably at least 20 °C, most preferably at least 30 °C above the condensation temperature of the carboxylic acid at operating pressure. In one embodiment, the temperature in the solvent recovery unit is at most 20 °C, preferably at most 10 °C, more preferably at most 5 °C, most preferably at most 0 °C below the condensation temperature of the absorbing solvent at operating pressure.

Typically, the pressure is at least at least 100 %, more preferably at least 110 %, even more preferably at least 120 %, most preferably at least 130 % of the condensation pressure of the absorbing solvent at operating temperature. Typically, the pressure is at most 100 %, preferably at most 90 %, more preferably at most 80 %, even more preferably at most 70 %, most preferably at most 50 % of the condensation pressure of the carboxylic acid at operating temperature.

In one embodiment, steam is fed at the bottom of the solvent regeneration (desorption) unit to hydrolyze any esters that may have been formed in the C_3-C_6 carboxylic acid/solvent mixture.

It is preferred that at least 80 wt%, more preferably at least 90 wt%, even more preferably at least 95 wt%, yet even more preferably at least 98 wt% of the C_3-C_6 carboxylic acid present in the stream fed to the solvent recovery unit comprising C_3-C_6 carboxylic acid and absorbing solvent is recovered.

It is further preferred that at least 80 wt%, more preferably at least 90 wt%, even more preferably at least 95 wt%, yet even more preferably at least 98 wt% of the solvent present in the stream fed to the solvent recovery unit comprising C_3-C_6 carboxylic acid and absorbing solvent is recovered.

Typically, the C_3-C_6 carboxylic acid product stream of the solvent recovery unit comprises C_3-C_6 carboxylic acid in a concentration of at least 70 wt%, preferably at least 80 wt%, more preferably at least 90 wt%, more preferably at least 95 wt%, even more preferably at least 99 wt%, yet even more preferably at least 99.5 wt%, most preferably at least 99.9 wt%.

Based on the amount of C_3-C_6 carboxylic acid present in the aqueous stream provided to the absorption unit, at least 50 wt%, more preferably at least 75 wt%, even more preferably at least 90 wt%, yet even more preferably at least 95 wt%, most preferably at least 99 wt% of C_3-C_6 carboxylic acid is recovered in the process as defined herein.

In a preferred embodiment, at least a portion of the stream of the solvent recovery unit comprising the absorbing solvent, typically the bottom stream of a distillation unit, is recirculated to the absorption unit. Typically, at least

20 wt%, preferably at least 50 wt%, more preferably at least 70 wt%, most preferably at least 90 wt% of the recovered solvent stream is recirculated to the absorption unit. In one embodiment, the entire bottom stream comprising the absorbing solvent is recirculated to the absorption unit.

In the absorption column typically a top stream comprising or substantially consisting of water vapour, and optionally other gases lighter than water, is produced. Water may be recovered from this top stream using a condensation step, for example by cooling down the top stream of the absorption unit to a lower temperature, for example room temperature, so that the water can be recovered as a liquid stream.

The water vapour top stream of the absorption unit may further comprise entrained absorbing solvent. Typically, said top stream of the absorption unit comprises no more than 3 vol%, preferably at most 1 vol%, more preferably at most 0.3, even more preferably at most 0.1, most preferably at most 0.01 vol% of entrained absorbing solvent. Said entrained absorbing solvent may be recovered by liquid-liquid separation from the liquid water formed in the aforementioned condensation step. Advantageously, such liquid-liquid separation occurs spontaneously upon condensation due to the preferred poor miscibility of water and the absorbing solvent. In a preferred embodiment, the absorbing solvent thus recovered is at least partially recirculated to the absorption unit either as a separate stream or by mixing with a recirculated absorbing solvent stream from the solvent recovery unit.

The top stream comprising C_3-C_6 carboxylic acid originating from the solvent recovery unit may be further treated downstream, for example to further remove water by (azeotropic) distillation, pervaporation, etc., and/or other purification methods available in the art to obtain the purity and specifications for C_3–C_6 carboxylic acid products according to market requirements.

Detailed description of the drawing

In **Figure 1**, a vapour stream **4** comprising water and C_3–C_6 carboxylic acid is fed to an absorption column **5** to which further an absorbing solvent **6** is fed. C_3–C_6 carboxylic acid is absorbed by the absorbing solvent, which exits the absorption column as "fat" solvent stream **7**. A vapour stream comprising water and other gaseous compounds exits the absorption column as stream **8**.

Stream **7** comprising fat absorbing solvent and absorbed C_3–C_6 carboxylic acid is fed supplied to a solvent recovery (desorption) unit, comprising a distillation unit **9** equipped with condenser section **9a** and reboiler section **9b**. Desorbed C_3–C_6 carboxylic acid leaves distillation unit **9** as stream **10**, while absorbing solvent now depleted of absorbed C_3–C_6 carboxylic acid exits distillation unit **9** as stream **11**. The C_3–C_6 carboxylic acid-depleted absorbing solvent stream **11** may be partially recirculated to absorption column **5** as absorbing solvent recirculation stream **12**. C_3–C_6 carboxylic acid stream **10** may be further purified downstream.

The vapour stream **8** comprising water and other gaseous compounds obtained as a top stream from absorption column **5** is fed to a condensation unit **13**, where water is removed via stream **14**. A product stream comprising gaseous compounds is removed via stream **15**, from where it may undergo further separation and/or purification further downstream.

In condensation unit **13**, spontaneous separation from the condensed water of absorbing solvent entrained in vapour stream **8** originating from absorption column **5** may occur. This separated absorbing solvent stream **16** may at least partially be recirculated to absorption column **5** via recirculation stream **17**.

CLAIMS

1. A process for the recovery of C_3-C_6 carboxylic acid from a vaporous aqueous stream, comprising

providing a vaporous aqueous stream comprising C_3-C_6 carboxylic acid,

contacting said vaporous aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water vapour,

feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent,

and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit,

wherein the absorbing solvent is an oxygen-containing organic compound having

(i) a Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid as determined at 25 °C of 15 $MPa^{1/2}$ or less, preferably 12 $MPa^{1/2}$ or less, more preferably 10 $MPa^{1/2}$ or less;

(ii) a 1-octanol/water partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, preferably at least 0.5, more preferably at least 1.0, even more preferably at least 1.5, yet even more preferably at least 2.0, most preferably at least 3.0; and

(iii) a boiling point at atmospheric pressure that is at least 5 °C higher, preferably at least 10 °C higher, more preferably at least 20 °C higher than the boiling point of C_3-C_6 carboxylic acid.

2. Process according to claim 1, wherein the oxygen-containing absorbing solvent is a compound selected from the group consisting of alcohols, ethers, esters and acids, more preferably alcohols.

3. Process according to claim 1 or 2, wherein the alcohol is an aromatic, olefinic or aliphatic, branched or linear, primary, secondary or tertiary alcohol having 5-20, preferably 6-18, more preferably 6-16 carbon atoms, most preferably 8-16 carbon atoms, preferably a cyclic or aromatic alcohol having 6 to 20 carbon atoms, a linear aliphatic alcohol having 6 to 14 carbon atoms or a branched aliphatic alcohol having 5 to 14 carbon atoms.

4. A process for the recovery of C_3-C_6 carboxylic acid from a vaporous aqueous stream, comprising

providing a vaporous aqueous stream comprising C_3-C_6 carboxylic acid,

contacting said aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in an absorption unit, to produce a first stream comprising absorbing solvent and C_3-C_6 carboxylic acid and a second stream comprising water,

feeding said first stream comprising absorbing solvent and C_3-C_6 carboxylic acid to a solvent recovery unit, to produce a third stream comprising C_3-C_6 carboxylic acid and a fourth stream comprising absorbing solvent,

and optionally recycling at least a portion of the fourth stream comprising absorbing solvent to the absorption unit,

wherein the absorbing solvent is a cyclic or aromatic alcohol having 6 to 20 carbon atoms, a linear aliphatic alcohol having 6 to 14 carbon atoms or a branched aliphatic alcohol having 5 to 14 carbon atoms.

5. Process according to any one of claims 2-4, wherein the alcohol is selected from the group consisting of phenol, benzyl alcohol, alkyl phenols, creosol, xylenols, guaiacol (2-methoxyfenol), cresols, phenoxy ethanol, naphthol, 1-hexanol, 2-hexanol, 3-hexanol, 1-octanol, 2-octanol, 1-decanol, 2-decanol, 1-dodecanol, 2-dodecanol, 2-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 2-methyl-2-pentanol, 2-methyl-1-pentanol, 2,3-dimethyl-1-butanol, 2,2-dimethyl-1-butanol, 2,3-dimethyl-2-butanol, 3,3-dimethyl-2-butanol, 4-methyl-1-pentanol (iso-hexanol), 4-methyl-2-pentanol, 2-ethyl-1-butanol, 5-methyl-2-hexanol, 3-methyl-2-hexanol, 2,2-dimethyl-1-pentanol, 4,4-dimethyl-1-pentanol, 2-ethyl-1-hexanol (iso-octanol), di-isobutyl carbinol, methylisobutyl carbinol, pinacolyl alcohol, 2-propyl heptanol, 3-methyl-1-butanol (isopentyl alcohol), 2-methyl-1-butanol, 2-benzyloxy-ethanol, 2-phenoxy ethanol, 2-butoxy-ethanol, cyclohexanol, methyl cyclohexanol, methyl cyclopentanol, trimethyl cyclohexanols, cyclohexanemethanol, methyl cyclohexanemethanol, pinacol, citronellol, menthol and isoborneol.

6. Process according to any one of the preceding claims, wherein before contacting the vaporous aqueous stream comprising C_3-C_6 carboxylic acid with an absorbing solvent in the absorption unit, said aqueous stream is concentrated using reverse osmosis, carboxylic acid-selective pervaporation, L/L extraction or adsorption-desorption using a solid adsorbent.

7. Process according to claim 5 or 6, which further comprises condensing the second stream comprising water from the absorption unit to produce liquid water,

optionally separating entrained absorbing solvent from said top stream,

and optionally recirculating at least a portion of the separated entrained absorbing solvent to the absorption unit.

8. Process according to any one of the preceding claims, wherein the aqueous stream comprising C_3-C_6 carboxylic acid has a concentration of at least 0.1 wt%.

9. Process according to any one of the preceding claims, wherein the ratio (wt/wt) of absorbing solvent to C_3-C_6 carboxylic acid supplied to the absorption unit is in the range of from 100:1 to 0.1:1, preferably in the range of from 50:1 to 0.25:1, more preferably in the range of from 40:1 to 0.5:1.

10. Process according to any one of the preceding claims, wherein the aqueous stream comprising C_3-C_6 carboxylic acid originates from the oxidative dehydrogenation of an alkane containing 3 to 6 carbon atoms, preferably propane.

11. Process any one of the preceding claims, wherein the aqueous stream comprising C_3-C_6 carboxylic acid originates from the oxidation of an alkene containing 3 to 6 carbon atoms, preferably propylene.

12. Process according to any one of the preceding claims, wherein the aqueous stream comprising C_3-C_6 carboxylic acid comprises acrylic acid or methacrylic acid, preferably acrylic acid.

13. Process according to any one of the preceding claims, wherein the C_3-C_6 carboxylic acid product stream of the solvent recovery unit comprises C_3-C_6 carboxylic acid in a concentration of at least 70 wt%, more preferably at least 90 wt%, more preferably at least 95 wt%, even more preferably at least 99 wt%, yet even more preferably at least 99.5 wt%, most preferably at least 99.9 wt%.

14. Process according to any one of the preceding claims, wherein at least 50 wt%, more preferably at least 75 wt%, even more preferably at least 90 wt%, yet even more preferably at least 95 wt%, most preferably at least 99 wt% of C_3-C_6 carboxylic acid is recovered, based on the amount of C_3-C_6 carboxylic acid present in the aqueous effluent stream provided to the absorption step.

15. Use of an oxygen-containing organic compound having

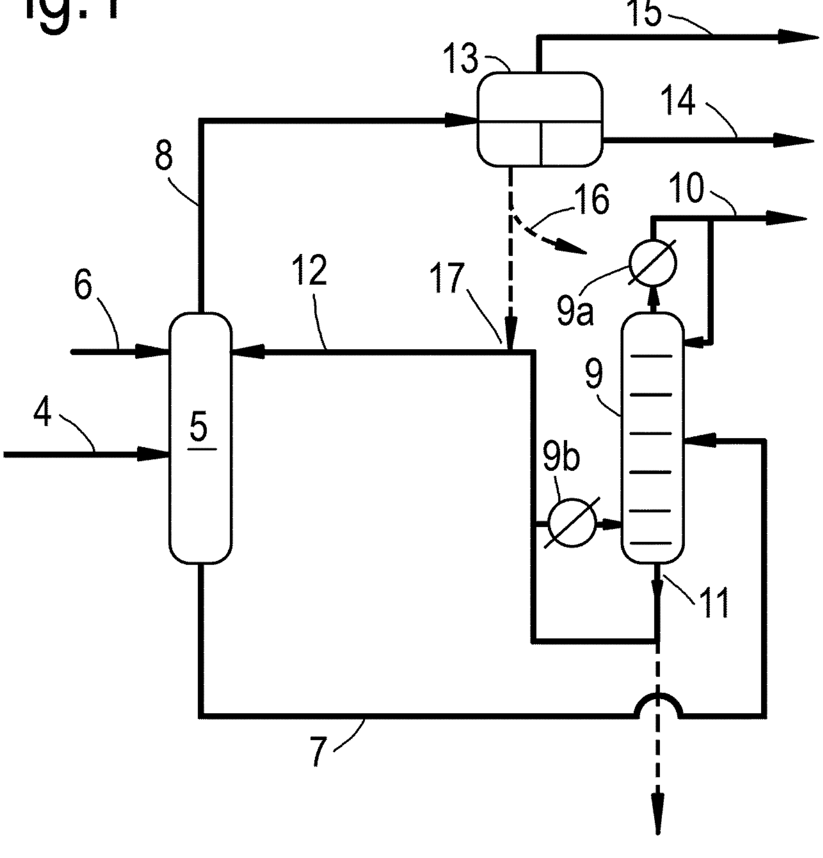
(i) a Hansen solubility parameter distance R_a with respect to C_3-C_6 carboxylic acid as determined at 25 °C of 15 $MPa^{1/2}$ or less, preferably 12 $MPa^{1/2}$ or less, more preferably 10 $MPa^{1/2}$ or less;

(ii) a 1-octanol/water partition coefficient $\log P_{OW}$ as determined at 25 °C and pH 7 of at least 0, preferably at least 0.5, more preferably at least 1.0, even more preferably at least 1.5, yet even more preferably at least 2.0, most preferably at least 3.0; and

(iii) a boiling point of at least 125 °C, preferably at least 140 °C, more preferably at least 160 °C, even more preferably at least 180 °C, most preferably at least 200 °Cat atmospheric pressure

as a solvent for absorbing C_3-C_6 carboxylic acid from a water-containing vapour stream.

Fig.1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/082706

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C57/07
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 458 396 A (DEGUSSA) 15 December 1976 (1976-12-15) page 1, lines 14-17,64-89 page 1, line 90 - page 2, line 18 example 1 page 2, lines 61-62, 109-113 page 3, lines 3-5,44-55 -----	1-15

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 6 March 2017	Date of mailing of the international search report 17/03/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Delanghe, Patrick

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/082706

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