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(54) **Title**: METHOD TO RECOVER ORGANIC TERTIARY AMINES FROM WASTE SULFURIC ACID

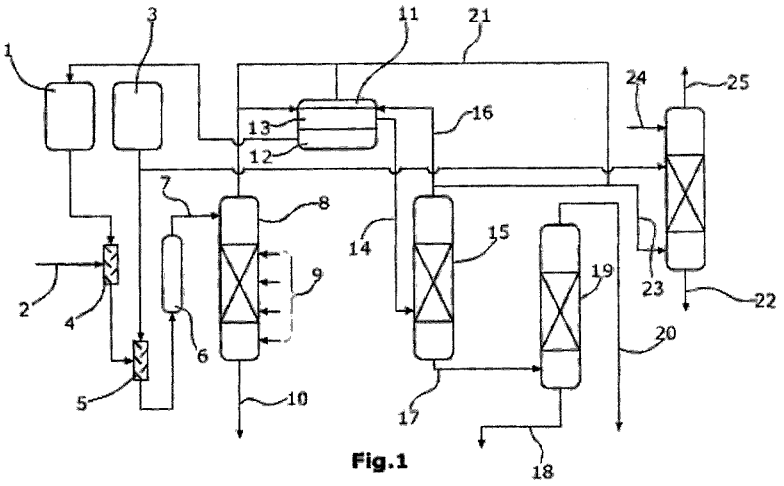


Fig.1

(57) **Abstract**: The present invention describes a method to recover organic tertiary amines from waste sulfuric acid comprising the following steps: a) reacting i) waste sulfuric acid comprising organic tertiary amines with ii) ammonia in an amount sufficient to obtain a pH of 9.5 or higher and b) separating the organic tertiary amines from the reaction mixture obtained in step a) wherein during the separation the pH of the reaction mixture is adjusted at a pH of 9.5 or higher.

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Method to recover organic tertiary amines from waste sulfuric acid

The invention relates to a method to recover organic tertiary amines from waste sulfuric acid as well as the use of said method to produce ammonium sulfate.

Waste sulfuric acid containing organic tertiary amines is obtained in many chemical plants and is a waste product from various chemical reactions.

The organic tertiary amines do have an economic value and as a consequence, it is desirable to recover the tertiary amines from the waste sulfuric acid. Further, waste sulfuric acid can be converted to ammonium sulfate which is commonly used as a fertilizer. However, it is a requirement for a good inorganic fertilizer that the total amount of organic compounds (TOC) is as low as possible.

It is known that waste sulfuric acid under reclamation of SO_2 can be treated thermally, whereby the contained amines are however lost. The production of SO_2 to the detriment of the contained amines is economically disadvantageous.

DE 101 46 689 A describes a method to recover organic amines from catalysts containing amines by distillative separation.

DE 35 22 470 A describes the recovery of amine- and metallic components in polyphenylene ether synthesis by separation using caustic soda.

DE 44 16 571 describes the recovery of amine from acidic solutions by the addition of alkali bases followed by distillation.

CN 1883790 describes the recovery of amines by neutralization with inorganic bases of oxide origin (NaOH, KOH, $Ca(OH)_2$, $CaCO_3$). In so doing the created sulfates must either be disposed of or processed using large amounts of energy (evaporation, drying) in order to obtain a usable by-product. Also, due to the mole masses of the oxide, bases require relatively large mass shares. In case of calcium bases, the created calcium sulfate already precipitates during the

reaction and therefore, the suspension must either be diluted or thoroughly blended at substantial costs.

DE 35 45 196 A1 discloses a process to recover tertiary aliphatic amines from waste sulfuric acid with ammonia. However, the yield of the tertiary amines recovered by the process disclosed in DE 35 45 196 A1 is too low and, as a consequence, the total amount of organic compounds which remain in the ammonium sulfate obtained from the process is too high. Thus, the process disclosed in the prior art requires a further purification step in order to reduce the amount of organic compounds in the dry ammonium sulfate to an acceptable level, i.e. a total amount of organic compounds (TOC), preferably of less than 1, more preferably less than 0.5 weight percent based on the dried ammonium sulfate obtained by the process. The TOC is determined in that a sample is oxidized and the amount of generated CO_2 is measured. The TOC can be determined according to the standard method DIN EN 1484-H3. Further, for an acceptable fertilizer it is particular important to keep the amount of organic tertiary amine in the ammonium sulfate composition as low as possible. Additionally, the process disclosed in DE 35 45 196 A1 does not recover the economically valuable tertiary amines from the waste sulfuric acid in a sufficient amount.

Therefore, it was an object of the present invention to overcome the problems present in the prior art and in particular, it was an object to significantly increase the yield of tertiary amines recovered from waste sulfuric acid. Further, it was an object to significantly reduce the total amount of organic compounds in the ammonium sulfate obtained from the process to recover the tertiary amine.

It has surprisingly been found that the problems associated with the methods to recover organic tertiary amines from waste sulfuric acids in the prior art can be solved by a method which uses ammonia and which controls the pH during the separation process.

The invention accordingly provides a method to recover organic tertiary amines from waste sulfuric acid comprising the following steps:

a) reacting

i) waste sulfuric acid comprising organic tertiary amines with

ii) ammonia in an amount sufficient to obtain a pH of 9.5 or higher and

b) separating the organic tertiary amines from the reaction mixture obtained in step a) wherein during the separation the pH of the reaction mixture is adjusted to a pH of 9.5 or higher.

The solution to the above-mentioned problems is surprising since in general to release amines from their ammonium salts, bases need to be used having a basicity of an order of magnitude higher than the corresponding amines. This applies, for example, to the bases described in CN 1883790 or DE-C-44 16 571.

Ammonia, on the other hand, has a comparable or lower basicity than the amines to be reclaimed such as triethylamine and many other amines.

In principle all tertiary amines are suited as organic amines to be recovered from the waste sulfuric acid by the method according to the present invention. The tertiary amines form corresponding hydrogen sulfates (below also referred to as organyl ammonium hydrogen sulfate) with sulfuric acid. Preferred tertiary amines are especially those comprising up to 20 carbon atoms, in particular up to 12 carbon atoms per nitrogen atom. Examples of amines which can be recovered from waste sulfuric acid by the method according to the present invention are selected from the group comprising trimethylamine, triethylamine, diethylpropylamine, tri-n-propylamine, triisopropylamine, ethyldiisopropylamine, tri-n-butylamine, triisobutylamine, tricyclohexylamine, ethyldicyclohexylamine, N,N-dimethylaniline, N,N-diethylaniline, benzyldimethylamine, pyridine, substituted pyridines such as picoline, lutidine, cholidine or methylethylpyridine, N-methylpiperidine, N-ethylpiperidine, N-methylmorpholine, N,N-dimethylpiperazine, 1,5-diazabicyclo[4.3.0]-non-5-en, 1,8-diazabicyclo-[5.4.0]-undec-7-en, 1,4-diazabicyclooctane, tetramethylhexamethylendiamine, tetramethylethylendiamine, tetramethylpropylendiamine, tetramethylbutylendiamine, 1,2-dimorpholylethan, pentamethyldiethyltriamine, pentaethyldiethylentriamine, pentamethyldipropylentriamine, tetramethyldi-

aminomethane, tetrapropyldiaminomethane, hexamethyltriethylentetramine, hexamethyltripropylenetetramine, diisobutylentriamine and triisopropylen-triamine.

Especially preferred is triethylamine.

Ammonia is an inexpensive, easily available chemical basic product and due to its low molecular weight has a highly favorable mass balance.

Ammonia can be used in gaseous or liquid form. According to the invention the partial pressure of the ammonia to be used can be between 0.1 and 300 bar and is limited only by the compressive strength of the used equipment. Ammonia can be used neat or as a mixture with other gases.

Ammonia can be used as a solution in other solvents, preferably as an aqueous solution. The aqueous solution can be obtained commercially or be produced directly from the reaction by introducing gaseous or liquid ammonia in water. The heat of solution can either be removed or retained by transferring the heated solution to the following reaction step. To avoid the exhalation of ammonia it is preferred to work at elevated pressure, e.g. a pressure of higher than 1 bar, preferably 1,5 to 10 bar. In step a) of the method to recover organic tertiary amines from waste sulfuric acid of the present invention, ammonia in gaseous or dissolved form is brought to the reaction with waste sulfuric acid comprising organic tertiary amines.

The ammonia is mixed with the waste sulfuric acid in an amount sufficient to obtain a pH of 9.5 or higher. According to a preferred embodiment of the method of the present invention the pH in step a) is preferably ranging from 9.8 to 12, i.e. the ammonia is added to the waste sulfuric acid in an amount sufficient to obtain a pH ranging from 9.8 to 12, more preferably from 10, or higher than 10, to 11.5.

During the reaction of waste sulfuric acid with ammonia, first the free sulfuric acid is neutralized followed by conversion of organyl ammonium hydrogen sulfate

to the corresponding amines. The reaction can be conducted batchwise, e.g. in an agitating machine or continuously in a pump reactor with or without agitation means. In the latter case, a static mixer is also suited, which in turn can be equipped with a temperature equalizer.

In a preferred embodiment of the method according to the present invention the reaction in step a) is conducted in a plug flow reactor. The plug flow reactor is preferred since the reaction can be conducted at elevated pressure and elevated temperature.

The reaction according to step a) of the method of the present invention is preferably conducted under an elevated pressure, preferably under pressure ranging from 2 to 12 bar, more preferably from 7 to 10 bar.

The temperature at which the reaction in step a) is conducted is preferably ranging from 95 to 150 °C, more preferably 100 to 140 °C, most preferably from 110 to 130 °C.

In order to avoid precipitation of ammonium sulfate by exceeding the solubility limit during or after the reaction, water can be added to the reaction mixture. This can be done by diluting the employed waste sulfuric acid with water before the reaction, by adding water during the reaction or by diluting the obtained ammonium sulfate solution after completion of the reaction.

The produced reaction heat can be removed using typical cooling devices known to the person skilled in the art. However, according to a preferred embodiment, the released reaction heat of the reaction of step a) is used in separation step b) for the distillative elimination of the organic tertiary amines. In case the reaction in step a) has been conducted under pressure and elevated temperature the expanded reaction mixture can be directly conveyed to the distillation column. Preferably the method is conducted at temperatures which work at the boiling point of the free amine or if present, the boiling temperature of the amine/water azeotrope or above. In case the reaction heat is not sufficient for distillation an

additional heating may be required. For example, in the case of triethylamine the preferred temperature is between 75 and 105 °C at 1 bar.

Further, according to a preferred embodiment of the present method, the energy released in step a) is at least partially used to evaporate the water in the concentration process in order to produce the solid ammonium sulfate, i.e. the reaction heat can be used to evaporate the water from the aqueous ammonium sulfate solution obtained by the method of the present invention.

Preferably an excess of ammonia is mixed with the waste sulfuric acid in order to achieve the required pH of 9.5 or higher.

Solutions which are suitable as waste sulfuric acids contain preferably 0.1 to 100 % by weight of the respective organyl ammonium hydrogen sulfate. Solutions may also contain free sulfuric acid and water. A typical waste sulfuric acid can for example, comprise 35 % by weight triethylammonium hydrogen sulfate, 45 % by weight sulfuric acid, 16 % by weight water and minor amounts of organic components.

In step b) of the method of the present invention the organic tertiary amines are separated from the reaction mixture obtained in step a) wherein during the separation the pH of the reaction mixture is adjusted at a pH of 9.5 or higher. Preferably the pH is adjusted to a range from 9.8 to 12, more preferably from 10, or higher than 10, to 11.5.

The separation of the released amines from the reaction mixture obtained in step a) can be done by distillation, extraction and through phase separation. Distillative separation is especially advantageous for amines with a low boiling point and amines with good water solubility. The above applies especially to amines that form an azeotrope with water. Distillative separation can be done directly from the reaction vessel or in a two stage apparatus.

According to a preferred embodiment the thermal energy of the products obtained at the still head of the distillation column may be used to heat the feed flow, e.g. the ammonia feed or the feed comprising the reaction mixture.

Low solubility amines in ammonium sulfate solution can be obtained through phase separation. Also, the ammonium sulfate solution can be extracted with a suitable solvent. Preferably, the organic tertiary amine is separated from the reaction mixture by extraction with an organic liquid, preferably a liquid hydrocarbon, more preferably an aliphatic liquid hydrocarbon comprising at least 6 carbon atoms, especially octane. However, the type of solvent is only limited by the stability of the used substances, the solubility of the ammonium sulfate solution and the following separability from the extracted amine.

The methods for the separation of the released amines can be applied individually or in combination.

According to an especially preferred method of the present invention the organic tertiary amine, preferably triethylamine, is separated from the reaction mixture obtained in step a) in a distillation column. In order to maintain a pH of 9.5 or higher during the separation in a distillation column, ammonia is preferably added to the distillation column. Preferably during the distillation ammonia is added to the distillation column in a counter flow to the reaction mixture obtained in step a).

According to a preferred embodiment, during the distillation the reaction mixture obtained in step a) is continuously fed to the upper part of a distillation column and the ammonia is continuously fed at the lower part or the middle part of the distillation column. The position of the ammonia feed to the distillation column can be used to control the pH of the reaction mixture to be separated during the separation process. The amount of ammonia and consequently the adjusted pH-value influence the capacity of the column with respect to separation of the tertiary amines from the aqueous ammonium sulfate solution. The closer the ammonia feed is to the bottom of the distillation column the higher the pH of the reaction mixture in the bottom of the column. The pH value referred to in step b)

of the method of the present invention is in case of a separation in a distillation column, the minimum pH value measured in the column between the feed of the reaction mixture and the feed of the ammonia.

Likewise, the position of the ammonia feed to the distillation column also influences the pH value of the aqueous solution comprising ammonium sulfate in the bottom of the column. In a preferred embodiment, the ammonia feed is placed at a position of the distillation column such that the aqueous solution, which is essentially free of the organic tertiary amine, in the lower part of the column has a pH ranging from 5 to 7.

Excess of ammonia can be reintroduced to the process according to the invention. This can be done purposely, e.g. by washing the exhaust containing ammonia with the employed waste sulfuric acid.

According to a preferred embodiment the organic tertiary amine, preferably triethylamine, is recovered in a yield of at least 99.0%, more preferably 99.5%.

According to a further embodiment of the present invention the method of the invention is used to produce ammonium sulfate. The ammonium sulfate solution obtained by the method of the invention represents a quickly recoverable, easily dosable, valuable nitrogen fertilizer. No additional processing is required prior to use. The ammonium sulfate content of the solution can be set as desired by the water content of the used waste sulfuric acid, the addition of water before, during or after the reaction and/or distillative removal of water taking into account the solubility limit of ammonium sulfate in water. Also possible is complete water removal using current methods such as distillation or spray drying, whereby ammonium sulfate is produced as a solid that can be used as a fertilizer.

According to a preferred embodiment, the method of the invention further comprises a dewatering step of the recovered tertiary amine which can optionally be followed by a further distillation of the dewatered amine.

A preferred embodiment of the process of the invention is illustrated by means of the following Figure 1. Figure measures known per se, e.g. addition of stabilizer, are not shown.

Figure 1 shows a method to recover triethylamine from waste sulfuric acid comprising triethylamine.

Figure 1 shows a schematic diagram of a process of the present invention.

Reference Signs

1	water reservoir
2	ammonia supply
3	waste sulfuric acid reservoir
4	first plug flow reactor
5	second plug flow reactor
6	pipe reactor
7	feed for the reaction mixture
8	distillation column
9	ammonia feed
10	flow for the ammonium sulfate solution
11	separator
12	water phase
13	organic phase
14	feed for the organic phase
15	dewatering column
16	feed for an azeotrope of water and tertiary amine
17	flow for the tertiary amine
18	flow for high boiler
19	distillation column
20	flow for the purified tertiary amine
21	ammonia comprising gases
22	flow of washing liquid
23	ammonia supply
24	water supply
25	exhaust gas

Gaseous ammonia is added via ammonia supply (2) to a first plug flow reactor (4) and diluted with water from a water reservoir (1). The aqueous ammonia solution is conveyed to a second plug flow reactor (5) where it is brought into contact with the waste sulfuric acid from the waste sulfuric acid reservoir (3). The waste sulfuric acid and the aqueous ammonia solution are reacted in a pipe reactor (6) and subsequently conveyed to a distillation column (8). The distillation column (8) has different ammonia feeds (9) which can be used to adjust the pH value during the separation process in the column. In the bottom of column (8) the ammonium sulfate solution is obtained which can be released from column (8) by flow (10). The triethylamine-water azeotrope is distilled off and conveyed to the phase separator (11) wherein the azeotrope is separated in a water phase (12) and an organic phase (13) which comprises the triethylamine. The organic phase is fed via feed (14) to the dewatering column (15). The azeotrope of water and triethylamine distilled off in the dewatering column (15) is conveyed via feed (16) to the separator (11). The triethylamine obtained at the bottom of dewatering column (15) is conveyed via flow (17) to distillation column (19). In distillation column (19) the purified triethylamine is distilled off via flow (20). From the bottom of distillation column (19) high boiling organic residues can be separated via flow (18). Ammonia containing gases are conveyed via line (21) and (23) to a column with a flow (22) and a water supply (24) and a supply from the waste sulfuric acid reservoir (3). Exhaust gas which is essentially free from ammonia can be released from the column via line (25).

The ammonia containing washing liquid released via flow (22) can be reintroduced in the process.

a) Separation of triethylamine in a distillation column

195 g of ammonia mixed with 755 g of water is reacted with 900 g of waste sulfuric acid consisting of 148 g water, 400 g H_2SO_4 and 334 g triethylammoniumhydrogensulfate (equivalent to 171 g of triethylamine) and additional 700 g of water.

The reaction mixture exhibits a pH value of 10. Subsequently, the reaction mixture is fed to the upper part of a distillation column while at the lower part of the distillation column ammonia is fed to the column in a counter flow fashion in order to keep the pH of the reaction mixture above 10. The pH value of the mixture in the column can be adjusted by the position of the ammonia feed at the lower part of the column.

Different pH values have been adjusted and the amount of triethylamine recovered has been determined. The weight-% of triethylamine recovered is based on the total weight of triethylamine present in the waste sulfuric acid.

Table 1: Examples 1 and 2 and Comparative Examples 3 to 5

Example	pH-value determined during separation	weight-% of triethylamine recovered
1 (according to the invention)	9.5	93.0
2 (according to the invention)	10.1	99.0
3 (comparative)	9.0	68.0
4 (comparative)	7.0	2.0
5 (comparative example 2 of DE 35 45 196)	not mentioned	92.6%

b) Separation of triethylamine by extraction with dichloromethane

530 g ice and 870 g of waste sulfuric acid consisting of 145 g water, 393 g H_2SO_4 and 308 g triethylammoniumhydrogensulfate (= equivalent to 158 g of triethylamine) are added to 683 g of an aqueous ammonia solution (25 wt.-% ammonia). The reaction mixture obtained shows a pH of 7.2. The mixture is subsequently divided in two equal parts (part 1 and part 2).

To part 2 54 g of an aqueous ammonia solution (25 wt.% ammonia) is added to obtain a pH of 10.1. Part 1 and part 2 are each 3 times extracted with 200 g dichloromethane at 25°C. The organic phases are subsequently dried with sodium sulfate, filtered and washed with dichloromethane to obtain 750 g of a dichloromethane solution.

The amount of extracted triethylamine is determined by gas chromatography.

Table 2: Separation of triethylamine by extraction at different pH-values

Example	pH adjusted to	Triethylamine recovered in wt.-%
Part 1 (comparative)	7.2	1.75
Part 2 (according to the invention)	10.1	80.6

Claims

1. Method to recover organic tertiary amines from waste sulfuric acid comprising the following steps:

a) reacting i) waste sulfuric acid comprising organic tertiary amines with

ii) ammonia in an amount sufficient to obtain a pH of 9.5 or higher and

b) separating the organic tertiary amines from the reaction mixture obtained in step a) wherein during the separation the pH of the reaction mixture is adjusted to a pH of 9.5 or higher.

2. Method according to claim 1 wherein the organic tertiary amine is separated from the reaction mixture obtained in step a) in a distillation column.

3. Method according to claim 2 wherein during the distillation ammonia is added to the distillation column.

4. Method according to claim 2 or 3 wherein during the distillation ammonia is added to the distillation column in a counter flow to the reaction mixture obtained in step a).

5. Method according to claim 4 wherein during the distillation the reaction mixture obtained in step a) is continuously fed to the upper part of a distillation column and the ammonia is continuously fed to the lower part or the middle part of the distillation column.

6. Method according to claim 5 wherein the ammonia feed to the distillation column is positioned such that the aqueous solution which is essentially free of organic tertiary amine and which comprises the ammonium sulfate in the lower part of the column has a pH ranging from 5 to 7.

7. Method according to claim 1 wherein the organic tertiary amine is separated from the reaction mixture by extraction with an organic liquid, preferably a liquid

hydrocarbon, more preferably an aliphatic liquid hydrocarbon comprising at least 6 carbon atoms, especially octane.

8. Method according to at least one of claims 1 to 7 wherein the pH in step a) and/or step b) ranges from 9.8 to 12.

9. Method according to at least one of claims 1 to 8 wherein the organic tertiary amine is triethylamine.

10. Method according to at least one of claims 1 to 9 wherein the organic tertiary amine is recovered in a yield of at least 99.0%.

11. Method according to at least one of claims 1 to 10 wherein the waste sulfuric acid comprises 0.1 to 100 % by weight of the organic tertiary amine as organyl ammonium hydrogen sulfate.

12. Method according to at least one of claims 1 to 7 wherein the released reaction heat of the reaction in step a) is used in the separation step b) for the distillative elimination of the organic tertiary amine.

13. Method according to at least one of claims 1 to 12 wherein step a) is conducted under elevated pressure, preferably a pressure ranging from 2 to 12 bar, more preferably from 7 to 10 bar.

14. Method according to at least one of claims 1 to 13 wherein the reaction in step a) is conducted at a temperature ranging from 90 to 150 °C, preferably 100 to 140 °C, more preferably from 110 to 130 °C.

15. Use of the method according to at least one of claims 1 to 14 to produce ammonium sulfate.

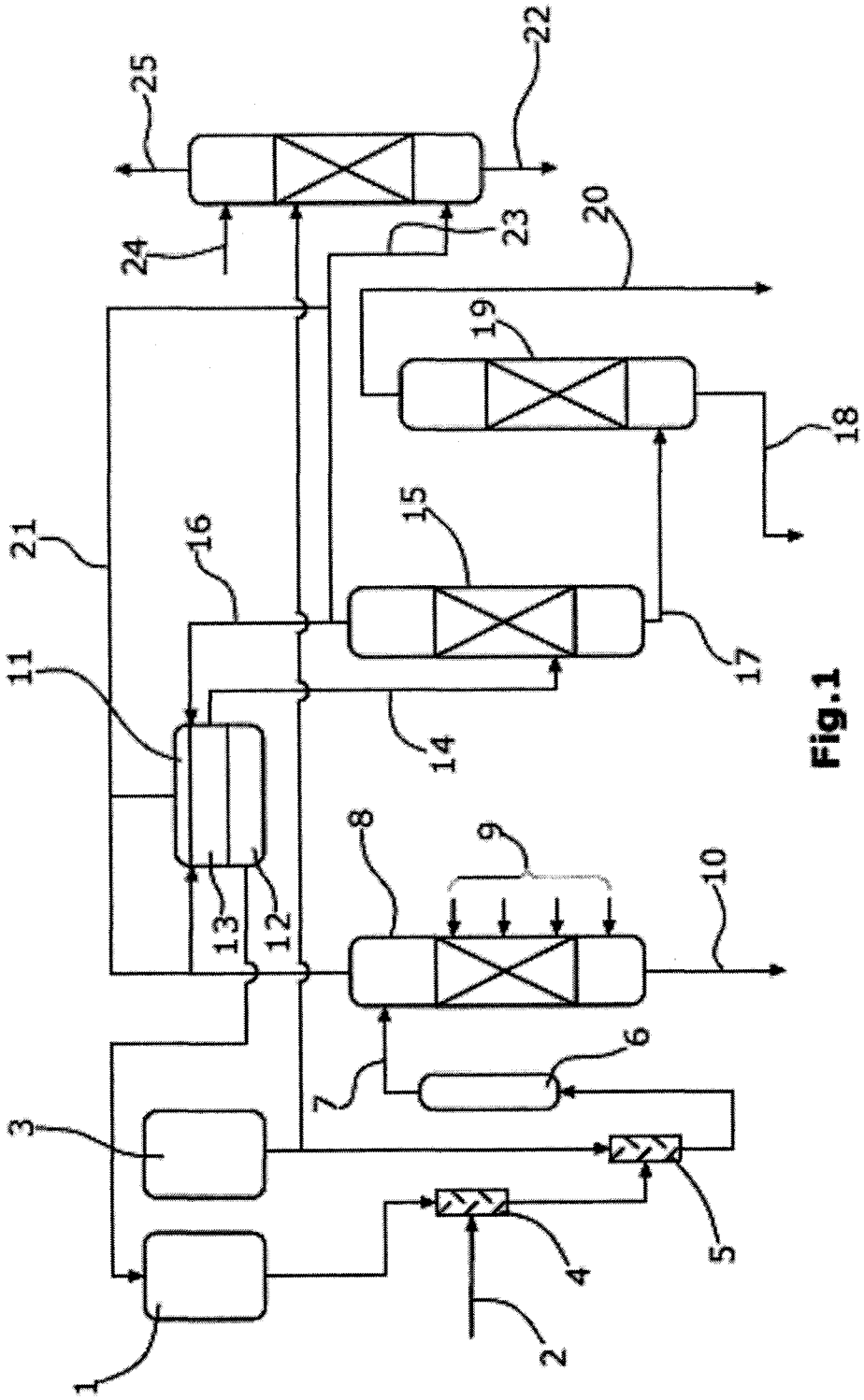


Fig.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/055788

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C209/86 C07C211/05 C01C1/242
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 C01C

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 practical, search terms used)
EPO-Internal, 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	DE 35 45 196 A1 (HOECHST AG [DE]) 25 June 1987 (1987-06-25) cited in the application column 1, line 37 - line 56 column 2, line 40 - line 49 column 3; example 2 -----	1-15
A	DE 44 16 571 C1 (GIEBELER EBERHARD DR [DE]) 7 December 1995 (1995-12-07) cited in the application abstract column 5, line 53 -----	1,15
A	WO 2007/079944 A1 (DSM IP ASSETS BV [NL]; PETERS ALEXANDER VOLKER [DE]; KROOSHOF GERARDUS) 19 July 2007 (2007-07-19) abstract page 5, line 19 -----	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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"&" document member of the same patent family

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

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3545196 A1	25-06-1987	NONE	
DE 4416571 C1	07-12-1995	AT 167663 T	15-07-1998
		AU 2342795 A	05-12-1995
		BR 9507711 A	23-09-1997
		CA 2187428 A1	23-11-1995
		CN 1148845 A	30-04-1997
		CZ 9603012 A3	13-08-1997
		WO 9531430 A1	23-11-1995
		EP 0759900 A1	05-03-1997
		ES 2120744 T3	01-11-1998
		JP 2929557 B2	03-08-1999
		JP 9507681 T	05-08-1997
		PL 317207 A1	17-03-1997
		RU 2145596 C1	20-02-2000
		US 5808159 A	15-09-1998
WO 2007079944 A1	19-07-2007	CN 101356151 A	28-01-2009
		EA 200801697 A1	30-10-2008
		EP 1971569 A1	24-09-2008
		JP 2009523144 T	18-06-2009
		KR 20080108082 A	11-12-2008
		US 2010274057 A1	28-10-2010