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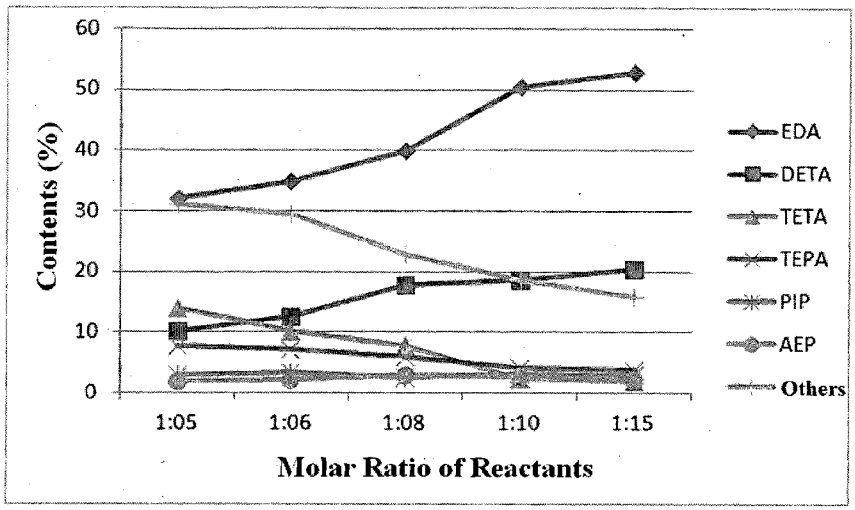
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(54) Title: METHOD FOR PRODUCING ETHYLENEAMINES



(57) Abstract: The present invention relates to method for producing ethyleneamines that includes: reacting ethylenedichloride with ammonia water under conditions optimizing the molar ratio of ethylenedichloride to ammonia in a defined range to produce amine compounds, ammonium chloride, and water; and isolating the amine compounds, ammonium chloride, and water, respectively. The present invention provides a continuous process for producing ethyleneamines using ethylenedichloride and ammonia by efficiently controlling the composition of the ethyleneamine product in accordance with the supply and demand of ethyleneamines to optimize the distribution of ethyleneamines.

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TITLE OF THE INVENTION

METHOD FOR PRODUCING ETHYLENEAMINES

BACKGROUND OF THE INVENTION

(a) Field of the Invention

The present invention relates to a process for producing ethyleneamines. In particular, the present invention relates to a method for producing ethyleneamines by performing the reaction of ethylenedichloride and ammonia water in the optimized manner so as to flexibly control the composition of the product and the distribution of ethyleneamines, based on the supply and demand of ethyleneamines.

(b) Description of the Related Art

Ethyleneamines were firstly synthesized by A.W. Hoffmann from ethylenedichloride and alcoholic ammonia, and industrially, these are prepared from ethylenedichloride and ammonia according to the technology of UCC Inc. (US).

Ethyleneamines can be prepared by Ethylenedichloride (EDC) process or Ethylene Oxide (EO) process, and the basic reactions are as follows:

[EDC process]

$C_2H_4Cl_2 + 4NH_3 \rightarrow C_2H_8N_2 + 2NH_4Cl$

(EDC + Ammonia → Ethylenediamine (EDA) + Ammonium chloride)

[EO process]

$C_2H_4O + 2NH_3 \rightarrow C_2H_8N_2 + H_2O$

(EO + Ammonia → EDA + Water)

Among them, the EDC method needs the process for recovering ammonia from ammonium chloride formed because it uses excessive ammonia, and sodium hydroxide is used on this account.

[Ammonia recovery process]

$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$

When ammonium chloride is reacted with the sodium hydroxide in order to recover ammonia, sodium chloride produced from the reaction is included into the mixture of ethyleneamines, simultaneously with water. Then, the reaction products are isolated and purified into the individual components in the subsequent processes, after removing water which is introduced initially or produced during the reaction of recovering ammonia.

The EDC process involves reacting EDC (Ethylenedichloride) with liquid ammonia or ammonia water under conditions of about 100 °C and 50 bar to yield ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and so forth. The EDC process which yields hydrochloric acid, ammonium chloride, or the like that entails difficulty in facility management and intensified corrosion to cause high maintenance cost.

The EO process involves reacting EO (Ethylene Oxide) with ammonia in the presence of a cobalt catalyst under conditions of about 150 to 230 °C and 200 bar to yield ethylenediamine (EDA), diethylenetriamine (DETA), aminoethylethanolamine (AEEA), and so forth. The EO process requires higher reaction temperature and higher pressure compared with the EDC process. However, the EO process generates water as a by-product, and then is easier to manage with less trouble.

Therefore, it has been needed to study the development of the process for producing ethyleneamines, in accordance with the supply and demand of ethyleneamines, to flexibly control the composition of the product and the distribution of ethyleneamines.

SUMMARY OF THE INVENTION

It is an aspect of the present invention to provide a method for effectively producing ethyleneamines that efficiently controls the composition of the product and optimizes the distribution of ethyleneamines, in accordance with the supply and demand of ethyleneamines.

The present invention provides a method for producing ethyleneamines that includes the steps of: reacting ethylenedichloride with ammonia water having a concentration of 20 % to 80 % to produce amine compounds, ammonium chloride, and water; and isolating the amine compounds, ammonium chloride, and water, respectively; where the ethylenedichloride is reacted with the ammonia water to have the molar ratio of ethylenedichloride to ammonia in the range from 1:5 to 1:15.

The amine compounds may comprise at least one selected from the group consisting of ethylenediamine (EDA), diethylenetriamine (DETA), piperazine (PIP), aminoethylpiperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), monoethanolamine (MEA), aminoethylethanolamine (AEEA), and hexaethyleneheptamine (HEHA).

The reaction producing the amine compounds may be carried out in the

manner of a continuous process.

The reaction producing the amine compounds may be carried out under the condition of 50 to 180 °C.

The reaction producing the amine compounds may be carried out under the condition of 80 to 180 bar.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the results of an experiment varying the composition ratio of reactants according to one exemplary embodiment of the present invention.

Fig. 2 is a graph showing the results of an experiment varying the concentration of ammonia water according to another exemplary embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

Hereinafter, the method for producing ethyleneamines according to the concrete embodiment of the present invention is explained in more detail. However, the followings are only for the understanding of the present invention and the scope of the present invention is not limited to or by them, and it is obvious to a person skilled in the related art that the embodiments can be variously modified in the scope of the present invention.

In addition, "comprises, " "comprising," "includes," "including," "contains," or "containing" means to include any components (or ingredients) without particular limitation unless there is no particular mention about them in this

description, and it cannot be interpreted as a meaning of excluding an addition of other components (or ingredients).

In the course of the repeated studies on the preparation of ethyleneamines by reacting ethylenedichloride with ammonia water, the inventors of the present invention have found it out that ethyleneamines can be produced with the composition of the product flexibly controlled in accordance with ethyleneamine supply and demand situations then the reaction for producing ethyleneamines is carried out under optimized process conditions such as the composition ratio of reactants.

In accordance with one exemplary embodiment of the present invention, there is provided a method for producing ethyleneamines that includes reacting ethylenedichloride with ammonia water. The method for producing ethyleneamines according to the present invention comprises the steps of reacting ethylenedichloride with ammonia water having a concentration of 20 % to 80 % to produce amine compounds, ammonium chloride, and water; and isolating the amine compounds, ammonium chloride, and water, respectively; wherein the ethylenedichloride is reacted with the ammonia water to have the molar ratio of ethylenedichloride to ammonia in the range from 1:5 to 1:15

The term "ethyleneamines" as used herein refers to all amine compounds, that is, all compounds containing at least one ethylene group and at least one amine group and includes a number of polyamines (heavy amines) together with ethylenediamine. The ethyleneamines, that is, the amine compounds may include at least one selected from the group consisting of ethylenediamine (EDA), diethylenetriamine (DETA), piperazine (PIP),

aminoethylpiperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), monoethanolamine (MEA), aminoethylethanolamine (AEEA), and hexaethyleneheptamine (HEHA). Here, diethylenetriamine (DETA), piperazine (PIP), aminoethylpiperazine (AEP), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), monoethanolamine (MEA), aminoethylethanolamine (AEEA), and hexaethyleneheptamine (HEHA), except for ethylenediamine (EDA), are commonly called "polyamines (or heavy amines)".

The reaction for producing the amine compounds may be carried out under the temperature conditions ranging from 50 °C to 180 °C, preferably from 100 °C to 150 °C. The reaction temperature is 50 °C or higher in view of the starting of the reaction, and 180 °C or lower with a view to minimizing the generation of by-products and securing easiness of operation.

Further, the reaction for producing the amine compounds may be carried out under the pressure conditions ranging from 80 bar to 180 bar, preferably from 100 bar to 150 bar. The pressure for the reaction is 80 bar or higher in view of the starting of the reaction, and 180 bar or lower with a view to minimizing the generation of by-products and securing easiness of operation.

The reaction for producing amine compounds may be performed in the manner of a continuous process. A tubular reactor can be used in the continuous process. In the continuous process, the reaction is performed under dynamic pressure and then the amine compounds are produced in a continuous manner.

In the present invention, the reaction between ethylenedichloride and ammonia water may be carried out under condition that the molar ratio of ethylenedichloride to ammonia is in the range from 1:5 to 1:15. The molar ratio of ethylenedichloride to ammonia may be 1:5 or greater in view of improving the conversion rate of ethylenedichloride. Also, the molar ratio of ethylenedichloride to ammonia may be 1:15 or less to optimize the amount of water being recycled, and it enhances the efficiency of the operation and reduces the operating costs.

Particularly, the molar ratio of ethylenedichloride to ammonia can be flexibly controlled to optimize the distribution of ethylenediamine (EDA) and polyamines (heavy amines) as the product. For example, the reaction between ethylenedichloride and ammonia water may be carried out to have the molar ratio of ethylenedichloride to ammonia in the range from 1:5 to 1:12, preferably from 1:5 to 1:10, more preferably from 1:5 to 1:8, in order to maximize the contents of polyamines (heavy amines) and minimize the contents of ethylenediamine (EDA) among the product. Otherwise, the reaction between ethylenedichloride and ammonia water may be carried out to have the molar ratio of ethylenedichloride to ammonia in the range from 1:7 to 1:15, preferably from 1:8 to 1:15, more preferably from 1:10 to 1:15, in order to maximize the contents of ethylenediamine (EDA) and minimize the contents of polyamines (heavy amines) among the product.

The concentration of ammonia water may be 20 to 80 wt% (% by weight). Here, the concentration of ammonia water means the weight of ammonia (e.g., 20 g to 80 g) included per unit weight (e.g., 100 g) of water.

The concentration of ammonia water may be 20 wt% or greater in view of optimizing the used amount of water and enhancing the efficiency of the reaction. Also, the concentration of ammonia water may be 80 wt% or less in view of enhancing the efficiency of the operation and reducing the operating costs. Particularly, the concentration of ammonia water can be flexibly controlled to optimize the distribution of ethylenediamine (EDA) and polyamines (heavy amines) as the product. For example, the ammonia water may be used in a high concentration, i.e., preferably 30 to 80 wt%, more preferably 40 to 80 wt%, most preferably 50 to 80 wt%, in order to maximize the contents of polyamines (heavy amines) and minimize the contents of ethylenediamine (EDA) among the product. Otherwise, the ammonia water may be used in a low concentration, i.e., preferably 20 to 65 wt%, more preferably 20 to 60 wt%, most preferably 20 to 50 wt%, in order to maximize the contents of ethylenediamine (EDA) and minimize the contents of polyamines (heavy amines) among the product.

The amine compounds, ammonium chloride, and water, which are produced from the above reaction, can be carried out of a separation process, such as neutralization, extraction, or the like. The neutralization process may be applied to remove ammonium chloride by converting it into sodium chloride (NaCl) through reaction with sodium hydroxide. The extraction process may be applied to isolate a little of the soluble salt included in the amine compounds by selective dissolving it with a solvent.

In the process for producing ethyleneamines according to the present invention, the distribution of ethyleneamines can be optimized by using an

ammonia water having the concentration of 28 % under the condition of making the molar ratio of ethylenedichloride to ammonia in the range of 1:15 to 1:10. For instance, ethylenediamine (EDA) can be produced in the contents of 55 wt% or less, or from 25 wt% to 55 wt%, preferably 50 wt% or less, more preferably 45 wt% or less, most preferably 40 wt% or less. Also, polyamines (heavy amines) can be produced in the contents of 45 wt% or greater, or from 45 wt% to 75 wt%, preferably 50 wt% or greater, more preferably 55 wt% or greater, most preferably 60 wt% or greater.

According to the present invention, the conversion rate of ethylenedichloride can be calculated by analyzing the content of chloride ion, and the analysis of the resultant ethyleneamines can be carried out using gas chromatography (GC).

In the present invention, those other than described above herein may be added or omitted under necessity and not intended to limit the scope of the present invention.

As explained, according to the present invention, a variety of ethyleneamines can be effectively produced by adjusting the conditions for the process of reacting ethylenedichloride with ammonia water, in accordance with the supply and demand of ethyleneamines, so as to flexibly control the composition of the product and the distribution of ethyleneamines.

Examples

Hereinafter, preferable examples and comparative examples are

presented for understanding the present invention. However, the following examples are only for illustrating the present invention and the present invention is not limited to or by them.

Example 1

40% ammonia water and ethylenedichloride (EDC; $C_2H_4Cl_2$) were introduced into a reactor to be 1:5 of the molar ratio for ethylenedichloride to ammonia (NH_3). The reaction was carried out under the pressure of 120 bar while maintaining the temperature of the reactor to be 120 °C.

After finishing the reaction, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 32.1 wt% of EDA, 10.2 wt% of DETA, 13.9 wt% of TETA, 7.8 wt% of TEPA, and 2.0 wt% of AEP, and the rest of the product was the other heavy amines. The analysis results are presented in the following Table 1.

Example 2

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 1, except for applying in 1:6 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to ammonia (NH_3).

Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 34.9 wt% of EDA, 12.7 wt% of DETA, 10.2 wt% of TETA, 7.2 wt% of TEPA, and 2.2 wt% of AEP. The analysis results are presented in the following Table 1.

Example 3

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 1, except for applying in 1:8 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to ammonia (NH_3).

Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 40.0 wt% of EDA, 17.8 wt% of DETA, 7.9 wt% of TETA, 6.0 wt% of TEPA, and 2.9 wt% of AEP. The analysis results are presented in the following Table 1.

Example 4

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 1, except for applying in 1:10 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to ammonia (NH_3).

Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 50.4 wt% of EDA, 18.7 wt% of DETA, 2.3 wt% of TETA, 4.2 wt% of TEPA, and 2.8 wt% of AEP. The analysis results are presented in the following Table 1.

Example 5

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 1, except for applying in 1:15 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to ammonia (NH_3).

Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 52.9

wt% of EDA, 20.5 wt% of DETA, 1.8 wt% of TETA, 3.8 wt% of TEPA, and 2.1 wt% of AEP. The analysis results are presented in the following Table 1.

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5
Reactants Ratio	1:5	1:6	1:8	1:10	1:15
EDA	32.101	34.946	39.983	50.384	52.854
DETA	10.211	12.697	17.775	18.683	20.515
TETA	13.941	10.204	7.853	2.261	1.844
TEPA	7.819	7.165	6.048	4.194	3.846
PIP	2.928	3.297	2.611	3.081	2.953
AEP	1.972	2.158	2.887	2.756	2.145
Others	31.028	29.533	22.843	18.641	15.843
Total	100.000	100.000	100.000	100.000	100.000

* Reactants Ratio is the composition of reactants, EDC : ammonia water (i.e., molar ratio of ethylenedichloride to ammonia)
* EDA: ethylenediamine, DETA: diethylenetriamine, TETA: triethylenetetramine, TEPA: tetraethylenepentamine, PIP: piperazine, AEP: aminoethylpiperazine
* unit is wt%

The results of an experiment varying the composition ratios of reactants according to one exemplary embodiment of the present invention are shown in the graph of FIG. 1.

As shown in Table 1, Examples 1 to 5 in which the conditions for the process of producing the amine compounds are given in the optimum range according to the present invention end up with the EDC conversion rate of 100 % and the distribution of ethylenediamine (EDA) is optimized with the higher composition of reactants. Particularly, Example 1 which was carried out in the range of 1:5 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to

ammonia, is given that the content of ethylenediamine (EDA) is minimized at 32.101 wt% and the contents of polyamines (heavy amines) including DETA, TETA, TEPA, PIP, AEP, and others are maximized at 67.899 wt% . Also, Example 5 which was carried out in the range of 1:15 of the molar ratio for ethylenedichloride (EDC, $C_2H_4Cl_2$) to ammonia, is given that the content of ethylenediamine (EDA) is maximized at 52.854 wt% and the contents of polyamines (heavy amines) including DETA, TETA, TEPA, PIP, AEP, and others are minimized at 47.146 wt% .

Example 6

28% ammonia water and ethylenedichloride (EDC; $C_2H_4Cl_2$) were introduced into a reactor to be 1:10 of the molar ratio for ethylenedichloride (EDC; $C_2H_4Cl_2$) to ammonia (NH_3). The reaction was carried out under the pressure of 120 bar while maintaining the temperature of the reactor to be 120 °C.

After finishing the reaction, the conversion rate of EDC was 100 %. The analysis measured by gas chromatography (GC) showed that the product was composed of 52.3 wt% of EDA, 19.4 wt% of DETA, 2.7 wt% of TETA, 3.8 wt% of TEPA, and 2.5 wt% of AEP, and the rest of the product was the other heavy amines. The analysis results are presented in the following Table 2.

Example 7

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 6, except

for using the ammonia water with 52%. Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 43.2 wt% of EDA, 16.7 wt% of DETA, 8.5 wt% of TETA, 6.9 wt% of TEPA, and 1.8 wt% of AEP. The analysis results are presented in the following Table 2.

Example 8

The reaction of ammonia water and ethylenedichloride was carried out substantially according to the same method as disclosed in Example 6, except for using the ammonia water with 60%. Here, the conversion rate of EDC was 100 %. The analysis measured by a gas chromatography (GC) showed that the product was composed of 39.4 wt% of EDA, 12.7 wt% of DETA, 11.3 wt% of TETA, 9.2 wt% of TEPA, and 1.8 wt% of AEP. The analysis results are presented in the following Table 2.

[Table 2]

	Example 4	Example 6	Example 7	Example 8
Concentration	40 %	28 %	52 %	60 %
EDA	50.384	52.329	43.220	39.383
DETA	18.683	19.354	16.660	12.683
TETA	2.261	2.652	8.520	11.260
TEPA	4.194	3.772	6.928	9.194
PIP	3.081	2.774	2.162	3.080
AEP	2.756	2.518	1.848	1.755
Others	18.641	16.601	20.662	22.645
Total	100.000	100.000	100.000	100.000

*Concentration – concentration of ammonia water
* EDA: ethylenediamine, DETA: diethylenetriamine, TETA: triethylenetetramine, TEPA: tetraethylenepentamine, PIP: piperazine, AEP: aminoethylpiperazine
* unit is wt%

The results of an experiment varying the concentration of ammonia water according to another embodiment of the present invention are shown in the graph of FIG. 2.

As shown in Table 2, Examples 4 and 6 to 8 in which the conditions for the process of producing the amine compounds are given in the optimum range according to the present invention end up with the EDC conversion rate of 100 % and the distribution of the ethylenediamine (EDA) product maximized with the lower concentration of ammonia water. Particularly, Example 8 which was carried out by using the ammonia water with 60% concentration, is given that the content of ethylenediamine (EDA) is minimized at 39.383 wt% and the contents of polyamines (heavy amines) including DETA, TETA, TEPA, PIP, AEP, and others are maximized at 60.617 wt% . Also, Example 6 which was carried out by using the ammonia water with 28% concentration, is given that the content of ethylenediamine (EDA) is maximized at 52.329 wt% and the contents of polyamines (heavy amines) including DETA, TETA, TEPA, PIP, AEP, and others are minimized at 47.146 wt% .

Comparative Example 1

As in the catalytic reaction process according to the prior art, a mixture including 49.6 wt% of EDA, 1.9 wt% of PIP, 24.3 wt% of DETA, 2 wt% of AEP, 21 wt% of heavies, and 1.2 wt% of other amines was added into an EDC reactor to activate a reaction in the fixed-bed reactor. The reaction was maintained under the condition of the pressure at 800 psig and the temperature ranges from 145 °C to 155 °C. Also, 0.0003 wt% of hydrogen was added to

maintain the activity of the catalyst. The catalyst as used herein was a heterogeneous Ni-Re (6.8:1.8 wt%) catalyst, and used with an alumina or silica support. According to the analysis results, the product was composed of 37.3 wt% of EDA, 25.4 wt% of DETA, 21.1 wt% of TETA, 5.6 wt% of TEPA, 3.7 wt% of AEP, 4.9 wt% of PIP, and 2.0 wt% of other amines.

Comparative Example 2

As in the reaction process involving an addition of ethylenediamine (EDA) according to the prior art, a 1 L reactor was filled with 200 g of water, supplied with 236 g of ammonia, and then heated up to 100 °C. The pressure of the reactor was 25 kg/cm^2G, and the concentration of ammonia water was 51.5 wt%. Then, 92.9 g of EDC was added into the reactor, which is maintained at 100 °C. After 6 minutes, 29.7 g of EDA was added so that the molar ratio of EDA to EDC was 0.51. When the reaction was completed in 30 minutes after the addition of EDC, the reactor was cooled down to the room temperature. Then, sodium hydroxide was added to neutralize ammonium chloride and amine hydrochloride. The final product was analyzed by gas chromatography (GC). The analytical results showed that the product was composed of 23.3 wt% of EDA, 34.4 wt% of DETA, 18.7 wt% of TETA, 8.6 wt% of TEPA, 4.9 wt% of AEP, 2.7 wt% of PIP, and 7.7 wt% of other amines.

As described above, Comparative Example 1 controlled the product distribution by the use of the "Ni-Re catalyst." However, the present invention can control the product without using a catalyst. Also, Comparative Example 2

controlled the product distribution by "addition of separate EDA." On the contrary, the present invention can control the product without adding separate "EDA." Therefore, the present invention is superior to the conventional processes such as Comparative Examples 1 and 2, in the aspects of enhancing the process efficiency and reducing the cost.

While this disclosure has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

WHAT IS CLAIMED:

1. A method for producing ethyleneamines, comprising the steps of:

reacting ethylenedichloride with ammonia water having a concentration of 20 % to 80 % to produce amine compounds, ammonium chloride, and water; and

isolating the amine compounds, ammonium chloride, and water, respectively;

wherein the ethylenedichloride is reacted with the ammonia water to have the molar ratio of ethylenedichloride to ammonia in the range from 1:5 to 1:15.

2. The method according to Claim 1, wherein the amine compounds comprises at least one selected from the group consisting of ethylenediamine, diethylenetriamine, piperazine, aminoethylpiperazine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, monoethanolamine, aminoethyleneethanolamine, and hexaethyleneheptamine.

3. The method according to Claim 1, wherein the reaction for producing the amine compounds is carried out in the manner of a continuous process.

4. The method according to Claim 1, wherein the reaction for producing the amine compounds is carried out under the condition of 50 to 180 °C.

5. The method according to Claim 1, wherein the reaction for producing the amine compounds is carried out under the condition of 80 to 180 bar.

FIG. 1

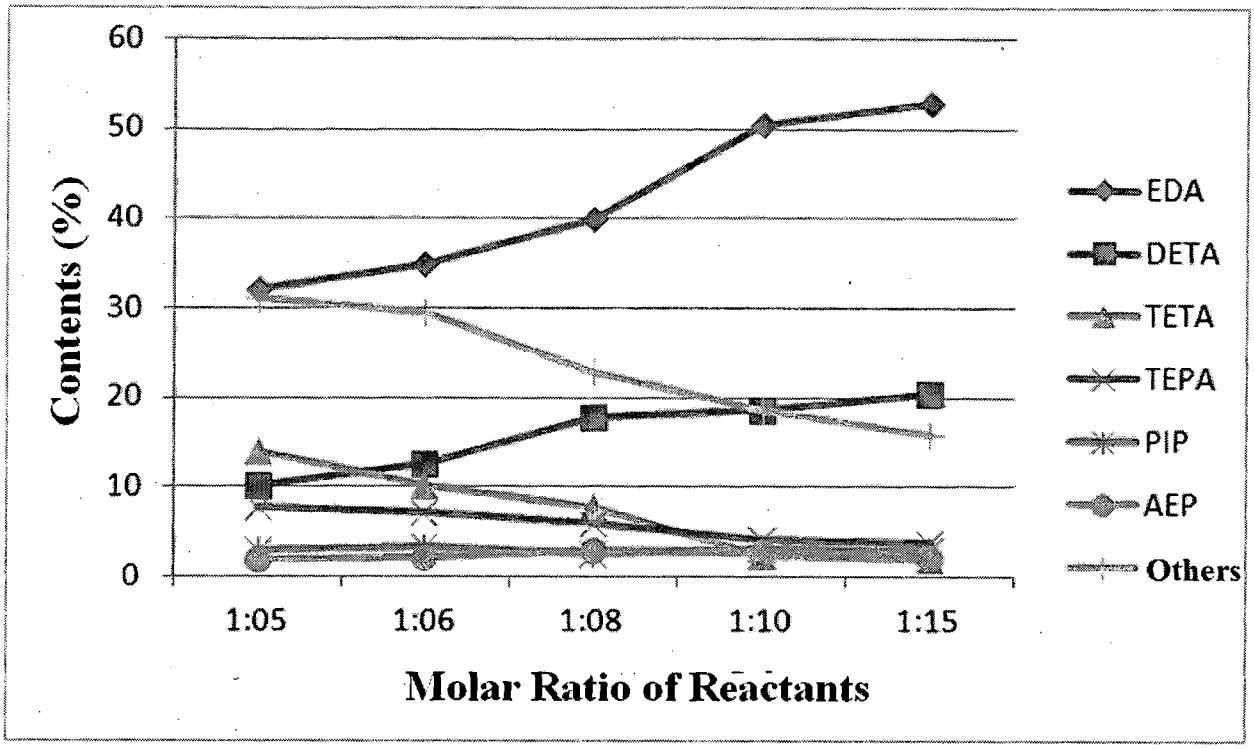
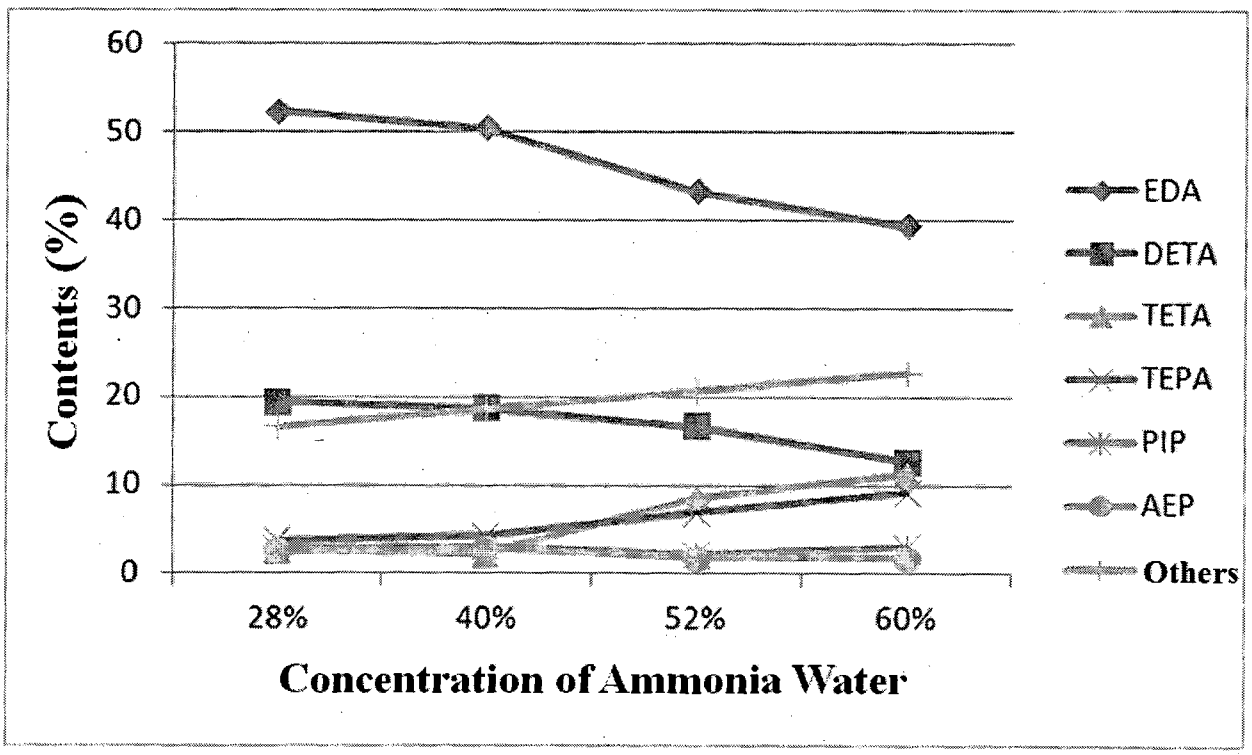

60
50
40
30
20
10
0
Contents (%)
1:05
1:06
1:08
1:10
1:15
Molar Ratio of Reactants
EDA
DETA
TETA
TEPA
PIP
AEP
Others

FIG. 2


60
50
40
30
20
10
0
Contents (%)
28%
40%
52%
60%
Concentration of Ammonia Water
EDA
DETA
TETA
TEPA
PIP
AEP
Others

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2013/004366

A. CLASSIFICATION OF SUBJECT MATTER

C07C 209/24(2006.01)i, C07C 209/86(2006.01)i, C07C 211/21(2006.01)i, C07B 61/00(2006.01)i

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 209/24; C07D 239/04; C07D 241/04; C07C 209/00; C07C 209/08; C07C 209/86; C07C 211/21; C07B 61/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal), Google & Keywords:ethylenedichloride, ammonia, ethyleneamine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010-0087681 A1 (PETRAITIS DAVID M. et al.) 08 April 2010 See the abstract; paragraphs [0026]-0033]; and claims 1-7.	1-5
X	HUNTSMAN Advanced Technology Center, `ETHYLENAMINES, A global profile of products and services` (2007) See page 1, lines 4-9; page 2, lines 1-3; and Table 2.1.	1-5
X	US 3183269 A (DINO COSTABELLO, NOVARA et al.) 11 May 1965 See column 1, lines 14-51; and claim 1.	1-5
X	KR 10-1999-0009059 A (SAMSUNG FINE CHEMICALS CO., LTD.) 05 February 1999 See the abstract; example 1; and claim 1.	1-5
A	US 2008-0249307 A1 (VAN CAUWENBERGE GUNTHER et al.) 09 October 2008 See the abstrat; and Scheme 1.	1-5

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"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	Date of mailing of the international search report
23 September 2013 (23.09.2013)	**23 September 2013 (23.09.2013)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2013/004366

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		US 7626058 B2	01/12/2009
		WO 2007-042466 A1	19/04/2007