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(54) Title: MINIMIZING WATER CONTENT IN ETHANOLAMINE
PRODUCT STREAMS

(57) Abstract: Systems and methods are provided for reducing
the water content from approximately 0.15% -0.19% by
weight to approximately 0.01-0.03% by weight in an ethano-
lane product stream in a non-reactive distillation column.
The reduced water content can be achieved by increasing the
processing conditions at the drying column by approximately
5% to approximately 20%, more preferably to approximately
10%. The increased processing conditions at the drying
column can result in an increased bottom stream flow rate and
an increased reboiler duty. The reboiler duty of the drying
column can be increased by up to 2 % to achieve said level of
water content. The bottom stream flow rate can be increased
by up to approximately 12% to achieve said level of water content.

[Continued on next page]
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MINIMIZING WATER CONTENT IN ETHANOLAMINE PRODUCT STREAMS

TECHNICAL FIELD

[0001] The present invention relates to a process for the production of ethanolamines, specifically, to a process for minimizing the water content in ethanolamine product streams, such as a monoethanolamine ("MEA") product stream.

BACKGROUND

[0002] Ethanolamines, individually and in combination have many uses in the chemical industries. For example, ethanolamines can be used as corrosion inhibitors, lubricants and scouring agents for gas sweetening, detergents and specialty cleaners, concrete admixtures, flexible urethane foam catalysts, personal care products, photographic emulsions, solvents, dyes intermediates, rubber accelerator, emulsifiers, ink additives, oil additives, alkalization of water in steam cycles of power plants and nuclear plants with pressurized water reactors, pesticides and pharmaceutical intermediates, natural gas is also used as acid gas absorption solvent. Ethanolamines can also be used in the semiconductor field for wafer cleaning and photoresist striping applications because of their surfactant properties. Global demand for ethanolamines is increasing, and is projected to exceed 1.605 million tons by 2015.

[0003] Ethanolamines are flammable, corrosive, colorless, viscous liquids that are produced by the reaction of ammonia (NH₃) and halohydrins or ethylene oxide (C₂H₄O) (EO). EO, however, is more widely used for commercial processes. To produce ethanolamines commercially, aqueous ammonia and ethylene oxide are contacted in a single stage or multi stage reaction chamber at a temperature of 50°C to 257°C. There are three types of ethanolamines: MEA (H₂NCH₂CH₂OH); Diethanolamine (HN(CH₂CH₂OH)₂), also referred to as DEA; and Triethanolamine (N(CH₂CH₂OH)₃), also referred to as TEA. The formation of MEA, DEA or TEA depends on whether an ammonia molecule reacts with 1, 2 or 3 EO molecules. The reactions have a parallel consecutive mechanism, so that the three products (MEA, DEA and TEA) are obtained simultaneously. Water is used as a catalyst in ethanolamine reactions.

[0004] Due to the demand for ethanolamines in the petrochemical industry, needs exist for producing higher-yield ethanolamine product streams via a cost-effective process.

SUMMARY
[0005] Embodiments of the present invention can include a system and method for producing an ethanolamine product stream in a non-reactive distillation column. The method can include: mixing an ammonia solution containing approximately 30% to approximately 40% by weight ammonia with ethylene oxide in a reactor to create a resultant product stream, wherein said resultant product stream includes ethanolamines, unreacted ammonia and water; removing approximately 30% to approximately 50% by weight of the unreacted ammonia and approximately 50% to approximately 70% by weight of water from the resultant product stream to create a stripped product stream, wherein the stripped product stream includes ethanolamines and approximately 30% to approximately 50% by weight of water; operating a vacuum drying column at adjusted processing conditions, wherein said processing conditions are selected from: the stripped product stream flow rate, reflux rate at the vacuum drying column, condenser heat duty at the vacuum drying column, reboiler heat duty at the vacuum drying column, bottom rate at the vacuum drying column and a combination comprising at least one of the foregoing, and where said adjusted processing conditions are approximately 5% to approximately 20% above a base case value of the selected processing conditions; transferring the stripped product stream to a stage of the vacuum drying column to create a dehydrated product stream; and removing a portion of residual water from the stripped product stream at the vacuum drying column to create a dehydrated product stream, wherein said dehydrated product stream includes ethanolamines and approximately 0.01% to approximately 0.03% by weight of water.

[0006] Additional features, advantages, and embodiments of the invention are set forth or apparent from consideration of the following detailed description, drawings and claims. Moreover, it is to be understood that both the foregoing summary of the invention and the following detailed description are exemplary and intended to provide further explanation without limiting the scope of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The accompanying drawings, which are included to provide a further understanding of the invention and are incorporated in and constitute a part of this specification, illustrate preferred embodiments of the invention and together with the detailed description serve to explain the principles of the invention. In the drawings like elements are numbered alike and are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.
[0008] FIG. 1 is a schematic representation of an ethanolamine production process according to one embodiment.

[0009] FIG. 2 illustrates an ASPEN™ simulation of a drying column for the production of ethanolamine according to one embodiment.

DETAILED DESCRIPTION

[0010] Embodiments of the present invention can provide an improved process for minimizing the water content in ethanolamine product streams from vacuum distillation columns in a non-reactive distillation apparatus. This invention can be practiced over a wide range of processing conditions including but not limited to the concentrations of reactants, flow rates of reactants, temperatures, and pressures. The process 100 can be conducted in the presence or absence of a catalyst, wherein the catalyst is preferably water. The process 100 can be conducted in aqueous or non-aqueous phase. A desired output product in the process 100 can be manipulated to contain various ratios of MEA, DEA, and TEA by selecting appropriate processing conditions. The process as described herein are exemplary processes only and used for illustrative purposes. Other variations and combinations of steps and components can be used as necessary.

[0011] Now referring to FIG. 1, there is shown a schematic representation of an ethanolamine production process according to one embodiment. The process 100 can include a reactor 105, in which EO can be reacted with excess ammonia and water in an aqueous solution to form an ethanolamine reaction product containing MEA, DEA and TEA; an ammonia stripper 107 for stripping the unreacted ammonia from the reaction product and for removing the excess ammonia and some water by distillation; a vacuum drying column 112 for evaporating water from the stripped reaction product to create a dehydrated reaction product; and an amine distillation component for separating the dehydrated reaction product into MEA, DEA and TEA. In some alternatives, the process 100 can also include an ammonia absorber 110 and ammonia solution storage 103 for recycling the excess ammonia stripped from the reaction product, which can be fed to the reactor 105 through line 104. Ammonia solution storage 103 can also be fed to ammonia absorber 110 through line 111. In some alternatives, the process 100 can also include EO storage 101. In some alternatives, the ammonia stripper 107, the drying column 112, and the distillation or splitter columns can be carried out with one or more plate-type columns. In some alternatives, the one or more plate-type columns can include a reaction zone (top section) and a stripping zone (bottom section). In some alternatives, the columns can include multiple plates or stages, for example, from 5 -
20 stages. The reactor 105 used in the process 100 can be an isothermal reactor, an adiabatic reactor or other known reactor. A tubular reactor externally cooled by circulating water can be used. In some alternatives, the length of the reactor 105 can be approximately 2 meters to approximately 35 meters. In some alternatives, the diameter of the reactor 105 can be approximately 0.2 meters to approximately 0.5 meters.

[0012] The invention will be illustrated in more detail with reference to the following examples, but it should be understood that the present invention is not deemed to be limited thereto. Unless otherwise stated, all examples were based upon simulations.

EXAMPLES

Example 1 - Base Case at Drying Column 112

[0013] Now referring to FIG. 2, there is shown an ASPEN™ simulation of a drying column for the production of ethanolamine according to one embodiment. A simulation model can be developed to evaluate the process 100 and component of the process 100. The model can be validated against actual plant behavior. Data from actual plant behavior can be input into the model and can be used to tweak the model. The model can be developed using Aspen™ simulation software (Aspen Plus™ and Aspen Custom Modeler™) or other simulation software, such as Simulation Sciences (SimSci) Pro/II™. The model can use processing conditions data, e.g., from a plant in Saudi Arabia, capable of producing approximately 90,000 - 110,000 tons of ethanolamine per year. The plant can also be capable of producing approximately 700,000 tons of Mono-ethylene glycol (MEG) per year. In some alternatives, the model can be developed with Oxiteno process flow diagram (PFD) data for the ethanolamine production process. These simulations can be labeled as the base case. In some alternatives, the process 100 can utilize six stages of tubular reactors 105 connected in series with intercoolers between the reactors 105. In some alternatives, the intercoolers can consist of a bundle of U-tubes, maintained at temperatures from approximately 37°C to approximately 70°C. More preferably, the temperatures of the U-tubes can be maintained at temperatures from approximately 41°C-43°C to approximately 60°C - 63°C. The temperature at the tubular reactors 105 can be cooled down from approximately 60°C - 63°C at the outlet of each stage of the tubular reactors 105 to approximately 41°C - 43°C, where it can be fed to the inlet of each stage of the tubular reactors 105 by means of an intercooler using a circulating or evaporating coolant as the cooling media. In some alternatives, the coolant can be water.
An aqueous ammonia feed from ammonia storage 103 can be introduced to the first stage of the reactor via line 104. An alkylene oxide, such as EO from EO storage 101 can also be introduced to the first stage of the reactor 105 via line 102. In some alternatives, the ammonia feed from ammonia storage 103 and the EO feed from EO storage 101 can be combined before being introduced to the first stage of the reactor 105. In some alternatives, the aqueous ammonia solution can include approximately 30-40% by weight of ammonia and 50-70% by weight of water.

More preferably, the ammonia solution can include approximately 33-35% by weight of ammonia and approximately 62% by weight of water. In some alternatives, the % by weight of ammonia can be maintained below 50% to increase the production of MEG. In some alternatives, the ethanolamines produced by the process 100 can be recycled back into reactor 105 in order to adjust the desired MEA: DEA: TEA ratio. In some alternatives, approximately 1-5% by weight of MEA can be added to the aqueous ammonia solution. In some alternatives, approximately 1-5% by weight of DEA can be added to the aqueous ammonia solution. More preferably, approximately 2.7% by weight MEA and approximately 2.2% by weight DEA can also be added to the aqueous ammonia solution. In some alternatives, the ammonia in the aqueous ammonia solution can be freshly added ammonia, recycled ammonia, or combinations thereof. In some alternatives, the fresh ammonia can be fed directly into a reactor 105 or at some other point in the process 100 (e.g., to the ammonia stripper 107). In some alternatives, ammonia suitable for the reaction can be anhydrous or a solution of ammonia and water.

In some alternatives, the required EO for the reaction can be split evenly across the stages of the reactor 105. The flow of EO to each stage of the reactor 105 via line 102 can be maintained from approximately 1,500 kilograms per hour (kg/hr) to approximately 1,800 kg/hr. More preferably, the flow of EO to each stage of the reactor 105 can be maintained at 1,714.2 kg/hr to produce the desired EO conversion at the outlet of each stage of the reactor 105. In some alternatives, the EO flow rate to each stage of the reactor 105 can be one sixth of the total EO flow rate for line 102, for example, one-sixth of a total EO flow rate of 10,285 kg/hr.

The flow rate of the EO can ensure that approximately eighty-six percent of the EO can be converted in the reactions occurring at the first four stages of the reactor 105.
Approximately ninety-nine percent of the EO can be converted in the reaction occurring at the fifth stage of the reactor 105 and greater than ninety-nine percent of the EO can be converted in the reaction occurring at the sixth stage of the reactor 105. In some alternatives, the EO flow rate to each stage of the reactor 105 can depend on the production rate of the ethanolamines. The pressure at each stage of the reactor 105 can be maintained from approximately 15 barg to approximately 30 barg. More preferably, the pressure at each stage of the reactor 105 can be maintained at approximately 19 barg to approximately 24 barg to avoid the evaporation of EO and ammonia. The reactions in the reactor 105 can form a reaction product effluent, which can contain ethanolamines, unreacted/excess ammonia, any other unreacted components (e.g., water and the like), and optionally one or more reaction by-products, such as MEG.

[0018] The resultant product stream can be introduced via line 106 above the fourth stage of the ammonia stripper 107, which can contain approximately sixteen stages. The feed rate for line 106 can be from approximately 58,170 kg/hr to approximately 58,190 kg/hr. More preferably, at a feed rate of 58,180 kg/hr. The ammonia stripper 107 can remove the excess or unreacted ammonia from the reaction product effluent. The ammonia stripper 107 can operate at a pressure of approximately 1 barg to approximately 5 barg, and more preferably, from approximately 3.5 barg to approximately 3.6 barg. A flow, which includes approximately 35-45% by weight ammonia and 40-60% by weight of water, negligible quantities of ethanolamines and MEG can be collected from the head of the ammonia stripper 107 via line 108 and conveyed to an ammonia absorber 110. More preferably, the flow can include approximately 40% by weight of unreacted ammonia, approximately 59% by weight of water, negligible quantities of ethanolamines and MEG. The overhead vapors of the ammonia stripper 107 can be cooled and condensed and then fed to an ammonia absorption column 110 via line 108. Fresh ammonia makeup can be fed into the ammonia absorption column 110 and both streams can form part of the aqueous ammonia feed to the reactor 105 via line 104. The temperature at the top of the ammonia stripper 107 can be approximately 130°C to approximately 140°C, and more preferably approximately 133.6°C to approximately 135.2°C. A second flow containing ethanolamines, byproducts and the remaining water can be extracted at the foot of the ammonia stripper 107 via line 109 and fed to drying column 112 where a dehydrated mixture of ethanolamines can be obtained by the evaporation of the remaining water. The temperature at the foot of the ammonia stripper 107 can be approximately 150°C to approximately 165°C, and more preferably from approximately 158.2°C to approximately 159.6°C. The second flow can contain approximately 35-50% by
weight, water, and more preferably, approximately 40-43% by weight of water. In some
alternatives, part of the flow collected from the head of the ammonia stripper 107 via line
108, which can include approximately 90-99% by weight of water and negligible quantities of
ethanolamine can be refluxed into the drying column 112 at a stage below the sixteenth stage
via line 201. More preferably, the flow includes approximately 98.31% by weight of water
and negligible quantities of ethanolamine.

[0019] The stripped resultant product effluent from line 109 can be introduced to the
drying column 112 above the second stage of the drying column at a feed rate from
approximately 20,000 kg/hr to approximately 30,000 kg/hr. More preferably, the feed rate
can be approximately 24.61 kg/hr. More preferably, the resultant product effluent from line
109 can be introduced at the ninth stage of the drying column 112. The drying column 112
can remove any water still present in the stripped resultant product effluent by evaporation of
the remaining water. The water can leave the drying column 112 as a vapor via line 113. In
some alternatives, the vapor can be added as a recycled water stream to the drying column
112 to ensure that no MEA, DEA or TEA leaves the drying column 112 together with the
vapor. In some alternatives, water recovered from the drying column 112 via line 113 can be
recycled for use in the ammonia absorber 110. In some alternatives, a portion of the water
recovered from the drying column 112 via line 113 can also be recycled for use throughout
the process 100 via line 114. The drying column 112 can be operated at a pressure from
approximately 260 millibar (mbar) to approximately 280 mbar, and more preferably from
approximately 270 mbar to approximately 273 mbar. Pressure measured in millibar as
described herein refers to absolute pressure. The drying column 112 can include a heat
exchanger 202 and a condenser 206, where line 204 feeds material from the drying column
112 to the condenser 206 through line 205. The condenser 206 can have a reflux ratio from
approximately 0 to approximately 1, and more preferably a reflux ratio of 0.2. The condenser
206 can keep the top stages of the drying column 112 at a temperature of approximately 55°C
to approximately 75°C, and more preferably from approximately 66.7°C to approximately
67°C. The condenser 206 can feed material back to the drying column 207 and byproduct can
leave the condenser 206 through line 207. In some alternatives, the heat exchanger 202 can
be a thermosiphon or a forced circuit reboiler. Traditionally, a reboiler 202, with a duty of
approximately 7,000 kilowatts (kW) to approximately 8,500 kW, and more preferably
approximately 7,483 kW to approximately 7,548 kW can keep the bottom stages of the
drying column 112 at a temperature of approximately 140°C to approximately 160°C. More
preferably, the temperature at the bottom stages of the drying column 112 can be
approximately 147.5°C to approximately 150.2°C. The dehydrated resultant product stream can contain approximately 0.01% by weight of water, ethanolamines and byproducts can be fed to the distillation component of the process 100 via line 115 for separation into MEA, DEA and TEA. The distillation component of the process 100 can be further divided into an MEA distillation column 116, DEA splitter column 119, DEA distillation column 122 and TEA distillation column 125. Table 3 below shows the production rates of ethanolamines, water and byproducts that can be recovered from MEA distillation column 116.

[0020] MEA product leaves MEA distillation column 116 through line 117, while the remaining feed in the MEA distillation column 116 is fed to the DEA splitter column 119 through line 118. DEA byproduct leaves the DEA splitter column 119 through line 120, while the remaining feed in the DEA splitter column 119 is fed to DEA distillation column 122 through line 121. DEA product leaves the DEA distillation column 122 through line 123, while the remaining feed in the DEA distillation column 122 is fed to the TEA distillation column 125 through line 124. TEA product leaves TEA distillation column 125 through line 126, while unreacted product and byproducts leave TEA distillation column 125 through line 127.

Example 2 - 110% of base case processing conditions at the drying column 112

[0021] The production of ethanolamines as described in Example 1 was further modeled to simulate increased processing conditions data at the drying column 112. The processing conditions data at the drying column 112 was increased by approximately 5% to approximately 20% over the base case data, and more preferably by approximately 10%. The processing conditions include, but are not limited to flow rates of the stripped product effluent, reflux rate, condenser heat duty, reboiler heat duty, and bottom flow rate of the drying column 112. This simulation was labeled as 110% of base case. Now referring to FIG.2, the stripped product from line 109 can be introduced to the ninth stage of the drying column 112 at a feed rate of approximately 20,000 kg/hr to approximately 30,000 kg/hr, and more preferably at approximately 29,109 kg/hr. In some alternatives, the concentrated resultant product effluent can contain 40-43% by weight of water. Part of the flow collected from the head of the ammonia stripper 107 via line 108, which can contain approximately 98.31% by weight (wt %) of water and negligible quantities of ethanolamines can be fed to the drying column 112 via line 201. In some alternatives, the feeds from lines 109 and 201 can be combined prior to being fed to the drying column 112, for example, at the ninth stage. The drying column 112 can be operated at a pressure of approximately 270 mbar to
approximately 273 mbar. The temperature at the top of drying column 112 can be approximately 66.7°C. The temperature at the bottom of the drying column 112 can be approximately 150.2°C. The flow rate of line 201 can be approximately 1,808.77 kg/hr. A second flow, which can contain ethanolamines, and byproducts can be collected at the bottom of drying column 112, for example, at the eighteenth stage 210, and fed to a heat exchanger 202 via line 203. The sixteenth stage 209 and seventeenth stage 208 are also illustrated in FIG. 2. Ethanolamines can be distilled and returned to the drying column 112 via line 204. The ethanolamine rich stream can exit the reboiler 202 via line 115 at a flow rate of approximately 16,640 kg/hr for further processing by the MEA distillation column 116, DEA splitter column 119, DEA distillation column 122 and TEA distillation column 125. In certain embodiments, by increasing the processing conditions for the base case by approximately 5% to approximately 20%, more preferably by approximately 10% at the drying column 112, the reboiler 202 duty can be adjusted from approximately 7,548 kW to approximately 9,099 kW. In certain embodiments, the bottom stream flow rate of the drying column 112 can be adjusted from approximately 14,798 kg/hr to approximately 16,640 kg/hr. The water content of the ethanolamine product stream exiting the drying column 112 via line 115 can contain approximately 0.03% by weight of water.

[0022] Table 1 shows the processing conditions for the feeds via lines 109 and 201 at the inlet of drying column 112. Temperature was measured in degrees Celsius (°C), pressure in bar gage (barg), feed in the drying column in kilograms per hour (kg/hr), and the amount of the components in percent by weight (wt %).

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Drying Column 112</th>
<th>PFD 100%</th>
<th>Simulation at base case</th>
<th>Simulation at 110% of base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td></td>
<td>158.24</td>
<td>49.9</td>
<td>158.24</td>
<td>49.9</td>
</tr>
<tr>
<td>Pressure barg</td>
<td>3.6</td>
<td>6.1</td>
<td>3.6</td>
<td>6.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Feed in to the Drying Column kg/hr</td>
<td>24611.26</td>
<td>1808.77</td>
<td>24611.26</td>
<td>1808.77</td>
<td>29109</td>
</tr>
<tr>
<td>H₂O wt %</td>
<td></td>
<td>40</td>
<td>98.31</td>
<td>40</td>
<td>98.31</td>
</tr>
<tr>
<td>MEA wt %</td>
<td></td>
<td>21.37</td>
<td>1.61</td>
<td>21.37</td>
<td>1.61</td>
</tr>
<tr>
<td>DEA wt %</td>
<td></td>
<td>21.48</td>
<td>0.03</td>
<td>21.48</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Table 2: Drying Column Outlet Parameters

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Drying column 112</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFD</td>
<td>Simulation at Base Case</td>
</tr>
<tr>
<td>Load</td>
<td>%</td>
<td>100</td>
</tr>
<tr>
<td>Top Temp</td>
<td>°C</td>
<td>67</td>
</tr>
<tr>
<td>Pressure</td>
<td>mbar</td>
<td>270</td>
</tr>
<tr>
<td>Reflux Rate</td>
<td>kg/hr</td>
<td>1600</td>
</tr>
<tr>
<td>Bottom Temp</td>
<td>°C</td>
<td>150.2</td>
</tr>
<tr>
<td>Pressure</td>
<td>mbar</td>
<td>273</td>
</tr>
<tr>
<td>Condenser Heat Duty, Qc</td>
<td>kW</td>
<td>8860</td>
</tr>
<tr>
<td>Qc Design</td>
<td>kW</td>
<td>10986</td>
</tr>
<tr>
<td>Reboiler Heat Duty, Qr</td>
<td>kW</td>
<td>7483</td>
</tr>
<tr>
<td>Qr Design</td>
<td>kW</td>
<td>8914</td>
</tr>
<tr>
<td>Bottom rate</td>
<td>kg/hr</td>
<td>14798</td>
</tr>
</tbody>
</table>

Table 3: Drying Column Production Rates and Quality

<table>
<thead>
<tr>
<th>Description</th>
<th>Units</th>
<th>Drying column 112</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFD</td>
<td>Simulation at Base Case</td>
</tr>
<tr>
<td>Load</td>
<td>%</td>
<td>100</td>
</tr>
<tr>
<td>Production of Drying Column</td>
<td>kg/hr</td>
<td>14798.00</td>
</tr>
<tr>
<td>112 feed to the MEA Column</td>
<td></td>
<td></td>
</tr>
<tr>
<td>116 through line 115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>wt %</td>
<td>0.01</td>
</tr>
<tr>
<td>MEA</td>
<td>wt %</td>
<td>35.73</td>
</tr>
<tr>
<td>DEA</td>
<td>wt %</td>
<td>35.72</td>
</tr>
<tr>
<td>TEA</td>
<td>wt %</td>
<td>27.73</td>
</tr>
<tr>
<td>MEG</td>
<td>wt %</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Based on the results above, the amount of water present in the ethanolamine product stream from the drying column 112 can be reduced from approximately 0.01% to approximately 0.03% by weight of water by adjusting the processing conditions at the drying column 112 by approximately 5% to approximately 20%, more preferably to approximately 10%. The increased processing conditions can result in an increase to the reboiler 202 duty and the bottom stream flow rate of the drying column 112. In some alternatives, the reboiler 202 duty can be increased from approximately 8,914 kW to approximately 9,099 kW, an increase of approximately 2%. In some alternatives, the bottom stream flow rate can be increased from approximately 14,798 kg/hr to approximately 16,640 kg/hr, an increase of approximately 12.4%. In some alternatives, the increased reboiler 202 duty and the bottom stream flow rate can play a significant role to minimize the amount of water in the ethanolamine product stream exiting the drying column 112.

MEA product stream from the actual plant can contain significantly more water than the simulations as a result of the imbalance in flow at the plant, i.e., the flow at the plant may not be stable. Table 3 shows that the bottom stream of the drying column 112 for the actual plant production data can be approximately 16,816 kg/hr at 110% of a production load, which may result in an increase in the water content of the MEA product stream to more than 0.2% by weight of water. The simulation results discussed above show the same concept, where the water content of the MEA product stream can be increased to more than 0.2% by weight of water when the bottom stream of drying column 112 can be approximately 16,816 kg/hr. To minimize water content in the MEA product stream up to 0.01 - 0.03% by weight of water, the bottom stream of the drying column 112 can be reduced from approximately 16,816 kg/hr to approximately 16,640 kg/hr and the reboiler duty of the drying column 112 can be increased by up to 2% to achieve said level of water content.

The method disclosed herein include(s) at least the following embodiments:

Embodiment 1: A method for producing an ethanolamine product stream in a non-reactive distillation column, comprising: mixing an ammonia solution comprising approximately 30% to approximately 40% by weight ammonia with ethylene oxide in a reactor to create a resultant product stream, wherein said resultant product stream comprises ethanolamines, unreacted ammonia and water; removing approximately 30% to approximately 50% by weight of the unreacted ammonia and approximately 50% to approximately 70% by weight of water from the resultant product stream to create a stripped product stream, wherein the stripped product stream comprises ethanolamines and
approximately 30% to approximately 50% by weight of water; operating a vacuum drying column at adjusted processing conditions, wherein said processing conditions are selected from: the stripped product stream flow rate, reflux rate at the vacuum drying column, condenser heat duty at the vacuum drying column, reboiler heat duty at the vacuum drying column, bottom rate at the vacuum drying column and a combination comprising at least one of the foregoing, and where said adjusted processing conditions are approximately 5% to approximately 20% above a base case value of the selected processing conditions; transferring the stripped product stream to a stage of the vacuum drying column to create a dehydrated product stream; and removing a portion of residual water from the stripped product stream at the vacuum drying column to create a dehydrated product stream, wherein said dehydrated product stream comprises ethanolamines and approximately 0.01% to approximately 0.03% by weight of water.

[0029] Embodiment 2: The method of Claim 1, wherein the dehydrated product stream is transferred to one or more columns for the recovery of monoethanolamine, diethanolamine and triethanolamine.

[0030] Embodiment 3: The method of Claim 1 or Claim 2, wherein the ammonia solution comprises approximately 50% to approximately 70% by weight of water, approximately 1% to approximately 5% by weight of monoethanolamine, and approximately 1% to approximately 5% by weight of diethanolamine.

[0031] Embodiment 4: The method of Claim 3, wherein the ammonia solution comprises approximately 33% by weight ammonia, approximately 62% by weight of water, approximately 2.7% of monoethanolamine, and approximately 2.2% of diethanolamine.

[0032] Embodiment 5: The method of any of Claims 1-4, wherein the ethanolamines are selected from monoethanolamine, diethanolamine, triethanolamine and combinations comprising at least one of the foregoing.

[0033] Embodiment 6: The method of any of Claims 1-5, wherein the unreacted ammonia is recycled and added to the ammonia solution.

[0034] Embodiment 7: The method of any of Claims 1-6, wherein the vacuum drying column is operated at a pressure from approximately 260 mbar to approximately 280 mbar and a temperature at top stages of the vacuum drying column from approximately 550°C to approximately 750°C, and a temperature at bottom stages of the vacuum drying column from approximately 1400°C to approximately 1600°C.
Embodiment 8: The method of any of Claims 1-7, wherein the reactor is operated at a temperature of approximately 37oC to approximately 70oC and a pressure of approximately 15 barg to approximately 30 barg.

Embodiment 9: The method of any of Claims 1-8, wherein the vacuum drying column comprises a heat exchanger selected from thermosiphon, a reboiler, and combinations comprising at least one of the foregoing.

Embodiment 10: The method of Claim 9, wherein the heat exchange is a reboiler.

Embodiment 11: The method of any of Claims 1-10, wherein the adjusted processing conditions are increased by approximately 10% above the base case value.

Embodiment 12: The method of any of Claims 1-11, wherein the adjusted processing conditions increase the reboiler duty from approximately 7,000 kiloWatts to approximately 10,000 kiloWatts.

Embodiment 13: The method of Claim 12, wherein the reboiler duty is increased from approximately 7,483 kiloWatts to approximately 9,099 kiloWatts.

Embodiment 14: The method of any of Claims 1-11, wherein the reboiler duty is at least 9,099 kiloWatts.

Embodiment 15: The method of any of Claims 1-14, wherein the adjusted processing conditions increase bottom flow rate from approximately 14,000 kg/hr to approximately 17,000 kg/hr.

Embodiment 16: The method of Claim 15, wherein the bottom flow rate increases from approximately 14,798 kg/hr to approximately 16,816 kg/hr.

Embodiment 17: The method of Claim 16, wherein the bottom flow rate is at least 16,816.41 kg/hr.

Embodiment 18: The method of any of Claims 1-16, wherein the base case value comprises the stripped product stream at a flow rate of approximately 14,798 kg/hr, a reflux rate of approximately 1,600 kg/hr, a condenser heat duty of approximately 8,860 kiloWatts, a reboiler heat duty of approximately 7,483 kiloWatts, and a bottom rate of approximately 14,798 kg/hr.

Embodiment 19: The method of any of Claims 1-18, wherein the reactor comprises a multi-stage reactor.

Embodiment 20: The method of Claim 19, wherein the multi-stage reactor comprises six stages.
[0048] Although the foregoing description is directed to the preferred embodiments of the invention, it is noted that other variation and modifications will be apparent to those skilled in the art, and may be made without departing from the spirit or scope of the invention. Moreover, features described in connection with one embodiment of the invention may be used in conjunction with other embodiments, even if not explicitly stated above.

[0049] In general, the invention may alternately comprise, consist of, or consist essentially of, any appropriate components herein disclosed. The invention may additionally, or alternatively, be formulated so as to be devoid, or substantially free, of any components, materials, ingredients, adjuvants or species used in the prior art compositions or that are otherwise not necessary to the achievement of the function and/or objectives of the present invention. The endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of "less than or equal to 25 wt %, or 5 wt % to 20 wt %," is inclusive of the endpoints and all intermediate values of the ranges of "5 wt % to 25 wt %," etc.). Disclosure of a narrower range or more specific group in addition to a broader range is not a disclaimer of the broader range or larger group. "Combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. Furthermore, the terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to denote one element from another. The terms "a" and "an" and "the" herein do not denote a limitation of quantity, and are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. "Or" means "and/or." The suffix ")" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the film(s) includes one or more films). Reference throughout the specification to "one embodiment", "another embodiment", "an embodiment", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments.

[0050] The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity). The notation "± 10%" means that the indicated measurement can be from an amount that is minus 10% to an amount that is plus 10% of the stated value. The terms "front", "back", "bottom", and/or "top" are used herein, unless otherwise noted, merely for convenience of description, and are not limited to
any one position or spatial orientation. "Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. A "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0051] All cited patents, patent applications, and other references are incorporated herein by reference in their entirety. However, if a term in the present application contradicts or conflicts with a term in the incorporated reference, the term from the present application takes precedence over the conflicting term from the incorporated reference.

[0052] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or may be presently unforeseen may arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they may be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.
CLAIMS

1. A method for producing an ethanolamine product stream in a non-reactive distillation column, comprising:
   - mixing an ammonia solution comprising approximately 30% to approximately 40% by weight ammonia with ethylene oxide in a reactor to create a resultant product stream, wherein said resultant product stream comprises ethanolamines, unreacted ammonia and water;
   - removing approximately 30% to approximately 50% by weight of the unreacted ammonia and approximately 50% to approximately 70% by weight of water from the resultant product stream to create a stripped product stream, wherein the stripped product stream comprises ethanolamines and approximately 30% to approximately 50% by weight of water;
   - operating a vacuum drying column at adjusted processing conditions, wherein said processing conditions are selected from: the stripped product stream flow rate, reflux rate at the vacuum drying column, condenser heat duty at the vacuum drying column, reboiler heat duty at the vacuum drying column, bottom rate at the vacuum drying column and a combination comprising at least one of the foregoing, and where said adjusted processing conditions are approximately 5% to approximately 20% above a base case value of the selected processing conditions;
   - transferring the stripped product stream to a stage of the vacuum drying column to create a dehydrated product stream; and
   - removing a portion of residual water from the stripped product stream at the vacuum drying column to create a dehydrated product stream, wherein said dehydrated product stream comprises ethanolamines and approximately 0.01% to approximately 0.03% by weight of water.

2. The method of Claim 1, wherein the dehydrated product stream is transferred to one or more columns for the recovery of monoethanolamine, diethanolamine and triethanolamine.

3. The method of Claim 1 or Claim 2, wherein the ammonia solution comprises approximately 50% to approximately 70% by weight of water, approximately 1% to
approximately 5% by weight of monoethanolamine, and approximately 1% to approximately 5% by weight of diethanolamine.

4. The method of Claim 3, wherein the ammonia solution comprises approximately 33% by weight ammonia, approximately 62% by weight of water, approximately 2.7% of monoethanolamine, and approximately 2.2% of diethanolamine.

5. The method of any of Claims 1-4, wherein the ethanolamines are selected from monoethanolamine, diethanolamine, triethanolamine and combinations comprising at least one of the foregoing.

6. The method of any of Claims 1-5, wherein the unreacted ammonia is recycled and added to the ammonia solution.

7. The method of any of Claims 1-6, wherein the vacuum drying column is operated at a pressure from approximately 260 mbar to approximately 280 mbar and a temperature at top stages of the vacuum drying column from approximately 55°C to approximately 75°C, and a temperature at bottom stages of the vacuum drying column from approximately 140°C to approximately 160°C.

8. The method of any of Claims 1-7, wherein the reactor is operated at a temperature of approximately 37°C to approximately 70°C and a pressure of approximately 15 barg to approximately 30 barg.

9. The method of any of Claims 1-8, wherein the vacuum drying column comprises a heat exchanger selected from thermosiphon, a reboiler, and combinations comprising at least one of the foregoing.

10. The method of Claim 9, wherein the heat exchange is a reboiler.

11. The method of any of Claims 1-10, wherein the adjusted processing conditions are increased by approximately 10% above the base case value.
12. The method of any of Claims 1-11, wherein the adjusted processing conditions increase the reboiler duty from approximately 7,000 kiloWatts to approximately 10,000 kiloWatts.

13. The method of Claim 12, wherein the reboiler duty is increased from approximately 7,483 kiloWatts to approximately 9,099 kiloWatts.

14. The method of any of Claims 1-11, wherein the reboiler duty is at least 9,099 kiloWatts.

15. The method of any of Claims 1-14, wherein the adjusted processing conditions increase bottom flow rate from approximately 14,000 kg/hr to approximately 17,000 kg/hr.

16. The method of Claim 15, wherein the bottom flow rate increases from approximately 14,798 kg/hr to approximately 16,816 kg/hr.

17. The method of Claim 16, wherein the bottom flow rate is at least 16,816.41 Kg/hr.

18. The method of any of Claims 1-16, wherein the base case value comprises the stripped product stream at a flow rate of approximately 14,798 kg/hr, a reflux rate of approximately 1,600 kg/hr, a condenser heat duty of approximately 8,860 kiloWatts, a reboiler heat duty of approximately 7,483 kiloWatts, and a bottom rate of approximately 14,798 kg/hr.

19. The method of any of Claims 1-18, wherein the reactor comprises a multi-stage reactor.

20. The method of Claim 19, wherein the multi-stage reactor comprises six stages.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>EP 2 177 501 A1 (SULZER CHEMTECH AG [CH]) 21 April 2010 (2010-04-21) abstract claims 1, 8</td>
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* 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

"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)

"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

"Z" document member of the same patent family

Date of the actual completion of the international search

24 June 2015

Date of mailing of the international search report

02/07/2015

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