Fig. 1

(57) Abstract: The present invention reacts ethylenediamine with one or more additional ethylenamines in the presence of a transamination catalyst to provide a different, preferably more desirable product mix of one or more ethylenamines.
A PROCESS TO SELECTIVELY MANUFACTURE DIETHYLENETRIAMINE (DETA) OR OTHER DESIRABLE ETHYLENAMINES VIA CONTINUOUS TRANSAMINATION OF ETHYLENEDIAMINE (EDA), AND OTHER ETHYLENEAMINES OVER A HETEROGENEOUS CATALYST SYSTEM

PRIORITY CLAIM

The present non-provisional patent Application claims priority under 35 U.S.C. § 119(e) from United States Provisional patent application having serial number 61/195,404 filed on October 6, 2008, by Cook et al. and entitled "A PROCESS TO SELECTIVELY MANUFACTURE DIETHYLENETRIAMINE (DETA) OR OTHER DESIRABLE ETHYLENAMINES VIA CONTINUOUS TRANSAMINATION OF ETHYLENEDIAMINE (EDA), AND OTHER ETHYLENEAMINES OVER A HETEROGENEOUS CATALYST SYSTEM," which application is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to manufacturing one or more ethyleneamines by subjecting one or more ethyleneamines to a transamination reaction.

BACKGROUND OF THE INVENTION

Methods of making ethyleneamines via transamination are known. See, e.g., U.S. Patent Numbers 7,053,247 (Lif et al.) and 7,393,978 (Frauenkron et al.), U.S. Publication Number 2007/0100144 (Frauenkron et al.), and GB 1508460.

U.S. Patent Number 7,053,247 (Lif et al.) relates to a process for the manufacture of diethylenetriamine and higher polyethylenepolyamines by a transamination of ethylenediamine.

U.S. Patent Number 7,393,978 (Frauenkron et al.) relates to a process for the preparation of ethyleneamines, in particular diethylenetriamine (DETA), by continuous reaction of ethylenediamine (EDA) in the presence of a heterogeneous catalyst, where the reaction is carried out in a reaction column.

U.S. Publication Number 2007/0100144 (Frauenkron et al.), relates to the preparation of ethyleneamines by reacting monoethanolamine (MEOA) with ammonia in the presence of a catalyst in a reactor and separating the resulting reaction product, where ethylenediamine (EDA) obtained in the separation is reacted in a separate reactor in the presence of a catalyst to give diethylenetriamine (DETA).
and the resulting reaction product is passed to the separation of the reaction product resulting from the first reactor.

There is still a need for improved processes that make ethylenediamines via transamination. For example, many transamination processes have a limited selectivity towards the product mix of ethylenediamines that is produced. If the selectivity does not at least closely match market demand, the process tends to be inefficient because more of an undesired product is typically made so as to produce a quantity of desired ethylenediamine. Improved selectivity of the ethylenediamine product mix could allow production to be tailored to market demand so as to improve operating costs and the like.

SUMMARY OF THE INVENTION

The present invention reacts ethylenediamine with one or more additional ethylenediamines in the presence of a transamination catalyst to provide one or more ethylenediamines. The selectivity of the transamination reaction can be controlled to produce a desired ethylenediamine product based on a given transamination feed stream and operating conditions. Advantageously, a relatively less desirable ethylenediamine product mix (e.g., coming from a relatively less controllable ethylenediamine production process such as reductive amination) can be converted into a more desirable ethylene product mix by subjecting the less desirable ethylenediamine product mix to a transamination process according to the present invention. So as market demands for particular ethylenediamine(s) changes, a process according to the present invention can use a less desirable mix of ethylenediamine(s) and produce a more desirable/valuable product mix of ethylenediamines that maximizes the amount of desirable ethylenediamine(s) produced and minimizes the amount of less desirable ethylenediamines. As another advantage, the process can be implemented as a stand alone/modular facility or integrated into an existing ethylenediamines unit.

According to one aspect of the present invention, a process for the manufacture of one or more ethylenediamines by a transamination reaction, includes the step of reacting ethylenediamine with one or more additional ethylenediamines in the presence of a transamination catalyst to provide the one or more ethylenediamines. The one or more additional ethylenediamines are selected from the group consisting
of: diethylenetriamine, triethylenetetramine, tetraethylenepentamine, aminoethylethanolamine, aminoethylpiperazine, piperazinoethylethylenediamine, heavy polyamine and combinations thereof.

According to another aspect of the present invention, a process for the manufacture of one or more ethyleneamines by a transamination reaction includes the step of reacting a first mixture in the presence of a transamination catalyst to provide a second mixture. The first mixture comprises ethylenediamine and one or more additional ethyleneamines. The one or more additional ethyleneamines are selected from the group consisting of: diethylenetriamine, triethylenetetramine, tetraethylenepentamine, aminoethylethanolamine, aminoethylpiperazine, piperazinoethylethylenediamine, heavy polyamine and combinations thereof. At least two ethyleneamines in the first mixture are present in an amount that is different than the amount of the corresponding two ethyleneamines in the second mixture.

According to another aspect of the present invention, a process for the manufacture of one or more ethyleneamines by a transamination reaction includes the step of reacting ethylenediamine with one or more additional ethyleneamines in the presence of a transamination catalyst in a fixed bed reactor to provide the one or more ethyleneamines.

According to another aspect of the present invention, a process for the manufacture of one or more ethyleneamines by a transamination reaction includes the step of reacting ethylenediamine in the presence of a transamination catalyst to provide the one or more ethyleneamines. The catalyst includes a) a support portion having an acidic mixed metal oxide including a transitional alumina and a second metal oxide, wherein the second metal oxide has a weight percentage that is less than the weight percentage of alumina; and b) a catalyst portion having one or more metals selected from the group consisting of cobalt, nickel, and copper, wherein there is no, or less than 0.01 wt. % rhenium in the catalyst, and the catalyst portion is 25 wt. % or less of the catalyst.

According to another aspect of the present invention, a process for the manufacture of one or more ethyleneamines by a transamination reaction, includes the step of reacting ethylenediamine in the presence of a transamination catalyst to
provide the one or more ethyleneamines. The catalyst includes a) a support portion comprising an acidic mixed metal oxide comprising a transitional alumina and a second metal oxide; and b) a catalyst portion comprising nickel and rhenium, wherein: the second metal oxide has a weight percentage that is less than the weight percentage of alumina, the catalyst portion is 25 weight percent or less of the catalyst composition, the catalyst portion comprises nickel in an amount in the range of 2 to 20 weight percent, based upon total catalyst composition weight, and there is no boron in the catalyst portion.

According to another aspect of the present invention, a modular reaction system for the manufacture of one or more ethyleneamines by a transamination reaction includes: a) a reactor comprising a transamination catalyst; and b) program instructions to cause ethylenediamine to react with one or more additional ethyleneamines in the presence of the transamination catalyst to provide the one or more ethyleneamines.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The advantages of the present invention, and the manner of attaining them, will become more apparent and the invention itself will be better understood by reference to the following description of the embodiments of the invention taken in conjunction with the accompanying drawing, wherein:

**FIG. 1** - is a block diagram schematically illustrating a process according to the present invention for the preparation of one or more ethyleneamines by a transamination reaction.

**DETAILED DESCRIPTION**

The embodiments of the present invention described below are not intended to be exhaustive or to limit the invention to the precise forms disclosed in the following detailed description. Rather the embodiments are chosen and described so that others skilled in the art may appreciate and understand the principles and practices of the present invention.

All publications and patents mentioned herein are incorporated herein by reference in their respective entirities for the purpose of describing and disclosing, for example, the constructs and methodologies that are described in the publications which might be used in connection with the presently described invention. The
publications discussed above and throughout the text are provided solely for their
disclosure prior to the filing date of the present application. Nothing herein is to be
construed as an admission that the inventor is not entitled to antedate such disclosure
by virtue of prior invention.

A process for the manufacture of one or more ethyleneamines according to
the present invention uses a feed of one or more ethyleneamines for a transamination
reaction.

Ethyleneamines that can be used in a process according to the present
invention are well known and can include one or more of ethylenediamine (EDA),
diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine
(TEPA), piperazine (PIP), aminoethylpiperazine (AEP), aminoethylethanolamine
(AEEA), piperazinoethylethylenediamine (PEEDA), heavy polyamine (HPA), and
combinations thereof. HPA is a mixture of linear, branched, and/or cyclic
ethyleneamines, the structures of which can be deduced from the chemistry of
 manufacture and knowledge of the structures present in TETA and TEPA. The
structures of the principle components of HPA can contain six or more nitrogen
atoms per molecule.

The amount of one or more ethyleneamines after the transamination reaction
is controllably different than the amount of the corresponding ethyleneamine(s)
before the transamination reaction. Advantageously, a relatively less desirable
ethyleneamine product mix (e.g., coming from a relatively less controllable
ethyleneamine production process such as reductive amination) can be transformed
into a more desirable ethyleneamine product mix by subjecting the less desirable
ethyleneamine product mix to a transamination process according to the present
invention. For example, a process according to the present invention can subject a
reactant mixture that has a relatively high amount of one or more ethyleneamines
other than diethylenetriamine (DETA), and produce a product mixture that is
relatively high in DETA. For example, a reactant mixture could have relatively high
amounts of ethylenediamine (EDA) or EDA and piperazine (PIP), while the product
mixture produced according to the invention could be relatively high in DETA. As
another example, a product mix that is relatively high in amounts of the oligomers
triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) can be produced
by subjecting a feed that is relatively high in amounts of EDA and/or DETA to a transamination reaction according to the present invention. In certain embodiments, desirable ethyleneamine product mixes can be produced according to the present invention with relatively little or no aminoethylethanolamine (AEEA) produced as a co-product and lower amounts of undesirable cyclic ethyleneamines relative to the desired ethyleneamines.

The source of the one or more ethyleneamines that are subjected to a transamination reaction according to present invention can be raw materials, materials delivered from an upstream process (e.g., an upstream process or processes that makes the ethyleneamine(s) such as reductive amination, ethylene dichloride and ammonia, and condensations), or a combination of these. For example, in certain embodiments, one or more ethyleneamines that are produced in a reductive amination reaction can be used as feed for a transamination process according to the present invention. See co-pending U.S. Provisional Patent Application titled "METHOD OF MANUFACTURING ETHYLENEAMINES" by David M. Petraitis et al., bearing Attorney Docket Number 67686 (DOW0021/P1), and filed on even date herewith, the entirety of which reference is incorporated herein by reference. See also, co-pending U.S. Provisional Patent Application titled "METHODS FOR MAKING ETHANOLAMINE(S) AND ETHYLENEAMINE(S) FROM ETHYLYENE OXIDE AND AMMONIA, AND RELATED METHODS" by David Do et al., bearing Attorney Docket Number 67691 (DOW0019/P1), and filed on even date herewith, the entirety of which reference is incorporated herein by reference.

Transamination is a transfer of an amino group from one chemical compound to another, or the transposition of an amino group within a chemical compound. Transamination is also disclosed in U.S. Provisional Patent Application titled "METHODS OF MAKING CYCLIC, N-AMINO FUNCTIONAL TRIAMINES" by Stephen W. King, bearing Attorney Docket Number 67685 (DOW0020/P1), and filed on even date herewith, the entirety of which reference is incorporated herein by reference.
Optionally, one or more additional components can be combined with the ethyleneamine reactants prior to and/or within the transamination reactor. For example ammonia (NH₃) can be included in the transamination feed stream to minimize the extent of unfavorable reaction(s). As another example, hydrogen can be included in the transamination feed stream in an amount sufficient to affect catalyst activity and product selectivity. Exemplary amounts of hydrogen include 0.001 to 10.0 mole % based on liquid feed.

The transamination reaction can be practiced in any suitable reactor. These include batch reactor, continuous fixed bed reactors, slurry bed reactors, fluidized bed reactors, catalytic distillation reactors, combinations of these, and the like. In certain embodiments, a fixed bed reactor is preferred. A fixed bed reactor includes catalyst pellets that are held in place and do not substantially move with respect to fixed reference frame. At least a portion of the reactor feed material passes over (flows past) the catalyst pellets and reacts to form product(s).

The reactor conditions can be set so as to form a desired product mix given the reactor feed and catalyst(s) used. Preferably, the reactor conditions are relatively moderate so as to reduce operating costs and the like. A preferred transamination reaction temperature can be a temperature in the range of from 130°C-180°C, preferably in the range of from 130°C-170°C, even more preferably in the range of from 130°C-160°C. A preferred transamination reaction pressure can be a pressure in the range of from 200-2000 psig. A preferred transamination reaction reactor space velocity can be in the range of from 5-50 gram moles of ethyleneamines per kilogram of catalyst per hour. In preferred embodiments, a transamination reaction according to the present invention can have feed conversions of 25% or more, e.g., in the range of from 25% to 65%.

Any catalyst that can catalyze a transamination reaction can be used in a process according to the present invention. Such catalysts are well known. A preferred catalyst includes a hydrogenation catalyst or dehydrogenation catalyst. A hydrogenation catalyst can be made of nickel (Ni), copper (Cu), cobalt (Co), ruthenium (Ru), rhenium (Re), rhodium (Rh), platinum (Pt), palladium (Pd), and combinations thereof. Any catalyst support that can support a catalyst for a transamination reaction can be used in a process according to the present invention.
Catalyst supports are well known and include, e.g., metal oxide. In preferred embodiments, a mixed metal oxide is used, and more preferably a transitional alumina containing silica is used.

One preferred catalyst includes nickel and rhenium as described in co-pending U.S. Provisional Patent Application titled "LOW METAL CATALYST COMPOSITIONS INCLUDING ACIDIC MIXED METAL OXIDE AS SUPPORT" by Stephen W. King et al., bearing Attorney Docket Number 67688 (DOWOO16/PI), and filed on even date herewith, the entirety of which reference is incorporated herein by reference. And yet another preferred combination includes nickel, cobalt, or copper, or combinations thereof as described in co-pending U.S. Provisional Patent Application titled "LOW METAL LOADED, ALUMINA SUPPORTED, CATALYST COMPOSITIONS AND AMINATION PROCESS" by Stephen W. King et al., bearing Attorney Docket Number 66049 (DOWOO15/PI), and filed on even date herewith, the entirety of which reference is incorporated herein by reference. Such catalysts show significantly improved selectivity to ethylenediamine. Advantageously, such catalyst can achieve much improved selectivity at relatively moderate temperature and pressure conditions. For example, such catalyst can achieve the desired product selectivity at a temperature in the range of from 110°C to 180°C, preferably from 130°C to 160°C, and a pressure of 2000 psig or less.

One or more ammonia recovery systems can be used in the process of making ethyleneamines according to the present invention. An ammonia recovery system separates ammonia, and optionally one or more additional components (e.g., hydrogen), from a fluid stream. An ammonia recovery system can be positioned anywhere in the overall process as desired. Preferably, one or more ammonia recovery systems are used in a manner that minimizes the number of ammonia recovery systems and/or other process units. The recovered ammonia can be used in any desired manner. For example, depending on the purity level of the recovered ammonia, the recovered ammonia may be recycled to another point in the process such as the inlet of a reactor. Advantageously, such recovered ammonia can be used as "make-up' ammonia for a reactor where ammonia is consumed in a reaction.
Ammonia recovery systems can be any type of ammonia recovery system known in the art. For example, an ammonia recovery system can utilize distillation columns, multiple single stage separators, compressors, chillers and/or absorbers in many different combinations and the like.

The one or more ethyleneamines made by a process according to the present invention can be separated and recovered by any method known in the art. For example, the ethyleneamines can be refined using conventional distillation technology known in the art. Preferably, dividing wall columns are used.

Other separation techniques can include (membranes, melt crystallization, reactive distillation).

A transamination process according to the present invention can be used in a stand alone (modular) system or it can be integrated with a larger system that makes one or more ethyleneamines which could be used as a feed for the transamination process according to the present invention. As used herein, a "modular" reaction system for the manufacture of one or more ethyleneamines by a transamination reaction means a stand alone system that can have EDA and other ethyleneamines introduced directly as raw feed or a stand alone system that has been integrated into a larger system (e.g., an existing system) and can have EDA and other ethyleneamines introduced from an upstream process. Larger systems into which a modular transamination reaction system according to the present invention could be integrated into include systems that can produce one or more ethyleneamines such as an ethylene dichloride (EDC) based system, a condensation based system, and/or a reductive animation based system. An example of the present invention integrated into a reductive amination system is further described in co-pending U.S. Provisional Patent Application titled "METHOD OF MANUFACTURING ETHYLENEAMINES" by David M. Petraitis et al., bearing Attorney Docket Number 67686 (DOW0021/P1), and filed on even date herewith, the entirety of which reference is incorporated herein by reference. See also, co-pending U.S. Provisional Patent Application titled "METHODS FOR MAKING ETHANOLAMINE(S) AND ETHYLENEAMINE(S) FROM ETHYLENE OXIDE AND AMMONIA, AND RELATED METHODS" by David Do et al.,
bearing Attorney Docket Number 67691 (DOWOO 19Pl), and filed on even date herewith, the entirety of which reference is incorporated herein by reference.

Advantageously, because of the relatively high selectivity of ethyleneamine product mix that can be achieved by a process according to the present invention, a modular transamination system according to the present invention can be incorporated (e.g., retrofitted) with other systems (e.g., reductive amination systems) such that the feed for the transamination system comes from one or more upstream processes that may not have such desirable selectivity in the ethyleneamines product mix. Preferably, a modular system has its own refining train. Also, such a modular system can include a processing unit such as a computer or the like to carry out program instructions (e.g., programming code) of a process according to the present invention.

The present invention will now be further illustrated by reference to the exemplary schematic flow diagram shown in FIG. 1.

FIG. 1 shows a block diagram schematically illustrating a process according to the present invention for the preparation of one or more ethyleneamines by a transamination reaction. A source of one or more ethyleneamines is fed to a transamination reactor via stream. The source of ethyleneamines can include ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), piperazine (PIP), aminoethylpiperazine (AEP), and heavy polyamine (HPA), or mixtures thereof. As shown, a source of hydrogen gas and a source of ammonia can optionally be combined with the ethyleneamines from source and fed to reactor via lines and , respectively. As shown, reactor produces an effluent having a product mix of ethyleneamines that include ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), piperazine (PIP), aminoethylpiperazine (AEP), and heavy polyamine (HPA). The amount of each ethyleneamine coming out of reactor is controllably different than the amount of each ethyleneamine going into reactor because of how the transamination reaction is performed. Advantageously, a relatively less desirable ethyleneamine product mix (e.g., coming from a relatively less controllable ethyleneamine production process such as reductive amination) can be transformed into a more
desirable ethyleneamines product mix by subjecting the less desirable ethyleneamines product mix to a transamination process according to the present invention. The effluent from reactor 50 is fed to ammonia recovery unit 60 via line 55. Ammonia recovery unit 60 separates ammonia from the ethyleneamines and sends the ammonia overhead via line 67. The ethyleneamines are sent to product refining system 70 via line 65 where the ethyleneamines can be separated into individual ethyleneamine species. Optionally, one or more ethyleneamines that are separated in product refining system 70 can be combined with the ethyleneamines from source 20 via stream 77 and fed to reactor 50.

EXAMPLES

Catalyst Preparation

The catalysts used in the Examples 1-5 below were prepared as described below. Precursor salts of the Nickel (Ni) and Rhenium (Re) were dissolved in 70-80°C water to form an impregnation solution. The final volume of the impregnation solution was adjusted to equal the adsorption volume required for the number of times that the carrier was impregnated, and the quantities of the precursor salts were those calculated to give the metal compositions provided in the examples. In each case the carrier was impregnated to incipient wetness by the addition of the appropriate amount of impregnation solution and gently agitated until all the liquid was adsorbed. The sample was then placed in a muffle furnace and calcined in air for one hour at 340°C. When the support had cooled, additional impregnations were performed until all of the solution had been added. A calcination step at 340°C was done after each impregnation. Prior to use, the catalyst compositions were reduced in hydrogen by ramping the temperature at 3°C/min to 230°C, holding at 230°C for one hour, and then ramping at 3°C/min to 340°C, and holding for 3 hours. The catalyst compositions were allowed to cool under hydrogen to ambient temperature, after which they were stabilized by adding a flowing stream of 1% oxygen in nitrogen gas until the exotherm ceased. At no time was the exotherm allowed to exceed about 70°C.
The following examples were prepared using a process flow similar to that illustrated in FIG. 1. Ethylenediamine is pumped up to reaction pressure of 600-1000 psi and heated to a temperature of 140-160°C. Hydrogen mole percent (based on feed) from 0.1 to 10.0 is then added. The EDA hydrogen mixture is the feed upflow to a reactor containing ca. 274 grams of a heterogeneous Ni-Re (6.8: 1.8 wt percent) catalyst on a 1/16” alumina silica (80:20) support. Reactor outlet product is sent to ammonia recovery to remove the feed H2 and the ammonia created in the process. The ammonia free material is then analyzed before being sent to a recovery system consisting of conventional distillation columns to recover EDA, PIP, DETA, TETA and Heavies. The data is presented as weight percents based on the total ethylenediamine content.

Example 1
Table 1 below shows the process is highly selective to DETA and TETA while keeping the level of cyclics (PIP, AEP, PEEDA) low. Also, the process can be operated at pressures from approximately 600 psia to 1000 psia at different EDA space velocities, hydrogen concentrations and temperatures while still maintaining good selectivity to acyclic products.
Table 1

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Product composition (w%)

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EDA conversion, %

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<th>8.52</th>
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<tr>
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<td>DETA/PIP</td>
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<td>23.1</td>
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<td>43.2</td>
<td>23.0</td>
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<td>1.2</td>
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<td>0.6</td>
<td>1.1</td>
<td>1.1</td>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>(DETA+TETA)/PIP</td>
<td>6.2</td>
<td>9.8</td>
<td>29.5</td>
<td>24.2</td>
<td>17.0</td>
<td>12.6</td>
<td>6.2</td>
<td>12.71</td>
<td>43.8</td>
<td>3.0</td>
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</tbody>
</table>

5 Example 2

Table 2 below shows the results of feeding EDA/DETA over the heterogeneous catalyst. A higher level of TETA is produced as compared to an EDA only feed while still maintaining low levels of cyclic materials.
Table 2

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T (ºC)</td>
<td>148.1</td>
<td>148.5</td>
<td>151.3</td>
<td>153.6</td>
<td>147.6</td>
<td>149.1</td>
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<tr>
<td>P (psi)</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
</tr>
<tr>
<td>Hz, mole % in Feed</td>
<td>4.2</td>
<td>4.4</td>
<td>4.3</td>
<td>4.3</td>
<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td>SV EDA, gmol/hr/kgs</td>
<td>13.5</td>
<td>13.4</td>
<td>13.6</td>
<td>13.5</td>
<td>12.4</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Feed (wt%)  | EDA | PIP | DETA | AEP | T-TETA | OTHER |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96.04</td>
<td>96.92</td>
<td>96.94</td>
<td>95.58</td>
<td>91.07</td>
<td>91.14</td>
</tr>
</tbody>
</table>

Product composition (wt%)  | EDA | PIP | DETA | AEP | T-TETA | OTHER |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(no NCO)</td>
<td>72.28</td>
<td>70.94</td>
<td>65.42</td>
<td>59.12</td>
<td>68.38</td>
<td>66.25</td>
</tr>
</tbody>
</table>

EDA conversion, %  | 32.60 | 34.39 | 40.36 | 47.19 | 38.91 | 41.43 | 46.87 | 53.96 |

Selectivity  |  |

Example 3

Table 3 below shows the results of feeding EDA/PIP over the heterogeneous catalyst. As compared to the table above, it can be seen that at similar EDA conversions, the DETA/PIP ratio is improved (Note: the PIP in the feed is subtracted from the PIP produced in the product).
Table 3

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
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<th>146.1</th>
<th>148.2</th>
<th>150.8</th>
<th>148.2</th>
<th>152.1</th>
<th>155.9</th>
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</thead>
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<tr>
<td>T (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (psia)</td>
<td></td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
</tr>
<tr>
<td>H₂, mole % in Feed</td>
<td></td>
<td>4.0</td>
<td>4.5</td>
<td>4.1</td>
<td>4.3</td>
<td>4.3</td>
<td>4.4</td>
</tr>
<tr>
<td>SV EDA, gmol/hr/kgcat</td>
<td></td>
<td>14.0</td>
<td>13.4</td>
<td>13.9</td>
<td>13.5</td>
<td>13.6</td>
<td>13.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feed (wt%)</th>
<th>EDA</th>
<th>PIP</th>
<th>DETA</th>
<th>AEP</th>
<th>I-TETA</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98.54</td>
<td>98.54</td>
<td>98.55</td>
<td>96.43</td>
<td>96.37</td>
<td>96.37</td>
</tr>
<tr>
<td>PIP</td>
<td>1.45</td>
<td>1.46</td>
<td>1.45</td>
<td>3.57</td>
<td>3.63</td>
<td>3.63</td>
</tr>
<tr>
<td>DETA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AEP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-TETA</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Product composition (wt%)</th>
<th>EDA</th>
<th>PIP</th>
<th>DETA</th>
<th>AEP</th>
<th>I-TETA</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td>(no NH₃)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>78.03</td>
<td>73.45</td>
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<td>71.64</td>
<td>63.76</td>
<td>53.93</td>
</tr>
<tr>
<td>PIP</td>
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<td>3.60</td>
<td>4.61</td>
<td>5.84</td>
<td>7.65</td>
<td>10.96</td>
</tr>
<tr>
<td>DETA</td>
<td>17.47</td>
<td>20.47</td>
<td>23.08</td>
<td>20.06</td>
<td>24.15</td>
<td>27.35</td>
</tr>
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<td>AEP</td>
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<td>0.07</td>
<td>0.12</td>
<td>0.07</td>
<td>0.18</td>
<td>0.50</td>
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<tr>
<td>I-TETA</td>
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<td>2.14</td>
<td>3.65</td>
<td>5.76</td>
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<td>0.01</td>
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<td>0.02</td>
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<tr>
<td>I-TETA</td>
<td>0.11</td>
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<td>0.31</td>
<td>0.19</td>
<td>0.42</td>
<td>0.93</td>
</tr>
<tr>
<td>OTHER</td>
<td>0.01</td>
<td>0.03</td>
<td>0.07</td>
<td>0.03</td>
<td>0.11</td>
<td>0.34</td>
</tr>
</tbody>
</table>

| EDA conversion, % | 23.74 | 28.90 | 34.18 | 29.11 | 37.97 | 48.82 |
| Selectivity       |       |       |       |       |       |       |

Note DETA:PIP; TETA:PIP; and (DETA + TETA)/PIP calculated by subtracting PIP fed from PIP in the product mix.

Example 4

Table 4 below shows the results of feeding EDA/TETA over the heterogeneous catalyst. Note that the DETA:PIP and TETA:PIP (Note that TETA is calculated by subtracting the TETA fed from TETA in the product mix) are improved over EDA only feed at similar EDA conversions. Additionally, more AEP is formed at similar EDA conversions.
Table 4

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>146.3</th>
<th>148.8</th>
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<th>151.3</th>
<th>155.1</th>
<th>152.9</th>
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<th>143.4</th>
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</thead>
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<tr>
<td>T (°C)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P (psi)</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
<td>815</td>
</tr>
<tr>
<td>H2, mole % in Feed</td>
<td>5.7</td>
<td>4.6</td>
<td>4.5</td>
<td>4.3</td>
<td>4.7</td>
<td>4.0</td>
<td>3.9</td>
<td>4.0</td>
</tr>
<tr>
<td>SV EDA, gmoi/hr/gcat</td>
<td>13.5</td>
<td>13.5</td>
<td>13.5</td>
<td>13.6</td>
<td>14.1</td>
<td>14.0</td>
<td>13.7</td>
<td>13.5</td>
</tr>
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</table>

Feed (wt%)

<table>
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<tr>
<th></th>
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<th>EDA</th>
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<th>EDA</th>
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</table>

Product composition (wt%)

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<tr>
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<th>EDA</th>
<th>EDA</th>
<th>EDA</th>
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<td>78.83</td>
</tr>
<tr>
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<td></td>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<td>19.80</td>
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<td>22.75</td>
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<tr>
<td></td>
<td>AEP</td>
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<td>AEP</td>
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<td>6.29</td>
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<td>7.01</td>
<td>4.32</td>
<td>4.57</td>
</tr>
<tr>
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<td>0.10</td>
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<tr>
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<td>T-TETA</td>
<td>T-TETA</td>
<td>T-TETA</td>
<td>T-TETA</td>
<td>T-TETA</td>
<td>T-TETA</td>
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<tr>
<td></td>
<td>0.83</td>
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<td>1.21</td>
<td>1.21</td>
<td>1.72</td>
<td>1.41</td>
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</tr>
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<td>OTHER</td>
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</tr>
<tr>
<td></td>
<td>0.22</td>
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<td>0.37</td>
<td>0.37</td>
<td>0.72</td>
<td>0.52</td>
<td>0.07</td>
<td>0.09</td>
</tr>
</tbody>
</table>

EDA conversion, %

<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30.09</td>
<td>33.31</td>
<td>39.53</td>
<td>39.65</td>
<td>50.48</td>
<td>45.34</td>
<td>20.46</td>
<td>24.23</td>
</tr>
</tbody>
</table>

Selectivity

<p>| | | | | | | | | |</p>
<table>
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<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DETA/PIP</td>
<td>10.1</td>
<td>10.1</td>
<td>7.3</td>
<td>7.3</td>
<td>4.4</td>
<td>5.2</td>
<td>21.0</td>
<td>16.8</td>
</tr>
<tr>
<td>T-TETA/PIP</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>(DETA + T-TETA)/PIP</td>
<td>10.8</td>
<td>10.8</td>
<td>8.0</td>
<td>8.0</td>
<td>5.0</td>
<td>5.6</td>
<td>20.5</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Example 5

Table 5 below shows the results of feeding EDA/AEP over the heterogeneous catalyst. As can be seen from the results, additional PEEDA is formed compared to EDA only feed at similar EDA conversions.
Table 5

Reaction Conditions

<table>
<thead>
<tr>
<th></th>
<th>T (°C)</th>
<th>P (psia)</th>
<th>H₂, mole % in Feed</th>
<th>SV EDA, gmol/hrkcat</th>
<th>Feed (wt%)</th>
<th>Product composition (wt%)</th>
<th>EDA conversion, %</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>EDA</td>
<td>PIP</td>
<td>SV EDA, gmol/hrkcat</td>
</tr>
<tr>
<td></td>
<td>143.0</td>
<td>815</td>
<td>4.1</td>
<td>13.3</td>
<td>EDA 9625</td>
<td>367</td>
<td>0.09</td>
<td>21.68</td>
</tr>
<tr>
<td></td>
<td>146.7</td>
<td>815</td>
<td>3.9</td>
<td>13.6</td>
<td>96.24</td>
<td>3.69</td>
<td>0.08</td>
<td>27.51</td>
</tr>
<tr>
<td></td>
<td>150.3</td>
<td>815</td>
<td>4.5</td>
<td>13.0</td>
<td>96.24</td>
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</tr>
<tr>
<td></td>
<td>154.2</td>
<td>815</td>
<td>4.2</td>
<td>136.0</td>
<td>96.25</td>
<td>3.67</td>
<td>0.09</td>
<td>47.42</td>
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<tr>
<td></td>
<td>156.5</td>
<td>815</td>
<td>4.2</td>
<td>14.5</td>
<td>96.24</td>
<td>369</td>
<td>0.08</td>
<td>51.73</td>
</tr>
</tbody>
</table>

Other embodiments of this invention will be apparent to those skilled in the art upon consideration of this specification or from practice of the invention disclosed herein. Various omissions, modifications, and changes to the principles and embodiments described herein may be made by one skilled in the art without departing from the true scope and spirit of the invention.
WHAT I S CLAIMED IS:

1. A process for the manufacture of one or more ethyleneamines by a transamination reaction, comprising the step of reacting ethylenediamine with one or more additional ethyleneamines in the presence of a transamination catalyst to provide the one or more ethyleneamines, wherein the one or more additional ethyleneamines are selected from the group consisting of: diethylenetriamine, triethylenetetramine, tetraethylenepentamine, aminoethylethanolamine, aminoethylpiperazine, piperazinoethylethylenediamine, heavy polyamine and combinations thereof.

2. The process according to claim 1, wherein the catalyst comprises:
   a) a support portion comprising an acidic mixed metal oxide comprising a transitional alumina and a second metal oxide; and
   b) a catalyst portion comprising nickel and rhenium, wherein:
      the second metal oxide has a weight percentage that is less than the weight percentage of alumina,
      the catalyst portion is 25 weight percent or less of the catalyst,
      the catalyst portion comprises nickel in an amount in the range of 2 to 20 weight percent, based upon total catalyst weight, and
      there is no boron in the catalyst portion.

3. The process of claim 1, wherein the step of reacting comprises reacting a first mixture in the presence of a transamination catalyst to provide a second mixture, wherein the first mixture comprises the ethylenediamine and one or more additional ethyleneamines, and wherein at least two ethyleneamines in the first mixture are present in an amount that is different than the amount of the corresponding two ethyleneamines in the second mixture.

4. The process of claim 3, wherein all of the ethyleneamines in the first mixture are present in an amount that is different than the amount of the corresponding ethyleneamines in the second mixture.

5. The process of claim 1, wherein the catalyst comprises:
a) a support portion comprising an acidic mixed metal oxide comprising a transitional alumina and a second metal oxide, wherein the second metal oxide has a weight percentage that is less than the weight percentage of alumina; and

b) a catalyst portion comprising one or more metals selected from the group consisting of cobalt, nickel, and copper,

wherein there is no, or less than 0.01 wt. % rhenium in the catalyst, and the catalyst portion is 25 wt. % or less of the catalyst.

6. The process according to claim 5, wherein the catalyst portion is in the range of 3 wt. % to 18 wt. % of the catalyst.

7. The process according to claim 5, wherein the catalyst portion comprises two or three metals selected from the group consisting of cobalt, nickel, and copper.

8. The process according to claim 7, wherein the catalyst portion comprises cobalt and nickel in a weight ratio in the range of 1:9 to 9:1.

9. The process according to claim 5, wherein the catalyst portion comprises no rhenium, or less than 0.005 wt. % rhenium.

10. A process for the manufacture of one or more ethyleneamines by a transamination reaction, comprising the step of reacting ethylenediamine with one or more additional ethyleneamines in the presence of a transamination catalyst in a fixed bed reactor to provide the one or more ethyleneamines.

11. The process according to claim 10, wherein the one or more additional ethyleneamines are selected from the group consisting of: diethylenetriamine, triethylenetetramine, tetraethylenepentamine, piperazine, aminoethylpiperazine, aminoethylethanolamine, piperazinoethylhexamethylenediamine, heavy polyamine, and combinations thereof.

12. A process for the manufacture of one or more ethyleneamines by a transamination reaction, comprising the step of reacting ethylenediamine in the presence of a transamination catalyst to provide the one or more ethyleneamines, wherein the catalyst comprises:

a) a support portion comprising an acidic mixed metal oxide comprising a transitional alumina and a second metal oxide; and

b) a catalyst portion comprising nickel and rhenium, wherein:
the second metal oxide has a weight percentage that is less than the weight percentage of alumina,
the catalyst portion is 25 weight percent or less of the catalyst composition,
the catalyst portion comprises nickel in an amount in the range of 2 to 20 weight percent, based upon total catalyst composition weight, and
there is no boron in the catalyst portion.
13. The process according to claim 12, wherein the transitional alumina comprises delta alumina.
14. The process according to claim 13, wherein the transitional alumina further comprises one or more of gamma, theta or alpha alumina.
15. The process according to claims 12, wherein the ethylenediamine is reacted with one or more additional ethyleneamines in the presence of a transamination catalyst to provide one or more ethyleneamines.
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 practical, search terms used)
EPO-Internal, WPI Data

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<td>EP 0 197 611 A2 (UNION CARBIDE CORP [US]) 15 October 1986 (1986-10-15) column 4, line 14 - line 17 column 16, lines 5-7,33-37,40,48-54 column 17, line 16 - line 30 column 35, line 50 - column 36, line 19 column 36, line 33 - line 55 column 37, line 15 - line 49 claims 5,87</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document 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

Date of the actual completion of the international search
4 February 2010

Date of mailing of the international search report
10/02/2010

Name and mailing address of the ISA/European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Fax (+31-70) 340-3016

Authorized officer
Fitz, Wolfgang
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