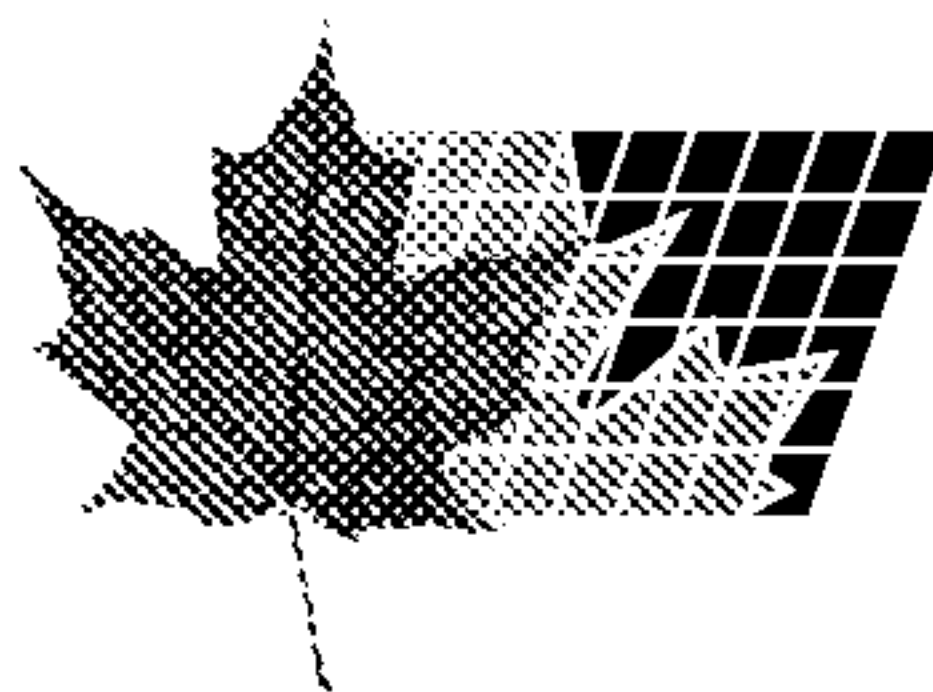




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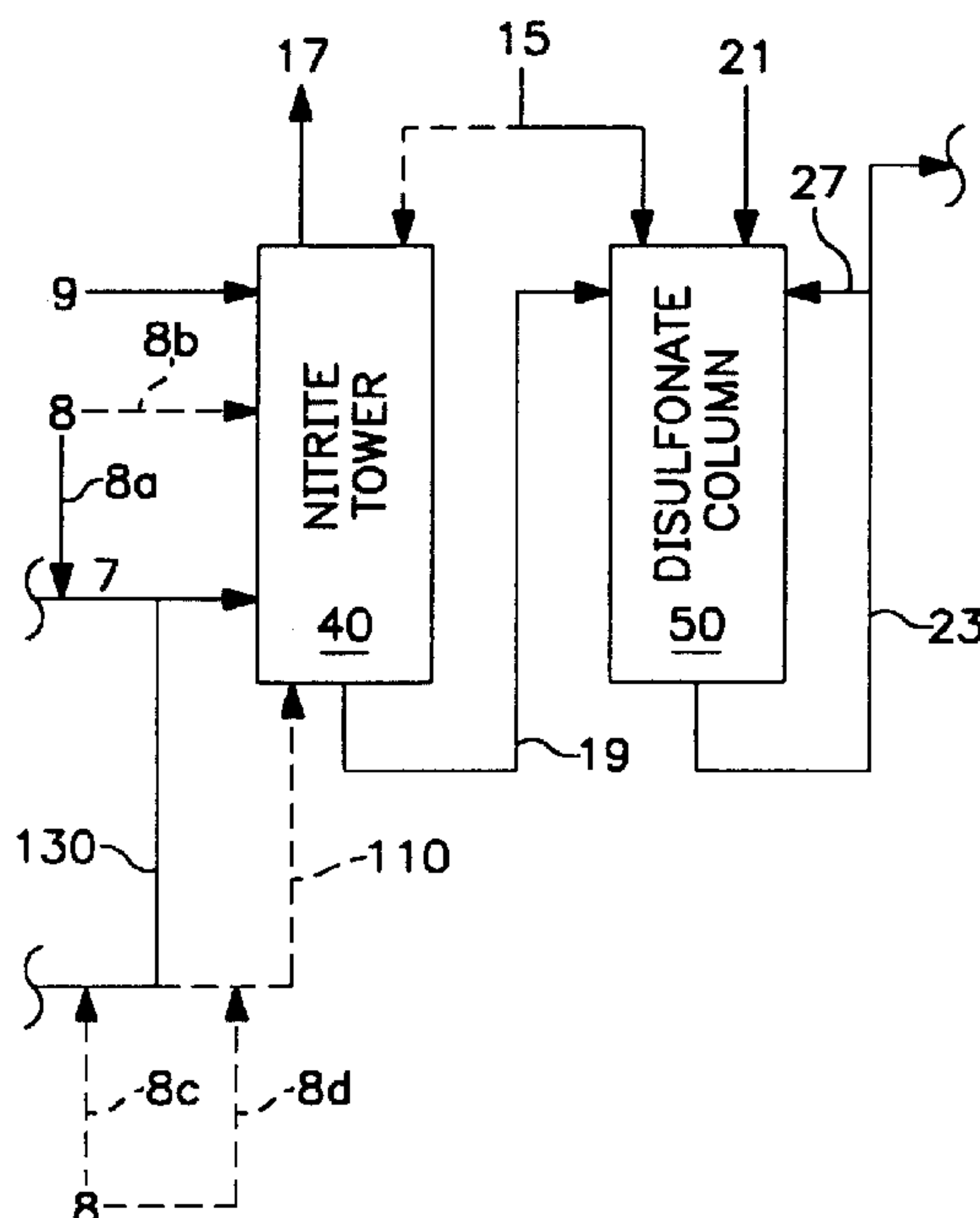
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(54) **METHODE DE PRODUCTION DU SULFATE**

**D'HYDROXYLAMINE DANS LE PROCESSUS CLASSIQUE DE
SYNTHESE DU CAPROLACTAME**

(54) **METHOD FOR PRODUCTION OF HYDROXYLAMINE**

**SULFATE IN THE CONVENTIONAL PROCESS FOR THE
SYNTHESIS OF CAPROLACTAM**



(57) An improvement in the conventional process for the production of caprolactam. The process involves: (a) reacting air with ammonia gas in an ammonia conversion zone to produce nitric oxide; (b) oxidizing a portion of the nitric oxide to nitrogen dioxide to produce an NO_x-rich process gas stream; (c) reacting the NO_x-rich stream with ammonium carbonate in a nitrating zone to produce ammonium nitrite; (d) reducing the ammonium nitrite to hydroxylamine diammonium sulfate; (e) hydrolyzing the hydroxylamine diammonium sulfate to hydroxylamine sulfate; (f) oximating the hydroxylamine sulfate with cyclohexanone to produce cyclohexanone oxime; and (g) converting the cyclohexanone oxime to caprolactam. The process is improved by adding supplemental oxygen downstream of the ammonia conversion zone to increase the quantity and rate of formation of nitrogen dioxide in the NO_x-rich process gas stream.

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Abstract

An improvement in the conventional process for the production of caprolactam. The process involves:

(a) reacting air with ammonia gas in an ammonia conversion zone to produce nitric oxide;

(b) oxidizing a portion of the nitric oxide to nitrogen dioxide to produce an NO_x-rich process gas stream;

(c) reacting the NO_x-rich stream with ammonium carbonate in a nitriting zone to produce ammonium nitrite;

(d) reducing the ammonium nitrite to hydroxylamine diammonium sulfate;

(e) hydrolyzing the hydroxylamine diammonium sulfate to hydroxylamine sulfate;

(f) oximating the hydroxylamine sulfate with cyclohexanone to produce cyclohexanone oxime; and

(g) converting the cyclohexanone oxime to caprolactam.

The process is improved by adding supplemental oxygen downstream of the ammonia conversion zone to increase the quantity and rate of formation of nitrogen dioxide in the NO_x-rich process gas stream.

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METHOD FOR PRODUCTION OF HYDROXYLAMINE SULFATE IN
THE CONVENTIONAL PROCESS FOR THE SYNTHESIS OF
CAPROLACTAM

5 BACKGROUND OF THE INVENTION

Caprolactam can be produced from three hydrocarbon feedstocks: cyclohexane, phenol, and toluene. Approximately 68% of the world's caprolactam capacity is produced from cyclohexane, 31% from phenol, and 1% from toluene. All of the cyclohexane and phenol-based production proceeds via the formation of cyclohexanone oxime. In 94% of the cyclohexane-based and phenol-based caprolactam capacity, the formation of this oxime requires an ammonia oxidation step.

In the processes involving ammonia oxidation, caprolactam production from cyclohexane or phenol can be broken down into the following steps:

- Oxidation of cyclohexane or hydrogenation of phenol, to synthesize cyclohexanone;
- Oxidation of ammonia to form nitric oxide, followed by various reaction steps to form a hydroxylamine salt;
- Synthesis of cyclohexanone oxime by reaction of cyclohexanone and the hydroxylamine salt; and
- Treatment of the cyclohexanone oxime with sulfuric acid followed by neutralization with aqueous ammonia to form caprolactam.

One such method for producing caprolactam is frequently referred to as the "conventional" or "Allied Signal" process. Such process is disclosed,

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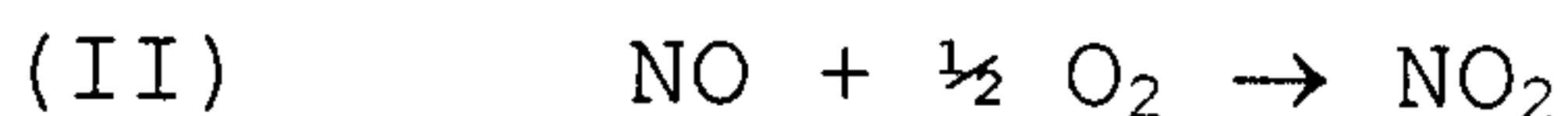
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for example, in Weissermel and Arp, Industrial Organic Chemistry (VCH Verlagsgesellschaft mbH 1993), pp. 249-258. In the conventional process, hydroxylamine sulfate ((NH₂OH)₂·H₂SO₄) and aqueous ammonia are reacted to synthesize the oxime. The hydroxylamine sulfate is produced by the Raschig process:

Catalytic air oxidation of ammonia to form nitric oxide:



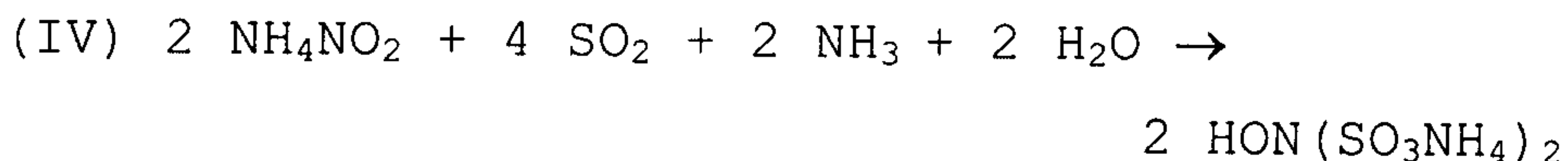
Continued oxidation of nitric oxide to form nitrogen dioxide:



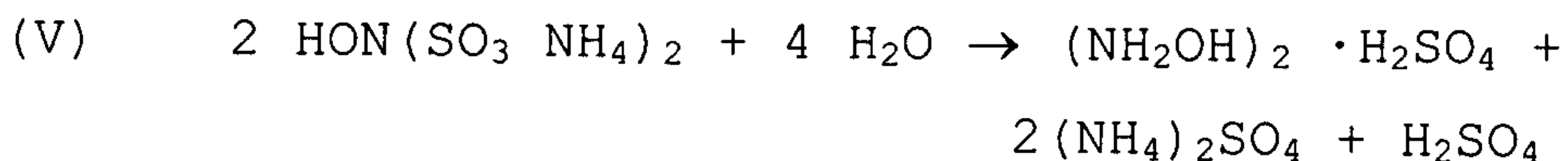
Synthesis of ammonium nitrite:



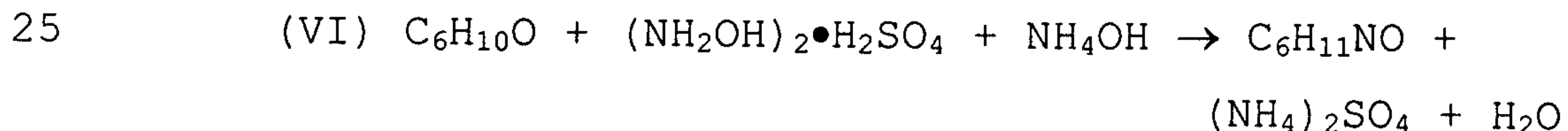
Reduction of ammonium nitrite to hydroxylamine diammonium sulfate:



Hydrolysis of hydroxylamine diammonium sulfate to hydroxylamine sulfate:



Oximating the cyclohexanone with the hydroxylamine sulfate to produce cyclohexanone oxime:



The process for forming hydroxylamine sulfate in the conventional process is shown in the flow sheet depicted in Figure 1 of the attached drawing. As shown therein, an air stream 3 is initially compressed in a compressor 10, introduced as a "primary" air

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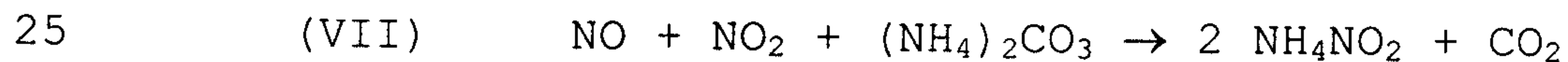
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stream through feed line 12 into admixture with a gaseous ammonia stream 1, and thereafter fed to a catalytic ammonia converter 20. Typically, 100% ammonia conversion and 95% selectivity to NO are achieved in that reaction. Upon exiting the converter, some of the NO is further oxidized to NO₂ to form an NO_x-rich process gas stream 2. The water formed in the ammonia oxidation is thereafter removed from the process stream in a condenser 30. Some of the NO₂ is absorbed in the water as it is condensed, producing a weak nitric acid condensate 5.

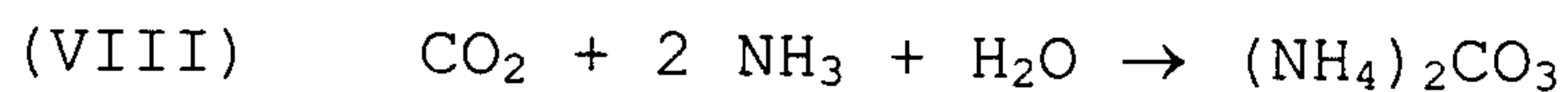
The NO_x-rich process gas stream 7 exiting the condenser 30 is then contacted countercurrently with an aqueous ammonium carbonate stream 9 in a trayed absorption tower 40, referred to as a "nitrite tower".

In the conventional process additional, "secondary" air is added either directly into the nitrite tower through line 11 or into the NO_x process stream through line 13. The amount of secondary air fed to the nitrite tower affects the relative concentrations of NO and NO₂ in the tower. An ammonia stream 15a may also be added to the tower to recover CO₂.

Ammonium nitrite is desirably formed in the nitrite tower, according to the reaction:



The CO₂ liberated in this reaction can be recovered in-situ as ammonium carbonate by reaction with the ammonia stream 15, according to the reaction:

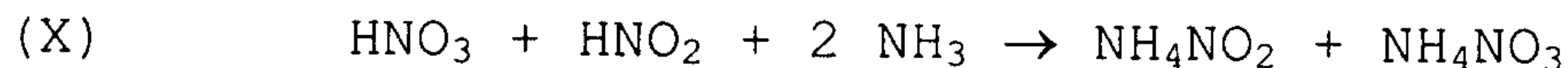
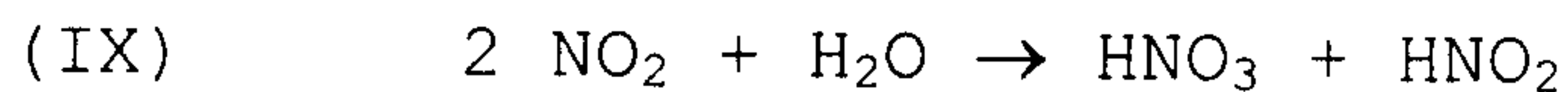


An undesired product, ammonium nitrate, is also formed in the nitrite tower by the following

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reactions:



Ammonia participating in reaction (X) may be derived
5 from the dissociation of the ammonium compounds formed
in these reactions.

The nitrite tower 40 must be operated to minimize
the formation of nitrate. To accomplish this, an
approximate 1:1 molar ratio of NO to NO₂ should be
10 maintained in the tower. In order to maintain such
ratio, secondary air is added to the nitrite tower in
the conventional process in amounts of about 5 to 10
volume % of the total air flow into the system.

The vent gas 17 exiting the nitriting tower must
15 be properly regulated to minimize the emission of NO_x.

An increase in production of hydroxylamine sulfate
typically results in a corresponding increase in NO_x
emission in the vent gas 17.

The nitrite-rich aqueous solution 19 is then
20 reacted with a sulfur dioxide stream 21 and an ammonia
stream 15b fed into a disulfonate column 50 to form
hydroxylamine diammonium sulfate. In some systems the
ammonia may rather be admixed with the nitrite-rich
aqueous solution 19 from the nitrite tower and the
25 mixture then introduced into the disulfonate column.

The hydroxylamine diammonium sulfate stream 23
removed from the disulfonate column is conventionally
hydrolyzed in a hydrolysis column 60 to form
hydroxylamine sulfate. A portion of the hydroxylamine
30 diammonium sulfate is recycled through line 27 to the
disulfonate column 50. The hydroxylamine sulfate

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solution exiting the hydrolysis column is then recovered from line 25 for use in the oximation process.

5 In view of the strict environmental regulation of NO_x emissions, the quantity of NO_x gases vented through line 17 cannot be increased. Accordingly, any increased hydroxylammonium sulfate production (and subsequent caprolactam production) must be obtained without any increase in NO_x emissions. This can be
10 accomplished by increasing the amount of air and ammonia fed to the process while increasing the plant size, e.g., the size of the nitrite tower 40 and air compressor 10. However, such an increase in equipment capacity requires substantial capital investment.

15 There is therefore a need for the development of improved techniques in the conventional process for producing caprolactam, by which increased amounts of hydroxylamine sulfate and, consequently, caprolactam can be produced without large capital investment, and
20 without increasing NO_x emissions.

SUMMARY OF THE INVENTION

The present invention provides just such an improvement in the conventional process for the
25 production of caprolactam involving:

(a) reacting air with ammonia gas in an ammonia conversion zone to produce nitric oxide;

(b) oxidizing a portion of the nitric oxide to nitrogen dioxide to produce an NO_x-rich process gas
30 stream;

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(c) reacting the NO_x-rich stream with ammonium carbonate in a nitriting zone to produce ammonium nitrite;

(d) reducing the ammonium nitrite to
5 hydroxylamine diammonium sulfate;

(e) hydrolyzing the hydroxylamine diammonium sulfate to hydroxylamine sulfate;

(f) oximating the hydroxylamine sulfate with cyclohexanone to produce cyclohexanone oxime; and

10 (g) converting the cyclohexanone oxime to caprolactam.

In accordance with the invention, the foregoing process is improved by adding supplemental oxygen downstream of the ammonia conversion zone to increase
15 the quantity and rate of formation of nitrogen dioxide in the NO_x-rich process gas stream. Desirably, secondary air, normally introduced into the nitriting zone (or into the NO_x-rich gaseous stream feeding into the nitriting zone) is rerouted to the ammonia
20 conversion zone to increase the production of nitric oxide formed in the ammonia conversion zone without increasing the level of NO_x contained in the gas vented from the nitriting zone.

Utilizing the improved technique of the
25 invention, desirably by rerouting the secondary air to the ammonia conversion zone and maintaining the volumetric percentage of ammonia fed to the conversion zone at a constant or increased level, the production of NO in the conversion zone is increased. By adding
30 supplemental oxygen according to the invention, both the amount and rate of conversion of NO to NO₂ are increased, thereby promoting formation of nitrite in

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the nitriting zone, without any adverse effect on the NO_x content of gases vented from the nitriting zone. Alternatively, the addition of supplemental oxygen may be used to lower NO_x emissions, with or without
5 rerouting of secondary air to the ammonia conversion zone, and with or without increases in nitrite (and consequently hydroxylamine sulfate and caprolactam) production. The invention also encompasses adding supplemental oxygen according to the invention without
10 rerouting secondary air to the ammonia converter, but increasing the volumetric percentage of ammonia fed to the conversion zone to increase production of NO. This ultimately results in an increase in formation of hydroxylamine sulfate and caprolactam without an
15 increase in NO_x emissions.

The method of the present invention thus facilitates an increase in hydroxylamine sulfate production in the conventional process for synthesizing caprolactam, while maintaining NO_x
20 emissions at constant, or decreased, levels. It is estimated that use of the method of the invention normally results in an increase of between about 5 and 15% in the production of hydroxylamine sulfate without increasing NO_x emissions. Furthermore, this is
25 accomplished without substantial capital investment, such as would otherwise be required to increase plant capacity. Moreover, by substituting oxygen for inert nitrogen present in the secondary air conventionally fed to the nitriting zone, the oxygen partial pressure
30 in the system may be increased and residence times for the intermediates formed in the various stages of the process may be lowered.

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In the production of nitric acid, it is known that direct injection of supplemental oxygen can boost nitric acid synthesis while controlling NO_x emissions.

Such addition of oxygen is described, for example, in
5 US Patent Nos. 4,183,906; 4,183,906; 4,235,858; and
5,167,935; UK Patent No. 803211; and EP published
Patent Applications Nos. 799794 and 808797. Oxygen
addition is also described in Kongshaug, Extension of
10 Nitric Acid Plant Capacity by Use of Oxygen, Nitric
Acid Symposium (1981); and by Faried et al., Boosting
Existing Nitric Acid Production, The Fertiliser
Society (1986). For example, EP 808797 describes an
improved process for nitric acid production in which
supplemental oxygen is added to the cooler/condenser,
15 the absorption tower, the ammonia converter, and/or
the bleacher, to cause an increase in nitric acid
production without increasing NO_x emissions. No
supplemental oxygen addition of this type is believed
to have been previously disclosed in connection with
20 the synthesis of caprolactam.

Feeding oxygen to the ammonia converter has been
employed in the BASF and Inventa processes for the
synthesis of caprolactam. (As described, for example,
in the Kirk Othmer Encyclopedia of Chemical
25 Technology, 4th edition, 4:831 (1992) and U.S. Patent
No. 5,777,163.) In these processes, however, no
supplemental oxygen is added downstream of the
converter. Also, the BASF and Inventa processes
differ substantially from the conventional process for
30 producing caprolactam in that they do not add air to
the ammonia converter, and do not involve the
formation of NO₂.

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BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

Fig. 1 is a schematic flow sheet of the
5 hydroxylamine sulfate section of the prior art
conventional process for the production of
caprolactam; and

Fig. 2 is a schematic flow sheet of a portion of
the conventional process reaction train as modified in
10 accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

All patent applications, patents, and literature
references cited in this specification are hereby
15 incorporated by reference in their entirety.

In accordance with the present invention, a
supplemental oxygen stream 8, (see Fig. 2) is injected
downstream of the ammonia converter 20 of the
hydroxylamine sulfate reaction train (Fig. 1) in the
20 conventional process for the synthesis of caprolactam.
As used herein, the term "supplemental oxygen" refers
to pure oxygen or any oxygen-enriched gaseous stream
containing more than about 50%, and preferably more
than about 90%, oxygen by volume. Suitable
25 supplemental oxygen sources include pipeline oxygen,
independent cryogenic oxygen plants or PSA/VPSA oxygen
plants, liquid oxygen tanks or oxygen-enriched air
streams.

The supplemental oxygen is injected in place of
30 the secondary air introduced to the nitrite tower in
the conventional process through lines 11 or 13
(Figure 1). In accordance with a preferred embodiment

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of the present invention, air that would otherwise have been employed as "secondary" air is instead fed through feed line 12 for introduction as primary air into the ammonia converter 20. Gaseous mixtures
5 containing about 8 to 12 mole % ammonia and about 18 to 20 mole % oxygen are thus introduced into the ammonia converter, and converted therein under the reaction conditions, e.g., temperature, pressure and catalyst, utilized in the conventional process to
10 produce gaseous reaction mixtures containing in mole %, about:

7 to 12% NO

11 to 18% H₂O67 to 72% N₂15 3 to 10% O₂

By thus increasing the flow of primary air introduced into the ammonia converter, the amount of NO formed therein is increased by about 5 to 15% as compared with ammonia oxidation step in the absence of the
20 addition of supplemental oxygen according to the invention .

The supplemental oxygen is admixed with the NO_x-rich process gas stream 7 introduced to the nitrite tower 40 in the proportion of about 1 to 2 moles of O₂
25 per mole of incremental NO produced in the ammonia converter (i.e., per mole of additional NO produced as a result of introducing additional primary air and ammonia according to the preferred embodiment of the invention). By thus increasing the amount of oxygen
30 introduced into the nitriting zone, both the quantity and rate of formation of NO₂ and ammonium nitrite are

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enhanced, without adversely affecting the desired NO:NO₂ ratio in the reaction mixture.

The supplemental oxygen may be added to the nitriting zone through any of the alternative streams shown in Fig. 2. For example, in one embodiment of the invention the supplemental oxygen stream 8 is injected via line 8a into the process gas line 15 entering the nitrite tower 40. Alternatively, the supplemental oxygen 8 may be injected through line 8b directly into the nitrite tower 40. It is also feasible to inject the supplemental oxygen 8 via lines 8c and 13 into process gas line 7, or via lines 8d and 11 directly into the nitrite tower. The invention also encompasses the direct addition of the supplemental oxygen at several locations in the nitrite tower. If injected at a single location, however, it is preferable to add the supplemental oxygen 8 via lines 8c and 13, or 8d and 11, as indicated above. The supplemental oxygen is preferably introduced into the nitrite tower under positive pressures of between about 2 and 20 psig, typically about 5 psig.

As noted above, practice of the improved method of this invention does not involve any capital investment of the order of that which would be required to, e.g., expand the capacity of the nitriting unit. Furthermore, retrofitting of existing plants to practice the improved technique of the invention can be easily carried out by providing the necessary supplemental oxygen supply lines and connecting them by conventional means to the relevant process line or process unit as outlined above.

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It is estimated that roughly 2.8 tons of oxygen may typically be consumed in the method of the invention for every additional ton of ammonia added to the ammonia converter, although the invention may be
5 practiced using lower and higher amounts of oxygen consumption.

While preferred embodiments of the process hereof are described hereinabove, it will be apparent to those skilled in the art that various changes may be
10 made therein without departing from the scope of the invention as defined in the claims appended hereto.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the production of caprolactam, which comprises:
 - (a) reacting air with ammonia gas in an ammonia conversion zone to produce nitric oxide;
 - (b) oxidizing a portion of the nitric oxide to nitrogen dioxide to thereby produce an NO_x-rich process gas stream;
 - (c) reacting the NO_x-rich stream with ammonium carbonate in a nitriting zone to produce ammonium nitrite;
 - (d) reducing the ammonium nitrate to hydroxylamine diammonium sulfate;
 - (e) hydrolyzing the hydroxylamine diammonium sulfate to hydroxylamine sulfate;
 - (f) oximating the hydroxylamine sulfate with cyclohexanone to produce cyclohexanone oxime; and
 - (g) converting the cyclohexanone oxime to caprolactam;the improvement comprising adding supplemental oxygen downstream of the ammonia conversion zone to increase the quantity and rate of formation of nitrogen dioxide in the NO_x-rich process gas stream.
2. The process of claim 1 further comprising rerouting secondary air from the nitriting zone to the ammonia conversion zone.
3. The process of claim 1 further comprising increasing the amount of ammonia gas added to the

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ammonia conversion zone to increase the production of nitric oxide formed in the ammonia conversion zone.

4. The process of claim 1 further comprising maintaining a substantially equimolar NO:NO₂ ratio in the NO_x-rich process gas stream in the nitriting zone.

5. The process of claim 1 wherein the supplemental oxygen is added into a secondary air stream providing air to the nitriting zone.

6. The process of claim 1 wherein the supplemental oxygen is added into a secondary air stream providing air to the NO_x-rich process gas stream upstream of the nitriting zone.

7. The process of claim 1 wherein the supplemental oxygen is added directly into the nitriting zone.

8. The process of claim 1 wherein the supplemental oxygen is added to the NO_x-rich process gas stream upstream of the nitriting zone.

9. The process of claim 1 wherein the supplemental oxygen is a gas comprising more than about 90 vol.% oxygen.

10. In a process for the production of caprolactam, which comprises:

(a) reacting air with ammonia gas in an ammonia conversion zone to produce nitric oxide;

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(b) oxidizing a portion of the nitric oxide to nitrogen dioxide to thereby produce an NO_x-rich process gas stream;

(c) reacting the NO_x-rich stream with ammonium carbonate in a nitriting zone to produce ammonium nitrite;

(d) reducing the ammonium nitrate to hydroxylamine diammonium sulfate;

(e) hydrolyzing the hydroxylamine diammonium sulfate to hydroxylamine sulfate;

(f) oximating the hydroxylamine sulfate with cyclohexanone to produce cyclohexanone oxime; and

(g) converting the cyclohexanone oxime to caprolactam;

the improvement comprising adding supplemental oxygen downstream of the ammonia conversion zone while simultaneously rerouting secondary air to the ammonia conversion zone to increase the production of nitric oxide formed in the ammonia conversion zone and the quantity and rate of formation of nitrogen dioxide in the nitriting zone, while maintaining a substantially equimolar NO:NO₂ ratio in the NO_x-rich stream in the nitriting zone.

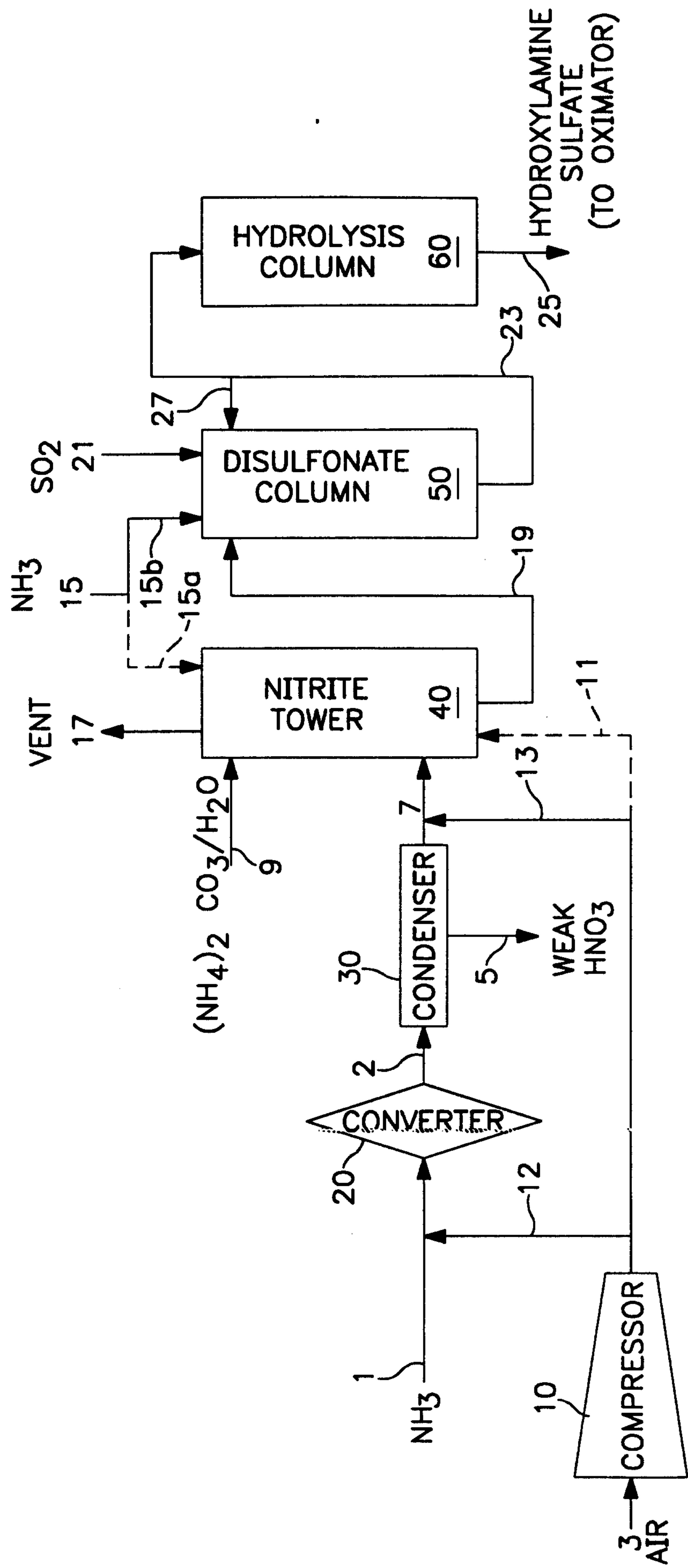


FIG. 1
PRIOR ART

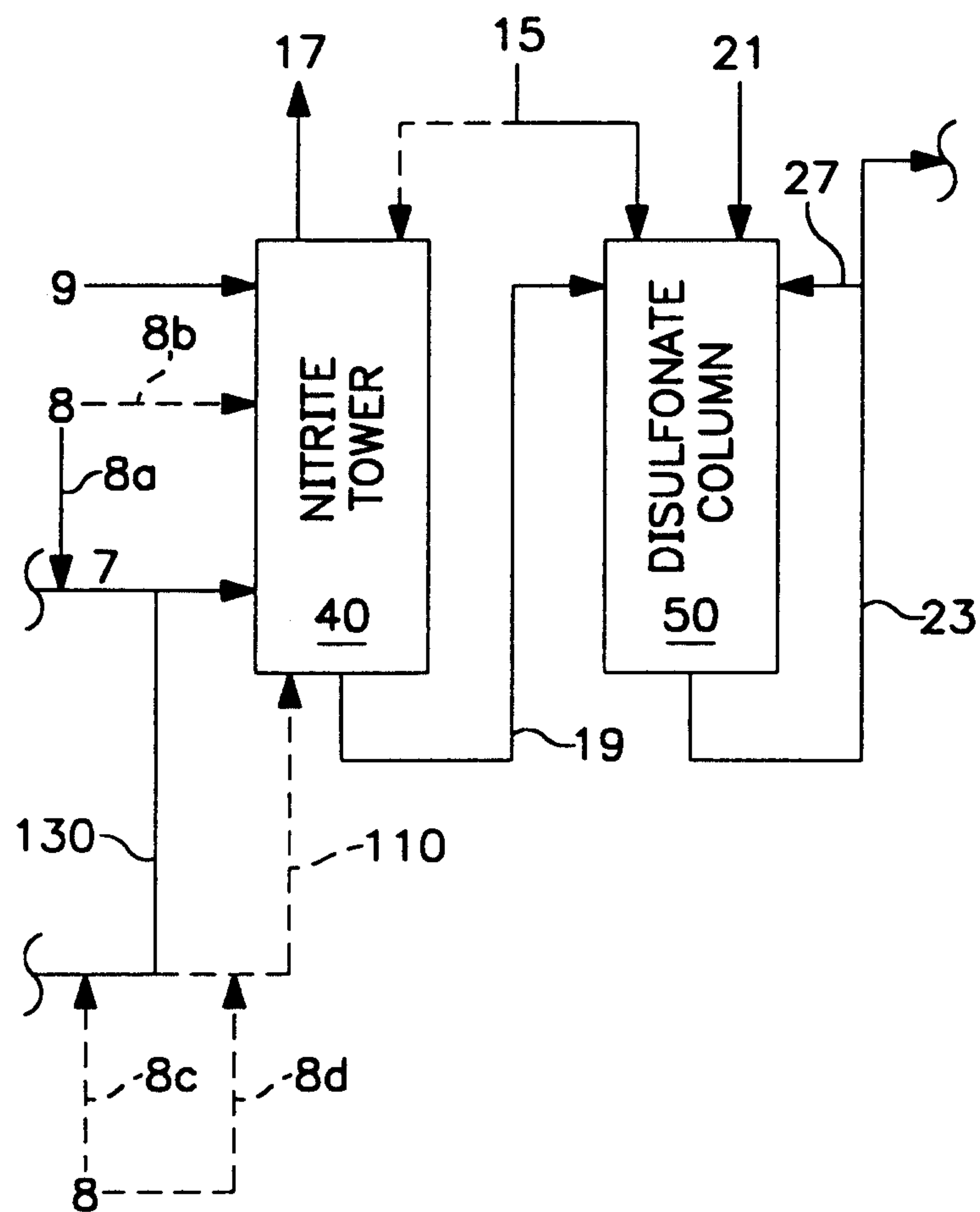


FIG. 2