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(54) **METHOD FOR TREATING REFINERY WASTE STREAMS IN A FLUID CATALYTIC CRACKING UNIT AND AN IMPROVED CATALYTIC CRACKING UNIT FOR PROCESSING REFINERY WASTE STREAMS**

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(57) **ABSTRACT**

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A method of processing the waste stream includes introducing the waste stream into the Fluid Catalytic Cracking Unit **10** such that waste stream is processed within the regenerator unit **12** or in CO boiler unit **13** such that the waste stream and the regenerator flue gas are burned within the regenerator unit **12** or the CO boiler unit **13**. The waste stream contains NH₃ and the NH₃ is converted to the NOx and N₂. The fluid catalytic cracking unit may further include an assembly for converting NOx to N₂. Flue gas from the CO boiler unit containing NOx and N₂ is fed to the assembly to NOx to N₂ within the assembly. The assembly for converting NOx to N₂ preferably includes a selective catalytic reduction unit **14** containing a catalyst, and wherein converting NOx to N₂ includes reacting the NOx with the catalyst to produce N₂ and H₂O.

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Related U.S. Application Data

(63) Continuation of application No. 12/232,942, filed on Sep. 26, 2008, now Pat. No. 8,114,272.

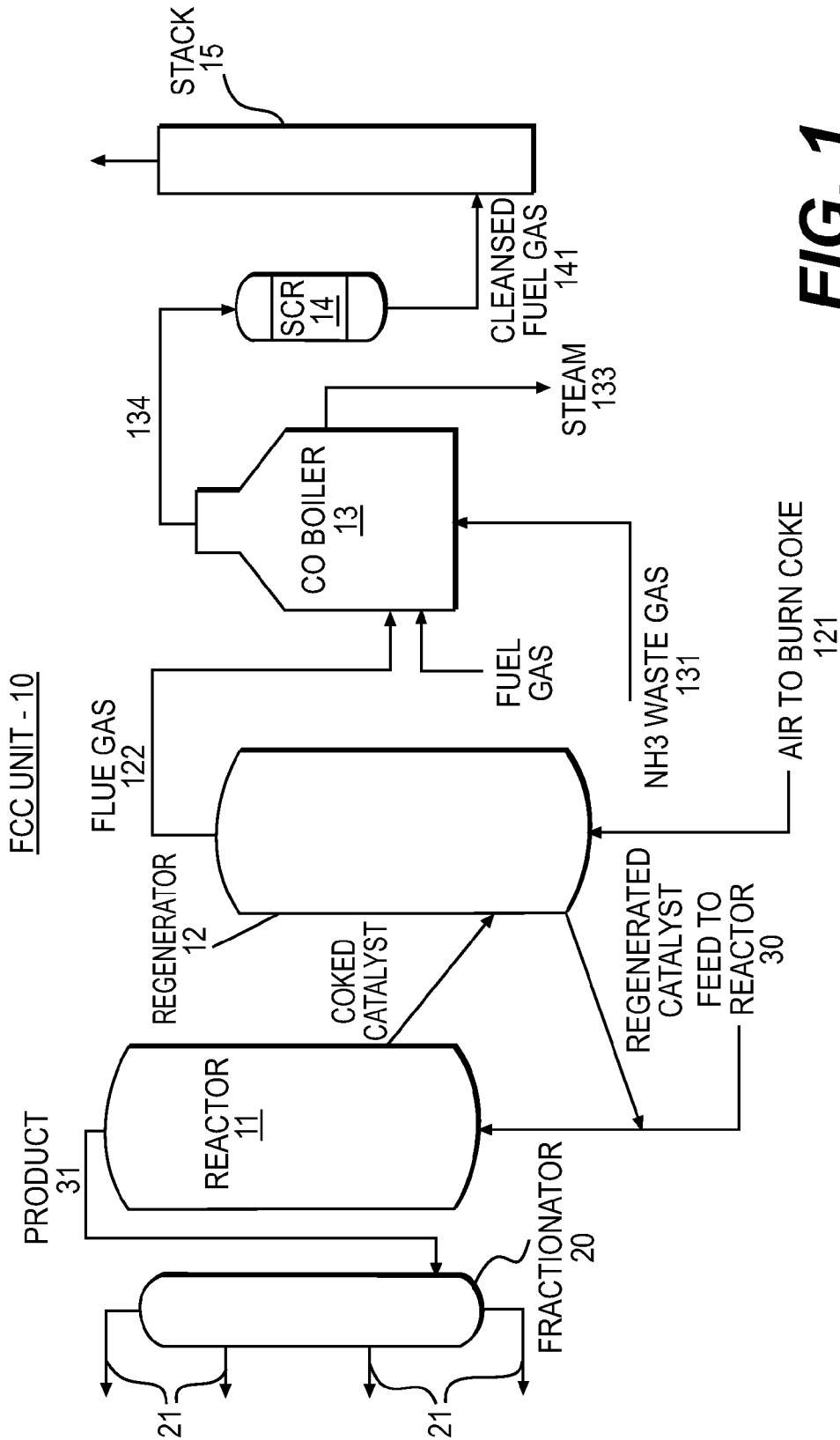
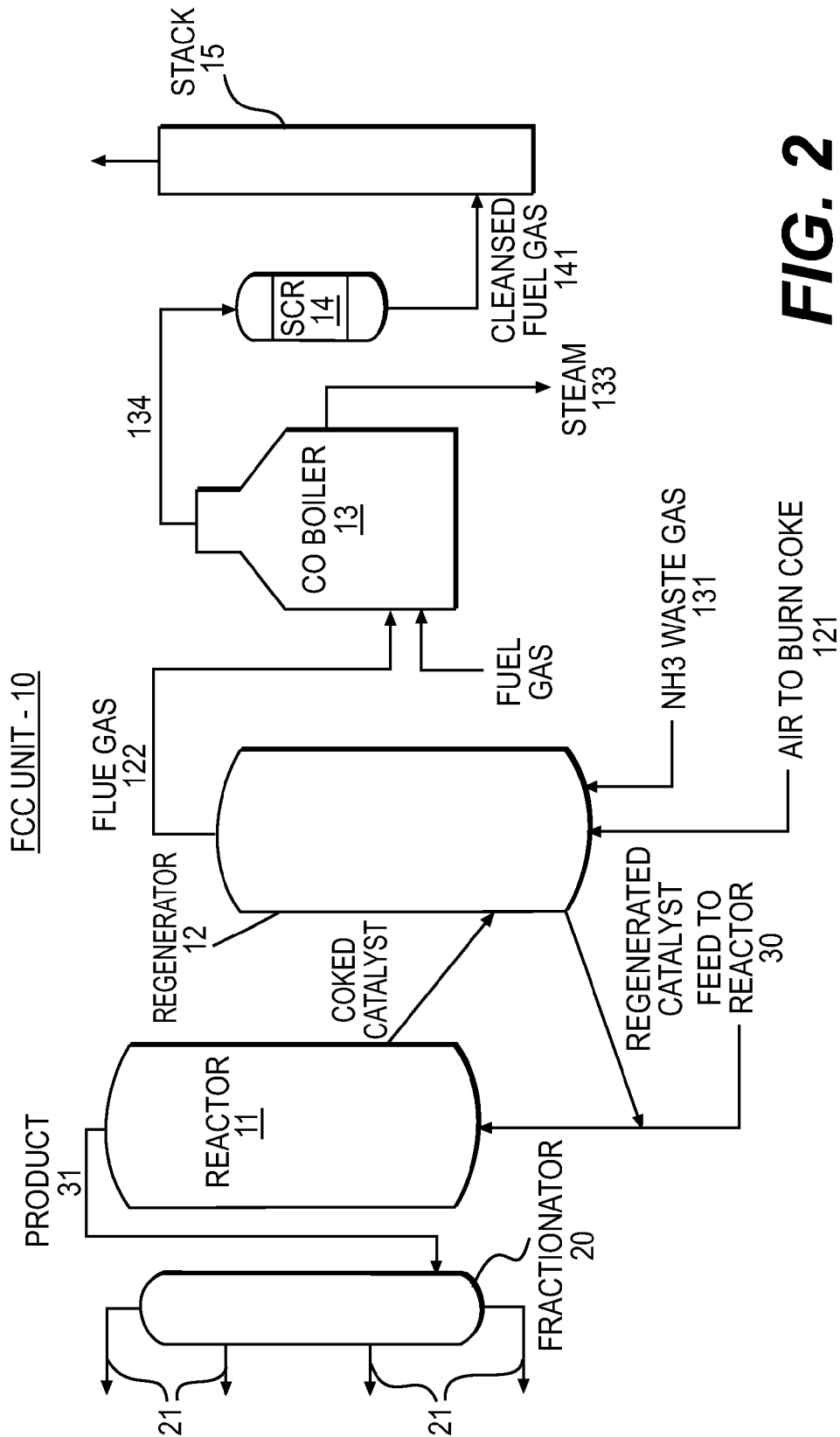


FIG. 1



**METHOD FOR TREATING REFINERY
WASTE STREAMS IN A FLUID CATALYTIC
CRACKING UNIT AND AN IMPROVED
CATALYTIC CRACKING UNIT FOR
PROCESSING REFINERY WASTE STREAMS**

CROSS REFERENCE TO RELATED
APPLICATIONS

[0001] This application is a continuation of U.S. patent application Ser. No 12/232,942, filed on Sep. 26, 2008.

FIELD OF THE INVENTION

[0002] This invention relates to a process for treating refinery waste streams. In particular, the present invention relates to a process for treating nitrogen-containing refinery waste streams while minimizing NOx emissions. More particularly, the present invention relates to the use of a fluid catalytic cracking (FCC) unit to process the nitrogen-containing refinery waste stream. This invention also relates to an improved FCC unit capable of processing nitrogen-containing refinery waste streams.

BACKGROUND OF THE INVENTION

[0003] Purified water and processed steam are used in many oil refinery operations. Purified water is often used in heat exchangers and various water-wash operations. Processed steam is used in pipestills, cokers, fluid catalytic cracking units, mid-distillate strippers, light distillate strippers and other applications. As a result of this use, significant quantities of contaminated sour refinery water are produced. The sour water may contain suspended and dissolved impurities, such as phenols, sulfides, ammonia, and other hydrocarbons. The processing of the sour water can generate a waste stream that is highly concentrated in ammonia, which must be disposed of in an environmentally safe manner. The sour water is typically stripped with steam to remove the impurities. In a two-stage stripping process, the sulfides are substantially stripped out in the first stage for processing in a sulfur plant. In the second stage, a waste stream consisting substantially of ammonia and steam is produced. The waste stream containing ammonia may be burned, but an undesirable by-product of this incineration is the generation of oxides of nitrogen (NOx) (i.e., NOx emissions). NOx emissions are highly regulated by regulatory agencies.

[0004] One approach for treating waste streams containing high concentrations of nitrogen, while minimizing NOx emissions, is offered by the John Zink Company. The John Zink Company's NOxidizer™ system uses a three stage incineration process to limit NOx formation. In the first stage, the waste stream and fuel are burned with less than the stoichiometric requirement of oxygen. The products of the combustion are cooled in the second stage and reoxidized in the third stage. The three stages are carried out in a series of refractory-lined vessels along with a high-intensity burner. While the process is effective in disposing of nitrogen-containing waste streams and reducing NOx emissions, the process requires a significant investment of capital along with significant yearly operating costs.

[0005] There is a need for a lower cost alternative for processing a nitrogen-containing waste stream while minimizing NOx emissions.

SUMMARY OF THE INVENTION

[0006] It is an aspect of the present invention to provide a method of processing a waste stream in a fluid catalytic cracking unit. The method includes introducing the waste stream into a portion of the fluid catalytic cracking unit and processing the waste stream within the fluid catalytic cracking unit.

[0007] In accordance with an aspect of the present invention, the fluid catalytic cracking unit includes a reactor unit for reacting a process stream with a catalyst contained therein, a regenerator unit for regenerating the catalyst, and a CO boiler unit for processing regenerator flue gas. The method of processing the waste stream includes introducing the waste stream into the CO boiler unit such that the waste stream and the regenerator flue gas are burned within the CO boiler unit. The waste stream contains NH₃ and the NH₃ is converted to NOx and N₂ in the CO boiler unit. The fluid catalytic cracking unit may further include an assembly for converting NOx to N₂. Flue gas from the CO boiler unit containing NOx is fed to the assembly to convert NOx to N₂ within the assembly. The assembly for converting NOx to N₂ preferably includes a selective catalytic reduction unit containing a catalyst, and wherein converting NOx to N₂ includes reacting the NOx with injected NH₃ and using the catalyst to produce N₂ and H₂O.

[0008] In accordance with another aspect of the present invention, the fluid catalytic cracking unit includes a reactor unit for reacting a process stream with a catalyst contained within the reactor unit. The fluid catalytic cracking unit also includes a regenerator unit for regenerating the catalyst and a CO boiler. The method of processing the waste stream includes introducing the waste stream into the regenerator unit. The waste stream contains NH₃. The waste stream is processed within the regenerator unit to convert a significant portion of the NH₃ to N₂. The waste stream containing NH₃ is burned within the regenerator unit as the catalyst is regenerated. The regenerator unit is operated at a sufficient temperature such that the NH₃ is converted to NOx and subsequently a significant portion is converted to N₂.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The invention will now be described in conjunction with the accompanying drawings in which like reference numerals describe like elements and wherein:

[0010] FIG. 1 is a schematic diagram of a fluid catalytic cracking unit for processing NH₃ waste gases in the CO boiler in accordance with an embodiment of the present invention; and

[0011] FIG. 2 is a schematic diagram of fluid catalytic cracking unit for processing NH₃ waste gases in the regenerator in accordance with another embodiment of the present invention

DETAILED DESCRIPTION OF PREFERRED
EMBODIMENTS

[0012] The present invention will now be described in greater detail in connection with the attached figure. A fluid catalytic cracking (FCC) unit is a primary conversion unit in most integrated refineries to convert heavier oils (e.g., heavy gas oil, vacuum gas oil or coker gas oil) into lighter products

(e.g., gasoline, naphtha and lighter gases). The FCC process works in the presence of a zeolitic catalyst with a riser or fluid bed reactor and a regenerator system. The reactor unit and the regenerator unit form the basis of the conventional FCC unit.

[0013] FIG. 1 illustrates a fluid catalytic cracking unit 10 in accordance with an aspect of the present invention. The FCC unit 10 includes a reactor unit 11 containing the zeolitic catalyst. The heavier oil feed or process stream 30 is fed into the reactor unit 11 where it is vaporized and cracked into smaller molecules of vapor by contact and mixing with the catalyst within the reactor unit 11. The vaporized process stream 31 is fed to a distillation column 20 to undergo fractionation where the process stream is separated into various lighter end products 21. The reaction within the reactor unit 11 produces a carbonaceous material or coke that deposits on the catalyst which reduces the catalyst activity. In order to maintain the effectiveness of the catalyst, the catalyst must be regenerated to burn off the deposited coke. The coked catalyst is fed to a regenerator unit 12 to burn off the coke. Air is fed into the regenerator unit 12 through a regenerator air line 121 to facilitate the regeneration process. The regenerated heated catalyst is then fed back to the reactor unit 11 for reaction with the process stream.

[0014] The regeneration of the catalyst in the regenerator unit 12 produces a flue gas 122 typically containing carbon dioxide (CO₂) and carbon monoxide (CO) gas. The amount of CO produced in the regeneration process is dependent upon the design of the unit 12, the temperature upon which regeneration occurs and the amount of excess oxygen (e.g., higher regeneration temperatures and higher excess oxygen produce lower quantities of CO). The flue gas from the regenerator unit 12 may be fed to a CO boiler unit 13 where the regenerator flue gas is typically burned with a fuel gas 131 to produce steam 133 for use in the refinery. As a result, the CO is burned, which limits CO emissions. The flue gas may then be subject to further processing to reduce contaminants before release into the environment through stack 15.

[0015] The combination of a reactor unit 11, a regenerator unit 12 and a CO boiler 13, if necessary, are considered to be conventional components in FCC units and whose operation and construction are well known in the fluid catalytic cracking art. Aspects of the present invention will now be described in greater detail in particular the use of the FCC unit to process NH₃ waste streams. The nitrogen-containing waste stream is introduced into the FCC unit at a predetermined location so that the NOx formed when the waste stream is burned can be reduced to molecular nitrogen before its release to the atmosphere. The predetermined location is dependent upon the design of the FCC unit, the unit operating temperatures and the provision of certain NOx reducing equipment.

[0016] In accordance with one embodiment of the present invention, a waste stream 132 containing NH₃ is fed into the CO boiler unit 13, where it combines with the regenerator flue gas 122 and a fuel gas 131, as shown in FIG. 1. In the CO boiler unit 13, the waste stream 131, the fuel gas 132 and the flue gas 122 are burned to produce steam 133, which may be used in other refinery applications. The NH₃ in the waste stream is converted to NOx and N₂ in the CO boiler unit 13. The flue gas 134 from the CO boiler unit 13 contains CO₂ and N₂ and certain amounts of NOx. The processing of the waste stream in the boiler unit 13 increases the NOx emissions from the CO boiler unit 13 from about 60-80 ppm up to about 200-300 ppm. The level of NOx contained in the flue gas 134

will require additional processing before the flue gas 134 can be released to the environment through the stack 15.

[0017] The flue gas 134 may undergo subsequent processing to reduce NOx prior to release to the atmosphere. In accordance with an aspect of the present invention, the flue gas is further processed using a selective catalytic reduction (SCR) unit 14, where the flue gas is exposed to a catalyst such that an acceptable amount of NOx is converted to N₂ and H₂O. The use of the SCR unit 14 after the CO boiler unit 13 will likely bring the NOx emissions down to less than 40 ppm. The cleansed flue gas 141 may then be released through stack 15. This combination is a low cost alternative for the processing of NH₃. The subsequent processing of the flue gas is not limited to the use of an SCR unit; rather, it is contemplated that the flue gas may be processed by selective non-catalytic reduction (e.g., a process marketed by ExxonMobil as the Thermal DeNOx process), wet gas scrubbing plus (WGS+) and oxidation of the flue gas with ozone followed by wet scrubbing.

[0018] In accordance with another aspect of the present invention, the nitrogen-containing waste stream can be processed by introducing the waste stream 123 with air from the regenerator air line 121 such that the waste stream 123 is introduced into the regenerator unit 12, as shown in FIG. 2. The nitrogen in the waste stream will initially burn to NOx in the regenerator unit 12. As NOx passes through the regenerator unit 12, NOx will be substantially converted to N₂ as it passes through the catalyst bed within the unit 12 and reacts with coke on catalyst. The coke on the catalyst reacts with the NOx to form molecular nitrogen. Depending on the design and operation of the regenerator, it may be possible to process the waste stream to remove NH₃ while maintaining acceptable NOx levels (e.g., on the order of 20-40 ppm) without the need for further processing or the need for any additional add-on NOx control devices. In the event that the NOx reduction is not at acceptable levels, it may be necessary to combine the present arrangement with an additional NOx control device (e.g., SCR unit, wet gas scrubbing plus, SNCR, etc.) in order to further reduce the presence of NOx to appropriate levels.

[0019] It will be apparent to those skilled in the art that various modifications and/or variations may be made without departing from the scope of the present invention. Thus, it is intended that the present invention covers the modifications and variations of the apparatus and methods herein, provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A method of processing a waste stream in a fluid catalytic cracking unit, comprising:
 - introducing the waste stream into the fluid catalytic cracking unit, wherein the waste stream contains NH₃; and
 - processing the waste stream within the fluid catalytic cracking unit, wherein processing the waste stream includes converting NH₃ to NOx and N₂.
2. The method according to claim 1, wherein the fluid catalytic cracking unit includes a reactor unit for reacting a process stream with a catalyst contained therein, and a regenerator unit for regenerating the catalyst, and wherein introducing the waste stream into the fluid catalytic cracking unit comprising introducing the waste stream into the regenerator unit.

3. The method according to claim 2, processing the waste stream within the fluid catalytic cracking unit includes burning the waste stream within the regenerator unit.

4. The method according to claim 3, wherein the fluid catalytic cracking unit further includes an assembly for converting NOx to N₂, and wherein processing the waste stream further includes converting NOx to N₂ within the assembly.

5. The method according to claim 4, wherein the assembly for converting NOx to N₂ includes a selective catalytic reduction unit containing a catalyst, and wherein converting NOx to N₂ includes reacting the NOx to N₂ within the assembly.

6. The method according to claim 2, wherein the fluid catalytic cracking unit includes a regenerator air line for introducing air to the regenerator unit for regenerating the catalyst, and wherein introducing the waste stream into the regenerator unit includes mixing with the waste stream with the air for introduction into the regenerator unit.

7. The method according to claim 6, processing the waste stream within the fluid catalytic cracking unit includes burning the waste stream within the regenerator unit.

8. The method according to claim 6, wherein the fluid catalytic cracking unit further includes an assembly for converting NOx to N₂, and wherein processing the waste stream further includes converting NOx to N₂ within the assembly.

9. The method according to claim 8, wherein the assembly for converting NOx to N₂ includes a selective catalytic reduction unit containing a catalyst, and wherein converting NOx to N₂ includes reacting the NOx with NH₃ over the catalyst to produce N₂ and H₂O.

10. The method according to claim 1, wherein the fluid catalytic cracking unit includes a regenerator unit for regenerating catalyst, wherein processing the waste stream comprising:

feeding the waste stream to the regenerator unit; and
burning the waste stream in the regenerator unit to convert the NH₃ to NOx and N₂.

11. The method according to claim 10, wherein the fluid catalytic cracking unit further includes an assembly for converting NOx to N₂, and wherein processing the waste stream further comprising:

processing the waste stream in the assembly by converting NOx to N₂.

12. The method according to claim 11, wherein the assembly for converting NOx to N₂ includes a selective catalytic reduction unit containing a catalyst, and wherein converting NOx to N₂ includes reacting the NOx with NH₃ over the catalyst to produce N₂ and H₂O.

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