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(54) Titre : PROCEDE DE PURIFICATION D'AMMONIAC, DE MELANGES D'AZOTE ET D'HYDROGENE, OU D'AZOTE, D'HYDROGENE ET D'AMMONIAC

(54) Title: METHOD FOR PURIFICATION OF AMMONIA, MIXTURES OF NITROGEN AND HYDROGEN, OR NITROGEN, HYDROGEN AND AMMONIA

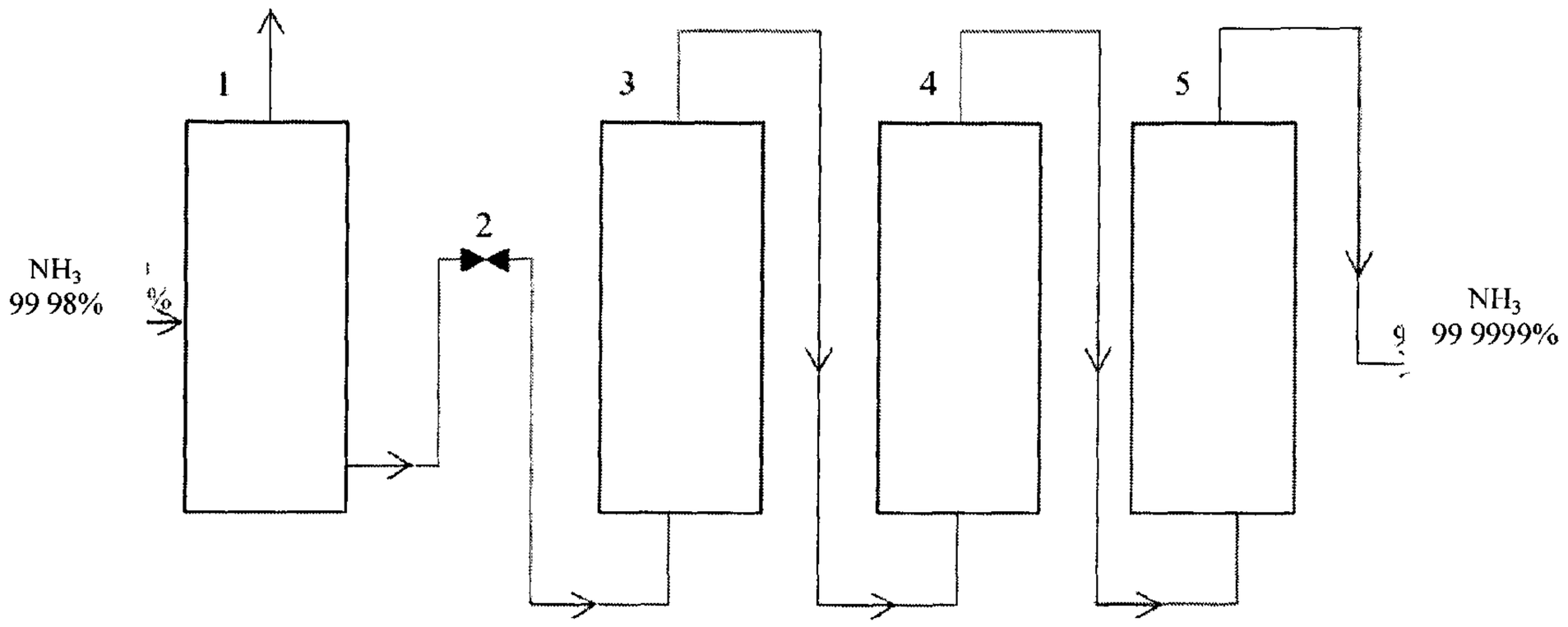


Fig. 1. Block diagram of the system according to Example 1.

(57) Abrégé/Abstract:
Method for purification of ammonia or mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia, according to which: a) ammonia or a mixture of gases under pressure of from 0.1 to 25 MPa is passed through a column packed with aluminium oxide with a large specific surface area; b) the ammonia or mixture of gases is then passed through a column packed with CaO, NaOH, KOH or an NaOH/KOH melt, separately or in a mixture, at 20 to 70°C and under pressure of from 0.1 to 25 MPa; c) next, the ammonia or mixture of gases is passed through a column packed with activated carbon having a specific area of 100÷3000 m^2 /g with sodium, potassium, caesium, magnesium, calcium, strontium, barium or cerium nitrates(V) or nitrates(III) deposited on its surface, separately or in a mixture; the aforementioned steps being realised in a serial process at a gas stream flow rate in the range of 100 dm^3/h to 1000 m^3/h.

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(54) Title: METHOD FOR PURIFICATION OF AMMONIA, MIXTURES OF NITROGEN AND HYDROGEN, OR NITROGEN, HYDROGEN AND AMMONIA

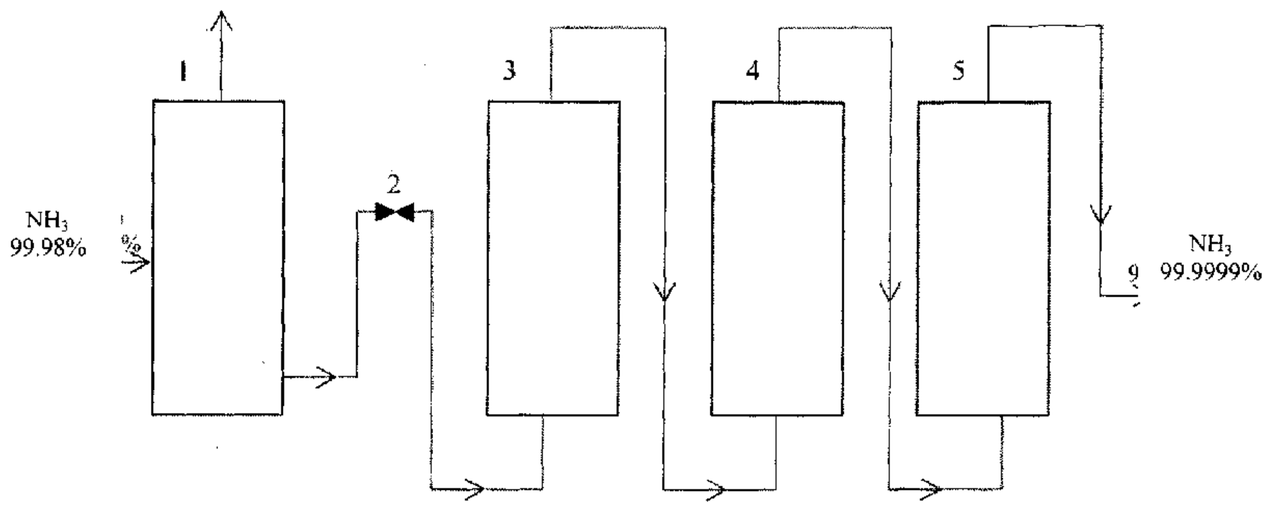


Fig. 1. Block diagram of the system according to Example 1.

(57) Abstract: Method for purification of ammonia or mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia, according to which: a) ammonia or a mixture of gases under pressure of from 0.1 to 25 MPa is passed through a column packed with aluminium oxide with a large specific surface area; b) the ammonia or mixture of gases is then passed through a column packed with CaO, NaOH, KOH or an NaOH/KOH melt, separately or in a mixture, at 20 to 70°C and under pressure of from 0.1 to 25 MPa; c) next, the ammonia or mixture of gases is passed through a column packed with activated carbon having a specific area of 100÷3000 m^2/g with sodium, potassium, caesium, magnesium, calcium, strontium, barium or cerium nitrates(V) or nitrates(III) deposited on its surface, separately or in a mixture; the aforementioned steps being realised in a serial process at a gas stream flow rate in the range of 100 dm^3/h to 1000 m^3/h.

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Method for purification of ammonia, mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia

The invention relates to a method for purification of ammonia, mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia to high purity.

Over the last few decades, scientific studies resulted in many discoveries in the field of electronics pertaining to the application of new materials. Nitrides of aluminium, gallium and indium are an especially attractive group of chemical compounds to be used in new electronic technologies. In the processes of synthesis of the said nitrides, ammonia with particularly high purity – less than 0.1 ppm of impurities – is used. On the other hand, a need arises for purification of the syngas (hydrogen and nitrogen) stream in ammonia synthesis, in which catalysts with higher efficiency than that of the conventional iron catalyst are used. Such catalysts are much more sensitive to impurities present in the syngas stream.

Purity of ammonia is connected both with purity of the syngas used for production of ammonia and with methods for purification of raw ammonia.

Methods for obtaining a syngas with proper purity (mixture of H_2 and N_2) are known and described in many sources of literature [W. Bobrownicki, S. Pawlikowski, „Technologia związków azotowych", WNT, Warsaw 1974; Information materials of Kellogg Brown & Root, http://www.kbr.com, dated 15.05.2012]. Final purification of the fresh gas from water vapour and carbon oxides is carried out by adsorption on molecular sieves or washing of the gas with a stream of liquid ammonia or liquid nitrogen. The purity of these gas streams is sufficient to obtain technical ammonia on a large commercial scale, but completely unsatisfactory for application of the obtained NH_3 in electronics. For this type of application, it is necessary to remove such impurities as $H_2O_{(g)}$, CO_x, CH_4, O_2 and Ar from ammonia.

In order to purify ammonia to high purity, two basic methods are used. The older one consists in passing gaseous ammonia containing 80 ppm of impurities under atmospheric pressure through liquid ammonia with dissolved metallic sodium. After purification, NH_3 contains 0.6 ppm of impurities in the form of oxygen-containing compounds [US4075306]. The other method for obtaining high-purity ammonia is fractional distillation of liquid ammonia under a pressure of 2÷30 MPa. Ammonia with 99.99% purity was purified to a level of 10 ppm of impurities [US7001490]. Distillation of liquid ammonia may be preceded by

stages of hydrocarbons and water removal by adsorption. The adsorption process is carried out using a known bed, e.g. granulated activated carbon for removal of hydrocarbons and calcium sulfate(VI) for removal of water. Such a process is known from the patent description US7297181, according to which ammonia with a purity of 99.9995% has been obtained.

Use of metallic sodium in the first method practically precludes its application in the field of electronics, because sodium is an element considered exceptionally inadvisable in semiconductor materials. In the next two methods, a process of distillation is used, requiring complex equipment and using a significant amount of energy.

The goal of the invention was to provide a method which allows for obtaining high-purity ammonia, technologically convenient on a large scale, and enables efficient purification of both syngas and impure ammonia.

The method for purification of ammonia, mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia, according to the invention, is a multi-staged process, consisting of the following steps:

a) ammonia or a mixture of gases under pressure of from 0.1 to 25 MPa is passed through a column packed with aluminium oxide with a large specific surface area, at room temperature, in order to bind oil residues;
b) the ammonia or mixture of gases is then passed through a column packed with CaO, NaOH, KOH or an NaOH/KOH melt, separately or in a mixture, at 20 to 70°C and under pressure of from 0.1 to 25 MPa, in order to preliminarily bind water vapour;
c) next, the ammonia or mixture of gases is passed through a column packed with activated carbon having a specific area of 100÷3000 m^2/g with sodium, potassium, caesium, magnesium, calcium, strontium, barium or cerium nitrates(V) or nitrates(III) deposited on its surface, separately or in a mixture, in order to remove a decisive majority of oxygen contained in the compounds that were not removed earlier (mainly H_2O and CO);

the aforementioned steps being realised in a serial process at a gas stream flow rate in the range of 100 dm^3/h to 1000 m^3/h.

In the case when the method according to the invention is used for purification of ammonia, additionally a preliminary stage of methane removal from above the liquid ammonia is applied by removal of the gas from above the liquid in the amount of 1÷100 dm^3/h.

In stages a) and b), ammonia, preferably decompressed to a pressure of from 0.1 to 0.8 MPa, is introduced to the columns.

In stage c), column packing activated before use with a stream of an inert gas (e.g. nitrogen) or hydrogen, or their mixture with a pressure of 0.1÷25 MPa, at 250÷700°C is used.

During the purification cycle, in stage c), the mixture of gases is passed through a column, preferably under pressure of from 0.1 to 25 MPa at 170÷425°C, while ammonia is passed through a column preferably under pressure of from 0.1 to 0.8 MPa at 170÷425°C.

In stage a), aluminium oxide with a specific area not lower than 50 m^2/g is used for the column packing.

The column packing of stage a) may be regenerated by exclusion of the column from the flow and passing a stream of an inert gas (e.g. nitrogen) or hydrogen or a mixture of these gases through it at 200÷700°C. The column packing of stage c) may be regenerated by exclusion of the column from the flow and passing a stream of an inert gas (e.g. nitrogen) or hydrogen or a mixture of these gases through it at 250÷700°C.

The solution according to the invention allows for obtaining ammonia or mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia, with a purity of 99.9999% using a technological apparatus with a simple construction and simultaneously using readily available chemical substances.

The method according to the invention is presented in more detail in embodiments. In all examples, measurements of ammonia purity were evaluated measuring the dew point in the gas.

Sets of columns for realisation of the method according to the invention are schematically shown in the embodiments in Figures 1 and 2.

Example 1

The system used is shown in Fig. 1. Technical liquid ammonia with a purity of 99.98% by wt. was purified. The gas was carried off at a rate of 30 dm^3/h from above liquid NH_3 in an intermediate tank (1) with a capacity of 1000 dm^3. Liquid ammonia from this tank was directed to decompression (2) and then, under pressure of 0.5 MPa, passed through a column (3) packed with aluminium oxide having a specific area of 90 m^2/g. Under the same pressure, the stream of ammonia was directed to a column (4) packed with CaO. The ammonia initially dried in this manner flowed through a column (5) with a carbon bed having a specific area of 500 m^2/g, saturated with a mixture of magnesium and calcium nitrates(V), which was dried and heated at 300°C under a stream of a hydrogen-nitrogen mixture with a molar ratio of 3:1. In the process, a stream of ammonia with a flow rate of 500 dm^3/h containing less than 1 ppm of impurities was obtained.

Example 2

The system used is shown in Fig. 2. A mixture of nitrogen and hydrogen (with a molar ratio of 1:3) containing 150 ppm of impurities was purified. A stream of gases under pressure of 7.5 MPa was passed through a column (1) packed with aluminium oxide having a specific area of 150 m^2/g. Under the same pressure, the stream of gases was directed to a column (2) packed with CaO. The gases initially dried in this manner flowed at 290°C through a column (3) with a carbon bed having a specific area of 800 m^2/g, saturated with calcium nitrate(V), which was dried and heated at 400°C under a stream of nitrogen. In the process, a stream of gases with a flow rate of 300 dm^3/min containing less than 0.5 ppm of impurities was obtained.

Example 3

The system used is shown in Fig. 2. A gaseous mixture of nitrogen and hydrogen (with a molar ratio of 1:3) containing an additional 5% by vol. of ammonia was purified. The level of impurities in the mixture was 100 ppm. A stream of gases under pressure of 6 MPa was passed through a column (1) packed with aluminium oxide having a specific area of 100 m^2/g. Under the same pressure, the stream of gases was directed to a column (2) packed with CaO. The gases initially dried in this manner flowed through a column (3) with a carbon bed having a specific area of 1200 m^2/g, saturated with calcium nitrate(V), which was dried and heated at 250°C under a stream of hydrogen and nitrogen mixture with a molar ratio of 1:3. In the process, a stream of gases with a flow rate of 200 dm^3/min and a composition the same as the one introduced containing less than 0.5 ppm of impurities was obtained.

AMENDED CLAIMS
received by the International Bureau on 17 January 2014 (17.01.2014)

Claims

1. Method for purification of ammonia or mixtures of nitrogen and hydrogen, or nitrogen, hydrogen and ammonia, using a step of hydrocarbons and water removal by adsorption, characterised in that:

a) ammonia or a mixture of gases under pressure of from 0.1 to 25 MPa is passed through a column packed with aluminium oxide with with a specific surface area not lower than 50 m^2/g,

b) the ammonia or mixture of gases is then passed through a column packed with CaO, NaOH, KOH or an NaOH/KOH melt, separately or in a mixture, at 20 to 70°C and under pressure of from 0.1 to 25 MPa,

c) next, the ammonia or mixture of gases is passed at 170-425°C through a column packed with activated carbon having a specific area of 100÷3000 m^2/g with sodium, potassium, caesium, magnesium, calcium, strontium, barium or cerium nitrates(V) or nitrates(III) deposited on its surface separately or in a mixture, and activated before use with a stream of an inert gas or hydrogen, or their mixture, with a pressure of 0.1-25 MPa and at 250-700°C,

the aforementioned steps being realised in a serial process at a gas stream flow rate in the range of 100 dm^3/h to 1000 m^3/h.

2. A method, according to claim 1, characterised in that for purification of ammonia, additionally a preliminary stage of methane removal from above the liquid ammonia is applied by removal of the gas from above the liquid in the amount of 1-100 dm^3/h.
3. A method, according to claim 1 or 2, characterised in that in stage a) and b), ammonia under pressure of from 0.1 to 0.8 MPa is introduced to the columns.
4. A method, according to claim 1, characterised in that in stage c), a mixture of gases is passed through a column under pressure of from 0.1 to 25 MPa.
5. A method, according to claim 1 or 2, characterised in that in stage c), ammonia is passed through a column under pressure of from 0.1 to 0.8 MPa.
6. A method, according to claim 1 or 2, characterised in that the column packing of stage a) is regenerated by passing a stream of an inert gas or hydrogen or a mixture of these gases through it at 200-700°C.

7. A method, according to claim 1 or 2, characterised in that the column packing of stage c) is regenerated by passing a stream of an inert gas or hydrogen or a mixture of these gases through it at 250-700°C.

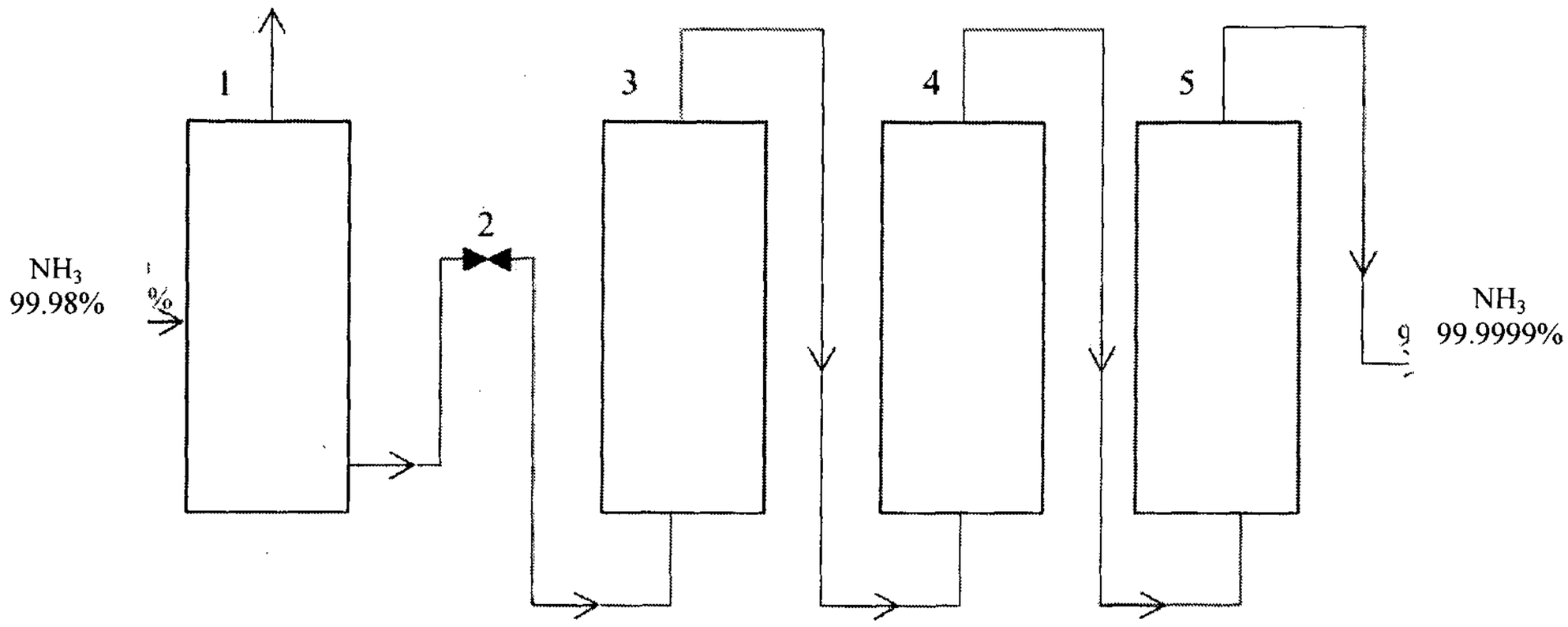


Fig. 1. Block diagram of the system according to Example 1.

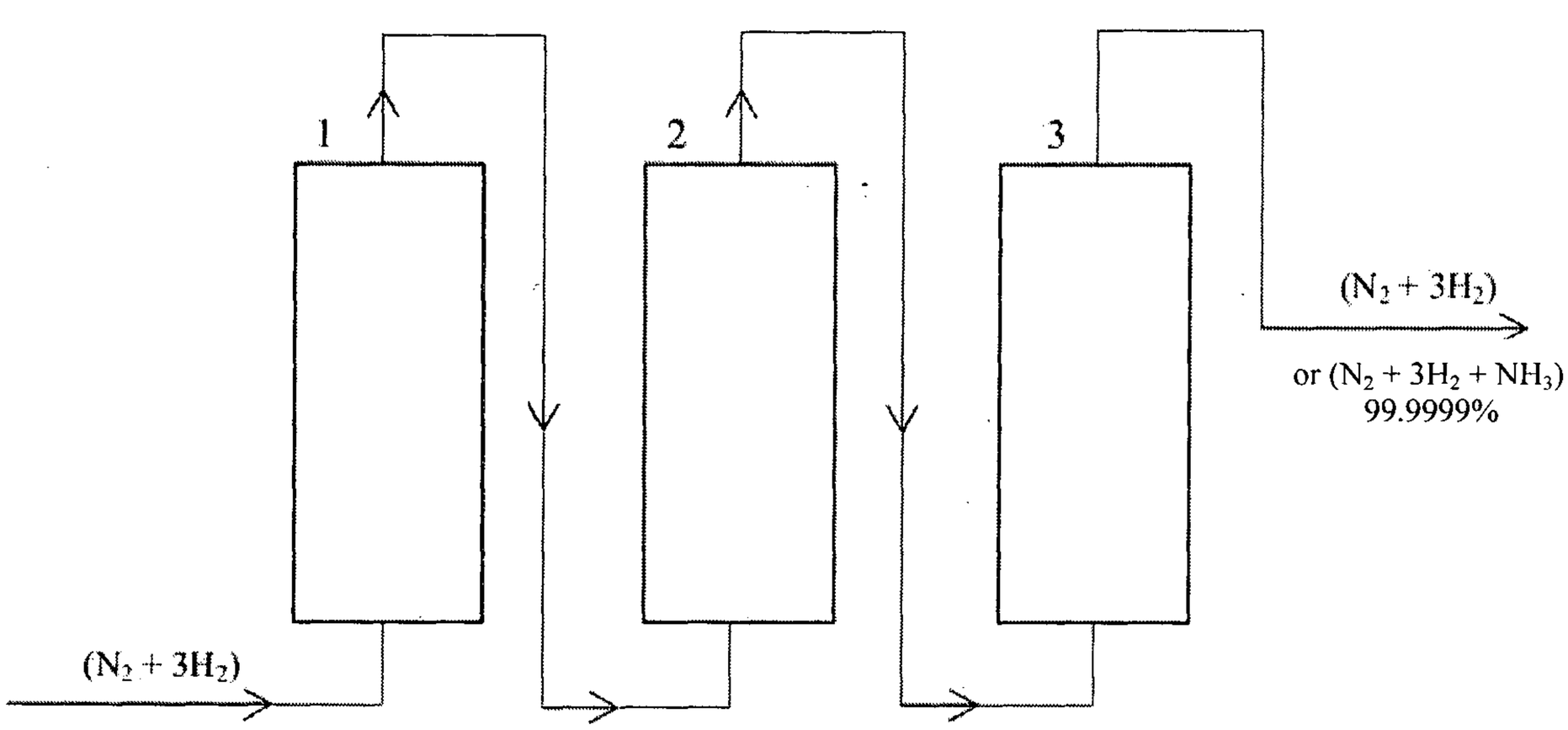


Fig. 2. Block diagram of the system according to Examples 2 and 3.

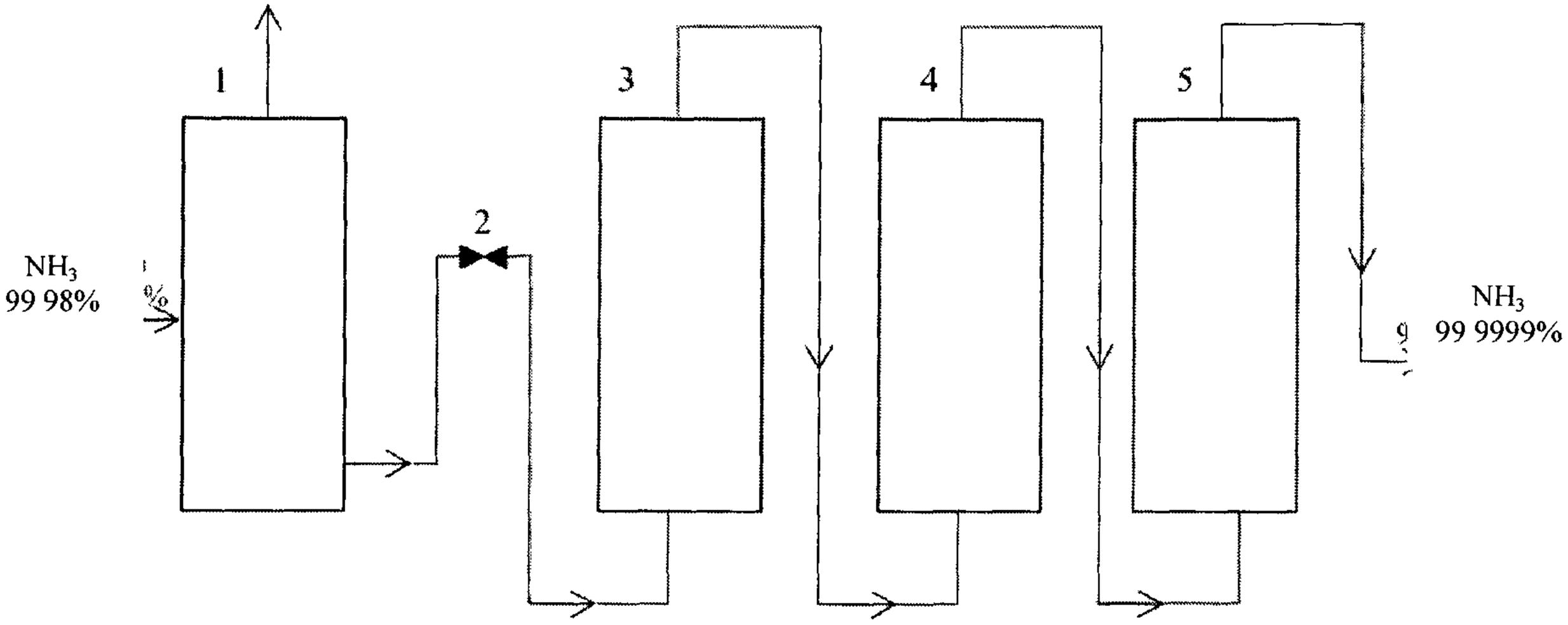


Fig. 1. Block diagram of the system according to Example 1.