the synthesis yields, avoiding costly treatments of the method effluents and improving the quality of the final product.

In one aspect, there is provided a method for preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and hydrocyanic acid (HCN), which comprises at least the following steps:

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods,

and HMTBN or HMSeBN is recovered.

It has been found that by combining determined values of the ratio of HCN to MTP and determined values of the pH of the reaction medium in the synthesis and extraction of the HCN, respectively, according to the above method, it is managed to promote the consumption of MTP in the reaction medium, which makes it possible to recover a stream of HMTBN or HMSeBN containing no or very little aldehyde and HCN. This method further has a major advantage in that to be implemented, the conventional production line can be adapted without substantial transformation.

The adjustment of the values respectively of the ratio of HCN to MTP and of the pH of the reaction medium, in the first step of the method, is necessary to promote the formation of the HMTBN or the HMSeBN, with a residual MTP concentration as low as possible.

With regard to the ratio of HCN to MTP, it is known that the equilibrium of the reaction leads to a low residual concentration of MTP when it is greater than 1. According to the disclosure, it is determined at a value of at least 1; advantageously this value remains close to 1, it can in particular vary from 1 to 2, the value of 2 having to be considered as maximum since beyond that the excess of HCN is highly detrimental economically. The pH of the reaction medium is determined at a value of at least 3.5, but it is preferably at least 4 and even better still at least 5, for an optimal reaction, which is an important parameter during the implementation of this synthesis on an industrial scale.

Before discussing the disclosure in detail, certain terms and expressions used in this text are defined.

By «value greater than or equal to» or «value of at least», is meant that the upper limit is obviously not unlimited. As previously said, the reaction of the MTP with the HCN is known to those skilled in the art and it is up to their general knowledge to estimate the value beyond which the concerned step can no longer be carried out.

any mixture of thereof), evaporation, distillation, membrane methods. In a preferred variant of the disclosure, the evaporation is used.

The extraction of the HCN makes it possible to recycle it at the step of reaction with the aldehyde. It can be directly recycled, it can also be treated by one or more operations before being reintroduced into the reaction medium.

The method of the disclosure can be carried out continuously, which is moreover a preferred mode of use of this method.

As previously stated, the applications of a method of the disclosure comprise the production of methionine, selenomethionine, 2-hydroxy-4-methylthiobutyric acid (HMTBA) and 2-hydroxy-4-methylselenobutyric (HMSeBA),

Thus, the disclosure provides a method for the production of methionine or selenomethionine, starting respectively from 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or from 2-hydroxy-4-methylselenobutyronitrile (HMSeBN), the method comprising at least the following steps:

the HMTBN or the HMSeBN is prepared by a method as defined above, generally or in any one of its variants, and

the HMTBN or HMSeBN is converted into methionine or selenomethionine, respectively, by one of the following ways:

a) converting HMTBN or HMSeBN directly into methionine or selenomethionine; by way of example, this conversion can be carried out in the presence of at least water and of a catalyst comprising at least one of alumina, titanium dioxide and zirconia, and optionally, even preferably in presence of ammonia, or

b) reacting HMTBN with NH_3 and CO_2 to produce methionine hydantoin which is saponified with a base such as NaOH, K_2CO_3, to produce Na or K methionine; this methionine is then acidified to form methionine,

as described for example in US5990349A, or

c) converting HMTBN or HMSeBN to 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or AMSeBN is converted into 2-amino-4-methylthiobutyramide (AMTBM) or 2-amino-4-methylselenobutyramide (AMSeBM), then

the AMTBM or AMSeBM is hydrolyzed to methionine or selenomethionine,

as described for example in WO01/60790A1, or

d) converting HMTBN or HMSeBN into 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or AMSeBN is converted into methionine or selenomethionine.

In another aspect, there is provided a method for producing the methionine or the selenomethionine, respectively from the 2-hydroxy-4-methylthiobutyronitrile

(HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN), characterized in that it comprises the following steps:

i) preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and from hydrocyanic acid (HCN), in which

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods, and

ii) the HMTBN or HMSeBN is converted into methionine or selenomethionine, respectively, by one of the following ways:

a) the HMTBN or the HMSeBN is converted directly to methionine or selenomethionine, or

b) the HMTBN is reacted with NH_3 and CO_2 to produce methionine hydantoin which is saponified with a base such as NaOH, K_2CO_3, to produce Na or K methionine; this methionine is then acidified to form methionine, or

c) the HMTBN or the HMSeBN is converted into 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or the AMSeBN is converted into 2-amino-4-methylthiobutyramide (AMTBM) or 2-amino-4-methylselenobutyramide (AMSeBM), then

the AMTBM or AMSeBM is hydrolyzed to methionine or selenomethionine, or

d) the HMTBN or the HMSeBN is converted into 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or the AMSeBN is converted into methionine or selenomethionine.

By way of example, the conversion of AMTBN or AMSeBN into methionine or selenomethionine, respectively, according to way d) can be carried out in the

presence of at least water and of a catalyst comprising at least one alumina, titanium dioxide and zirconia, and optionally in the presence of ammonia.

The disclosure also provides a method for producing the 2-hydroxy-4-methylthiobutyric acid (HMTBA) or the 2-hydroxy-4-methylselenobutyric acid (HMSeBA), respectively from the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN), the method comprising at least the following steps:

preparing the HMTBN or the HMSeBN by a method as defined above, generally or in any one of its variants, and

converting the HMTBN or HMSeBN to HMTBA or HMSeBA.

In another aspect, there is provided a method for producing the 2-hydroxy-4-methylthiobutyric acid (HMTBA) or 2-hydroxy-4-methylselenobutyric acid (HMSeBA), starting respectively from 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or 2-hydroxy-4-methylselenobutyronitrile (HMSeBN), characterized in that it comprises the following steps:

i) preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and from hydrocyanic acid (HCN), in which

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods, and

the HMTBN or the HMSeBN is converted into HMTBA or HMSeBA.

By way of example, the HMTBN or HMSeBN is converted into HMTBA or HMSeBA, in the presence of at least water, a weak acid such as acetic acid, formic acid and propionic acid, and a catalyst comprising at least one of alumina, titanium dioxide and zirconia.

The disclosure and its advantages are illustrated in the examples below.

<u>Example 1: Synthesis of HMTBN according to the invention in a molar ratio of HCN: MTP of 1.1: 1</u>

The HMTBN synthesis is carried out by bringing a stream of gaseous HCN containing 10% HCN, 61% N_2, 1% CO_2, 4% CO and 24% water, expressed as mass percentages, into contact with Liquid MTP. The molar ratio is 1.1:1. The medium is

buffered at pH=5 with a citric acid/sodium citrate mixture and the reaction takes place at 70°C.

The obtained HMTBN solution contains 70.5% (mass) of HMTBN, 4000 ppm of HCN, 1000 ppm of MTP and 29% (mass) of water.

The pH of this mixture is lowered to 2 by the sulfuric acid. The HCN is extracted from the mixture by evaporation, by heating said mixture to 65°C at 250 mbar. The final medium contains only 65 ppm of HCN and 1200 ppm of MTP, 72% (mass) of HMTBN and 27.9% (mass) of water.

The vapors are partly condensed. The remaining gases composed of 75% (mass) HCN, 9% (mass) air and 16% (mass) water are returned with the HCN stream to the synthesis.

The liquid composed of 97% (mass) water, 0.2% (mass) MTP and 2.8% (mass) HCN is returned with the MTP to the synthesis.

<u>Example 2: Synthesis of HMTBN according to the invention in a molar ratio of HCN: MTP of 1.05: 1</u>

CLAIMS

1. A method for preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and from hydrocyanic acid (HCN), characterized in that,

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods,

and the HMTBN or the HMSeBN is recovered.

2. The method according to claim 1, characterized in that the molar ratio of the HCN to MTP is adjusted to a value greater than or equal to 1.02.

3. The method according to claim 1 or 2, characterized in that the pH is adjusted and maintained at a value greater than or equal to 4, preferably greater than or equal to 5.

4. The method according to any one of the preceding claims, characterized in that it is carried out at a temperature ranging from 50 to 110°C.

5. The method according to any one of the preceding claims, characterized in that the pH is adjusted and maintained by a buffer solution selected from the pairs citric acid/sodium citrate, citric acid/caustic soda, sodium citrate/ phosphoric acid.

6. The method according to any one of the preceding claims, characterized in that, in the second step, the pH of the reaction medium is lowered to a value less than or equal to 2.2, in particular to a value less than or equal to 2, or even at a value less than or equal to 1.5.

7. The method according to any one of the preceding claims, characterized in that the pH of the reaction medium is lowered by an acid selected from sulfuric acid, nitric acid, hydrochloric acid and any mixture thereof.

8. The method according to any one of the preceding claims, characterized in that the extracted HCN is recycled in said method.

9. The method according to any one of the preceding claims, characterized in that it is continuously carried out.

10. A method for producing the methionine or the selenomethionine, respectively from the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-

4-methylselenobutyronitrile (HMSeBN), characterized in that it comprises the following steps:

i) preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and from hydrocyanic acid (HCN), in which

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods, and

ii) the HMTBN or HMSeBN is converted into methionine or selenomethionine, respectively, by one of the following ways:

a) the HMTBN or the HMSeBN is converted directly to methionine or selenomethionine, or

b) the HMTBN is reacted with NH_3 and CO_2 to produce methionine hydantoin which is saponified with a base such as NaOH, K_2CO_3, to produce Na or K methionine; this methionine is then acidified to form methionine, or

c) the HMTBN or the HMSeBN is converted into 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or the AMSeBN is converted into 2-amino-4-methylthiobutyramide (AMTBM) or 2-amino-4-methylselenobutyramide (AMSeBM), then

the AMTBM or AMSeBM is hydrolyzed to methionine or selenomethionine, or

d) the HMTBN or the HMSeBN is converted into 2-amino-4-methylthiobutyronitrile (AMTBN) or 2-amino-4-methylselenobutyronitrile (AMSeBN),

the AMTBN or the AMSeBN is converted into methionine or selenomethionine.

11. The method according to claim 10, characterized in that way a) is carried out in the presence of at least water and a catalyst comprising at least one of alumina, titanium dioxide and zirconia, and optionally in the presence of ammonia.

12. The method according to claim 10, characterized in that way d) is carried out in the presence of at least water and a catalyst comprising at least one of alumina, titanium dioxide and zirconia, and optionally in the presence of ammonia.

13. A method for producing the 2-hydroxy-4-methylthiobutyric acid (HMTBA) or 2-hydroxy-4-methylselenobutyric acid (HMSeBA), starting respectively from 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or 2-hydroxy-4-methylselenobutyronitrile (HMSeBN), characterized in that it comprises the following steps:

i) preparing the 2-hydroxy-4-methylthiobutyronitrile (HMTBN) or the 2-hydroxy-4-methylselenobutyronitrile (HMSeBN) from 3-methylthiopropanal (MTP) or 3-methylselenopropanal (MSeP), respectively, and from hydrocyanic acid (HCN), in which

the molar ratio of HCN to MTP or to MSeP is adjusted to a value greater than or equal to 1 and the pH is adjusted and maintained at a value greater than or equal to 3.5, to obtain a reaction medium in which the HMTBN or HMSeBN is formed,

then the pH of the reaction medium is lowered to a value less than or equal to 2.5 and the HCN is extracted from the reaction medium, the extraction is performed by stripping, evaporation, distillation or membrane methods, and

the HMTBN or the HMSeBN is converted into HMTBA or HMSeBA.

14. The method according to claim 13, characterized in that the HMTBN or the HMSeBN is converted into HMTBA or into HMSeBA, respectively, in the presence of at least water, a weak acid and a catalyst comprising at least one of alumina, titanium dioxide and zirconia.