(19) IPOS INTELLECTUAL PROPERTY OFFICE OF SINGAPORE

(11) Publication number: **SG 192565 A1**
(43) Publication date: **30.09.2013**
(51) Int. Cl: **C07C 319/20, C07C 323/25;**

(12) Patent Application

(21) Application number: **2013049465**
(22) Date of filing: **13.02.2012**
(30) Priority: **US 61/445,781 23.02.2011**

(71) Applicant: **EVONIK DEGUSSA GMBH RELLINGHAUSER STRAßE 1-11, 45128, ESSEN DE**

(72) Inventor: **BUSS, DIETER AM SIONITERHOF 44 50389 WESSELING DE**
STEURENTHALER, MARTIN RAIMUNDSTRAßE 132 60320 FRANKFURT DE
RINNER, MICHAEL R 29 KEPPEL BAY VIEW #10-87 SG-098417 SINGAPORE SG
KRETZ, STEPHAN ÜBER DER KIRCHE 4 63599 BIEBERGEMÜND DE
HASSELBACH, HANS JOACHIM DEUTSCHORDENSTR. 6 63571 GELNHAUSEN DE
FINKELDEI, CASPAR-HEINRICH SCHILLERSTRAßE 15 63755 ALZENAU DE
KÖRFER, MARTIN MAINSTRAßE 20 63796 KAHL DE
ZACCHI, PABLO HEINRICH-HOERLE-STR. 7 50354 HÜRTH DE

(54) **Title:**
METHOD FOR PRODUCING 2-HYDROXY-4-(METHYLTHIO)BUTANENITRILE FROM 3-(METHYLTHIO)PROPANAL AND HYDROGEN CYANIDE

(57) **Abstract:**
Abstract method is disclosed for the production of -hydroxy-4- (methyithio)butyronitrile, in 'which 3-mathyamercaptor oropionaidehyde is reacted with hydrogen cyanide in the ;presence of a base as catalyst in a main reaction zone to form the nitrile and residual amounts of gaseous hydrogen cyanide which leave the main reaction zone are absorbed in an absorption and ;post-reaction zone containing a mixture of 3-methylmercaptobrobionaidehyde and catalyst and optionally 2-hydroxy-4-(methyltheo)butyronitrile and are further reacted.

Abstract

A method is disclosed for the production of 2-hydroxy-4-(methylthio)butyronitrile, in which 3-methylmercapto-propionaldehyde is reacted with hydrogen cyanide in the presence of a base as catalyst in a main reaction zone to form the nitrile and residual amounts of gaseous hydrogen cyanide which leave the main reaction zone are absorbed in an absorption and post-reaction zone containing a mixture of 3-methylmercaptopropionaldehyde and catalyst and optionally 2-hydroxy-4-(methylthio)butyronitrile and are further reacted.

Method for producing 2-hydroxy-4-(methylthio)butanenitrile from 3-(methylthio)propanal and hydrogen cyanide

The invention relates to a catalytic method for the production of 2-hydroxy-4-(methylthio)butyronitrile (MMP-CN) from 3-(methylthio)propanal (= methylmercapto-propionaldehyde, MMP) and hydrogen cyanide (HCN). In particular, the invention describes a process for synthesizing storage-stable MMP-CN using stoichiometric amounts of prussic acid, the product containing superstoichiometric amounts of prussic acid, in relation to the unreacted MMP or to the MMP in equilibrium with MMP-CN.

2-Hydroxy-4-(methylthio)butyronitrile (MMP-cyanohydrin) is an intermediate for the synthesis of D,L-methionine and the methionine hydroxyl analog 2-hydroxy-4-methylthiobutyric acid (MHA). Methionine is an essential amino acid which is used, inter alia, as supplement in feedstuffs. MHA is a liquid methionine substitute having low bioavailability.

Prior art

From MMP, by reaction with hydrogen cyanide (prussic acid), MMP-cyanohydrin (2-hydroxy-4-(methylthio)butyronitrile) may be produced using suitable catalysts. Suitable catalysts are, e.g., pyridine or triethylamine. By hydrolysis of MMP-cyanohydrin with, e.g., mineral acids, MHA is obtained. Methionine is formed by reaction of MMP-cyanohydrin with ammonium hydrogencarbonate, with formation of hydantoin, which can be saponified with a base, e.g. potassium carbonate or sodium hydroxide. Methionine is liberated with carbon dioxide or sulfuric acid.

It is known, for example, from the patent US A 4 960 932, to produce methionine by a four-stage method. In the first step, by addition of HCN to MMP in the presence of triethylamine, the MMP-cyanohydrin is produced. The amount of HCN used corresponds to 1.05 mol in relation to the amount of MMP used. Then, the MMP-cyanohydrin, in a second step, is reacted with ammonia, whereby 2-amino-4-methylthiobutyronitrile is formed which, in a third step, is then hydrolyzed in the presence of a ketone and an alkali metal hydroxide, forming methylthiobutyramide which is finally saponified to form an alkali metal methioninate.

In the case of production of 2-hydroxy-4-methylthiobutyric acid (MHA), the 2-hydroxy-4-methylthiobutyronitrile is obtained by reacting MMP and HCN in a medium that contains pyridine or an amine (see patent US A 2 745 745, column 2, lines 52 to 55). Excess HCN is merely distilled off, e.g. in a vacuum. The resultant 2-hydroxy-4-methylthiobutyronitrile is then hydrolyzed with sulfuric acid, whereby the amide of 2-hydroxy-4-methylthiobutyric acid is directly formed, and finally 2-hydroxy-4-methylthiobutyric acid is formed. A similar method is also described in EP A 330 527 A1 or in US 4 912 257.

In addition, in WO 96/40631 A1, the production of MMP-cyanohydrin by reacting MMP with hydrogen cyanide in the presence of a suitable addition reaction catalyst is described. There it was found that triisopropanolamine, nicotinamide, imidazole, benzimidazole, 2-fluoropyridine, poly-4-vinylpyridine, 4-dimethylaminopyridine, picoline and pyrazine can serve as addition reaction catalysts for producing MMP-cyanohydrin. Furthermore, trialkylamines having three to eighteen carbon atoms in each of the alkyl

substituents bound to the nitrogen atom and tertiary amines in which at least one of the non-hydrogen substituents that are bound to the nitrogen atom according to the above description contains an aryl group can also serve for catalyzing the reaction between MMP and hydrogen cyanide to form MMP-cyanohydrin.

Preferably, in this case, the hydrogen cyanide is used in a molar excess of about 2%, based on MMP.

WO 2006/015684 A2 finally discloses a method for, in particular, continuous production of MMP or of MMP-cyanohydrin in which in each case heterogeneous amine catalysts are used for the addition reaction.

In addition, it is known from the patent US 5 756 803 to react an aldehyde with hydrogen cyanide in the presence of a buffer, by means of which the pH of the solution can be set above 4, amines being excluded. Quite generally, as buffer, mixtures of alkali metal salts of acids and acids, or mixtures of acids and alkali metal hydroxides can be used. The buffer is used in order firstly to avoid the decomposition of the starting materials and of the desired product and secondly to neutralize the acids used for stabilizing hydrogen cyanide. Likewise, here, HCN is added in a molar excess to the MMP, the molar excess preferably being in the range from 2% to 5%. In the reaction of MMP with HCN in the presence of the customarily used bases, although these increase the reaction rate under the conditions specified, they rapidly lead to a decomposition of the cyanohydrin formed and to decomposition of the aldehyde used at the start, forming a highly discolored solution.

In order to recover the residual amounts of unreacted HCN and MMP contained in the exhaust gas of the reactive absorber, said unreacted HCN and MMP are scrubbed using a water scrubber, the scrubbing water passing into the product. The water content in the product is approximately 48% by weight.

The substantial disadvantages of the methods previously described in the literature are that for achieving a high MMP-CN yield, high molar excesses of HCN have to be used. The excess amounts of HCN are lost in the methods described and are a great economic disadvantage. Furthermore, the catalysts used in the methods described also promote the formation of unwanted byproducts from the aldehydes used, which lead to contamination of the product which cannot be tolerated. One approach to solving this problem of formation of byproducts is described in US 5 756 803 with, of course, large amounts of water passing into the product, which firstly, for production of methionine, need to be at least partially removed and which secondly again promote the decomposition of the MMP-cyanohydrin which in each case is a not inconsiderable disadvantage. Therefore, the product described in US patent 5 756 803 is not storage stable and, for storage and in particular for transport, must be processed in a complex manner by means of removal of the water by distillation, which is a great economic disadvantage of the method.

Object of the invention

It was the object of this invention to provide a catalytic method which both catalyzes the reaction of aldehyde, in particular of MMP with hydrogen cyanide, and prepares a

storage-stable cyanohydrin in which the method should at the same time show marked improvements with regard to yields with respect to the aldehyde used and to the hydrogen cyanide.

Description of the invention

These and further objects are achieved by a method for the production of 2-hydroxy-4-methylthiobutyronitrile, in which 3-(methylmercapto)propionaldehyde is reacted with hydrogen cyanide in the presence of a base as catalyst in a main reaction zone to form the nitrile and residual amounts of gaseous hydrogen cyanide (HCN), which leave the main reaction zone are absorbed in an absorption and post-reaction zone containing a mixture of 3-(methylmercapto)-propionaldehyde and catalyst and optionally 2-hydroxy-4-(methylthio)butyronitrile and are further reacted.

The residual content of HCN reacts, owing to the absorption or condensation with the aldehyde to form the cyanohydrin. Owing to the effective removal of the HCN from the gas phase, it is possible, in contrast to the methods known in the literature to use a molar ratio of hydrogen cyanide to aldehyde of 0.99 to 1.01, which is a great economic advantage for the method.

The invention relates, in particular, to a method for the addition reaction of hydrogen cyanide to MMP in the presence of a base, in particular an amine, wherein the method is arranged in such a manner that residual contents of gaseous hydrogen cyanide are absorbed outside a main reaction zone at temperatures of about 0°C to 25°C into a liquid mixture of the aldehyde MMP and the reaction product

from MMP with hydrogen cyanide and catalyst and then further reacted with MMP.

By means of the method according to the invention, in general, aldehydes containing 1 to 6 carbon atoms which if desired are substituted with alkyl, alkoxy or alkylthio, are advantageously reacted with hydrogen cyanide.

It is preferred here that the mixture contained in the absorption and post-reaction zone originates at least partially from the main reaction zone. A dilution with foreign materials or foreign solvents is thereby prevented, in contrast to US 5,756,803.

The main reaction zone can contain either a stirred reactor or a loop reactor. Both embodiments lead to a rapid and good mixture and a rapid conversion of MMP and HCN.

The main reaction zone can also additionally contain a jet pump. This leads to a further intensification of mixing of the components and can be used concomitantly particularly advantageously for drawing HCN into the main reaction zone.

The post reaction can proceed as stated above between an HCN-containing gas and a liquid. It then takes place in an absorption and post-reaction zone which preferably contains a device for contacting a gas with a liquid, in particular a column such as, for example, a tray column, a packed-bed column, a bubble-column reactor, a droplet column or optionally a reactor having a mechanically agitated container, or a submerged jet reactor.

The absorption zone and the post-reaction zone can also be part of a loop reactor, which effects high mixing and rapid reaction of the components.

In the method according to the invention, substantially gaseous hydrogen cyanide is introduced into the main reaction zone, preferably a hydrogen-cyanide-containing product gas from a hydrogen cyanide production process.

The hydrogen cyanide content of the gas mixture used ranges from 1 to 99% by weight, preferably from 5 to 75% by weight, particularly preferably 6-22% by weight. The hydrogen cyanide is produced, in particular, by the Andrussow method as per DE 102007034715A1 or else by what is termed the BMA method in German ("**B**lausäure aus **M**ethan und **A**mmonik" [prussic acid from methane and ammonia]) as per DE 1041476 (reactor). Both methods are also described in Ullmann´s Encyclopedia of Industrial Chemistry, 1987 VCH-Verlagsgesellschaft mbH, chapter "Cyano Compounds Inorganic", section 1.2.1-1.2.2. The ammonia present is removed in each case from the product gas. The product gas from the Andrussow method (Andrussow gas) contains, after the removal of ammonia, typically about 10% by weight of hydrogen cyanide, in contrast, the product gas from the BMA method (BMA gas) contains about 70% by weight of hydrogen cyanide.

Thus, the typical product gas compositions of the Andrussow method have approximately the following contents: 10.3% by weight of HCN, 3.7% by weight of H_2O, 1.3% by weight of H_2, 75.8% by weight of N_2, 0.4% by weight of O_2, 6.3% by weight of CO, 0.6% by weight of CO_2, 0.4% by weight of CH_4, 1.3% by weight of Ar, those of the BMA method about 68.3% by

weight of HCN, 6.7% by weight of H_2O, 17.3% by weight of H_2, 3.6% by weight of N_2, 4% by weight of CH_4.

The direct use of the product gas has the considerable advantage that no upstream and energy-intensive liquefaction of the hydrogen cyanide need proceed and with corresponding coupling to a plant for producing hydrogen cyanide gas, considerable capital costs in corresponding process steps for the absorption and distillation of HCN are saved. The further gas fractions in addition to HCN surprisingly do not have a disadvantageous effect on the cyanohydrin yield.

The residual gas of the MMP-cyanohydrin production and hydrogen cyanide production can then be utilized jointly or burnt. In the latter case, the resultant energy can be reused for operating both methods, which means more degrees of freedom and a considerable economic advantage.

A preferred embodiment of the method according to the invention and a corresponding device are outlined in **Fig. 1**, which is described in more detail hereinafter:

When a tray column or a packed-bed column is used for the reactive absorption, the gas flow which contains the prussic acid is fed into the bottom phase (A) of the column (C) or preferably already contacted with the aldehyde solution via a gas blower (B), which aldehyde solution is circulated (8) by means of a pump (I). The temperature in the bottom phase of the column is set via a heat exchanger (J). The bottom phase (A) and the column (C), in particular, serve as the main reaction zone, the column C being able to be heated/cooled separately by means of a

heat exchanger (K). In this case the temperature of the streams (7) and (8) is selected in such a manner that the heat of reaction can be removed with cooling water corresponding to the ambient temperature and the reaction between aldehyde and HCN in column part (C) is 80 to 99.9% complete.

The aldehyde can be fed separately or together with the catalyst ((2),(3)). Preferably, the aldehyde or the aldehyde/catalyst mixture (2) + (3) is mixed with a substream (6) from the absorption and condensation part (E) of the column which is taken off from an intermediate bottom phase (D). The catalyst can also be fed, e.g., via the pathway (4). In this case, the catalyst should, via the pathway (13), also arrive in part in the top circuit. The residual amounts of HCN present in stream (6) are reacted with the supplied aldehyde in the dwell time vessel (G), the (second) post-reaction zone, completely or virtually completely to the cyanohydrin. Thereafter, the stream is cooled to 0°C to 25°C in the heat exchanger (H) in order to ensure condensation/absorption of HCN which is as complete as possible. In particular, the intermediate bottom phase (D), the absorption and condensation part (E) and the dwell time vessel (G) serve as absorption and post-reaction zone. Owing to the amounts of cyanohydrin present in the stream (5), and the cooling which is performed, the residual gases exiting at the column top also contain only very low residual amounts of the aldehyde, and so no additional scrubbing for recovery of the aldehyde from the residual gas is required. The cyanohydrin concentration can be set via corresponding metering from the column bottom phase (13), preferably in the range from 10% by weight to 70% by weight in stream (5). The purified gases are advantageously

passed into a combustion unit. The product exiting with stream (9) has a molar ratio of hydrogen cyanide to unreacted aldehyde of greater than 1, which contributes substantially to stabilizing the product. In addition, the product is clear and only slightly discolored, which underlines the extraordinarily high selectivity of this process procedure.

After passage through a post reactor (L), in which any residual fractions of the aldehyde present are reacted to completion to achieve equilibrium with hydrogen cyanide, the resulting product stream is mixed with an acid. For this purpose, a suitable mixing element (M) is used. The pH of the product (stream (11)) that is set in this case is between 1 and 4, preferably between 2 and 3.

If the aldehyde is MMP, as shown in Fig. 1, the MMP starting material stream of the method described generally has a small content of methylmercaptan (MC), the predomiant part of which would pass into the exhaust gas stream (12). This excess MC can also optionally be reacted with acrolein, which can be fed to the method, e.g. via stream (14), to form MMP and in succession with HCN to form MMP-CN and the yield thereby further increased.

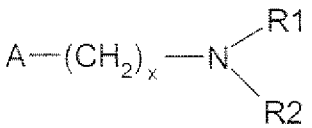
In the method according to the invention, the catalyst used can be low-molecular-weight or heterogeneous amines or solutions of inorganic bases, or mixtures of acids and low-molecular-weight amines. These are also needed in order to set the optimum pH range of approximately 4.5 to 6.0, preferably 5.0-5.5, that is required for the reaction, which is measured using a pH electrode ("Aquatrode Plus with Pt 1000" type, manufacturer: Metrohm Schweiz AG)

directly in the cyanohydrin having a typical water content of 2-14% by weight. The measurements are performed at a temperature of about 23° in a stirred vessel, the pH measurement being temperature-compensated. For following the reaction conditions close in time, and for elimination of measurement errors, at intervals of one hour, in each case the pH is measured 4 times with formation of the mean value, each measurement taking approximately 30 seconds. The measurement can, however, also be carried out directly during the reaction online in the reaction system at the temperature that is set there and converted to the pH at 23°C, which further simplifies the process control.

Low-molecular-weight amines, preferably having 1 to 36 carbon atoms, have the particular advantage of virtually unlimited miscibility with the reaction medium, which in turn favors a rapid reaction.

Low-molecular-weight amines which are preferred in this case are tri-(C_1-C_{12}-alkyl)amines, preferably triethylamine or triisopropanolamine, dialkylaralkylamines, preferably dimethylbenzylamine, dialkylarylamines, preferably N,N-dimethylaniline, heterocyclic amines, preferably nicotinamide, imidazole, benzimidazole, 2-fluoropyridine, 4-dimethylaminopyridine, picoline or pyrazine.

Alternatively, heterogeneous amines of the general formula



formula I

or polyvinylpyridine can also be used, wherein

R_1 and R_2 are hydrogen, alkyl having chain lengths between C_1 and C_{12}, aryl or heteroaryl;
R_1 can be different from R_2
X is a number between 0 and 6, and
A is a natural or synthetic resin, preferably a polystyrene. These and the advantages associated therewith, such as, for instance, easier separability, low entrainment in subsequent reaction stages, are already described in WO 2006/015684.

It is preferred in this case that the catalyst according to formula I is a polymer-bound base selected from the group of the homologous dialkylaminoalkylpolystyrenes or dialkylaminomacroreticular resins.

It is particularly preferred that the catalyst according to formula I is diethylaminoethylpolystyrene, diethylaminomethylpolystyrene, dimethylaminomethylpolystyrene, diethylaminomethylmacroreticular resin or dimethylaminoethylpolystyrene.

The inorganic base used can advantageously be alkali metal hydroxide, preferably NaOH or KOH, alkali metal cyanide, preferably NaCN or KCN, alkali metal carbonate, preferably Na_2CO_3 or K_2CO_3, or alkali metal hydrogencarbonate, preferably $NaHCO_3$ or $KHCO_3$, alone or in mixed form. These have the advantage of particularly high catalytic activity which in turn favors a very rapid reaction and also the low potential interference of the low salt fractions resulting therefrom in the subsequent method. However, here, extremely good mixing and temperature control must be ensured, so that no significant byproduct formation proceeds.

cyanohydrin is advantageous. This second post-reaction zone is operated at a similar temperature to the main reaction zone of 20°C to 80°C, preferably 40°C to 70°C, particularly preferably 45°C to 65°C. In this manner a rapid and virtually quantitative completion of the reaction of HCN and MMP to form MMP-cyanohydrin shortly upstream of the product discharge is ensured.

The method according to the invention is advantageously operated at an absolute pressure of 0.9 to 5 bar, preferably 1.0 to 3 bar, particularly preferably 1 to 1.5 bar. This has the effect that rapid degassing of the absorbed HCN from the solution and corresponding losses are prevented thereby.

The method according to the invention is, in addition, characterized in that a molar ratio of prussic acid to 3-(methylthio)propanal of 0.98 to 1.03, preferably 0.99 to 1.01 can be set. Firstly, losses of prussic acid are avoided thereby which, especially on an industrial scale, are a great economic disadvantage. Secondly, unwanted prussic acid breakdown products such as, e.g., polymeric prussic acid or the saponification product formic acid which has corrosive properties against various metallic materials, are avoided and corresponding disadvantageous effects in the downstream method stages to methionine are avoided thereby.

In the method according to the invention, preferably, a weight ratio of catalyst to 3-(methylthio)propanal of 0.00005 to 0.002 is used, particularly preferably 0.0001 to 0.001. This has the effect of a particularly low byproduct formation at the same time as a high reaction rate.

The method according to the invention can optionally be carried out batchwise, semicontinuously, or continuously, the continuous embodiment being particularly economical to operate on an industrial scale of greater than 10 000 tons/a.

The MMP-cyanohydrin produced according to the invention has the typical following composition:

MMP-CN: 86-97% by weight,

MMP: 0-1% by weight,

HCN: 0.05-0.5% by weight,

H_2O: 2-14% by weight,

Oligomers: 0.01-0.1% by weight.

The molar yields based on MMP are typically 99.50 to 99.99%.

The reaction product containing methylthiopropionaldehyde cyanohydrin (MMP-cyanohydrin) obtained in accordance with the method according to the invention can, particularly advantageously, be used directly for producing methionine and 2-hydroxy-4-methylthiobutyric acid. For this purpose, it is either aminated (aminonitrile pathway) or reacted with a mixture of ammonia and carbon dioxide (hydantoin pathway), in order to form methionine or hydrolyzed directly to form 2-hydroxy-4-methylthiobutyric acid (methioninehydroxy analogs, MHA). It has, furthermore, surprisingly been found that high-boiling MMP oligomers already present in MMP are for the most part reacted in the

method according to the invention to form the desired MMP-cyanohydrin. This is shown in that, e.g., the residue formed in the distillation of the products is markedly less after the reaction than before the reaction to form the MMP-cyanohydrin.

The present invention will be described in more detail with reference to the examples hereinafter.

Analytical methods used:

The H_2O content in MMP-CN was determined by the method of titration with biamperometric indication of the end point (Karl-Fischer titration).

For this purpose, 20-30 ml of titration medium (e.g. Hydranal Solvent 5, Fluka) were charged into the titration vessel and titrated to dryness using titration agent (e.g. Hydranal Titrant 5, Fluka). A sample quantity of approximately 500 mg was added to the initial charge that had been titrated to exhaustion (plastic disposable syringe) and titrated to the end point with titration agent. The exact sample weight was determined by differential weighing.

The procedure of this standard method is known to those skilled in the art (see, e.g., P. A. Bruttel, R. Schlink: *Wasserbestimmung durch Karl-Fischer-Titration* [Water determination by Karl-Fischer titration] Metrohm AG).

The free prussic acid content of the product was determined by the principle of ion chromatography (IC) using amperometric cyanide detection at an Ag working electrode,

the sample preparation having proceeded by separating off the free prussic acid from the sample matrix by means of preparative column chromatography.

The preparative cyanide removal was performed, e.g., at room temperature, on a PRP-X 300 separation column, 250 mm length × 4.1 mm internal diameter from Hamilton. The mobile phase consisted of a 5 mmolar sulfuric acid. At a flow rate of 1.0 ml/min, 100 µl of the sample solution (0.1 g of sample in 10 ml of mobile phase) were injected. The column eluate from 4 min to 8 min was collected in a 100 ml measuring flask, made up to the mark with ultrapure water and 100 µl were injected into the IC for cyanide determination.

Similarly to the sample solution, an NaCN calibration solution of known content was subjected to the preparative separation by means of column chromatography and 100 µl were injected into the IC for cyanide determination.

The ion-chromatographic cyanide determination was carried out at room temperature, e.g. on a Carbo Pac PA1 separation column, 250 mm in length × 4.0 mm internal diameter from Dionex. The mobile phase consisted of a solution of 1.5 g of sodium chloride and 1 ml of ethylenediamine in 1 l of a 50 mmolar sodium hydroxide solution. At a flow rate of 1.0 ml/min, 100 µl of sample solution or calibration solution were injected. The evaluation was performed by peak area comparison using the external standard method.

The procedure of this standard method is known to those skilled in the art.

As catalysts, advantageously, also mixtures of acids and the abovementioned low-molecular-weight amines can be used, in order to set the pH more readily in the desired range and to be able to stabilize it by the buffer action. Particularly advantageous in this case is the use of organic acids such as short-chain fatty acids, e.g. acetic acid, formic acid, citric acid, and organic sulfonic acids, e.g. trifluoromethanesulfonic acid or the use of mineral acids such as, e.g., sulfuric acid or phosphoric acid, in combination with the low-molecular-weight amines.

According to a further preferred embodiment of the invention, the temperature in the main reaction zone is selected in such a manner that the heat of reaction liberated can be given off to cooling water in accordance with the ambient temperature, which is a further great economic advantage of the method.

Correspondingly, the main reaction zone is operated at a temperature of 20°C to 80°C, preferably from 30°C to 70°C, particularly preferably from 35°C to 65°C. The reaction also proceeds comparatively rapidly in this range.

In the method according to the invention it is further preferred that the absorption and post-reaction zone is operated at a temperature of 0°C to 30°C, preferably from 4°C to 15°C. This ensures a particularly efficient absorption of the hydrogen cyanide and still makes possible thorough reaction of HCN with the MMP to form MMP-cyanohydrin.

Furthermore, the use of a second post-reaction zone just upstream of the product discharge point for the MMP-

The MMP-CN and MMP contents of the product were determined by means of isocratic ion exclusion chromatography on a cation exchanger with subsequent UV detection at 205 nm. The determination was carried out, e.g., on a PRP-X 300 separation column, 250 mm in length × 4.1 mm internal diameter from Hamilton at a temperature of 25°C. The mobile phase consisted of a 5 mmolar sulfuric acid. At a flow rate of 1.0 ml/min, 100 µl of the respective sample solution (0.5 g of sample for MMP determination or 0.06 g of sample for MMP-CN determination in 50 ml of solvent) were injected. The calibration proceeded by injecting suitable calibration solutions (0.5 mg of MMP in 50 ml of solvent, or 50 mg of MMP-CN in 50 ml of solvent).

The solvent consisted of a mixture of 500 µl of 0.5 molar H_2SO_4 and 5 ml of acetonitrile which was diluted to 50 ml with ultrapure water.

The evaluation proceeded by peak area comparison by means of the external standard method.

The procedure of this standard method is known to those skilled in the art.

The components in the HCN-containing starting material gas nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), prussic acid (HCN), water (H_2O), argon (Ar)/oxygen (O_2) (either/or), hydrogen (H_2) (only conditionally) and benzene as internal standard were determined by gas chromatography. The gas chromatograph 6890 (Agilent, based on the HP 6890) was used here. The gas chromatograph for this analysis was equipped with three separation columns: 1. HP-CPWAX 52CB 25m*0.32mm*0.2µm (here

NH3, HCN, water and benzene were separated), 2. molecular sieve 30m*0.32mm*12µm (here H_2, N_2, O_2, CO and methane were separated) and 3. Plot Q 30m*0.32mm*20µm (here CO_2 and benzene were separated), two thermal conductivity detectors (TCD), a pressure measuring unit and a mass flow meter (MFM) for helium. Column 1 was connected via a back injector to the back detector. Columns 2 and 3 were connected by a front injector to the front detector.

The procedure of this standard method is known to those skilled in the art.

The components methylmercaptan (MC) and methylmercaptopropionaldehyde (MMP) and acrolein (AC) of the residual gas exiting from the column top were determined by means of gas chromatography. In this case the gas chromatograph 7890A (Agilent) was used. The gas chromatograph was equipped for this analysis with a separation column (HP-INNOWAX 60m*0.32mm*0.25µm) and a back detector (FID). The procedure of this standard method is known to those skilled in the art.

Example 1

A setup as shown in Fig. 1 was used, having a column of 70 mm in diameter, which was equipped with 2 ordered packings (C) and (E) and which had heights in each case of 2500 and 1700 mm. Between the ordered packings were situated an intermediate bottom phase (D), from which a stream (6) can be taken off for operating a top circuit. Beneath the column was situated the column bottom phase having a volume of 4 liters. The diagram of this device is attached (see Figure 1).

With the stream (1), 8.98 kg/h of crude product gas from the production of hydrogen cyanide by the Andrussow method were fed via the gas blower (B) into the column bottom phase A which contained, based on weight: HCN: 8.87%, H_2O: 3.88%, H_2: 1.33%, N_2: 76.01%, O_2: 1.48%, CO: 5.67%, CO_2: 1.13%, CH_4: 0.39%. The incoming gas was mixed at the jet pump (B) with a circulating stream (8) of 300 kg/h. The temperature of the circulation stream was controlled here in such a manner that in the column bottom phase (A), at a filling state of 50%, a temperature of 50°C prevailed. The feed stream (7) onto the ordered packing (C), at 40 kg/h, had a temperature of 35°C.

The methylthiopropionaldehyde was introduced into the reactor (G) via the feed (2) at a throughput of 2.966 kg/h. The reactor contained, based on weight:

MMP: 96.46%, H_2O: 2.77%, MC: 0.2%. Via the feed line (3), at the same time 0.211 kg/h of a mixture of 99% by weight of MMP in the composition described above and 1% by weight of triethanolamine as catalyst were introduced into the reactor (G). The whole stream (5) consisting of the starting materials and the circulation stream (6) was 40 kg/h in the feed to the upper ordered packing (E) at a temperature of 6°C.

The molar starting material ratio HCN/MMP corresponded to 1. The product left the column bottom phase at 4.20 kg/h and had the following composition, based on weight: MMP-CN: 90.43%, H_2O: 7.82%, MMP: 0.14%, HCN: 0.16%, MC: 0.01%. The exhaust gas left the column top at 8.07 kg/h and had the following composition based on weight: HCN: 0.00%, MMP: 0.07%, MC: 0.05%, H_2O: 1.34%, H_2: 1.48%, N_2: 86.02%, O_2:

1.64%, CO: 6.31%, CO_2: 1.26%, CH_4: 0.44%. The gases were fed to a combustion plant.

Example 2

The setup of Example 1 was used.

With the stream (1), 8.94 kg/h of crude product gas of the production of hydrogen cyanide by the Andrussow method were fed via the gas blower (B) into the column bottom phase A which contained, based on weight: HCN: 8.9%, H_2O: 3.7%, H_2: 1.3%, N_2: 76.3%, O_2: 1.5%, CO: 5.6%, CO_2: 1.1%, CH_4: 0.4%. The incoming gas was mixed at the jet pump (B) with a circulating stream (8) of 280 kg/h. The temperature of the circulation stream was controlled in this case in such a manner that, in the column bottom phase (A), at a filling state of 50%, a temperature of 49.8°C prevailed. The feed stream (7) onto the ordered packing (C) had a temperature of 35°C at 40 kg/h.

The methylthiopropionaldehyde was introduced into the reactor (G) via the feed (2) at a throughput of 2.976 kg/h. It contained, based on weight:

MMP: 96.9%, H_2O: 2.8%, MC: 0.2%. Via the feed line (3), at the same time, 0.2 kg/h of a mixture of 99% by weight of MMP in the above described composition and 1% by weight of triethanolamine as catalyst was introduced into the reactor (G). In addition, 2 kg/h of the bottom phase product were introduced via the pathway (13) into the reactor (G). The whole stream (5) consisted of the starting materials and the circulation stream (6) and the product stream (13) was 42 kg/h in the feed to the upper ordered packing (E) at a

temperature of 5.5°C.

The molar starting material ratio HCN/MMP corresponded to 1. The product left the column bottom phase at 4.25 kg/h and had the following composition, based on weight:

MMP-CN: 90.06%, H_2O: 8.81%, MMP: 0.75%, HCN: 0.21%, MC: 0.01%. The exhaust gas left the column top at 7.88 kg/h and had the following composition based on weight:

HCN: 0.00%, MMP: 0.09%, MC: 0.10%, H_2O: 0.6%, H_2: 1.50%, N_2: 86.60%, O_2: 1.70%, CO: 6.40%, CO_2: 1.20%, CH_4: 0.50%. The gases were fed to a combustion plant.

Claims

1. Method for producing 2-hydroxy-4-(methylthio)butyronitrile, in which 3-methylmercaptopropionaldehyde is reacted with hydrogen cyanide in the presence of a base as catalyst in a main reaction zone to form the nitrile and residual amounts of gaseous hydrogen cyanide which leave the main reaction zone are absorbed in an absorption and post-reaction zone containing a mixture of 3-methylmercaptopropionaldehyde and catalyst and optionally 2-hydroxy-4-(methylthio)butyronitrile and are further reacted.

2. Method according to claim 1, characterized in that the mixture contained in the absorption and post-reaction zone originates at least partially from the main reaction zone.

3. Method according to claim 1, characterized in that the main reaction zone contains a stirred reactor or loop reactor.

4. Method according to claim 3, characterized in that the main reaction zone additionally contains a jet pump.

5. Method according to any one of claims 1 to 4, characterized in that the absorption and post-reaction zone contains a device for contacting a gas with a liquid, preferably a column, in particular a tray column, a packed-bed column, a bubble-column reactor, a droplet column or optionally a reactor having a mechanically agitated container, a submerged jet reactor or a jet pump.

6. Method according to any one of claims 1 to 5, characterized in that the absorption and post-reaction zones are part of a loop reactor.

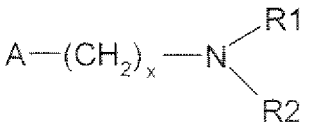
7. Method according to any one of claims 1 to 6, characterized in that substantially gaseous hydrogen cyanide is introduced into the main reaction zone, preferably a hydrogen-cyanide-containing product gas from a plant for producing hydrogen cyanide.

8. Method according to claim 7, characterized in that the hydrogen cyanide content of the gas used is 1 to 99% by weight, preferably 5 to 75% by weight, particularly preferably 6-22% by weight.

9. Method according to any one of claims 1 to 8, characterized in that the catalyst used is low-molecular-weight or heterogeneous amines, solutions of inorganic bases, or mixtures of acids and low-molecular-weight amines.

10. Method according to claim 9, characterized in that the low-molecular-weight amines are tri-(C_1-C_{12}-alkyl)amines, preferably triethylamine or triisopropanolamine, dialkylaralkylamines, preferably dimethylbenzylamine, dialkylarylamines, preferably N,N-dimethylaniline, heterocyclic amines, preferably nicotinamide, imidazole, benzimidazole, 2-fluoropyridine, 4-dimethylaminopyridine, picoline or pyrazine.

11. Method according to claim 9, characterized in that heterogeneous amines of the general formula



formula I

or polyvinylpyridine are used, wherein

R_1 and R_2 are hydrogen, alkyl having chain lengths between C_1 and C_{12}, aryl or heteroaryl;
R_1 can be different from R_2
X is a number between 0 and 6, and
A is a natural or synthetic resin, preferably a polystyrene.

12. Method according to claim 11, characterized in that the catalyst according to formula I is a polymer-bound base selected from the group of homologous dialkylamino-alkylpolystyrenes or dialkylaminomacroreticular resins.

13. Method according to claim 12, characterized in that the catalyst according to formula I is
diethylaminoethylpolystyrene,
diethylaminomethylpolystyrene,
dimethylaminomethylpolystyrene,
diethylaminomethylmacroreticular resin or
dimethylaminoethylpolystyrene.

14. Method according to claim 9, characterized in that the inorganic base used is alkali metal hydroxide, preferably NaOH or KOH, alkali metal cyanide, preferably NaCN or KCN, alkali metal carbonate, preferably Na_2CO_3 or K_2CO_3, or alkali metal hydrogencarbonate, preferably $NaHCO_3$ or $KHCO_3$, alone or in mixed form.

15. Method according to claim 9, characterized in that the acid used in the mixtures of acids and low-molecular-weight amines is organic acids, preferably short-chain fatty acids, in particular acetic acid, formic acid, citric acid, or organic sulfonic acids, preferably trifluoromethanesulfonic acid or mineral acids, preferably sulfuric acid or phosphoric acid.

16. Method according to any one of claims 1 to 15, characterized in that a pH of 4.5 to 6.0 is set, preferably 5.0-5.5, measured using a pH electrode at 23°C and a water content of 2 to 14% by weight in the main reaction zone and the absorption and post-reaction zone.

17. Method according to any one of claims 1 to 16, characterized in that the main reaction zone is operated at a temperature of 20°C to 80°C, preferably 30°C to 70°C, particularly preferably 35°C to 65°C.

18. Method according to any one of claims 1 to 17, characterized in that the absorption and post-reaction zone is operated at a temperature of 0°C to 30°C, preferably 4°C to 15°C.

19. Method according to any one of claims 1 to 18, characterized in that a further post-reaction zone is operated at a temperature of 20°C to 80°C, preferably 40°C to 70°C, particularly preferably 45°C to 65°C, upstream of the MMP-cyanohydrin product discharge site for completing the reaction of HCN and MMP to form the MMP-cyanohydrin.

20. Method according to any one of claims 1 to 19, characterized in that an absolute pressure of 0.9 to 5 bar, preferably 1.0 to 3 bar, particularly preferably 1 to 1.5 bar, is employed.

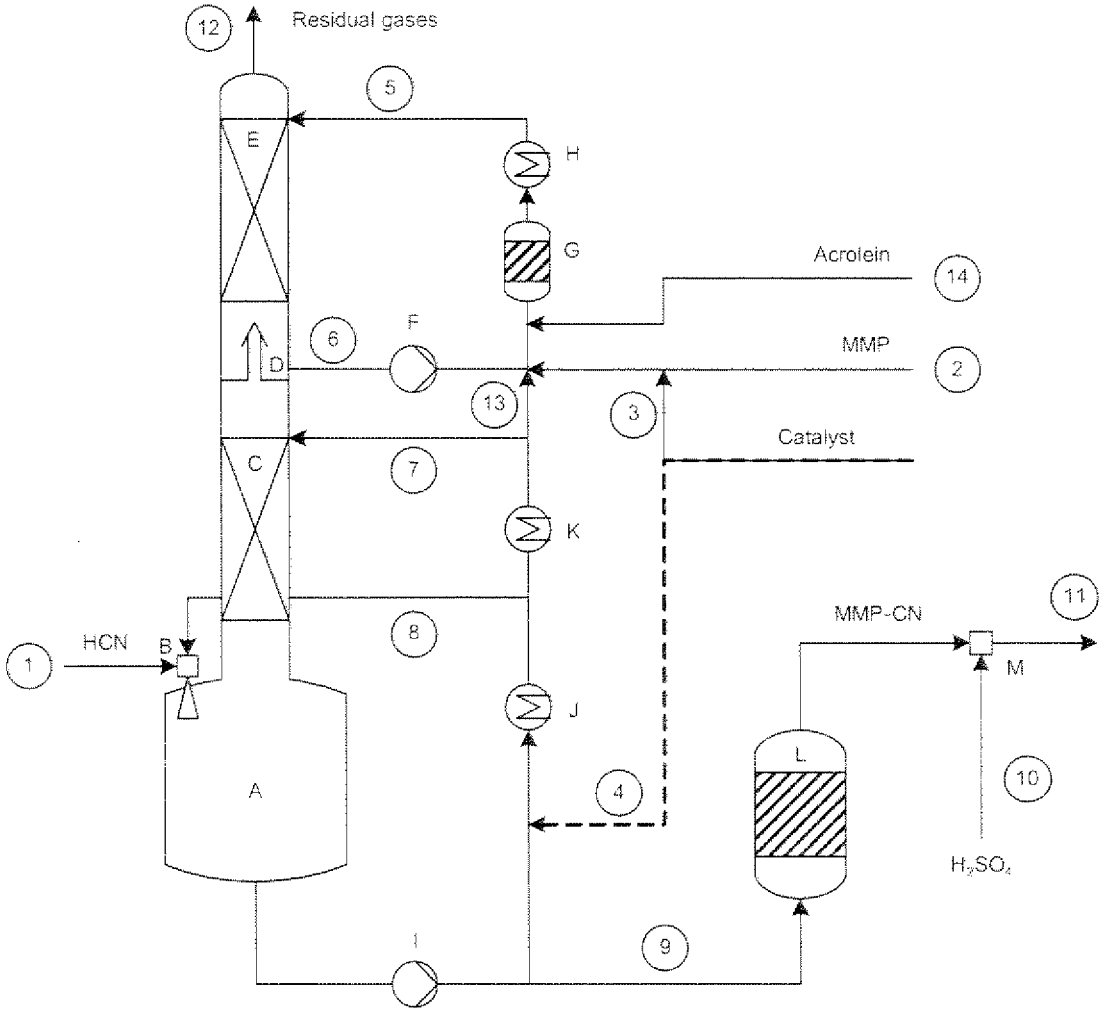
21. Method according to any one of claims 1 to 20, characterized in that the molar ratio of prussic acid to 3-(methylthio)propanal is 0.98 to 1.03, preferably 0.99 to 1.01.

22. Method according to any one of claims 1 to 21, characterized in that a weight ratio of catalyst to 3-(methylthio)propanal of 0.00005 to 0.002, preferably 0.0001 to 0.001, is used.

23. Method according to any of claims 1 to 22, characterized in that the method is carried out batchwise, semicontinuously, or continuously.

24. Use of a reaction product containing MMP-cyanohydrin produced according to any one of claims 1 to 23 for producing D,L-methionine or 2-hydroxy-4-methylthiobutyric acid.

Figure 1


12
Residual gases
5
E
H
G
Acrolein
14
F
6
D
MMP
2
13
3
Catalyst
C
7
K
11
MMP-CN
HCN
B
1
8
M
J
L
10
A
4
H_2SO_4
I
9