

Method for producing tetrahydrothiophene

[0001] The present invention relates to a process for the production of tetrahydrothiophene incorporating the treatment of the gaseous discharges. The present invention also relates to a process for the treatment of the gaseous discharges from a tetrahydrothiophene production unit.

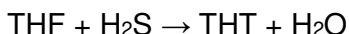
[0002] Tetrahydrothiophene is a compound exhibiting great industrial interest. It is known to be used as an additive in consumable gases to detect possible leaks due to its very characteristic odor. As a result, it is present in the gas injected into the domestic supply network, in gas transport networks, in storage units and in interconnections with other gas transport networks.

[0003] It is known to synthesize tetrahydrothiophene, hereinafter denoted THT, from 1,4-butanediol, hereinafter denoted BDO, or else from tetrahydrofuran, denoted THF, and from hydrogen sulfide, hereinafter denoted H₂S, in the presence of a heterogeneous catalyst.

[0004] It is accepted in the literature that the first *in situ* stage is the transformation of BDO into THF according to the following reaction:

$$1,4\text{-BDO} \rightarrow \text{THF} + \text{H}_2\text{O}$$

[0005] The second stage is the transformation of THF, in the presence of H₂S, into THT according to the following reaction:



[0006] In point of fact, the following side reactions can occur depending on the operating conditions:



[0007] In addition, this synthesis can generate degradation products, such as CO₂, ethylene and C₁ to C₄ mercaptans.

[0008] Furthermore, gaseous discharges, also called vent gases, are emitted throughout the production process. These discharges can contain the excess hydrogen sulfide possibly introduced into the circuit, cracking products, intermediate compounds, such as THF, and also significant amounts of THT. Usually, these discharges are incinerated, resulting in high emissions of sulfur oxides (SO₂) into the atmosphere, which are potentially responsible for acid rain. In point of fact, at the present time, these discharges are no longer tolerated. It should be noted that these gaseous discharges cannot be recycled as such in the main reaction because the presence of ethylene, propylene and butene results in very premature aging of the catalyst by the formation of gums and coke. Thus, to be recycled, these discharges must undergo very substantial bleeding in order not to recycle large amounts of C₂ to C₄ hydrocarbons. In point of fact, this bleeding also has the consequence of losing virtually

all of the THT and of the sulfur compounds or oxygen compounds present in these vent gases.

[0009] In point of fact, from the viewpoint of current ecological considerations, there today exists a real need for a process for the synthesis of THT which is more environmentally friendly, while retaining high yields.

[0010] One objective of the present invention is to provide a process for the preparation of THT which makes possible improved management of the gaseous discharges, and in particular which is more environmentally friendly.

[0011] Another objective of the present invention is to reduce the gaseous discharges, and in particular the amount of sulfur dioxide, emitted during the production of tetrahydrothiophene, after incineration of the discharges.

[0012] Another objective of the present invention is to provide a process for the preparation of tetrahydrothiophene which is more economical.

[0013] Finally, another objective of the present invention is to provide a process and/or a device for the treatment of the gaseous discharges which can be readily incorporated in a unit for the production of tetrahydrothiophene.

[0014] The process according to the invention meets all or some of the abovementioned objectives.

[0015] The present inventors have discovered, surprisingly, that the gaseous discharges can be recovered and treated by a gas-liquid extraction, with 1,4-butanediol as solvent of the extraction. The gas(vent gases)-liquid(1,4-butanediol) extraction according to the invention makes it possible in particular to cause the sulfur compounds, and also the tetrahydrofuran, contained in said vent gases to pass into the liquid 1,4-butanediol.

[0016] The term "sulfur compounds" is understood to mean compounds comprising at least one sulfur atom, preferably one sulfur atom. In particular, the term "sulfur compounds" is understood to mean tetrahydrothiophene and sulfur-containing byproducts, such as thiophene, dihydrothiophene, mercaptans and possibly hydrogen sulfide, these compounds having been entrained in the vent gases during the purification stage(s), preferably in the condensation and/or decanting and/or distillation stages, after stage a).

[0017] Thus, the gas-liquid extraction according to the invention makes it possible to recover sulfur compounds, and in particular tetrahydrothiophene, and also tetrahydrofuran, which is an intermediate of the reaction.

[0018] The process according to the invention uses one of the synthesis reactants, that is to say 1,4-butanediol, as solvent of the gas-liquid extraction stage. Thus, the recovery of sulfur compounds and of tetrahydrofuran uses the synthesis reactant, thus optimizing this recycling route.

[0019] Very advantageously, 1,4-butanediol enriched in sulfur compound(s) and optionally in tetrahydrofuran is used, preferably directly (for example without a purification stage), as reactant for forming tetrahydrothiophene. Thus, the process according to the present invention makes it possible to reintroduce advantageous compounds, which were hitherto incinerated, into the tetrahydrothiophene production process.

[0020] The extraction stage according to the invention exhibits the advantage of being able

to be easily incorporated in a tetrahydrothiophene production unit, because it treats only the vent gases. It thus consumes little energy and uses a simple device.

[0021] Said extraction also makes it possible to reduce the amount of vent gases to be treated by incineration and makes it possible to greatly reduce the release of sulfur dioxide into the atmosphere.

[0022] The process for the production of tetrahydrothiophene according to the invention is thus more economical and exhibits a better productivity, while at the same time being more environmentally friendly.

Brief description of the invention

[0023] Thus, one aspect of the present invention is a process for the production of tetrahydrothiophene comprising the following successive stages:

- a) reaction of 1,4-butanediol in the presence of hydrogen sulfide (H_2S), in the gas phase, in the presence of at least one catalyst, to form a stream (A) comprising tetrahydrothiophene, water and possibly unreacted hydrogen sulfide;
- b) condensation of the stream (A) to obtain a stream (B) rich in tetrahydrothiophene and vent gases (C) containing the noncondensables possibly formed on conclusion of stage a);
- c) at least one stage of purification, preferably by decanting, of the stream (B) with separation of the aqueous phase, of the organic phase constituting the stream (D) and of the vent gases (E);
- d) optionally at least one distillation of the stream (D) to isolate the tetrahydrothiophene from the vent gases (F);
- e) recovery of the tetrahydrothiophene isolated in stage c) and optionally in stage d), it being possible for stages b) and c) to be successive or simultaneous,
- f) gas-liquid extraction by means of a column, fed by one or more gas streams (G) comprising the vent gases (C) and/or the vent gases (E) and possibly the vent gases (F) and by a liquid stream of 1,4-butanediol, to form, at the column outlet, a gas stream (H) and a liquid stream (I) comprising enriched 1,4-butanediol;
- g) recycling of all or part of the stream (I) to the reaction a).

Brief description of the figure

[0024] [Fig. 1] is a diagram of the device implementing the claimed process.

Detailed description of the invention

[0025] Other characteristics, aspects, objects and advantages of the present invention will become even more clearly apparent on reading the description which follows.

[0026] It is specified that the expressions “from ... to ...” and “of between ... and ...” used in the present description should be understood as including each of the limits mentioned.

[0027] The term “enriched 1,4-butanediol” is understood to mean the 1,4-butanediol obtained after the gas-liquid extraction according to the invention, that is to say obtained after

stage f).

[0028] In particular, the enriched 1,4-butanediol is a composition comprising 1,4-butanediol and at least one sulfur compound, preferably comprising 1,4-butanediol and tetrahydrothiophene, and possibly sulfur-containing byproducts, such as thiophene and dihydrothiophene, and possibly tetrahydrofuran. In particular, said enriched 1,4-butanediol comprises between 0.1% and 20% by weight of tetrahydrothiophene, preferably between 1% and 10%, more preferentially between 1% and 5%, by weight of tetrahydrothiophene, with respect to the total weight of the enriched 1,4-butanediol.

[0029] More particularly, the term “enriched 1,4-butanediol” is understood to mean a composition comprising:

- 1,4-butanediol, preferably at least 50% by weight of 1,4-butanediol, more preferentially at least 80% by weight, preferentially again at least 90% by weight, of 1,4-butanediol, with respect to the total weight of the composition;
- tetrahydrothiophene, preferably between 0.1% and 20% by weight of tetrahydrothiophene, more preferentially between 1% and 10%, more preferentially still between 1% and 5%, by weight of tetrahydrothiophene, with respect to the total weight of the composition;
- possibly sulfur-comprising byproducts, preferably dihydrothiophene and/or thiophene;
- possibly tetrahydrofuran;
- possibly hydrogen sulfide;
- possibly water; and
- possibly noncondensable compounds.

[0030] Said composition can thus comprise:

- between 80% and 99% by weight of 1,4-butanediol, with respect to the total weight of the composition, and
- between 0.1% and 10%, preferably between 1% and 5%, by weight of tetrahydrothiophene, with respect to the total weight of the composition.

[0031] The term “vent gas” or “gaseous discharge” is understood to mean a gas phase comprising at least one sulfur compound as defined above and in particular recovered following at least one stage of separation or of purification of the stream (A), which follows on from the reaction a).

[0032] Said vent gases, and in particular the streams (C), (E) and (F), comprise at least one sulfur compound and possibly tetrahydrofuran.

[0033] These vent gases can comprise, indeed even consist of, tetrahydrothiophene, tetrahydrofuran, noncondensable compounds, water and sulfur-comprising byproducts, possibly hydrogen sulfide.

[0034] These vent gases can result from a condenser, from a decanting tank and/or from the overhead stream of the distillation column and/or from a bleed.

[0035] In particular, the vent gases or gaseous discharges according to the invention are normally regarded as waste and are usually sent to the incinerator.

[0036] The term “noncondensable compounds” is understood to mean compounds which remain in the gas state under the conditions of the stages of the process. Mention may be made, as noncondensable compounds, of CH₄, CO, CO₂, H₂ and N₂.

[0037] The process according to the invention comprises the abovementioned consecutive stages: stages a) to g). This process can comprise intermediate purification stages.

Stage a) - Reaction

[0038] During stage a), 1,4-butanediol is reacted with hydrogen sulfide to form a stream (A), preferably in the gas state, comprising tetrahydrothiophene, water, possibly unreacted hydrogen sulfide, possibly tetrahydrofuran and possibly sulfur-comprising byproducts. The stream (A) can also contain unreacted 1,4-butanediol. Olefins and/or noncondensables can also be present in the stream (A).

[0039] Thus, gas streams of hydrogen sulfide and 1,4-butanediol, each in the gaseous form, are introduced into a reactor. These reactants can arrive in the reactor via one and the same stream or else separately. Preferably, the reactants arrive via one and the same stream, the hydrogen sulfide stream being heated beforehand and making it possible to vaporize the liquid stream of 1,4-butanediol.

[0040] The reaction is carried out in the gas phase and preferably continuously. The catalyst or catalysts can be in a fixed bed in a reactor which is multitubular or nonmultitubular, isothermal or adiabatic, with plates. A multizone reactor or several reactors in series with identical or different catalysts, with or without multiple injection of BDO, can also be used.

[0041] The reaction temperature can be of between 200°C and 450°C, preferably between 200°C and 380°C. Preferably, the reaction temperature is of between 200°C and 360°C. Above this temperature, the catalyst may be physically damaged (in particular by sintering and coking). This temperature can change as a function of the duration of operation of the catalyst, which may be partially deactivated over time.

[0042] The pressure in the reactor can range from atmospheric pressure to 50 bar, preferably from 1 to 30 bar and more preferably from 1 to 10 bar.

[0043] The hydrogen sulfide/1,4-butanediol molar ratio can be of between 1 and 100, preferably between 1 and 50, more particularly between 1 and 10. The hydrogen sulfide is preferably in excess with respect to the 1,4-butanediol.

[0044] The flow rate of BDO with respect to the amount of catalyst can be of between 0.005 and 10 kg/h/kg of catalyst, preferably between 0.1 and 5 kg/h/kg of catalyst, more preferably between 0.1 and 1 kg of BDO kg/h/kg of catalyst.

[0045] The reactor contains a catalyst for the reaction for the formation of tetrahydrothiophene, preferably in the gas phase. Use may be made, among the catalysts which can be used, of silicas, aluminas or aluminosilicates. Preferably, the catalysts are aluminas more or less doped with alkali metal or alkaline earth metal oxides, preferably undoped.

[0046] Preferably, the catalyst used is an alumina containing an Na₂O content of less than 0.3% by weight, with respect to the total weight of the catalyst, such as Spheralite 505 sold by Axens.

[0047] A stream (A) comprising tetrahydrothiophene, water, possibly unreacted hydrogen sulfide, possibly tetrahydrofuran and possibly sulfur-comprising byproducts is thus obtained.

Stage b) – Condensation

[0048] The stream (A) resulting from stage a) is subjected to a stage of condensation by means of any conventional technique, preferably by means of one or more condensers or economizers. During the condensation, the stream (A) is in particular cooled as low as possible, to maximize the removal of water. Preferably, the stream (A) is condensed at a temperature of between 20°C and 70°C, for example between 30°C and 60°C. The condensation stage makes it possible to obtain a stream (B) rich in tetrahydrothiophene and vent gases (C) containing the noncondensables possibly formed on conclusion of stage a) and containing at least one sulfur compound and possibly tetrahydrofuran. Preferably, the vent gases (C) comprise tetrahydrothiophene, the noncondensables possibly formed on conclusion of stage a), possibly unreacted hydrogen sulfide, possibly tetrahydrofuran and possibly sulfur-comprising byproducts.

Stage c) – Purification, preferably by decanting

[0049] The stream (B) rich in tetrahydrothiophene is subjected to a purification stage. Preferably, it is a decanting stage so as to separate the organic phase from the aqueous phase containing the water generated during the reaction a). In addition, during this stage, vent gases are also removed. Thus, the organic phase (D) comprising the tetrahydrothiophene is separated from the aqueous phase. The vent gases are recovered in a gas stream denoted (E), which comprises at least one sulfur compound and possibly tetrahydrofuran. Preferably, the gas stream (E) comprises tetrahydrothiophene, possibly unreacted hydrogen sulfide, possibly tetrahydrofuran and possibly sulfur-comprising byproducts.

[0050] Preferably, the stream (B) is separated at a temperature of between 20°C and 70°C, preferably between 30°C and 60°C. The pressure can be of between 1 and 40 bar absolute.

Stage d) – Possible distillation

[0051] The stream (D), that is to say the organic phase resulting from the purification stage c), can be subjected to one or more distillations. This or these successive distillations make it possible to remove the compounds which are heavier than THT and/or the compounds which are lighter than THT.

[0052] According to one embodiment of the invention, two distillation columns can be used in series, the first to separate the heavy compounds and the second to separate the light compounds.

[0053] According to another embodiment of the distillation stage, the distillation is carried out with a partition column of DWC type, comprising 3 outlets: the top fraction comprising the light impurities, the bottom fraction comprising the heavy impurities and the intermediate fraction comprising the purified THT.

[0054] The distillation of stage d) can be carried out at a pressure of between 0.05 and 75 bar absolute, preferably between 1 and 30 bar absolute, more preferentially between 1 and 5 bar absolute.

[0055] The distillation of stage d) can be carried out at a temperature of between 20°C and 200°C, preferably between 40°C and 160°C, more preferentially between 60°C and 140°C.

[0056] The distillation can be carried out in any known type of distillation column. It can be a

column with plates (for example plates with caps, plates with valves or perforated plates) or with packing (for example with bulk or structured packing). The distillation can be carried out in a plate column, preferably comprising between 5 and 50 plates, more preferentially between 10 and 40 plates, for example between 25 and 30 plates. The distillation can also be carried out in a partition column (DWC for Divided Wall Column). The partition can be fixed or movable, for example with structured or bulk packing.

Stage e) – Recovery of the tetrahydrothiophene isolated in stage c) and/or d)

[0057] The tetrahydrothiophene is recovered on conclusion of stage c) and/or d) to be able to be stored or else to be able to be used directly in another synthesis stage.

Stage f) – Liquid-gas extraction

[0058] The purpose of the liquid-gas extraction stage is to recover the vent gases generated after the reaction stage a). It is possible to recover a single gas stream or else the totality of the gas streams of the production unit.

[0059] Preferably, the vent gases containing the noncondensables (C) resulting from the condensation stage b), the vent gases (E) resulting from the purification stage c) and possibly the gaseous fraction (F) resulting from the distillation stage d) can be recovered and combined in a stream (G). It would not be departing from the scope of the invention if the streams (C), (E) and (F) were to arrive separately in the liquid-gas extraction unit.

[0060] The liquid-gas extraction stage is carried out within a unit comprising at least one column. The latter is fed with one or more gas streams and with a liquid stream of 1,4-butanediol. At the column outlet, a gas stream (H) is generated comprising noncondensable compounds and possibly hydrogen sulfide, and a liquid stream (I) comprising enriched 1,4-butanediol.

[0061] The gas-liquid extraction can be carried out in at least one absorption column or in at least one tank, preferably with mechanical stirring. Said absorption column(s) is (are) chosen in particular from packed columns (for example bulk or structured packing), plate columns, bubble columns, spray columns and falling film columns, indeed even tanks with mechanical stirring. Preferably, one or more packed column(s), for example between 1 and 10 columns, is (are) used. Several absorption columns can be used, in parallel or in series. Preferably, the gas-liquid extraction is carried out in at least one absorption column or in at least one tank, preferably with mechanical stirring.

[0062] The flow rates of the gas (vent gases) phase and of the liquid (1,4-butanediol) phase depend on the type and on the number of columns. The vent gases and the liquid 1,4-butanediol enter the absorption column(s) cocurrentwise or countercurrentwise, preferably countercurrentwise. For example, the vent gases arrive via the bottom of the column(s) and the liquid 1,4-butanediol via the top of the column(s), with or without recirculation of the liquid phase to the column.

[0063] This type of system, making it possible to carry out a gas-liquid extraction, is generally referred to as “absorber” and, in the case of the present invention, “1,4-butanediol absorber”.

[0064] The gas-liquid extraction can be carried out at a temperature of between 25°C and

200°C, preferably between 25°C and 150°C, preferably between 25°C and 100°C, more preferentially between 40°C and 90°C. The gas-liquid extraction is carried out at a pressure of between 1 and 40 bar absolute, preferably between 1 and 10 bar absolute, more preferentially still between 1 and 5 bar absolute.

[0065] The ratio by weight of the vent gases with respect to the 1,4-butanediol can be of between 0.001 and 10, preferably between 0.1 and 3, more preferably between 0.5 and 2.

[0066] Stage f) makes it possible to pass the sulfur compounds and possibly the tetrahydrofuran into the liquid 1,4-butanediol and to reduce, indeed even to avoid, after incineration, the discharges of SO₂ to the atmosphere.

[0067] The vent gases thus treated (that is to say, at least one sulfur compound of which has been absorbed in the 1,4-butanediol) can subsequently be recovered, optionally incinerated, and released after incineration into the atmosphere with a reduced content of SO₂: preferably, said vent gases, after incineration, comprise virtually no or comprise no SO₂.

[0068] According to one embodiment of the process according to the invention, it is possible to recycle the gas stream (H) in the reaction stage a), it being possible for the stream (H) to be rich in hydrogen sulfide according to the amount of hydrogen sulfide introduced in the reaction a). This stream can be compressed using a compressor to subsequently be introduced into the reactor of stage a). A bleed can be present on this feed line, in order to remove possible impurities. This additional recycling stage also makes it possible to reduce the production of sulfur dioxide generated by the incineration of these vent gases and makes it possible to reduce the amount of fresh hydrogen sulfide introduced during stage a).

[0069] Preferably, the enriched 1,4-butanediol comprises between 0.1% and 20% by weight of tetrahydrothiophene, preferably between 1% and 10% by weight of tetrahydrothiophene, more preferentially between 1% and 5% by weight of tetrahydrothiophene, with respect to the total weight of the enriched 1,4-butanediol.

Stage g) – Recycling

[0070] The stream (I) comprising the enriched 1,4-butanediol is led, in all or in part, to stage a). It is thus used as reactant. It is optionally introduced as a mixture with fresh 1,4-butanediol. Preferably, the entire stream (I) is recycled in stage a). Preferably, the stream (I) is involved in stage a), without addition of fresh 1,4-butanediol.

[0071] The term “fresh 1,4-butanediol” is understood to mean a 1,4-butanediol which is not enriched within the meaning of the present invention, that is to say a 1,4-butanediol which has not been subjected to the gas-liquid extraction as according to the invention.

[0072] The stream (I) thus makes it possible to recycle the tetrahydrothiophene and the other sulfur compounds, which have passed into the vent gases. This stream also makes it possible to recycle the tetrahydrofuran possibly present in the vent gases.

[0073] The present invention also relates to a process for the treatment of the vent gases emitted by a unit for the production of tetrahydrothiophene from 1,4-butanediol and hydrogen sulfide, comprising the following stages:

- recovery of the vent gases resulting from a unit for the production of tetrahydrothiophene, said vent gases comprising at least one sulfur compound, preferably tetrahydrothiophene,

and possibly tetrahydrofuran;

- carrying out a gas-liquid extraction of said at least one sulfur compound, preferably tetrahydrothiophene, with liquid 1,4-butanediol, so as to obtain a liquid 1,4-butanediol enriched in sulfur compound(s), preferably in tetrahydrothiophene, and possibly tetrahydrofuran;
- optionally use of said enriched liquid 1,4-butanediol as reactant for the reaction for the production of tetrahydrothiophene from 1,4-butanediol and hydrogen sulfide.

[0074] All the elements of the process for the treatment of the vent gases are those defined for the process for the production of tetrahydrothiophene according to the invention.

Description of the figure

[0075] The appended figure 1 is a diagram representing an industrial installation for the production of tetrahydrothiophene according to the invention.

[0076] The reaction stage a) is carried out in the reactor R1 starting from 1,4-butanediol, which is wholly or partially enriched, and hydrogen sulfide.

[0077] The alcohol stream enters the reactor R1 via the pipe 1. The hydrogen sulfide stream enters the reactor R1 via the pipe 2. The stream A exiting the reactor R1 via the pipe 3 comprises tetrahydrothiophene, water, possibly unreacted hydrogen sulfide, possibly tetrahydrofuran, possibly sulfur-comprising byproducts, possibly olefins and possibly noncondensables.

[0078] The condensation stage b) is carried out in a device R2, such as a condenser. The device R2 is fed by the pipe 3 with stream A. The stream B, comprising the liquid tetrahydrothiophene, is evacuated from the device R2 via the pipe 4 and the vent gases C are evacuated via the pipe 5.

[0079] The decanting stage c) is carried out in the device R3. The aqueous phase is separated and removed via the pipe 6, the stream D comprising the tetrahydrothiophene is separated and evacuated via the pipe 7 and the vent gases E are removed via the pipe 8.

[0080] The distillation stage d) is carried out in the device R4. When a column of DWC type is used, the heavy impurities are removed via a pipe 9, the tetrahydrothiophene is isolated via a pipe 10 and the light impurities F are removed via a pipe 11.

[0081] The gas-liquid extraction stage f) is carried out in a device R5. The device is fed with liquid 1,4-butanediol by the pipe 12 and with vent gases G by the pipe 13. The pipe 13 recovers all of the vent gases and gaseous impurities generated during the separation and purification stages of the process, that is to say the pipe 5 recovering the vent gases C resulting from the condensation stage b), the pipe 8 recovering the vent gases E resulting from the decanting stage c) and the pipe 11 recovering the gaseous fraction F resulting from the distillation stage d). At the outlet of the device R5, the vent gases H are removed by the pipe 14 and the stream I of enriched liquid 1,4-butanediol, enriched in particular in tetrahydrothiophene, is evacuated by the pipe 15.

[0082] The pipe 15 conveys the enriched 1,4-butanediol to the reactor R1, in order for it to be used as reactant.

[0083] Depending on the amount of vent gases H recovered and on their composition (ac-

according to whether the hydrogen sulfide is introduced in excess in the reaction a)), it is possible to recover these vent gases and to reintroduce them in stage a).

[0084] The invention also relates to the use of a gas-liquid extraction device in a process for the production of tetrahydrothiophene, as defined above, for the recovery and the recycling of the vent gases produced after purification of the crude reaction product.

[0085] The examples which follow make it possible to illustrate the present invention but are not in any way limiting.

Examples

[0086] The process according to the invention was implemented. The gas-liquid extraction stage was carried out in a Norton IMTP adsorption column with a diameter of 400 mm and a packing height of 4 m. The pressure in the column is 3 bar absolute, with a bottom temperature of between 75°C and 80°C and a top temperature of 64°C. The ratio by weight of the vent gases with respect to the 1,4-butanediol is 1.13.

[0087] The gas streams at the inlet (stream entering from the pipe 13 in figure 1) and at the outlet (stream exiting from the pipe 14 in figure 1) of the reactor used to carry out the gas-liquid extraction of stage f) of the process were analyzed. The absorption efficiency could thus be calculated. These measurements appear in table 1 below.

	Absorption efficiency
H ₂ S	2.4%
CO ₂	0.8%
H ₂ O	90.8%
C ₂ to C ₄ Olefins	0.9%
C ₁ to C ₄ Mercaptans	15.4%
DHT/Thiophene	37.1%
THF	45.1%
THT	94.8%

Table 1

[0088] This test shows that 94.8% of the THT present in the vent gases is absorbed by the BDO, and thus recovered.

[0089] Depending on the production of the unit, if it is considered that 38 kg/h of THT were recovered, then the emission of 28 kg/h of SO₂ after incineration was avoided, i.e. 224 tons/year (for 8000 h/year of operation).

[0090] Another very great advantage of this absorption is the nonabsorption of the olefins. This is because more than 99% of the olefins pass through the absorber and will be virtually removed by the bleeding of this exiting gas phase and will not be recycled in the reaction.

[0091] Another advantage is also the nonabsorption of a noncondensable (CO₂) resulting from the cracking products. This is because the absorption of this noncondensable by the BDO absorption column would have led to an accumulation of noncondensables totally unacceptable for the process.

[0092] As regards the THF, which is the reaction intermediate, at least 45% of this product is recovered in these effluents, it being known that the content of THF in these effluents

increases with the aging of the catalyst.

For the other partially absorbed compounds, their recycling will result in them being found again in the purification stages downstream of the main reaction, apart from the hydrogen sulfide, which will react at the level of the main reaction.

Claims

1. A process for the production of tetrahydrothiophene comprising the following successive stages:

a) reaction of 1,4-butanediol in the presence of hydrogen sulfide (H_2S), in the gas phase, in the presence of at least one catalyst, to form a stream (A) comprising tetrahydrothiophene, water and possibly unreacted hydrogen sulfide;

b) condensation of the stream (A) to obtain a stream (B) rich in tetrahydrothiophene and vent gases (C) containing the noncondensables possibly formed on conclusion of stage a);

c) at least one stage of purification, preferably by decanting, of the stream (B) with separation of the aqueous phase, of the organic phase constituting the stream (D) and of the vent gases (E);

d) optionally at least one distillation of the stream (D) to isolate the tetrahydrothiophene from the vent gases (F);

e) recovery of the tetrahydrothiophene isolated in stage c) and optionally in stage d),

it being possible for stages b) and c) to be successive or simultaneous,

f) gas-liquid extraction by means of a column, fed by one or more gas streams (G) comprising the vent gases (C) and/or the vent gases (E) and possibly the vent gases (F) and by a liquid stream of 1,4-butanediol, to form, at the column outlet, a gas stream (H) and a liquid stream (I) comprising enriched 1,4-butanediol;

g) recycling of all or part of the stream (I) to the reaction a).

2. The process as claimed in claim 1, characterized in that the ratio by weight of the vent gases with respect to the 1,4-butanediol during stage f) is of between 0.001 and 10, preferably between 0.1 and 3, more preferably between 0.5 and 2.

3. The process as claimed in claim 1 or 2, characterized in that the gas-liquid extraction is carried out at a temperature of between 25°C and 200°C , preferably between 25°C and 150°C , preferably between 25°C and 100°C , more preferentially between 40°C and 90°C .

4. The process as claimed in any one of the preceding claims, characterized in that the gas-liquid extraction is carried out at a pressure of between 1 and 40 bar absolute, preferably between 1 and 10 bar absolute, more preferentially still between 1 and 5 bar absolute.

5. The process as claimed in any one of the preceding claims, characterized in that, during stage g), the entire stream (I) is recycled in stage a).

6. The process as claimed in any one of the preceding claims, characterized in that the enriched 1,4-butanediol comprises between 0.1% and 20% by weight of tetrahydrothiophene, preferably between 1% and 10% by weight of tetrahydrothiophene, more preferentially between 1% and 5% by weight of tetrahydrothiophene, with respect to the total weight of the enriched 1,4-butanediol.

7. The process as claimed in any one of the preceding claims, characterized in that the vent gases (C) resulting from stage a) comprise tetrahydrothiophene, the noncondensables possibly formed on conclusion of stage a), possibly unreacted hydrogen sulfide, possibly tetrahydrofuran and possibly sulfur-comprising byproducts.
8. The process as claimed in any one of the preceding claims, characterized in that the gas-liquid extraction is carried out in at least one absorption column or in at least one tank, preferably with mechanical stirring.
9. The process as claimed in any one of the preceding claims, characterized in that the stream (H) originating from the gas-liquid extraction stage is recycled in stage a).
10. The use of a gas-liquid extraction device in a process for the production of tetrahydrothiophene, as defined in any one of claims 1 to 9, for the recovery and the recycling of the vent gases produced after purification of the crude reaction product.