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(54) Title: METHOD FOR DRY HYDROCHLORINATION OF MASS FROM GLYCEROL HYDROCHLORINATION WITH HYDROCHLORIC ACID AND DEVICE FOR DRY HYDROCHLORINATION OF MASS FROM GLYCEROL HYDROCHLORINATION WITH HYDROCHLORIC ACID

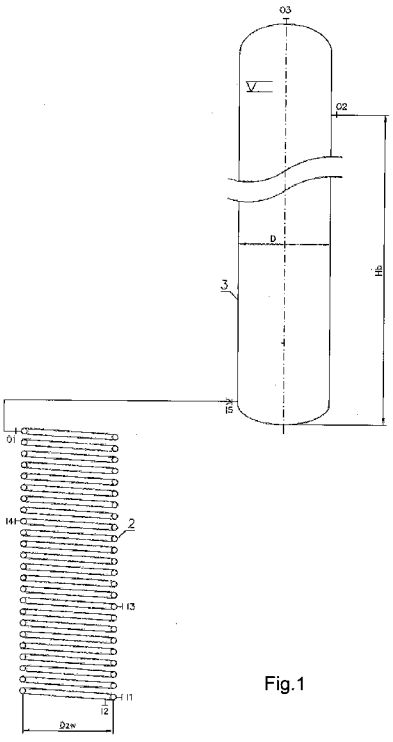

Fig.1

(57) Abstract: The invention relates to a method of dry hydrochlorination of mass from glycerol hydro¬ chlorination with hydrochloric acid and a device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid. According to the invention, in which the reaction of gaseous hydrogen chloride with non- reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a device for dry hydrochlorination in the pressure range of 5÷11 bar (a) at temperature of 120÷160°C, the method of dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, consists in the following: the mass from glycerol hydrochlorination with hydrochloric acid is introduced into the dispersion zone of a device (1) for dry hydrochlorination, and the reaction is initiated by introduction of gaseous hydrogen chloride; a forced turbulent flow of the liquid mass with gaseous hydrogen chloride in the dis¬ persion zone is formed until a diphase mixture is obtained; the diphase mixture is introduced into the bubbling zone consisting of a column reac¬ tor (3) of the device (1), tangentially in relation to its internal circumference; gaseous hydrogen chloride bubbles are allowed to flow freely upwards in the bubbling zone of the device (1), in a column of liquid with a defined height, the mixture of dichloropropanol isomers obtained as a result of the reaction is carried off from the device (1). According to the invention, in which the reaction of gaseous hydrogen chloride with non- reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a column reactor (3), the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, is characterized in that the device (1) includes a dispersion zone and a bubbling zone connected with it, while the bubbling zone consists of a column reactor (3).

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Method for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid and device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid

The invention relates to method for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid and device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid.

Quick development of fuels based on methyl esters of acids contained in rapeseed oil brings in a necessity to manage glycerol which is the second product of ester formation. Glycerol produced in this process on an industrial scale, is – apart from application for cosmetics industry – more and more often used for epichlorohydrin production.

Hydrochlorination of glycerol at 105÷120°C in the presence of concentrated acetic acid as a catalyst (Ł.A. Oszin; Promyszliennyje chlororganiczeskije produkty, Moscow, Izdatiestwo Chimija, 1978), added to the mass in the quantity of 2÷3% wt., is a commonly known method for synthesis of dichloropropanol isomers mixture of high concentration. The technological process includes the following stages: preparation of glycerol-acetic acid mixture, synthesis of dichloropropanols, neutralization of the post-reaction mass, and separation of pure dichloropropanols by rectification.

All newer methods for synthesis of concentrated mixture of dichloropropanol isomers are based on the method mentioned above, and they differ in catalysts used, engineering solutions of the apparatus, and carrying out the reaction under pressure.

In patent application No. WO 2006/100311, raw material base for production of glycerol and other polyols is claimed; in patent application No. WO 2005/021476, purity of the applied glycerol is claimed; and in patent application No. WO 2005/054167 – extension of the range of catalysts with organic mono- and dicarboxylic acids, and their anhydrides and organic derivatives. Differences in comparison to the method reported in the cited L.A. Oshin's publication concern engineering solutions and conditions of the reaction, such as application of a reactor cascade, a column reactor, a proper range of catalyst concentration in the reaction mass, method of its recovery for instance by crystallization. In patent application No. WO 2006/106154, composition of the post-reaction mass of glycerol hydrochlo-

rination, in which contents of sum of dichloropropanol isomers is higher than 10% molar and lower than 98% molar, is claimed.

A novelty in hydrochlorination method of glycerol, claimed in patent application No. WO 2006/20234, consists in carrying out the reaction under pressure from 2.5 to 44 bar at 50÷140°C. In the invention, catalysts of carboxylic acids, carboxylic acid anhydrides, acid chlorides, esters, lactones, lactans groups are used. From among of carboxylic acids, acids containing from 1 to 60 carbon atoms in the molecule are claimed. From among of carboxylic acid anhydrides, acetic acid anhydride, propionic acid anhydride, butyric acid anhydride etc. are claimed. From among of acid chlorides, 6-chlorohexanoic acid, 5-chloropentanoic acid, 4-chlorobutyric acid etc. are claimed. From among of esters, esters of glycerol, esters of ethylene glycol and esters of poly(propylene glycol) with carboxylic acids are claimed. From among of lactones and lactans, ε-caprolactone, γ-butyllactone, δ-valerolactone are claimed. While the reaction is being carried out, water forming as a result of it is not carried off, and the post-reaction mixture is subjected to distillations in order to separate the unreacted hydrogen chloride dissolved in water (hydrochloric acid), the concentrated reaction product being a mixture of 1,3- and 2,3-dichloropropanol isomers, and a residue consisting mostly of polyglycerols and their esters.

Patent application No. WO 2006/100317 claims utilization of metallic and non-metallic materials resistant to hydrochlorinating agents for production of equipment and piping for hydrochlorination reaction of polyols. Among metallic materials, tantalum, zirconium, titanium, platinum and their alloys, alloys of molybdenum, nickel and copper, and also alloys of gold and silver are claimed; and among non-metallic materials, elastomers, thermoplastics, glass, ceramic, metalloceramic laminates, fireproof materials, self-curing agents, impregnated graphite, carbon, glass, enamel, porcelain and stoneware are claimed. These materials are resistant in the temperature range from 0 to 200°C.

The invention according to Polish patent application No. P-383486 pertains to method of generation of a mixture of 1,3- and 2,3-dichloropropanols forming as a result of reaction of glycerol hydrochlorination with gaseous hydrogen chloride. The process is carried out in a cascade of four tank reactors with intersecting feeding of each reactor with gaseous hydrogen chloride and serial flow of the liquid reacting mass through the reactors, in the presence of adipic acid as a catalyst. Time spent by the mixture in the reactors is selected in a way ensuring the assumed conversion level of glycerol after the reactor, and the assumed

total contents of 1,2- and 1,3-dichlopropanols after the reactor; water from the reaction is collected together with a section of the formed mixture of 1,3- and 2,3-dichloropropanols in vapour phase from each of the cascade reactors, and separation of the concentrated product from the cascade reactor's decoction is carried out in a rectifying column with at least 28 theoretical plates, while the decoction is introduced on the plate between 10 and 18 theoretical plates from the bottom, and unreacted alpha- and beta-monochlorohydrins are returned to the reactor.

The invention according to Polish patent application No. P-383486 presents a method of generation of a mixture of 1,3- and 2,3-dichloropropanols, a raw material for epichlorohydrin production, of glycerol. Glycerol containing dissolved catalyst is introduced to an absorption column, and non-reacted gaseous hydrogen chloride from a flow reactor mixed with hydrogen chloride from condenser of a dehydration column is introduced in a countercurrent. The flow of partially reacted glycerol from the absorption column is directed to a flow reactor, fresh gaseous hydrogen chloride is introduced in a countercurrent. The flow after reaction from the flow reactor is directed to the dehydration column, condensed distillate is divided into reflux recirculated to the top of the dehydration column and solution of acidic dichloropropanols directed to epichlorohydrin production. Parameters of the whole process are chosen in a way ensuring conversion level not lower than 98% for gaseous hydrogen chloride, and not lower that 99% for glycerol.

Aim of the invention is to develop a more effective and more economic method and device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid.

According to the invention, in which the reaction of gaseous hydrogen chloride with non-reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a device for dry hydrochlorination in the pressure range of 5÷11 bar (a) at temperature of 120÷160°C, the method of dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, consists in the following:

- the mass from glycerol hydrochlorination with hydrochloric acid is introduced into the dispersion zone of a device for dry hydrochlorination, and the reaction is initiated by introduction of gaseous hydrogen chloride;
- a forced turbulent flow of the liquid mass with gaseous hydrogen chloride in the dispersion zone is formed until a diphase mixture is formed;

- the diphase mixture is introduced into the bubbling zone consisting of a column reactor of the device, tangentially in relation to its internal circumference;
- gaseous hydrogen chloride bubbles are allowed to flow freely upwards in the bubbling zone of the device, in a column of liquid with a defined height,
- the mixture of dichloropropanol isomers obtained as a result of the reaction is carried off from the device.

It is preferable when gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by direct contact of connections of conduits with the mass and with hydrogen chloride.

It is also preferable when gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by use of static mixers.

It is also preferable when gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by use of nozzles.

According to the invention, in which the reaction of gaseous hydrogen chloride with non-reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a column reactor, the device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, is characterized in that the device includes a dispersion zone and a bubbling zone connected with it, while the bubbling zone consists of a column reactor.

It is preferable when the dispersion zone consists of an external pipe coil, with outlet connector pipe is connected with inlet connector pipe of the column reactor.

It is also preferable when the dispersion zone consists of an integrated pipe coil with inlet connector pipe, coiled on the external side of the column reactor, while the lower section of the integrated pipe coil is located inside the column reactor.

It is preferable when cross-section area of the dispersion zone is of any shape.

Another preferred feature of the invention consists in that the ratio of length of the dispersion zone formed of the external pipe coil or of the integrated pipe coil to the height of the column reactor is in the range from 15:1 to 25:1.

It is preferable when the dispersion zone consists of an external casing enclosing the column reactor, while the lower section of the external casing is connected with the interior of the column reactor, and the upper section has an inlet connection pipe preferably located tangentially to the surface of the column reactor.

It is preferable when the dispersion zone is equipped along its length with one or more connector pipes supplying gaseous hydrogen chloride.

It is also preferable when the dispersion zone is equipped with a static mixer or nozzles.

The device according to the invention is shown in a example of embodiment in the Figures, where Fig.1 shows the device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid with an external pipe coil, Fig. 2 shows the device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid with an integrated pipe coil, and Fig. 3 shows the device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid with an external casing.

As it is shown in the example of embodiment in Fig. 1, the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid includes an external pipe coil (2) constituting dispersion zone, and a column reactor (3) constituting bubbling zone.

The external pipe coil (2) consists of coils of the external pipe coil (4) with internal diameter D_z and it is equipped with inlet connector pipe (I1), via which mass from glycerol hydrochlorination with hydrochloric acid flows into the external pipe coil (2).

The external pipe coil (2) is connected with the column reactor (3) via an outlet connector pipe (01).

The external pipe coil (2) it is equipped with connector pipes (I2, I3, I4), via which gaseous hydrogen chloride for hydrochlorination is supplied appropriately to the external pipe coil (2).

Via outlet connector pipe (O1), gaseous-liquid mixture flows out of the external pipe coil (2) to the column reactor (3), where hydrochlorination of the mass from glycerol hydrochlorination with hydrochloric acid is being concluded.

The post-reaction mass is carried off from the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid via lateral connector pipe (O2), and non-reacted hydrogen chloride is carried off via connector pipe (O3).

As it is shown in Fig. 2, the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid includes integrated pipe coil (5) constituting dispersion zone, and column reactor (3) constituting bubbling zone.

The integrated pipe coil (5) consists of coils winding round the external casing of the column reactor (3) and it is equipped with inlet connector pipe (I12), via which mass from glycerol hydrochlorination with hydrochloric acid flows into the integrated pipe coil (5).

The integrated pipe coil (5) it is equipped with connector pipes (I21, I31, I41), via which gaseous hydrogen chloride for hydrochlorination is supplied appropriately to the integrated pipe coil (5).

From the lower section of the integrated pipe coil (5), gaseous-liquid mixture flows to the column reactor (3), where hydrochlorination of the mass from glycerol hydrochlorination with hydrochloric acid is being concluded.

The post-reaction mass is carried off from the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid via lateral connector pipe (O11), and non-reacted hydrogen chloride is carried off via connector pipe (O21).

As it is shown in Fig. 3, the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid includes an external casing (6), constituting the dispersion zone, coiled around the tank reactor (3). The lower section of the external casing (6) is connected with the interior of the tank reactor (3), and the upper section is equipped with inlet connector pipe (I12).

The inlet connector pipe (I12) in the upper section of the external casing (6) is located tangentially in relation to wall surface of the column reactor (3) and mass from glycerol hydrochlorination with hydrochloric acid flows via connector pipe to the interior of the external casing (6).

The external casing (6), constituting the dispersion zone, coiled around the tank reactor (3), it is equipped with connector pipes (I22, I32, I42), via which gaseous hydrogen chloride for hydrochlorination is supplied appropriately to the interior of the external casing (6).

From the lower section of the external casing (6), gaseous-liquid mixture flows to the column reactor (3), where hydrochlorination of the mass from glycerol hydrochlorination with hydrochloric acid is being concluded.

The post-reaction mass is carried off from the device (1) for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid via lateral connector pipe (O12), and non-reacted hydrogen chloride is carried off via connector pipe (O22).

Construction of the reactor for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, in which the reaction of gaseous hydrogen chloride with non-reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in the pressure range of 5÷11 bar (a) at temperature of 120÷160°C, being a column reactor, in the presented embodiment examples, therefore resolves itself into the fact that the reactor is a structural connection of two reaction zones: the zone of dispersion of gaseous hydrogen chloride in the liquid mass and initiation of hydrochlorination in it, and the gas bubbling zone through a defined height of the liquid column enabling completion of hydrochlorination in it.

The dispersion zone of gaseous hydrogen chloride and initiation of reaction in it is formed by forced turbulent flow of the liquid mass with gaseous hydrogen chloride in a cross-section of any shape, while the route of the turbulent flow of the liquid mass with gaseous hydrogen chloride may range from top to bottom at the external section of the column reactor casing or be located outside the column reactor. Then, the diphase mixture flows from the bottom of the column reactor, tangentially in relation to its circumference, into the bubbling zone with free flow of gaseous bubbles upwards in a liquid column of defined height.

Any shape of the cross-section area of turbulent flow of the liquid mass with gaseous hydrogen chloride is circular cross-section, square cross-section, rectangular cross-section, triangular cross-section, trapezoidal cross-section, annular cross-section, or semicircular cross-section.

The ratio of the dispersion zone length to the bubbling zone height is in the range from 20 to 1.

The liquid mixture of non-reacted glycerol and monochlorohydrin isomers mixture in supplied in the topmost point of the dispersion zone of gaseous hydrogen chloride.

Gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by direct contact of connections of conduits with the mass and with hydrogen chloride, or by use of static mixers or nozzles.

Structure of the device for dry hydrochlorination with gaseous hydrogen chloride of mass from glycerol hydrochlorination with hydrochloric acid, allows to carry out reaction of synthesis of dichloropropanol isomers mixture in one device with the same yield and selectivity as the one obtained by carrying it out in other reactor systems cited in the state of the art. Owing to application of two reaction zones in one device: the dispersion zone and the bubbling zone, reactor structure becomes compact and easy to use practically for various scales of production of dichloropropanol isomers mixture.

Non-limiting examples of embodiment of the method and device according to the invention:

Example 1.

In the example shown in Fig. 1, a device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid is shown for production scale of mixture of sum of dichloropropanol isomers 16000 t/year. The dispersion zone of gaseous hydrogen chloride and initiation of hydrochlorination in it consists of 24 coils of pipe coil with coil diameter of 900 mm. Mass from glycerol hydrochlorination with hydrochloric acid flows into pipe coil with internal diameter of 50 mm via connector pipe (I1), and gaseous hydrogen chloride via connector pipes (I2, I3 and I4) appropriately. Gas-liquid mixture flows out via connector pipe (O1) to the column reactor, in which completion of hydrochlorination occurs. The connector pipes (I3, I4 and O1) are positioned in relation to the connector pipe (I2) in a way ensuring that the flow routes of the diphase mixture between the connector pipes (I2 and I3, I3 and I4), and (I4 and O1) were approximate. The connector pipe (I5) in the column reactor is positioned tangentially in relation to its circumference. Diameter of the column reactor D is 800 mm, and height of the liquid column is 5200 mm.

Example 2.

In the example shown in Fig. 2, a device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid is shown for production scale of mixture of sum

of dichloropropanol isomers 16000 t/year. Mass from glycerol hydrochlorination with hydrochloric acid flows into pipe coil with internal diameter of 50 mm via connector pipe (I1), and gaseous hydrogen chloride – with mass divided into three flows independent – via connector pipes (I2, I3 and I4). Contact of the liquid mass with gaseous hydrogen chloride marks the beginning of the dispersion zone and simultaneously initiation of reaction occurring in forced turbulent flow of the liquid mass with gaseous hydrogen chloride in circular, square, rectangular, triangular, trapezoidal or semicircular cross-section on the route from top to bottom at the external sections of the casing of the column reactor. Then, the diphase mixture flows into the bubbling zone with free flow of gas bubbles upwards in a liquid column of defined height, sufficient to obtain the assumed conversion level of the reagents. The following ratios of basic dimensions of the reactor should be kept:

$$\frac{Hd}{Hb} = 0.48$$

$$\frac{Hb}{D} = 6.5$$

Points of introduction of gaseous hydrogen chloride along height of the dispersion zone: division starting from the highest point: Hd/3.

The liquid post-reaction mass flows out via connector pipe (O11), and non-reacted hydrogen chloride – via connector pipe (O21).

Example 3.

In the example shown in Fig. 3, a device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid is shown for production scale of mixture of sum of dichloropropanol isomers 16000 t/year, in which the dispersion zone of gaseous hydrogen chloride in the liquid mass, and the bubbling zone through the defined height of the liquid column are located in one device. The liquid mass is supplied via connector pipe (I12), and gaseous hydrogen chloride – via connector pipes (I22, I32 and I42). Dispersion of gaseous hydrogen chloride and initiation of reaction occurs in annular space with diameter ratio D_z/D amounting to 1.125. The connector pipes (I22, I32 and I42) are positioned relation to height of the dispersion zone of gaseous hydrogen chloride in the liquid mass in a way ensuring the heights between the connector pipes (I22) and (I32), (I32) and (I42), and (I42) and the end of the dispersion zone are approximate. The ratio of height of the dispersion zone H_d to the bubbling zone height amounts to 0.50. The liquid post-reaction

mass flows out via connector pipe (O12), and non-reacted hydrogen chloride – via connector pipe (O22).

Claims

1. A method of dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, in which the reaction of gaseous hydrogen chloride with non-reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a device for dry hydrochlorination is carried out in a device for dry hydrochlorination in the pressure range of 5÷11 bar (a) at temperature of 120÷160°C, **characterized in that**:

- the mass from glycerol hydrochlorination with hydrochloric acid is introduced into the dispersion zone of a device (1) for dry hydrochlorination, and the reaction is initiated by introduction of gaseous hydrogen chloride;
- a forced turbulent flow of the liquid mass with gaseous hydrogen chloride in the dispersion zone is formed until a diphase mixture is obtained;
- the diphase mixture is introduced into the bubbling zone consisting of a column reactor (3) of the device (1), tangentially in relation to its internal circumference;
- gaseous hydrogen chloride bubbles are allowed to flow freely upwards in the bubbling zone of the device (1), in a column of liquid with a defined height;
- the mixture of dichloropropanol isomers obtained as a result of the reaction is carried off from the device (1).

2. Method according to claim 1, **characterized in that** gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by direct contact of connections of conduits with the mass and with hydrogen chloride.

3. Method according to claim 1, **characterized in that** gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by use of static mixers.

4. Method according to claim 1, **characterized in that** gaseous hydrogen chloride is introduced to the liquid mass in the dispersion zone in one, two or more points along its length, located between the point of the liquid mass introduction and the end of the dispersion zone, while introduction of gaseous hydrogen chloride to the liquid mass is realized by use of nozzles.

5. Device for dry hydrochlorination of mass from glycerol hydrochlorination with hydrochloric acid, in which the reaction of gaseous hydrogen chloride with non-reacted glycerol and monochlorohydrin isomers to a mixture of dichloropropanol isomers is carried out in a column reactor, **characterized in that** the device (1) contains a dispersion zone and a bubbling zone connected with it, while the bubbling zone consists of a column reactor (3).

6. Device according to claim 5, **characterized in that** the dispersion zone consists of an external pipe coil (2), with outlet connector pipe (01) is connected with inlet connector pipe (I5) of the column reactor (3).

7. Device according to claim 5, **characterized in that** the dispersion zone consists of an integrated pipe coil (5) with inlet connector pipe (I11), coiled on the external side of the column reactor (3), while the lower section of the integrated pipe coil (5) is located inside the column reactor (3).

8. Device according to claim 6 or 7, **characterized in that** cross-section area of the dispersion zone, and therefore of the integrated pipe coil (5) or of the external pipe coil (2), is of any shape.

9. Device according to claim 6 or 7, **characterized in that** the ratio of the dispersion zone length to the height of the column reactor (3) is in the range from 15:1 to 25:1.

10. Device according to claim 5, **characterized in that** the dispersion zone consists of an external casing (6) enclosing the column reactor (3), while the lower section of the external casing (6) is connected with the interior of the column reactor (3), and the upper section has an inlet connection pipe (I12).

11. Device according to claim 10, **characterized in that** the inlet connection pipe (I12) in the upper section of the external casing (6) is located tangentially in relation to the surface of the column reactor (3).

12. Device according to any one of the claims from 5 to 11, **characterized in that** the dispersion zone is equipped along its length with one or more connector pipes (I2, I3, I4, I21, I31, I41, I22, I32, I42,) supplying gaseous hydrogen chloride.

13. Device according to any one of the claims from 5 to 9, **characterized in that** the dispersion zone is equipped with a static mixer.

14. Device according to any one of the claims from 5 to 9, **characterized in that** the dispersion zone is equipped with nozzles.

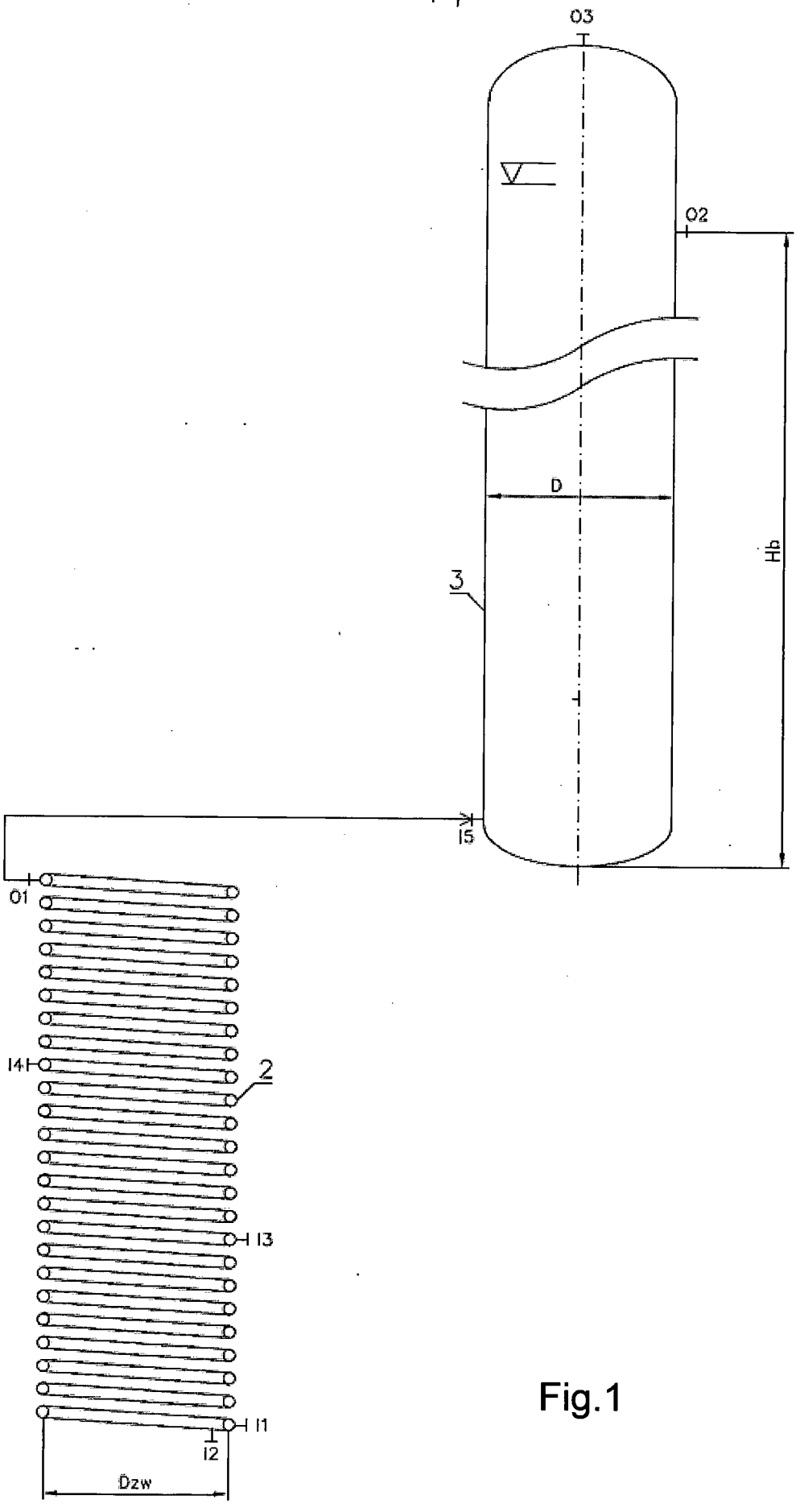

Fig.1

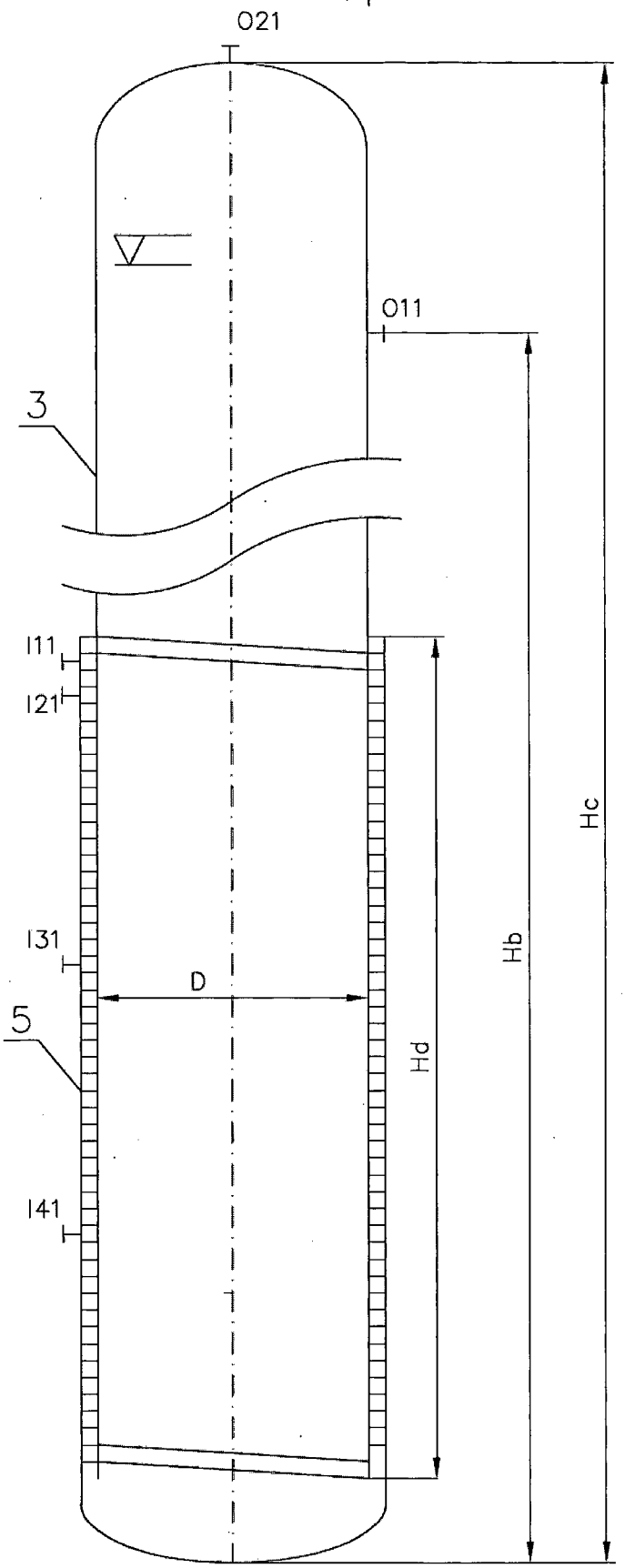

Fig.2

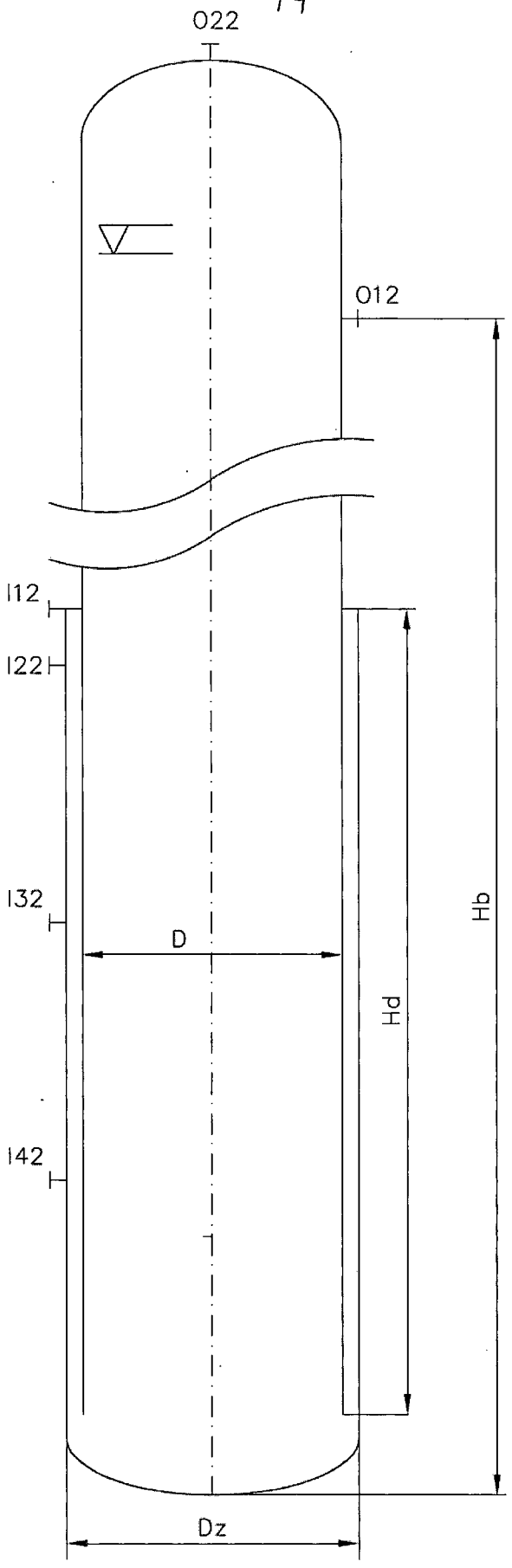

Fig.3

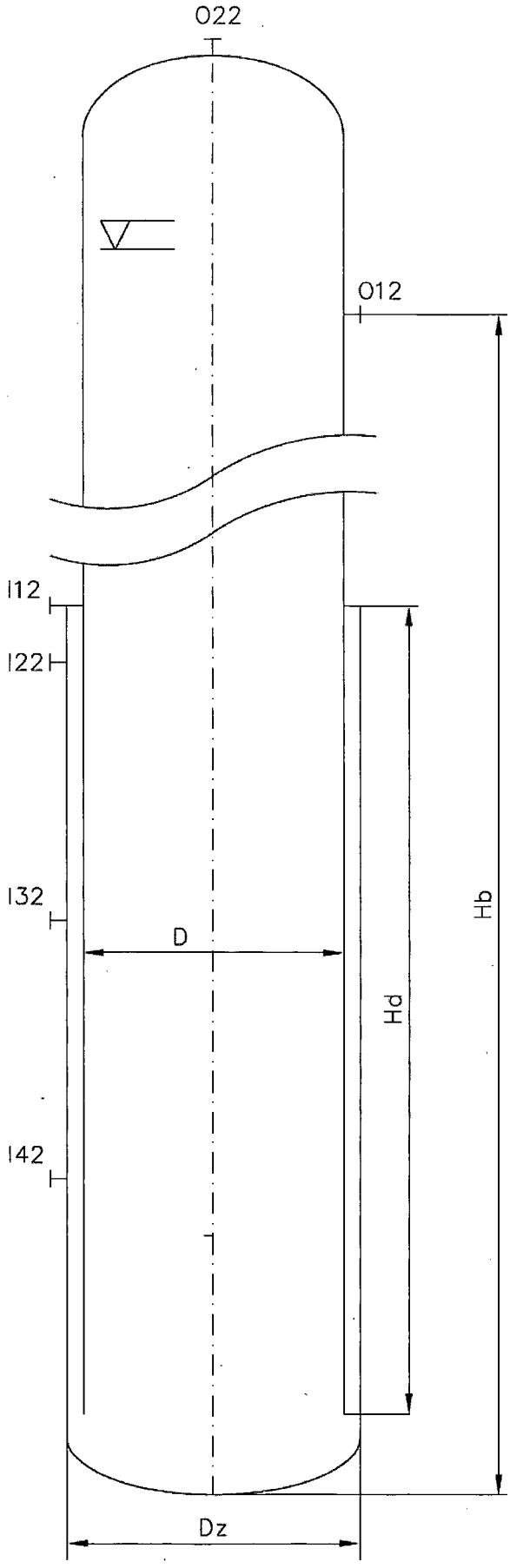

Fig.3

INTERNATIONAL SEARCH REPORT

International application No
PCT/PL2012/000013

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C31/36 C07C29/62 B01F3/04 B01F5/00 B01F5/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01F C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2010/022422 A1 (KANZLER WALTER [AT]) 4 March 2010 (2010-03-04)	5
A	claim 1 figure 1 example 1	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 July 2012	11/07/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	van Bergen, Marc

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