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(71) Applicant: **SOLVAY SA** [BE/BE]; Rue de Ransbeek, 310, B-1120 Bruxelles (BE).

(72) Inventor: **BRAUN, Max Josef**; 8 Varloh, 30900 Wedemark (DE).

(74) Agent: **MENVILLE, Laure**; 85 rue des Frères Perret, F-69192 Saint-Fons (FR).

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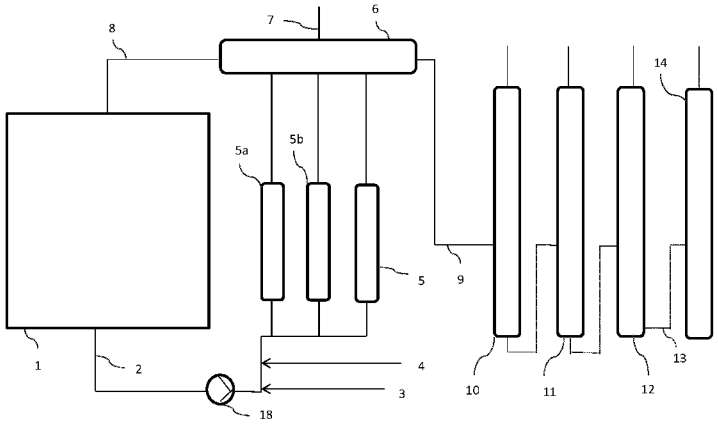
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(54) Title: A METHOD FOR PRODUCING A CHEMICAL COMPOUND AND APPARATUS THEREFOR

Figure 1



(57) Abstract: The invention relates to a method for the manufacture of chemical compounds wherein corrosive and/ or abrasive starting compounds, catalysts, intermediates or target compounds are involved; and a suitable reactor. The method is performed in a reactor at least partially made from or at least partially coated with material which is resistant to the reaction mixture, but has a low heat transfer coefficient, and where heat is supplied by a heat exchanger from a material which has a high heat transfer coefficient and high resistance to corrosion and/or abrasion. Preferably, the reactor is coated or at least partially coated with a (chloro)fluorosubstituted material, e.g. PTFE, and the heat exchanger is preferably constructed from silicon carbide. For example, hydrochlorofluorocarbons can be manufactured using HF as a starting compound, and antimony halides as catalyst.

WO 2016/079122 A1

A method for producing a chemical compound and apparatus therefor

The invention concerns a method for the manufacture of a chemical compound wherein the reaction mixture is corrosive or abrasive, and an apparatus therefor.

Chemical reactions often comprise a step wherein corrosive and/or abrasive constituents are contained in the reaction mixture. The abrasive and/or corrosive constituents may be introduced into the reaction in the form of respective starting material, they may be intermediates, a desired product or an undesired byproduct.

US published patent application 2004/0171896 for example discloses a process for the manufacture of fluorosubstituted compounds including a chlorine fluorine exchange reaction in the presence of adducts of antimony (V) halides with HF. It was observed that the resulting reaction mixture is very corrosive.

US published patent application 2005/0019487 states that alloys containing nickel and silicon and optionally aluminium are corrosion resistant materials suitable for such corrosive media.

Apparatus and parts of apparatus constructed from polyfluorinated, chlorofluorinated and perfluorinated material are often suitably corrosion resistant. The drawback of such material is the low heat transfer coefficient. Thus, it is difficult or impossible to economically perform reactions wherein heat must be provided or removed.

Object of the present invention is to provide an improved method for the manufacture of chemical compounds wherein corrosive and/or abrasive reaction mixtures are involved. Another object of the present invention is to provide an apparatus for the handling of such reaction mixtures. These and other objects are achieved by the invention as disclosed in the description and claims.

The invention relates to method for producing a chemical compound from at least one starting compound in a chemical reaction, optionally in the presence of at least one catalyst, providing a reaction mixture in a reactor at least partially made from or at least partially coated with a material of low heat conductivity, wherein heat is supplied or removed before, during and/or after performing the chemical reaction, wherein the at least one starting compound and /or the reaction mixture is corrosive and/or abrasive, and wherein the heat is supplied or

removed through an internal heat exchanger which is at least partially made from or at least partially coated with at least one carbide, wherein silicon carbide is preferred. In another aspect, the heat exchanger is an external heat exchanger.

Brief description of the drawings

Figure 1 shows an apparatus which is suitable for performing reactions which include corrosive and/or abrasive reactants. The apparatus includes heat exchangers arranged outside the reactor. The arrangement of the one or more heat exchangers outside the reactor is also denoted as "external heat exchanger".

Figure 2 shows an apparatus comprising a reactor with internally arranged heat exchangers.

Detailed description of the invention

In the present invention, the singular form is intended to include the plural, too. For example, the term "a method for the manufacture of a chemical compound" is intended to include the meaning "a method for the manufacture of chemical compounds"; "a material of low heat conductivity" is intended to include a mixture of materials comprising at least one material of low heat conductivity. Further, the term "a chemical reaction" is intended to denote a reaction comprising at least one reaction step, wherein reactions comprising several consecutive or simultaneous reaction steps are included in the term.

The term "corrosive" relates preferably to the ability of compounds to deteriorate, e.g. to dissolve, the metal or metal surface of reactors and reactor parts, e.g. walls, bottom, top, valves, lines, reactor internals like stirrers, deflector plates or baffle plates, media made from or coated with metal or metal alloys which parts may come into contact with at least part of the reaction mixture. Damaging of the metal surface by a chemical reaction of the metal with at least one compunds comprised in the reaction mixture, for example oxidation, is also related to by the term "corrosion". Generally, the term "corrosion" means any complete or partial destruction or erosion of the surface or wall of the metal of reactor or reactor parts due to chemical reaction of the metal with at least one compound comprised in the reaction mixture. The term "abrasive" preferably means that equipment and its parts which are – even only part time - in contact with the reaction media loose resistance towards reaction media. This often leads to mechanical partial deterioration, destruction or erosion of the metal or metal surface of reactors and reactor parts. In one aspect of the present invention, a reaction mixture is denoted as "corrosive" or "abrasive" if the interaction of the reaction mixture with a Hastelloy® C-4 reactor of 3 mm wall thickness at 100°C

for 1 hour diminishes the wall thickness to an extent of equal to or more than 30%, wherein equal to or less than 70% of the initial wall thickness remains, more preferably to an extent of equal to or more than 50%, wherein equal to or less than 50% of the initial wall thickness remains, and even more preferably to equal to or more than 70%, wherein equal to or less than 30% of the initial wall thickness remains. In another aspect of the present invention, a reaction mixture is denoted as "corrosive" or "abrasive" if the interaction of the reaction mixture with a reactor made of high grade stainless steel grade 1.4571 of 3 mm wall thickness at 100°C for 10 minutes diminishes the wall thickness to an extent of equal to or more than 30%, wherein equal to or less than 70% of the initial wall thickness remains, more preferably to an extent of equal to or more than 50%, wherein equal to or less than 50% of the initial wall thickness remains, and even more preferably to equal to or more than 70%, wherein equal to or less than 30% of the initial wall thickness remains.

According to the invention, the reaction is performed in a reactor at least partially made from material, or at least partially coated with material which is resistant to such deterioriation, but has a comparably low heat transfer coefficient. In this context, the term "a material of low heat conductivity" is intended to include a mixture of materials comprising at least one material of low heat conductivity.Preferably, the material has a heat conductivity at 25° of equal to or lower than 1 W/mK. Often, the reactor and/or reactor parts is or are at least partially made of or at least partially coated with a polyfluorinated polymer, a chlorofluorinated polymer, or a perfluoropolymer. Preferably, the reactor and/or reactor parts is or are made of or coated with a polyfluorinated polymer, a chlorofluorinated polymer, or a perfluoropolymer. Polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), polymeric ethylene chlorotrifluoroethylene (ECTFE), polymeric ethylene trifluoroethylene (ETFE), perfluoroalkoxy polymers (PFA) and fluorinated ethylene propylene (FEP) are cited as suitable polymers. Preferably, the reactor and/or reactor parts is or are at least partially made from or at least partially coated with polytetrafluoroethylene. More preferably, the reactor and/or reactor parts is or are made from or coated with polytetrafluoroethylene. Such parts and reactors are available, for example, from Dr. Schnabel GmbH, SGL Carbon Group, Limburg/Lahn, Germany.

The heat exchanger or heat exchangers is or are, respectively, at least partially made from at least one carbide. It is preferred that the heat exchanger or heat exchangers is or are substantially made from at least one carbide. The term

"carbide" intends to denote covalent carbides and interstitial carbides. Typical covalent carbides are silicon carbide and boron carbide.Silicon carbide (SiC) is preferred. Interstitial carbides include, but are not limited to, titanium carbide, hafnium carbide, zirconium carbide, vanadium carbide, niobium carbide, tantalum carbide, chromium carbode, molybdenum carbide and tungsten carbide. Where there is more than one crystalline form is possible for a given carbide, the invention includes all crystalline forms. Mixed carbides, for example titanium hafnium carbide, are also included in the term "carbide", Such heat exchangers, in particular heat exchangers made from SiC, were found to be corrosion resistant and resistant to abrasion. Heat exchangers made from SiC are most preferred according to the invention. SiC heat exchangers are available, for example, from Thaletec GmbH, Thale, Germany. The heat exchanger, or a plurality of two or more heat exchangers, may be arranged inside the reactor, or outside, for example, to heat or cool lines, pipes or a suitable reactor.

The corrosive, abrasive or corrosive and abrasive constituents of the reaction mixture may be introduced into the reaction mixture in the form of respective starting compounds, optionally including at least one compound of the group consisting of hydrogen halides and halogens, in particular HCl, chlorine and HF , which in combination are often much more corrosive than the isolated compounds alone. Further compounds which may be constituents from the beginning of the reaction are at least one catalyst or a combination of more than one catalyst, or they may be formed during a chemical reaction in the form of intermediates or in the form of desired products or by-products. For example, C1-C10 alkyl or C1 to C10 alkene compounds substituted by at least one Cl atom, e.g. compounds introduced into a reactor to perform a chlorine fluorine exchange reaction by using HF as fluorinating agent in presence of a catalyst. Preferred examples are unsaturated chlorinated C1 to C10 alkenes, especially chlorinated ethylenes, e.g. perchloroethylene, trichloroethylene, any dichloroethylene isomer, monochloroethylene or monochloroethylene isomer. Other preferred examples are C1-C10 alkyl compounds substituted by at least one Cl atom, e.g. compounds substituted by at least one Cl atom, e.g. 1,1-dichloro-2-chloro-2,2-difluoroethane or 1,1-dichloro-2,2,dichloro-2-fluoroethane.

In one embodiment, the method of the invention can be applied for at least one corrosive and/or abrasive starting compound, for example, HF, HCl or a halide, wherein HF is preferred, or mixtures thereof.

In another embodiment, the method of the invention can be applied for compounds supporting, influencing or accelerating chemical reactions, e.g. at least one corrosive and/or abrasive catalyst. For example, the method of the invention can be applied to reactions wherein at least one super acid is involved. A super acid is a medium in which the chemical potential of the proton is higher than in pure sulfuric acid. Super acids are, for example, HSO_3F, CF_3SO_3H, and especially, adducts of HF with antimony halides, especially adducts of HF with SbF_5, e.g. H_2FSbF_6. The method of the invention is suitable, for example, for chemical reactions involving at least one super acid as catalyst, especially as fluorination catalyst.

In still another embodiment, the method of the invention can be applied for producing or handling at least one intermediate compound which is corrosive and/or abrasive.

In yet another embodiment, the method of the invention can be applied for producing or handling at least one corrosive compound which is one or more desired product or byproducts, for example, in producing super acids to be used as catalysts.

Desired products or byproducts which can be manufactured according to the method of the invention including an HF addition reaction, a chlorine fluorine exchange reaction and/ or a rearrangement reaction, preferably in the presence of Sb(V) halide catalysts or their adducts with HF, are for example:

$CClF_2CHCl_2$ from CCl_3CHCl_2 or $CCl_2=CCl_2$.

$CClF_2CHCl_2$ from $CHCl_2CCl_2F$, and/or $CCl_2=CClF$

CF_3CHCl_2 from CCl_3CHCl_2, CCl_2FCHCl_2, $CClF_2CHCl_2$, $CClF_2CHClF$ or $CCl_2=CCl_2$.

CF_3CHF_2 from $CCl_2=CHCl$ or CCl_3CHCl_2.

CF_3CHF_2 from $CHCl_2CCl_2F$ and/or F1111 ($CCl_2=CClF$).

$CF_3CH_2CF_2CH_3$ from $CCl_3CH_2CCl_2CH_3$ or $CH_3=CCl=CH_2$, CCl_4 and HF

CH_2F_2 from CH_2Cl_2 and/or CH_2FCl.

$CF_3CF=CH_2$ from $CCl_3CHClCH_2Cl$ (including a dehydrofluorination reaction).

Trans-1-chloro-3,3,3-trifluoropropene from $CCl_3CH_2CHCl_2$ (including a dehydrofluorination reaction).

$CClF_2CCl_2F$ from CCl_3CCl_3.

CF_3CCl_3 from CCl_3CCl_3.

HFC-134a (CF_3 –CH_2F) or its precursor F133a (CF_3- CH_2Cl) by fluorination of trichloroethylene.

F 124 (CF_3CFHCl) and/or F125 (CF_3CHF_2) by fluorination of perchlorethylene or an intermediate, such as F121 ($CHCl_2CCl_2F$ and F1111 (CCl_2=CClF).

Other saturated and unsatured hydrochlorofluorocarbons and hydrofluorocarbons with, for example, a C1 to C10 backbone, from respective compounds with a lower degree of fluorine substitution.

For example, the method of the invention can be applied for reactions wherein hydrogen fluoride (HF) is involved, be it as starting compound, for example, in chlorine fluorine exchange reactions or in addition reactions; as intermediate, for example, in SN1 rearrangement reactions; as catalyst, for example, or in polymerization reactions; or as a reaction product, for example, in dehydrofluorination reactions.

A preferred embodiment of the invention relates to reactions wherein HF is a starting compound.

The method of the invention can also especially be applied for reactions involving at least one corrosive catalyst, e.g. for all super acids and combinations between all superacids and all their mixtures in the presence of some HF and/or HCl. For example, antimony (III) halides and antimonyantimony (V) halides, wherein antimony (V) halides are preferred, are applied as catalysts in chlorine fluorine exchange reactions and in reactions including the addition of HF to unsaturated carbon carbon bonds. Often, these catalysts are applied in the presence of HF, forming adducts with HF. HF and the adducts, for example, with $SbCl_xF_y$ forming $SbCl_xF_y \cdot HF$ or $SbCl_xF_y \cdot 2HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5, and especially, adducts wherein x is 0 or approximately 0, and y is 5 or approximately 5, are known to be very corrosive to metals, even to metals considered as resistant to corrosion, e.g. Monel metal or nickel. HF adducts of SbF_5, for example H_2FSbF_6, are super acids and can be used as catalysts or reactants in the method of the invention. The method of the invention can also be applied for reactions in which magic acid, FSO_3H-SbF_5, is involved.

Thus, another preferred embodiment of the invention relates to a reaction wherein at least one catalyst is present, and the at least one catalyst is at least one super acid or magic acid, and preferably, is selected from the group consisting of antimony halides and their adducts with hydrogen fluoride, more preferably,

wherein the catalyst comprises antimony (V) halides or their adducts with HF, and especially for reactions wherein the catalyst comprises $SbCl_xF_y$, $SbCl_xF_y \cdot HF$ or $SbCl_xF_y \cdot 2HF$ wherein x is an integer from 0 to 5, y an integer is from 0 to 5, and the sum of x and y is 5. Especially preferably, x is an integer from 0 to 1, and y is an integer from 4 to 5.

The method of the invention is especially suited for processes wherein Sb(III) halides and especially Sb(V) halides and their adducts with HF are employed as catalyst, as described above.

The method of the invention is preferably applied in processes for the manufacture of fluorosubstituted compounds. In these reactions, often hydrofluoric acid and/or the at least one antimony catalyst mentioned above are involved.

For example, the fluorination of $CCl_3C(O)Cl$ with HF in the presence of catalysts to form $CF_3(CO)F$ can be performed according to the invention.

The method of the invention is especially suited for the manufacture of fluorocarbons, hydrofluorocarbons and hydrochlorofluorocarbons in reactions involving at least one step of chlorine-fluorine exchange reactions, the addition of HF to unsaturated carbon-carbon bonds, or for rearrangement reactions, and for methods comprising two or more of such steps, preferably, in steps where at least one catalyst is involved. The method of the invention is preferred if, in addition to HF and/or at least one catalyst, especially an antimony (V) halide catalyst, the reaction mixture further comprises at least one intermediate and/or at least one target compound, or, preferably, at least one starting compound selected from the group consisting of: a halogenated carbon compound with 1 to 6 carbon atoms, and wherein the chemical reaction comprises a chlorine-fluorine exchange reaction; or a saturated halogenated carbon compound with 2 to 6 carbon atoms, and wherein the chemical reaction comprises at least one reaction step selected from the group consisting chlorine-fluorine exchange reaction and a rearrangement reaction; or an unsaturated halogenated carbon compound wherein the chemical reaction comprises at least one reaction step selected from the group consisting of a hydrogen-fluoride addition reaction, a chlorine-fluorine exchange reaction, and a rearrangement reaction.

More preferably, the reaction mixture comprises hydrogen fluoride and at least one halogenated carbon compound selected from the group consisting of $CHX=CX_2$, $CX_2=CX_2$, $C_aH_bCl_cF_d$ and $C_eH_fF_g$ wherein X is Cl or F; a is an integer from 2 to 6, b, c and d are integers equal to or greater than 1, and the sum

of b, c and d is 2a +2; and wherein e is an integer from 1 to 6, f is 1 or 2, g is an integer equal to or greater than 2 and the sum of e,f and g is 2e + 2.

Especially preferred, the at least one halogenated compound is selected from the group consisting of: $CCl_2=CCl_2$; $C_aH_bCl_cF_d$ wherein a is 2 or 3, b is 1 or 2, c is 1 or 2, d is an integer equal to or greater than 2, and the sum of b, c and d is 2a + 2; and $C_eH_fF_g$ wherein e is 2 or 3, f is 1 or 2, g is an integer equal to or greater than 2 and the sum of e, f and g is 2e + 2.

A most preferred embodiment relates to a method wherein $CCl_2=CCl_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5, to form $CHCl_2$-$CClF_2$ or $CHCl_2$-CF_3; or wherein $CHClF$-$CClF_2$ is rearranged in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5 to form $CHCl_2$-CF_3; or wherein $CHCl_2$-$CClF_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5 to form $CHCl_2$-CF_3.

Another preferred embodiment relates to rearrangement reactions. CF_3CHCl_2, for example, may be manufactured by addition of HF and chlorine fluorine exchange reactions starting with HF and $CCl_2=CCl_2$ in the presence of catalysts, e.g. in the presence of Sb catalysts, for example as described above. Often, $CClF_2CHClF$, CCl_2FCF_2 or both are contained as impurities. In downstream reactions, these impurities may form undesired byproducts. A suitable type of catalyst are, for example, super acids, especially adducts of HF and Sb (V) halides, especially those adducts as described above. Accordingly, the method of the invention preferably relates to the manufacture of isomerically pure CF_3CHCl_2 from impure CF_3CHCl_2 containing $CClF_2CHClF$, CCl_2FCHF_2 or both by a treatment in the presence of Hf and Sb(V) halides, especially in the presence of HF and SbF_5 forming $HSbF_6$ and/or $H_2F \cdot SbF_6$. This treatment is performed providing heat. The temperature is preferably in a range of from 50 to 150 °C, the pressure is preferably in a range of from ambient pressure (approximately 1 bar abs) and 6 bar (abs); temperature and pressure are selected such that the reaction is performed in the liquid phase. A detailed description can be found in US published patent application 2004/0171896.

Of course, addition reactions, chlorine fluorine exchange reactions and rearrangement reactions may be performed simultaneously. An example is the manufacture of pure CF_3CHCl_2 from $CCl_2=CCl_2$, and HF in the presence of

$SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5.The addition reaction and the chlorine fluorine exchange reaction provides some isomers, namely CF2ClCHClF and/or CCl_2FCHF_2 as described above. Simultaneously, a rearrangement reaction takes place according to the method of the invention, and pure CF_3CHCl_2 is obtained with, if at all, insignifcant traces of the isomers.

In a preferred embodiment, as mentioned above, the reaction is performed in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5; here, spent catalyst is preferably regenerated.

The regeneration can be performed in manners which are known in the art. For example, the regeneration can be effected by introducing elemental chlorine to the spent catalyst as described, for example, in US patent 2,005,710, or US published patent application 2005-0027147. Other methods for regeneration of the catalyst are described in US 3,806,589 where the catalyst is brought into an aqueous solution, ammonia is added, and finally the catalyst is recovered as $SbCl_3$ which could be oxidized with chlorine to produce $SbCl_5$; and in US 6,034,016 where tars are oxidized with chlorine to isolate purified catalyst.

The preferred method for regeneration of Sb(V)halide catalyst is described in US 2005-0027147 the whole content of which is incorporated herein for all purposes. Here, the spent catalyst is regenerated with elemental chlorine such that the chlorine does not come into contact with starting material or intermediates which could react with chlorine in an undesirable manner. For example, a part of the reaction mixutre is removed and returned from the reactor in a loop, and/or reactants are reacted in the mixture and possibly are removed by distillation before chlorine is added for regeneration.

The reaction mixture obtained according to the process of the invention may be either further reacted directly to obtain other final products, such as pharmaceuticals, agrochemicals, or their intermediates (e.g. as described below), or the raction mixture may be worked up.

For example, the rection mixture may be subjected to one or more distillation steps to obtain purified product. This can be done in a fractionation column or in several successive columns.

According to one aspect, the reaction mixture is subjected to a distillation comprising one or more, preferably at least 3 steps. Often, it is preferred to perform several distillation steps, preferably for removing in a first step lowest

boiling components, e.g. HCl, then low boiling components, e.g. HF, then CF_3CHCl_2, and finally $CClF_2CHCl_2$. The steps can be performed in a single distillation column, or in several subsequent distillation columns. It is preferred to remove the constituents with the lowest boiling point at a respectively high pressure, then compounds with higher boiling point at a lower pressure, and successively the constitutents with still higher boiling point, leaving the high boilers like polymers or tar in the last distillation column. For example, to remove HCl, the pressure is often rather high, e.g. in a range of from 18 to 30 bar (avbs). To remove HF, the pressure often is in a range of from 6 to 15 bar (abs). Constituents with higher boiling point are distilled at a pressure in a range of from atmospheric pressure to 5 bar (abs).

The products obtained by the method of the invention can be applied as such, e.g. as blowing agent, as solvent or as refrigerant.

Alternatively, they may be used as intermediates, to be further reacted to desired target compounds, e.g. intermediates for other reactions, intermediates for pharmaceuticals or agrochemicals, or pharmaceuticals or agrochemicals. Thus, the invention further relates to a process for the manufacture of an agrochemically or pharmaceutically active compound, wherein an agrochemically or pharmaceutically active compound or an intermediate of the agrochemically or pharmaceutically active compound is prepared according to the methods desribed above, and optionally wherein the intermediate is subsequently converted in one or more steps to form the agrochemically or pharmaceutically active compound.

For example, $CCl_2=CCl_2$ can be reacted according to the invention in a reaction including the addition of HF, a chlorine fluorine exchange reaction and an isomerisation reaction to form CF_3CHCl_2, or, depending on the reaction conditions, to form CHCl2$CClF_2$. This compound is then reacted with oxygen in a photocatalyzed reaction to form $CF_3C(O)Cl$ or $CClF_2C(O)Cl$, respectively. This reaction is described in US patent 3,883,407, US patent 5,545,298 (pressureless reaction in the absence of chlorine) and US patent 5,55569,782 (pressureless reaction in the presence of chlorine), the whole contents of all of the three patents incorporated herein for all purposes by reference. Said $CF_3C(O)Cl$ or $CClF_2C(O)Cl$ may be used as intermediate itself, for example, by reacting it with ethyl vinyl ethers for the manufacture of alkenones as described in US patent 7,405,328 B2 the whole content of which is incorporated herein by reference for all purposes. The reaction of CF3C(O)Cl or CClF2C(O)Cl may also

give a halogenated precursor of an alkenone, as described in WO2011003854. Such an alkenone and/or halogenated precursor of an alkenone can further be reacted to form heterocycles as described in WO2010037688. Said heterocycles are often suitable as active ingredients or intermediates of active ingredients of pharmaceuticals and/or agrochemicals, in particular fungicidal compounds. CF3C(O)Cl or CClF2C(O)Cl can also be reacted with ketene, followed by alcoholysis, reaction with orthoformate and subsequent reaction with heteroatom-containing building blocks, such as methyl hydrazine, optionally followed by reduction of a CClF2-group to CHF2-group to form as active ingredients or intermediates of active ingredients of pharmaceuticals and/or agrochemicals, in particular fungicidal compounds. Such reactions and reaction sequences are described, for example, in US2011297883, WO2013/171102, WO2012025469 and EP2687514. The whole content of all of the cited publications is hereby incorporated by reference.

The invention also concerns an apparatus for chemical reactions comprising a reactor made at least partially from or at least partially coated with a material of low heat conductivity, and an internal heat exchanger at least partially made from or at least partially coated with at least one carbide, in particular silicon carbide. The heat exchanger preferably is a plate heat exchanger or a tube bundle heat exchanger.

The invention further concerns an apparatus for chemical reactions comprising a reactor made at least partially from or at least partially coated with a material of low heat conductivity, and an external heat exchanger at least partially made from or at least partially coated with at least one carbide, in particular silicon carbide. The heat exchanger preferably is a plate heat exchanger or a tube bundle heat exchanger. The external heat exchanger often is particularly advantageous, as the reaction mixture often mixes very efficiently in the external heat exchanger, which can make additional stirrers inside the reactors redundant. Further, the external heat exchanger can also be designed as inlet for reactants, in particular in continous procdures, thus allowing an immediate and efficient mixing of the reactants, thus, for example, avoiding local large concentrations of reactants. External heat exchangers are further advantageously more accessible for maintenance or replacement.The material of the reactor is resistant to abrasive and/or corrosive deterioriation, but has a comparably low heat transfer coefficient. Preferably, the material has a heat conductivity at 25° of equal to or lower than 1 W/mK. Often, the reactor and/or

reactor parts is or are at least partially made of or at least partially coated with a polyfluorinated polymer, a chlorofluorinated polymer, or a perfluoropolymer. Polytetrafluoroethylene (PTFE), polychlorotrifluoroethylene (PCTFE), polymeric ethylene chlorotrifluoroethylene (ECTFE), polymeric ethylene trifluoroethylene (ETFE), perfluoroalkoxy polymers (PFA) and fluorinated ethylene propylene (FEP) are cited as suitable polymers. Preferably, the reactor and/or reactor parts is or are at leats partially made from or at least partially coated with polytetrafluoroethylene; and the reactor and/or parts of the reactor is/are especially preferably made from PTFE. Mixtures of two or more of the foregoing polymers are also suitable. Such parts and reactors are, for example, available from Dr. Schnabel GmbH, SGL Carbon Group, Limburg/Lahn, Germany.

The heat exchanger is at least partially made from at least one carbide, in particular silicon carbide (SiC). Such heat exchangers were found to be corrosion resistant and resistant to abrasion. SiC heat exchangers are available, for example, from Thaletec GmbH, Thale, Germany. The internal heat exchanger is a preferably a plate heat exchanger made from at least one carbide, preferably SiC, or a tube bundle heat exchanger made from at least one carbide, preferably silicon carbide. In another aspect, the heat exchanger is an external heat exchanger, which is a preferably a plate heat exchanger made from at least one carbide, preferably SiC, or a tube bundle heat exchanger made from at least one carbide, preferably silicon carbide.

In a very preferred embodiment, the apparatus comprises a reactor which is made from polytetrafluoroethylene, and an internal heat exchanger which is a plate heat exchanger made from silicon carbide, or a tube bundle heat exchanger made from silicon carbide. In another very preferred embodiment, the apparatus comprises a reactor which is made from polytetrafluoroethylene, and an external heat exchanger which is a plate heat exchanger made from silicon carbide, or a tube bundle heat exchanger made from silicon carbide.

The methods, processes and reactors as described in the present invention can be performed or operated in batch-wise or continuous manner, wherein continuous is preferred. In one aspect of the present invention, depending on the operation mode of the process and physical characteristics of reactants, catalysts and/or products, reactants and/or product streams are fed or withdrawn in solid, liquid or gas phase.

A particularly preferred apparatus will now be further explained by reference to figure 1.

A reactor (1), made, or preferably, coated on the inside with, for example from PTFE, serves to perform the reaction. Via line (2), reaction mixture is continuously or batchwise withdrawn from reactor (1). Via line (3), fresh $CCl_2=CCl_2$ is supplied into line (2), and via line (4), fresh HF. Withdrawn reaction mixture is fed by means of pump (18) to the bottom of heat exchangers (5), (5a) and (5b) made from SiC, and heated therein; for the sake of simplicity, lines for passing hot heat transfer fluid into the heat exchangers are omitted. The heated mixture is then fed into tank (6). 10 % by weight of the reaction mixture is withdrawn continuously through line (7) into a regeneration loop wherein the catalyst is treated with elemental chlorine to regenerate it. Regenerated may be fed to the tank (6), into line (8) or into the ractor (1). A part of the reaction mixture – which contains, as described above, fresh $CCl_2=CCl_2$ and HF - is withdrawn from tank (6) and returned, via line (8), into the reactor (1), another part of the reaction mixture from tank (6) is withdrawn via line (9) and fed into distillation tower (10).

In another aspect, instead of withdrawing mixture from the tank (6) for catalyst regeneration, mixture could be withdrawn directly from reactor (1) or from line (2) or otherwise.

In one embodiment, the apparatus is coupled with one or more distillation columns, which are operated at suitable pressure. Lowest boiling components, in particular HCl, generally leave via the top of column (10), the bottom is fed into distillation tower (11). The second lowest boiling compositions, in particular HF, leave via the top of column (11), the bottom of column (11) is fed into distillation tower (12) wherein the third lowest boiling compositions, in particular purified CF_3CHCl_2, are withdrawn via the top of column (12) . Higher boiling components are withdrawn from the bottom of column (12) via line (13) and fed into column (14). From the top of column (14), wherein the fourth lowest boiling compositions, inparticular purified CF_3CHCl_2, arewithdrawn. Highest boling components can be withdrawn from the bottom of column (14).

An alternative arrangement of the heat exchangers is given in figure 2. Here, the heat exchangers are located inside the reactor. A hot heat transfer fluid is passed via line (15) into tube bundle heat exchangers (16) which are constructed from at least one carbide, in particular silicon carbide. Heat transfer fluid is withdrawn from the heat exchangers (15) via line (17).

The advantage of the method and the apparatus of the invention is for example that a material with high corrosion resistance but low heat transfer capacity, combined with a material of high heat transfer capacity and high corrosion resistance, can be applied together for chemical reactions, especially for reactions involving HF and antimony halides and their adducts with HF.

The invention further concerns a method for producing a chemical compound from at least one starting compound in a chemical reaction, optionally in the presence of at least one catalyst, providing a reaction mixture in an apparatus comprising a reactor and a heat exchanger which are at least partially made from or at least partially coated with at least one carbide, wherein the at least one starting compound and /or the reaction mixture is corrosive and/or abrasive. A preferred carbide is silicon carbide. In one aspect, the reactor and the heat exchanger are integrated; in another aspect, the reactor and the heat exchanger are separate entities linked through suitable lines. The apparatus can be configured to function either on a microreactor scale, lab scale or tonne scale. More than one apparatus can be combined in order to provide suitable reaction conditions and turnover. Suitable apparatus are available, for example, from Chemtrix BV, Geleen, The Netherlands. The method can be applied in batch-wise mode or continuous mode, wherein continuous mode is preferred. The method is particularly preferred for reactions involving at least one corrosive catalyst. Detailed aspects of the preferred methods, in particular catalysts used, preferred starting materials and products, are disclosed in the description above. A most preferred aspect relates to a method wherein $CCl_2=CCl_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5, to form $CHCl_2$-$CClF_2$ or $CHCl_2$-CF_3; or wherein $CHClF$-$CClF_2$ is rearranged in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5 to form $CHCl_2$-CF_3; or wherein $CHCl_2$-$CClF_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5 to form $CHCl_2$-CF_3.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

The following examples, with reference to figure 1, are intended to explain the invention further without the intent to limit it.

Example 1: Manufacture of CF_3CHCl_2 and $CClF_2CHCl_2$

The reaction is performed in a reactor (1) coated with PTFE, having an internal volume of approximately 20 m^3, approximately 1,500 kg of $SbCl_5$ are given. 7.5 metric tons of HF and 6,500 kg of CCl_2=CCl_2 are fed into reactor (1) through lines (3) and (4) via heat exchangers (5), (5a) and (5b). The temperature of the reaction mixture is brought to at least 80 °C and kept there. $SbCl_5$ is converted to form a super acid, namely, the adduct of HF and SbF_5. Continuously, reaction mixture is withdrawn from reactor (1) via line (2) and pump (18), and continuously, HF and CCl_2=CCl_2 are introduced through lines (3) and (4) into line (2). The resulting mixture is passed through heat exchangers (5), (5a) and (5b) into tank (6). After some time, it is observed that the catalyst activity diminishes, and now, 10% by weight of the reaction mixture are withdrawn from tank (6) via line (7); in a loop, the catalyst is regenerated by contact with chlorine. The solution containing regenerated catalyst is returned to reactor (1). Another part of the reaction mixture of tank (6) is withdrawn via line (9) and fed into four subsequent distillation towers (10) to (14) to isolate HCl, HF, CF_3CHCl_2 and $CClF_2CHCl_2$, respectively.

Example 2: Manufacture of $CF_3(CO)Cl$ from CF_3CHCl_2

CF_3CHCl_2, obtained in column (13), is supplied to a photo reactor in gaseous form, mixed with O_2 and a low amount of Cl_2, and reacted without imposing additional pressure by providing UV light irradiation into the photo reactor. The resulting mixture of HCl, $CF_3C(O)Cl$ and unreacted O_2 and CF_3CHCl_2 is separated by distillation.

Example 3: Manufacture of $CClF_2(CO)Cl$ from $CClF_2CHCl_2$

$CClF_2CHCl_2$, obtained in column (14), is supplied to a photo reactor in gaseous form, mixed with O_2 and a low amount of Cl_2, and reacted without imposing additional pressure by providing UV light irradiation into the photo reactor. The resulting mixture of HCl, $CClF_2C(O)Cl$ and unreacted O_2 and $CClF_2CHCl_2$ is separated by distillation.

Example 4: Purification of CF_3CHCl_2

Approximately 7 metric tons of CF_3CHCl_2 which contains 10% by weight of $CClF_2CHCl_2$ and 0.1 % by weight of CCl_2FCHF_2 are given into reactor (1). Approximately 1.7 metric tons of SbF_5 and 1.5 metric tons of HF are added. The reaction mixture is circulated by means of pump (2) and brought to 110 °C by

means of heat exchangers (5), (5a) and (5b). The residence time in the reactor is at least about 30 minutes. Continuously, reaction mixture is withdrawn from tank (6) into the regeneration loop and to distillation columns (10), (11) and (14) to separate pure CF_3CHCl_2.

CLAIMS

1. A method for producing a chemical compound from at least one starting compound in a chemical reaction, optionally in the presence of at least one catalyst, providing a reaction mixture in a reactor at least partially made from or at least partially coated with a material of low heat conductivity, wherein heat is supplied or removed before, during and/or after performing the chemical reaction, wherein the at least one starting compound and /or the reaction mixture is corrosive and/or abrasive, and wherein the heat is supplied or removed through a heat exchanger which is at least partially made from or at least partially coated with at least one carbide.

2. The method of claim 1 wherein the heat exchanger is an external heat exchanger.

3. The method of claims 1 or 2, wherein the at least one carbide is silicon carbide.

4. The method of anyone of claims 1 to 3wherein at least one starting compound is hydrogen fluoride.

5. The method of anyone of claims 1 to 4 wherein at least one catalyst is present, and wherein the at least one catalyst is selected from the group consisting of antimony halides and antimony halide adducts with hydrogen fluoride.

6. The method of claim 5 wherein the at least one catalyst comprises $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5.

7. The method of anyone of claims 1 to 6 wherein the material of low heat conductivity has a heat conductivity at 25° of equal to or lower than 1 W/mK.

8. The method of anyone of claims 1 to 7 wherein the reactor is at least partially made of or is at least partially coated with a polyfluorinated polymer, a chlorofluorinated polymer, or a perfluoropolymer.

9. The method of anyone of claims 1 to 8 further comprising a starting compound selected from the group consisting of: a halogenated carbon

compound with 1 to 6 carbon atoms, and wherein the chemical reaction comprises a chlorine-fluorine exchange reaction; or a saturated halogenated carbon compound with 2 to 6 carbon atoms, and wherein the chemical reaction comprises at least one reaction step selected from the group consisting chlorine-fluorine exchange reaction and a rearrangement reaction; or an unsaturated halogenated carbon compound wherein the chemical reaction comprises at least one reaction step selected from the group consisting of a hydrogen-fluoride addition reaction, a chlorine-fluorine exchange reaction, and a rearrangement reaction.

10. The method of anyone of claims 1 to 9 wherein the reaction mixture comprises hydrogen fluoride and at least one halogenated carbon compound selected from the group consisting of $CHX=CX_2$, $CX_2=CX_2$, $C_aH_bCl_cF_d$ and $C_eH_fF_g$ wherein X is Cl or F; a is 2 to 6, b, c and d are integers equal to or greater than 1, and the sum of b, c and d is 2a +2; and wherein e is an integer from 1 to 6, f is 1 or 2, g is an integer equal to or greater than 2 and the sum of e, f and g is 2e + 2.

11. The method of anyone of claims 1 to 10 wherein $CCl_2=CCl_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5, to form $CHCl_2$-$CClF_2$ or $CHCl_2$-CF_3; or wherein $CHClF$-$CClF_2$ is rearranged in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5 to form $CHCl_2$-CF_3; or wherein $CHCl_2$-$CClF_2$ is reacted with hydrogen fluoride in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, to form $CHCl_2$-CF_3.

12. The method of anyone of claims 1 to 11 wherein the reaction is performed in the presence of $SbCl_xF_y$ or $SbCl_xF_y \cdot HF$ wherein x is an integer from 0 to 5, y is an integer from 0 to 5, and the sum of x and y is 5, and wherein spent catalyst is regenerated.

13. The method of any one of claims 1 to 12 wherein the reaction mixture is subjected to a distillation comprising at least 3 steps.

14. A process for the manufacture of an agrochemically or pharmaceutically active compound, comprising the method according to anyone

of claims 1 to 13, wherein an agrochemically or pharmaceutically active compound or an intermediate of the agrochemically or pharmaceutically active compound is prepared according to the method according to anyone of claims 1 to 13, and optionally wherein the intermediate is subsequently converted in one or more steps to form the agrochemically or pharmaceutically active compound.

15. An apparatus for chemical reactions comprising a reactor at least partially made from or at least partially coated with a material of low heat conductivity, preferably polytetrafluoroethylene, and a heat exchanger made from or coated with at least one carbide, in particular silicon carbide, peferably wherein the heat exchanger is a plate heat exchanger or a tube bundle heat exchanger.

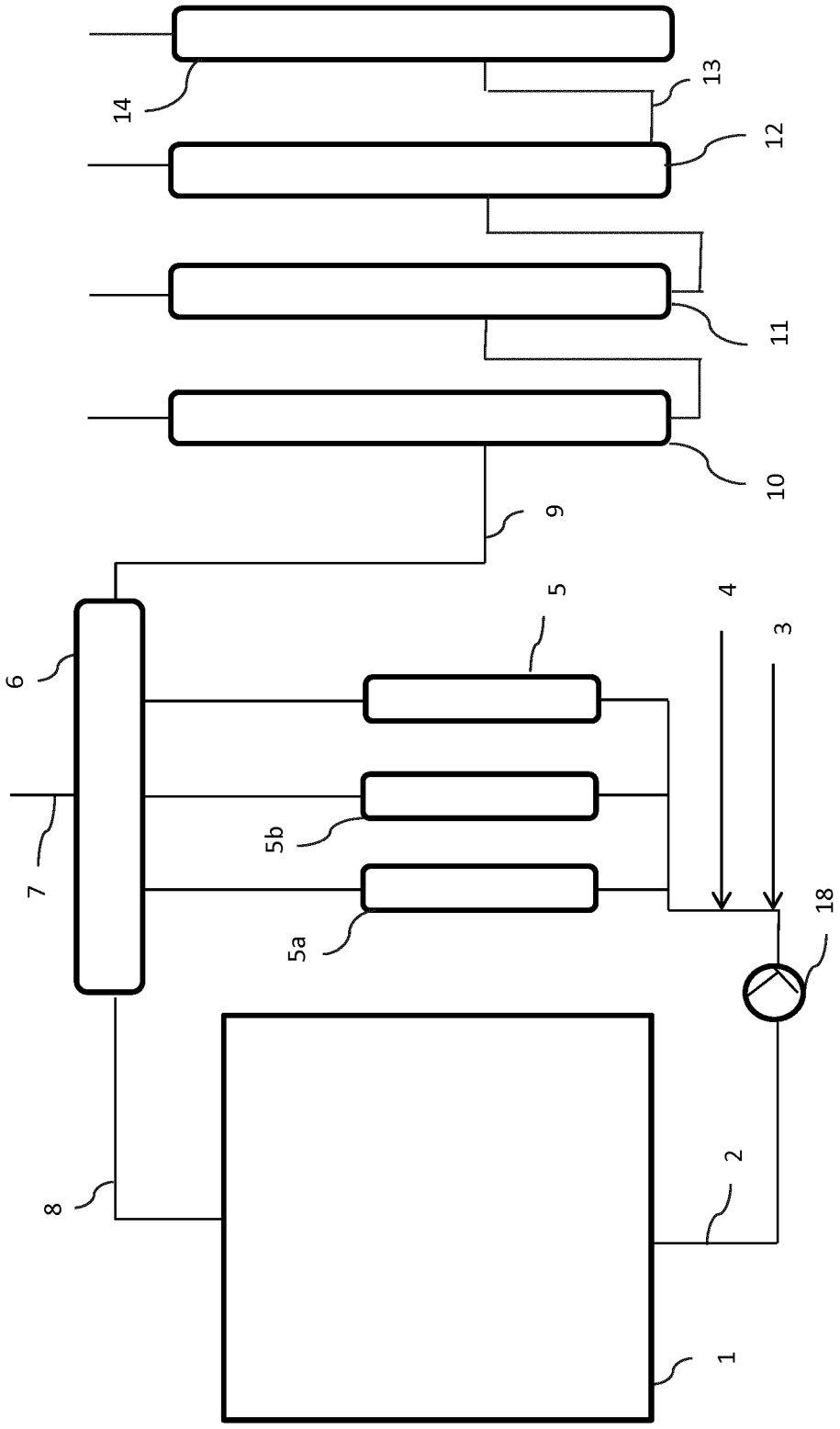


Figure 1

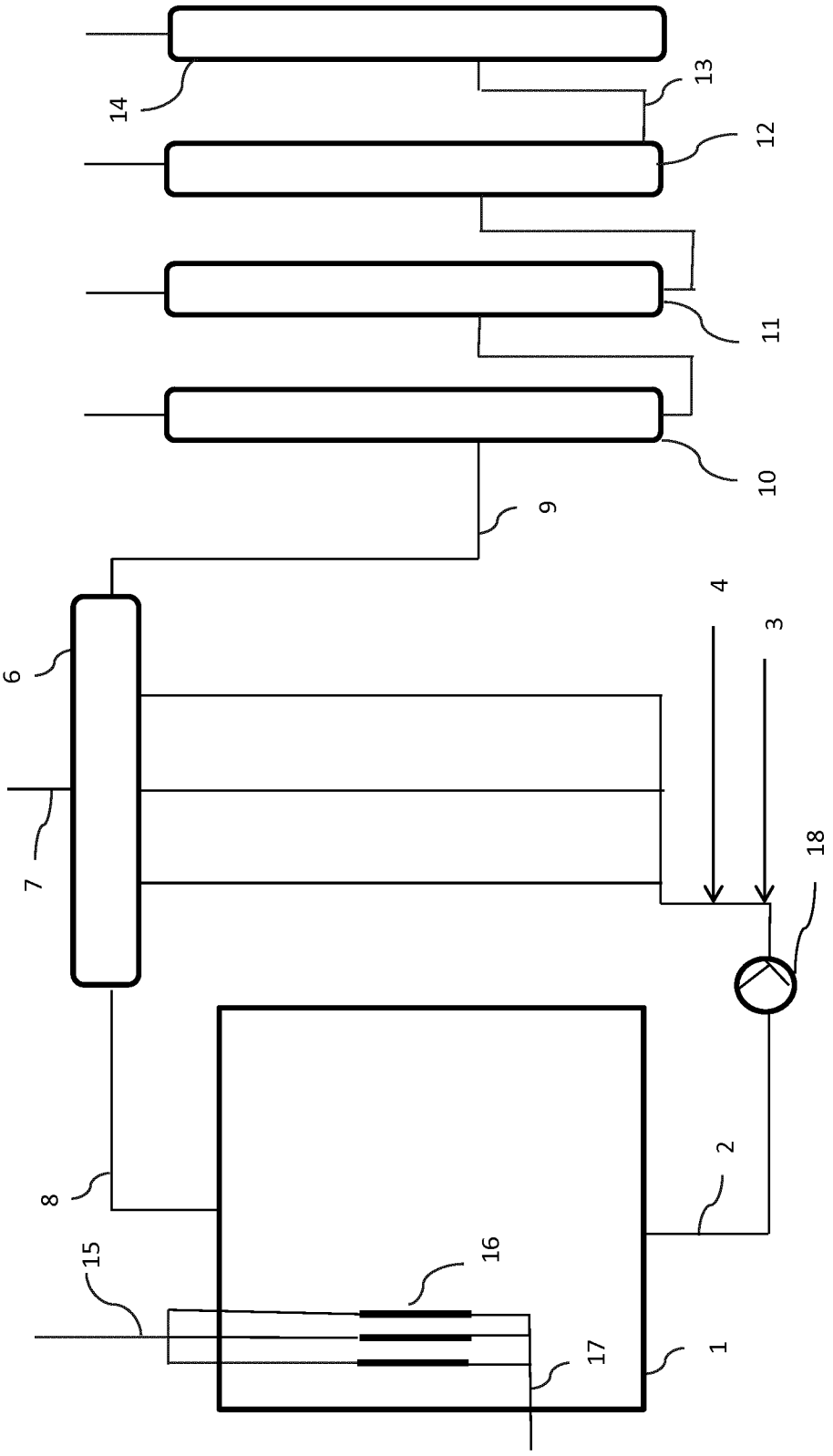


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/076834

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J19/02 B01J19/00 C07C17/358 C07C17/20
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)
B01J 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/089457 A1 (DEVIC MICHEL [FR] ET AL) 28 April 2005 (2005-04-28) paragraphs [0008], [0010], [0015], [0035] - [0038], [0043], [0044]	1-15
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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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
19 April 2016	28/04/2016

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	Veronesi, Sergio

1

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/076834

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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