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(54) **CLEAN PROCESS FOR PREPARING CHLOROFORMYL SUBSTITUTED BENZENE**

SAUBERES VERFAHREN ZUR HERSTELLUNG VON CHLOROFORMYLSUBSTITUIERTEM BENZOL

PROCÉDÉ PROPRE DE PRÉPARATION DE BENZÈNE SUBSTITUÉ PAR UN CHLOROFORMYLE

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(56) References cited:
CN-A- 102 206 157 **US-A- 4 165 337**
US-A- 4 165 337 **US-A1- 2011 278 174**

- **NORMAN RABJOHN ET AL: "The Chloromethylation of Toluene and Conversion of p-Xylyl Chloride to Terephthaloyl Chloride", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 76, no. 21, 1 November 1954 (1954-11-01), pages 5479-5481, XP055426475, US ISSN: 0002-7863, DOI: 10.1021/ja01650a066**
- **JAVIER PÉREZ-RAMÍREZ ET AL: "Sustainable chlorine recycling via catalysed HCl oxidation: from fundamentals to implementation", ENERGY & ENVIRONMENTAL SCIENCE, vol. 4, no. 12, 30 September 2011 (2011-09-30), page 4786, XP055426537, ISSN: 1754-5692, DOI: 10.1039/c1ee02190g**
- **None**

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Description

FIELD OF THE INVENTION

[0001] The present invention pertains to the field of chemical technology, and relates to a clean process of preparing a chloroformyl-substituted benzene. The process of the present invention is done by oxidation of a tail gas hydrogen chloride from a chlorination reaction and a chloroacylation reaction and recycling of the resulting oxidation product chlorine gas into the chlorination reaction. The present invention provides a clean process of preparing a polymer-grade chloroformyl-substituted benzene.

DESCRIPTION OF RELATED ART

[0002] In the prior art, preparation methods for chloroformyl-substituted benzenes mainly are: photochlorination method (see DE31 468 68, JP47-130931), sulfoxide chloride method, phosphorus trichloride method, phosphorus pentachloride method, and phosgene method. The sulfoxide chloride method is most commonly used (see, for example, CN102516060A, CN102344362A). However, the method requires the use of phthalic acid having a high purity of 99.99% as a raw material, which results in a high cost of the method. Moreover, these methods all suffer from a problem of generation of environmentally unfriendly by-products such as hydrogen chloride, sulfur dioxide, carbon dioxide, phosphorous acid. These by-products cause inconveniences to subsequent treatments of products and likely lead to environmental pollution.

[0003] The photochlorination method may use methyl aromatic compounds as raw materials, but the amount of the by-product hydrogen chloride is enormous. For example, a study shows that chlorination of o- or p-xylyl chloride is possible by using light (Norman Rabjohn et al. The Chloromethylation of Toluene and Conversion of p-xylyl chloride , Journal of the American Chemical Society, vol. 76, n°21, 1954-11-01, pages 5479-5481). However, as by-products are formed, the yields and purity of the obtained compounds are sometimes low. Moreover, the document US 4165337 discloses a method for producing isophthaloyl dichloride and terephthaloyl dichloride. The reaction is performed under UV irradiation, but large amounts of hydrogen chloride are produced during the process. How to deal with the large amount of hydrogen chloride has become an issue to be urgently solved. Currently, the main measure actually adopted in the industry is to absorb hydrogen chloride with water to prepare low-value, inexpensive hydrochloric acid for sale; since hydrochloric acid is inexpensive and has a limited market demand, the preparation of hydrochloric acid from hydrogen chloride has become a burden rather than a resource. Another measure is to neutralize hydrogen chloride with a base for direct discharge; however, with increasing sophistication of environmental laws and regulations, environmental protection standards of various ways of discharge have become very stringent.

[0004] The method of preparing chlorine gas directly from the by-product hydrogen chloride can not only achieve closed circulation of chlorine element, but also achieve zero emissions in the reaction process, which greatly improves the level of energy saving and emission reduction in the industry, reduces the cost, and eliminates pollution to the environment. Up to now, the methods of preparing chlorine gas from hydrogen chloride can be divided into three main categories: electrolytic method, direct oxidation method, and catalytic oxidation method. The electrolytic process has a high energy consumption and uses an ionic membrane that needs to be frequently replaced, resulting in a very high cost, wherein the cost per ton chlorine gas recovered is greater than 4,000 RMB. The direct oxidation method suffers from a low yield and cannot be industrialized. In contrast to the electrolytic method and the direct oxidation method, the catalytic oxidation method, particularly the Deacon catalytic oxidation, exhibits a highest potential for industrialization.

[0005] Industrial chlorine gas used in many productions in the chlorination industry is required to be ≥99.6% (vol%). Therefore, for chlorine gas obtained from the Deacon reaction, a high-purity chlorine gas capable of being recycled can be obtained only after a problem of separation of the resulting mixed gas from the reaction is solved. Particularly, in the prior art, in order to recover chlorine gas from a mixed gas from oxidation of hydrogen chloride, a separation method of hydrogen chloride by absorption thereof with water is generally adopted, for example, CN102502498A, US2008/0159948A1, which will cause generation of a large amount of dilute hydrochloric acid and thus require further treatments.

[0006] In view of the above, there is a need in the art for a clean process for producing chloroformyl-substituted benzenes with low cost, good quality and no pollution that is capable of achieving closed circulation of chlorine resources. The key of the clean process lies in oxidation process of hydrogen chloride and separation process of a product gas stream. Once the critical processes are solved, a high-purity chlorine gas can be obtained, thus achieving recycle of chlorine gas. The clean production process of chloroformyl-substituted benzenes is the key to achieve industrialization of related chemical industries, for example, aramid industry.

SUMMARY OF THE INVENTION

[0007] The present invention is defined in the claims. An object of the present disclosure is to provide a clean process of preparing a chloroformyl-substituted benzene. The process of the present disclosure solves the existing problems in the art, achieves closed circulation of chlorine resources, fundamentally eliminates pollution caused by by-products, and provides a product with low cost and hight quality.

[0008] The present disclosure is achieved by the following technical solution: firstly, reacting a methyl aromatic hydrocarbon of formula $(X)_aC_6H_{6-a-b}(CH_3)_b$ or a pendant alkyl chloride thereof with chlorine gas (e.g. under illumination conditions) to prepare trichloromethyl-substituted benzene; further reacting the resulting trichloromethyl-substituted benzene to prepare chloroformyl-substituted benzene; subjecting the resulting HCl gas to catalytic oxidation according to the Deacon reaction to generate chlorine gas for further use in the chlorination of the methyl aromatic hydrocarbon to prepare the trichloromethyl-substituted benzene. Representative equations of the overall technical process are as follows: $(X)_aC_6H_{6-a-b}(CH_3)_b + 3bCl_2 = (X)_aC_6H_{6-a-b}(CCl_3)_b + 3bHCl$ $(X)_aC_6H_{6-a-b}(CCl_3)_b + (X)_aC_6H_{6-a-b}(COOH)_b = 2(X)_aC_6H_{6-a-b}(COCl)_b + bHCl$ or $(X)_aC_6H_{6-a-b}(CCl_3)_b + bH_2O= (X)_aC_6H_{6-a-b}(COCl)_b + 2bHCl$ $4bHCl + bO_2 = 2bCl_2 + 2bH_2O$.

[0009] For simplicity, only the methyl aromatic hydrocarbon is shown in the above equations. Those skilled in the art can understand that the pendant alkyl chloride of the methyl aromatic hydrocarbon will be subjected to similar reactions.

[0010] The chlorine gas obtained by the oxidation is introduced into the chlorination reaction again as a raw material. Altogether, the total equation for preparing the bis-(chloroformyl)-benzene of the present disclosure is: $(X)_aC_6H_{6-a-b}(CH_3)_b + bCl_2 + (X)_aC_6H_{6-a-b}(COOH)_b + bO_2 = 2(X)_aC_6H_{6-a-b}(COCl)_b + 2bH_2O$.

[0011] Those skilled in the art can understand that the reactions for preparing the acyl chloride using water and the trichloromethyl-substituted benzene also have a similar total equation.

[0012] $(X)_aC_6H_{6-a-b}(CH_3)_b$ is a methyl aromatic compound (a pendant alkyl chloride thereof also applies to the present disclosure), $(X)_aC_6H_{6-a-b}(CCl_3)_b$ is trichloromethyl-substituted benzene, $(X)_aC_6H_{6-a-b}(COOH)_b$ is a corresponding aromatic acid, and $(X)_aC_6H_{6-a-b}(COCl)_b$ is chloroformyl-substituted benzene. In the formulas of the compounds of the present application, X is a chlorine, bromine or fluorine atom, a is an integer selected from 0, 1, 2, 3, 4 and 5, b is an integer selected from 1, 2, 3 and 4, and $a+b\leq 6$. The term "corresponding aromatic acid" in the present application means that a substituent on a parent nucleus of the aromatic acid and a substituent on a parent nucleus of the methyl aromatic hydrocarbon are located at the same substitution position or corresponding substitution positions; the substituent on the parent nucleus of the aromatic acid and the substituent on the parent nucleus of the methyl aromatic hydrocarbon may also be the same.

[0013] The term "pendant alkyl chloride of the methyl aromatic compound" in the present application means a compound where hydrogen atoms of a alkyl group in the aromatic compound are not completely substituted by chlorine atoms; the target product of the photochlorination reaction in the present application, i.e. trichloromethyl-substituted benzene, means a product where hydrogen atoms of a alkyl group in the aromatic compound are completely substituted by chlorine atoms.

[0014] A clean process of preparing the chloroformyl-substituted benzene comprises the following steps:

step 1 (chlorination reaction): reacting a methyl aromatic hydrocarbon of formula $(X)_aC_6H_{6-a-b}(CH_3)_b$ or a pendant alkyl chloride thereof with chlorine gas (e.g. under illumination conditions) to prepare a trichloromethyl-substituted benzene and obtain a by-product hydrogen chloride;
step 2 (chloroacylation reaction): further reacting the resulting trichloromethyl-substituted benzene in step 1 with the corresponding aromatic acid of formula $(X)_aC_6H_{6-a-b}(COOH)_b$ or water to prepare the chloroformyl-substituted benzene and to obtain a by-product hydrogen chloride;
step 3 (catalytic oxidation of the by-product hydrogen chloride): subjecting the collected by-product hydrogen chloride in steps 1 and 2 to catalytic oxidation in the presence of a catalyst (the Deacon reaction) to prepare chlorine gas;
step 4 (separation of the gas stream from step 3): separating a product gas steam from step 3 to obtain gas streams containing chlorine, containing oxygen, and/or containing hydrogen chloride;
step 5 (recycling of the separated substances): introducing the gas stream containing chlorine separated in step 4 as a raw material into the chlorination reaction including step 1; and
optionally, introducing the gas streams containing hydrogen chloride and/or containing oxygen separated in step 4 as a raw material into the catalytic oxidation of the by-product hydrogen chloride in step 3.

[0015] In the clean process of preparing the chloroformyl-substituted benzene according to the present disclosure, a purification step of the trichloromethyl-substituted benzene further may or may not exist after the chlorination reaction; and a purification step of chloroformyl-substituted benzene further may or may not exist after the chloroacylation reaction.

[0016] The process of the present disclosure is a completely green chemical process, without any wastes except for normal losses during the purification and reaction. The process of the present disclosure achieves a clean production of chloroformyl-substituted benzene, particularly a raw material for preparing aramid, polymer-grade bis-(chloroformyl)-benzene, and thus has important economic value and social benefit for producing high-performance aramid fibers at low cost.

[0017] The present disclosure has the following advantageous effects.

1) In the present disclosure, the by-product hydrogen chloride generated in the chlorination and chloroacylation steps during the process of producing chloroformyl-substituted benzene, for example, bis-(chloroformyl)-benzene, is further subjected to the catalytic oxidation to prepare chlorine gas, and the obtained chlorine gas is recycled to the chlorination reaction, thereby achieving closed circulation of chlorine element, and thus reducing the production cost and reducing the environmental pollution.

2) The catalytic oxidation in step 3 of the present disclosure is the key and core to achieve recycling of chlorine resources, and in the step, the resulting product gas stream in the catalytic oxidation of hydrogen chloride is directly circulated without separation thereof, achieving the dissipation effect of heat during the Deacon reaction and prolonging the lifetime of catalysts, and also the use of heat carried by the circulated product gas stream itself reduces the fuel cost in preheating a feed gas containing hydrogen chloride, further saving the industrialization cost.

3) In step 4, the present disclosure adopts a separation method comprising condensation, drying, and adsorption steps to separate the product gas stream of step 3, and the separation method optionally further comprises a liquefaction step. The separation method of the present disclosure does not produce a large amount of dilute hydrochloric acid because a water washing step is not present. Particularly, when the hydrogen chloride concentration in the chlorine gas after oxygen gas is removed by condensation, drying, and adsorption is low, a further liquefaction step is not required. Because the chlorine gas containing a small amount of hydrogen chloride gas is directly recycled to a chlorination step, for example, step 1, the presence of the small amount of hydrogen chloride does not affect the reaction between the chloride gas and the methyl aromatic hydrocarbon to produce the trichloromethyl-substituted benzene.

The separation method of the product gas stream in step 4 of the present disclosure has the advantages of simple process flow, environmental friendliness, low energy consumption, high separation efficiency, and low cost, and the purity of chlorine gas in the gas stream containing chlorine recovered by the separation method is up to ≥99.6% (vol%), which can meet the quality requirements of chlorine feed gas in the photochlorination reaction.

4) In the process of the present disclosure, in addition to closed circulation of chlorine resources, other substances generated during the production of the product may also be recycled, thereby achieving a clean production. For example, hydrogen chloride and/or oxygen gas that is not completely reacted in the catalytic oxidation in step 3 can be subjected to the catalytic oxidation again after being separated.

5) According to the process of the present disclosure, the polymer-grade chloroformyl-substituted benzene, for example, bis-(chloroformyl)-benzene, can be obtained, and the production cost is lower than that of the conventional process by above 30%.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a flow diagram of a clean process of preparing bis-(chloroformyl)-benzene.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The methods for preparing chloroformyl-substituted benzene in the prior art all suffer from the problems of a lot of by-products, difficulties in handling, low product yield, and serious environmental pollution, etc. In order to obtain a high quality of chloroformyl-substituted benzene, enormous economic and environmental costs are required.

[0020] After extensive research and experimentation, the present inventors creatively combine chlorination of the methyl aromatic hydrocarbon, synthesis of chloroformyl-substituted benzene, and oxidation of hydrogen chloride to prepare chlorine gas into a complete process (also with the improvement of the oxidation process of hydrogen chloride and the separation process of the mixed gas), wherein a large amount of hydrogen chloride generated during the chlorination and the chloroacylation is subjected to the catalytic oxidation to prepare chlorine gas and the resulting chlorine gas is introduced into the chlorination process again, achieving recycling of chlorine element. The whole process is a clean production process.

[0021] The whole clean production process is carried out in the following steps:

[0022] Step 1 (chlorination reaction): reacting a methyl aromatic hydrocarbon of formula $(X)_aC_6H_{6-a-b}(CH_3)_b$ or a pendant alkyl chloride thereof with chlorine gas (e.g. under illumination conditions) to prepare a trichloromethyl-substituted benzene and obtain a by-product hydrogen chloride, where X is a chlorine, bromine or fluorine atom, a is an integer selected from 0, 1, 2, 3, 4 and 5, b is an integer selected from 1, 2, 3 and 4, and a+b≤6.

[0023] The term "pendant alkyl chloride of the methyl aromatic compound" in the present application means a compound where hydrogen atoms of a alkyl group in the aromatic compound are not completely substituted by chlorine atoms; the target product of the photochlorination reaction in the present application, i.e. trichloromethyl-substituted benzene, means a product where hydrogen atoms of a alkyl group in the aromatic compound are completely substituted by chlorine atoms.

[0024] During the chlorination reaction of the present disclosure, the resulting trichloromethyl-substituted benzene is optionally subjected to further purification or directly fed to the chloroacylation reaction, and the resulting by-product hydrogen chloride is recovered for use in step 3.

[0025] The chlorination reaction of the present disclosure relates to a photochemical method for preparing trichloromethyl-substituted benzene, characterized in that a methyl aromatic hydrocarbon of formula $(X)_aC_6H_{6-a-b}(CH_3)_b$ or a pendant alkyl chloride thereof is reacted with chlorine gas under illumination conditions to prepare trichloromethyl-substituted benzene, where the illumination has a light source wavelength of about 350 nm-700 nm and a light amplitude of no more than about 200 nm, and where chlorine gas feeding is initiated under conditions of a reaction temperature of about 0°C-85°C and an illuminance of about 2000 Lux-about 55000 Lux, for a first reaction stage where the reaction temperature is no more than about 120°C at the illuminance; and then the remaining amount of chlorine gas is fed at a higher reaction temperature until the reaction is completed. In a preferred aspect of the method, the light source preferably is an LED lamp.

[0026] The present inventors have found that, in the first reaction stage of chlorination, it is advantageous to consume preferably at least about 1/6 of a total amount of chlorine gas required by the reaction before increasing the temperature and illuminance. In some preferred aspects of the present disclosure, about 1/6-about 1/2 of the total amount of chlorine gas required by the reaction is consumed in the first reaction stage; and preferably, about 1/4-about 1/3 of the total amount of chlorine gas required by the reaction is consumed in the first reaction stage.

[0027] The present inventors have found that, the reaction temperature in the first reaction stage of chlorination is preferably about 55-85°C.

[0028] The present inventors have found that, the illuminance in the first reaction stage of chlorination is about 5000Lux-about 55000Lux, preferably about 20000Lux-about 55000Lux, more preferably about 35000Lux-about 45000Lux.

[0029] The present inventors have found that, in the reaction after the first reaction stage of chlorination, the remaining amount of chlorine gas is fed at a reaction temperature of no more than about 350°C and at an illuminance of no more than about 100000Lux.

[0030] The process following the first reaction stage of chlorination according to the method of the present disclosure may be a single reaction stage or divided into several reaction stages such as two, three, four, five, six, seven, eight, nine, or ten reaction stages. In the process following the first reaction stage, the illuminance is optionally increased when the temperature is increased in each stage. Preferably, the process following the first reaction stage in the photochlorination reaction may be further divided into second and third reaction stages. In the second reaction stage, the reaction temperature is controlled to be about 120°C-about 160°C, the incoming illuminance is about 10000Lux-about 70000Lux, and 1/4-2/5 of the total amount of chlorine gas is fed; and in the third reaction stage, the temperature is controlled to be about 160°C-about 300°C, the incoming illuminance is about 50000Lux-about 100000Lux, and the remaining amount of chlorine gas is fed. In the second and third reaction stages, increasing the temperature and increasing the illuminance may be performed in any order.

[0031] The LED in the chlorination according to the method of the present disclosure preferably has a peak wavelength ranging from 350 nm-490 nm or 460 nm-490 nm.

[0032] The light source in the chlorination according to the method of the present disclosure preferably has a light amplitude of no more than about 50 nm, preferably about 10 nm-about 30 nm, more preferably about 10 nm-about 25 nm.

[0033] In the reaction system of the chlorination reaction according to the method of the present disclosure, preferably, no solvent and initiator are added.

[0034] The expression "total amount of chlorine gas" in the chlorination of the present disclosure means the amount of chlorine gas required for complete chlorination of hydrogen atoms on side chains in the methyl aromatic hydrocarbon, which is at least a theoretical molar amount for chlorination of the raw material methyl aromatic compound. Taking xylene as an example, the total amount of chlorine gas is a molar amount that is at least six times the number of moles of the raw material xylene. Preferably, the total amount of chlorine gas in the chlorination of the present disclosure is a molar amount that is above six times the number of moles of xylene. The excess amount of chlorine gas may be conventionally determined. Preferably, for saving the reaction time, fed amounts of chlorine in the respective stages herein may be adjusted depending on the monitored reaction results.

[0035] The term "light amplitude" in the present disclosure means the wavelength range at half peak height of light emission by the light source, not the peak wavelength of light. For example, a light amplitude of 50 nm means that the wavelength range at half peak height of light emission by the light source is no more than 50 nm. The peak wavelength of the LED light source in the present disclosure may vary from 350 nm-700 nm, and for any given wavelength, the light source of incident light in the present disclosure enables the light amplitude to be controlled within 50 nm, for example peak amplitude 50 nm at 465 nm, peak amplitude 50 nm at 360 nm, peak amplitude 50 nm at 586 nm. The present inventors have found that the LED light source also has the advantage of less heat generation, and thus the cost of the production equipment can be reduced, for example no additional cooling device is needed. In contrast, for the photochlorination reaction using a high-pressure mercury lamp as a light source, a corresponding cooling device is required (for example, see US5514254).

[0036] The illuminance in the present disclosure may be determined by a conventional instrument such as illuminometer in the art. The wavelength in the present disclosure may be determined by a conventional instrument such as monochromator in the art.

[0037] The term "about" in the present disclosure means that with respect to temperature, positive or negative variation of a stated value is no more than 2.5°C (expressed as the stated value ± 2.5°C), preferably the stated value ± 2.5°C, ±2°C or ±1°C; means that with respect to illuminance, positive or negative variation of a stated value is no more than 2500Lux (expressed as the stated value ± 2500Lux), preferably the stated value ± 2500Lux, ± 2000Lux, ± 1500Lux, ± 1000Lux, ± 500Lux, ± 200Lux or ± 100Lux; means that with respect to wavelength, positive or negative variation of a stated value is no more than 5 nm (expressed as the stated value ± 5 nm), preferably the stated value ± 4 nm, ±3 nm or ±1 nm; and means that with respect to light amplitude, positive or negative variation of a stated value is no more than 3 nm (expressed as the stated value ± 3 nm), preferably the stated value ±2 nm or ±1 nm.

[0038] In the reaction system of the chlorination reaction according to the present disclosure, preferably, no solvent and initiator are added, and more preferably, no components other than xylene and chlorine are added. At various stages in the chlorination of the present disclosure, the reaction progression may be monitored by conventional sampling and detection methods such as gas chromatography, so as to suitably adjust the parameters described above, thereby saving the reaction time. The description about the durations for three stages is not limiting and the reaction time at each stage may be freely adjusted depending on the monitored results of chlorination progression. The speed of feeding chlorine gas herein is not limited to a particular feeding rate. When the expression such as slowly, gradually is used to describe the speed of feeding chlorine gas, its meaning is not unclear, because the speed of feeding chlorine gas may be adjusted by those skilled in the art depending on the monitoring results of the reaction.

[0039] The product prepared by the method of the present application has a high purity value. In some embodiments, trichloromethyl-substituted benzene with a purity of between about 70%-about 75%, between about 75%-about 80%, between about 80%-about 85%, between about 85%-about 90%, between about 90%-about 95%, or between about 95%-about 99.9% is directly obtained after the reaction, and preferably with a purity of between about 90.0%-about 90.5%, between about 90.0%-about 91.0%, between about 90.0%-about 91.5%, between about 90.0%-about 92.0%, between about 90.0%-about 92.5%, between about 90.0%-about 93.0%, between about 90.0%-about 93.5%, between about 90.0%-about 94.0%, between about 90.0%-about 94.5%, between about 90.0%-about 95.0%, between about 90.0%-about 95.5%, between about 90.0%-about 96.0%, between about 90.0%-about 96.5%, between about 90.0%-about 97.0%, between about 90.0%-about 97.5%, between about 90.0%-about 98.0%, between about 90.0%-about 98.5%, between about 90.0%-about 99.0%, between about 90.0%-about 99.1%, between about 90.0%-about 99.2%, between about 90.0%-about 99.3%, between about 90.0%-about 99.4%, between about 90.0%-about 99.5%, between about 90.0%-about 99.6%, between about 90.0%-about 99.7%, between about 90.0%-about 99.8%, or between about 90.0%-about 99.9% is directly obtained after the reaction.

[0040] If desired, trichloromethyl-substituted benzene obtained from the chlorination in the present disclosure may also be further purified via a conventional purification method such as recrystallization, rectification, or molecular distillation. The molecular distillation is preferred in the present disclosure.

[0041] The method of the present application may be run in a batch or continuous mode, preferably in a continuous mode.

[0042] Step 2 (chloroacylation reaction): further reacting the resulting trichloromethyl-substituted benzene in step 1 to prepare a chloroformyl-substituted benzene and to obtain a by-product hydrogen chloride.

[0043] The resulting chloroformyl-substituted benzene optionally is further purified or directly collected as a finished product; and the resulting by-product hydrogen chloride is recovered for use in step 3.

[0044] The chloroacylation reaction of the present disclosure comprises the following steps:

i) fully melting the trichloromethyl-substituted benzene at an elevated temperature, adding water or the corresponding aromatic acid of formula $(X)_aC_6H_{6-a-b}(COOH)_b$ and a catalyst, and stirring thoroghly; wherein X is a chlorine, bromine or fluorine atom, a is an integer selected from 0, 1, 2, 3, 4 and 5, b is an integer selected from 1, 2, 3 and 4, and a+b≤6. The substituent on the parent nucleus of the aromatic acid and the substituent on the parent nucleus of the methyl aromatic hydrocarbon in step 1 may also be the same; and
ii) heating the reaction system to maintain the reaction, for example to 90-125°C, thereby obtaining a reaction mixture of the chloroacylation.

[0045] Preferably, trichloromethyl-substituted benzene and the corresponding aromatic acid are dosed in step i) at a stoichiometric molar ratio, for example bis-(trichloromethyl)-benzene and phthalic acid are dosed at a molar ratio of preferably 1:1.01-1.03. The catalyst in step i) is a Lewis acid, for example, aluminum trichloride, zinc chloride, ferric chloride, preferably ferric chloride; and particularly, when trichloromethyl-substituted benzene is reacted with water in step i), preferably, a small amount of the corresponding aromatic acid of formula $(X)_aC_6H_{6-a-b}(COOH)_b$ is also present.

The amount of the catalyst added in step i) is preferably 0.2%-0.3% of the mass of trichloromethyl-substituted benzene.

[0046] If desired, the resulting chloroformyl-substituted benzene from the chloroacylation may also be further purified via an optional purification method such as rectification, distillation, molecular distillation, or recrystallization. The rectification is preferred in the present disclosure.

[0047] The method of the present application may be run in a batch or continuous mode, preferably in a continuous mode.

[0048] Step 3 (catalytic oxidation of the by-product hydrogen chloride): subjecting the collected by-product hydrogen chloride in steps 1 and 2 to catalytic oxidation in the presence of a catalyst (the Deacon reaction) to prepare chlorine gas.

[0049] Optionally, the by-product hydrogen chloride gas is first pre-purified by a cryogenic or adsorption process to remove organic impurities before the catalytic oxidation. For example, hydrogen chloride gas may be purified by adsorption, and suitable adsorbent materials include, for example, activated carbon, aluminum oxide, titanium oxide, silica, ferric oxide, silica gel, zeolite, and a molecular sieve. **In one aspect, step 3 of the present disclosure is directed to a method for preparing chlorine gas through catalytic oxidation of hydrogen chloride, comprising the steps of:**

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2) providing a gas stream containing hydrogen chloride and a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a first reactor of the one or more reactors, and providing a gas stream containing hydrogen chloride and/or a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a downstream reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
3) directly returning a part of a product gas stream from a last reactor of the one or more reactors from the catalytic oxidation to any of the one or more reactors without separation thereof; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

[0050] The method of the present application may be run in a batch or continuous mode, preferably in a continuous mode.

[0051] In another aspect, step 3 of the present disclosure is directed to a method for preparing chlorine gas through catalytic oxidation of hydrogen chloride, comprising the steps of:

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2) providing a gas stream containing hydrogen chloride and a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a first reactor of the one or more reactors, and providing a gas stream containing hydrogen chloride and/or a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a downstream reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
3) before directly returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, preferably to a feed inlet of any of the one or more reactors, mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

[0052] In one preferred embodiment of step 3 of the present disclosure, the gas stream containing hydrogen chloride and the gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride are provided to the first reactor of the one or more reactors, and the gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride is provided to a downstream reactor of the one or more reactors; and the gas streams containing oxygen for oxidation of a gas stream containing hydrogen chloride provided to the reactors are portions of a desired amount of a gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride that are distributed among the reactors in any ratio as desired, preferably equally distributed into corresponding parts according to the number of the reactors.

[0053] The preferred embodiment further preferably provides a method comprising the steps of:

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2a) providing a gas stream containing hydrogen chloride and a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a first reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;

2b) providing a product gas stream from the first reactor of the one or more reactors to a downstream reactor of the one or more reactors through a heat exchanger, providing a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to the downstream reactor of the one or more reactors, and successively providing a product gas stream from the previous reactor and a gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride to a remaining downstream reactor of the one or more reactors;
3) before returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, preferably to a feed inlet of any of the one or more reactors, mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

[0054] In another particular preferred embodiment of step 3 of the present disclosure, an oxygen content in the gas stream containing oxygen entering each of the reactors is greater than a theoretical oxygen consumption required for oxidation of the gas stream containing hydrogen chloride entering said reactor. The particularly preferred embodiment may be implemented by, for example, the method comprising: providing a gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride and a gas stream containing hydrogen chloride to a first reactor of the one or more reactors, and providing a gas stream containing hydrogen chloride to a downstream reactor of the one or more reactors; wherein the gas streams containing hydrogen chloride are portions of a gas stream containing hydrogen chloride to be oxidated that are distributed among the reactors in any ratio as desired, preferably equally distributed into corresponding parts according to the number of the reactors.

[0055] The particular preferred embodiment further preferably provides a method comprising the steps of:

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2a) providing a gas stream containing oxygen for oxidation of hydrogen chloride and a gas stream containing hydrogen chloride to a first reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
2b) providing a product gas stream from the first reactor of the one or more reactors to a downstream reactor of the one or more reactors through a heat exchanger, providing a gas stream containing hydrogen chloride to the downstream reactor of the one or more reactors, and successively providing a product gas stream from the previous reactor and a gas stream containing hydrogen chloride to a remaining downstream reactor of the one or more reactors;
3) before returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, preferably to a feed inlet of any of the one or more reactors, mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

[0056] Further, in returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, the part of the product gas stream from the last reactor of the one or more reactors is preferably returned to each of the provided one or more reactors without separation thereof; and more preferably, before returning to a feed inlet of each of the one or more reactors, the part of the product gas stream from the last reactor of the one or more reactors is mixed with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride, which then is fed to said reactor for the catalytic oxidation. On the one hand, the method of the present disclosure can dilute the concentration of the feed reaction gas entering each of the one or more reactors to prevent the vigorous reaction at the inlet of said reactor and thus avoid the formation of too many hot spots; on the other hand, after the mixing is performed, the method of the present disclosure increases the feed temperature of the feed reaction gas, for which the preheating is not essentially required.

[0057] Further, in returning a part of a product gas stream from the last reactor of the one or more reactors to each of the provided one or more reactors without separation thereof, the returned product gas stream may be distributed among the one or more reactors in any ratio, for example, reasonably distributed depending on the operation conditions of the one or more reactors; wherein preferably, the returned product gas stream is equally distributed into corresponding parts according to the number of the one or more reactors, for respectively being returned to the one or more reactors. The one or more reactors in step 3 of the present application preferably are a adiabatic reactor. A heat exchanger may be connected between the reactors for reaction heat removal, namely, a heat exchanger is optionally present after each reactor. Preferably, the heat exchanger disposed after the last reactor is a gas heat exchanger, and the heat exchangers disposed after the rest of the reactors may be those well-known to a person skilled in the art, such as a tube bundle heat exchanger, plate heat exchanger, or gas heat exchanger.

[0058] It is preferred in the present application that, the remainder (or all after the reaction in step 3 is completed, and a person skilled in the art also can understand that the last portion of the product gas stream may not be returned) of the product gas stream (at a high temperature) from the catalytic oxidation in step 3 is passed through the gas heat exchanger before separation thereof, wherein the heat exchange is preferably performed in the gas heat exchanger using the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter the first reactor as a cooling medium; preferably, the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride after being heat exchanged is mixed with a part of the returned product gas stream out of the third-stage reactor before being provided to the first reactor, and then is fed to the first reactor for the catalytic oxidation of hydrogen chloride. The temperature of the product gas stream is reduced after the heat exchange. The temperature of the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride as the cooling medium is increased after the heat exchange, and then the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride after being heat exchanged is provided to the first reactor for the catalytic oxidation of hydrogen chloride; preferably, the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride after being heat exchanged is mixed with a part of the returned product gas stream out of the third-stage reactor before being provided to the first reactor, and then is fed to the first reactor for the catalytic oxidation of hydrogen chloride.

[0059] The providing a part or all of the product gas steam from step 3 for separation thereof in step 4 to obtain gas streams containing chlorine gas, containing oxygen, and/or containing hydrogen chloride in step 4 of the present disclosure means that a part or all of the product gas steam in step 3 is subjected to dehydration and removal of (some residues of) the gas stream containing hydrogen chloride and the gas stream containing oxygen, to obtain the gas stream containing chlorine.

[0060] It is preferred in the present application that (unreacted and residual) hydrogen chloride and/or oxygen gas separated in step 4 from the product gas stream may be provided again to the catalytic oxidation of step 3. The separated hydrogen chloride (or vaporized hydrochloric acid) and/or oxygen gas in step 4 may also be returned to the one or more reactors in step 3.

[0061] In all embodiments of the present disclosure, preferably, a volume ratio of the part of the product gas stream returned to the one or more reactors without separation thereof in step 3 (returned product gas stream) to the remainder of the product gas stream (remaining product gas stream) is 0.25:0.75-0.75:0.25, preferably 0.35:0.65-0.45:0.55.

[0062] In all embodiments of the present disclosure, preferably, a feed volume ratio of the gas stream containing hydrogen chloride (calculated based on pure hydrogen chloride) to the gas stream containing oxygen gas (calculated based on pure oxygen) for oxidation of the gas stream containing hydrogen chloride is 1:2-5:1, preferably 1:1.2-3.5:1, more preferably 1:1-3:1.

[0063] In one preferred embodiment of step 3 of the present disclosure, a feed volume ratio of the gas stream containing hydrogen chloride (calculated based on pure hydrogen chloride) to the gas stream containing oxygen gas (calculated based on pure oxygen) for oxidation of the gas stream containing hydrogen chloride is 2:1-5:1.

[0064] In another particular preferred embodiment of step 3 of the present disclosure, a feed volume ratio of the gas stream containing hydrogen chloride (calculated based on pure hydrogen chloride) to the gas stream containing oxygen gas (calculated based on pure oxygen) for oxidation of the gas stream containing hydrogen chloride is 1:2-2:1, preferably 0.9:1.1-1.1:0.9.

[0065] In all embodiments of the present disclosure, preferably, the pressure within the one or more reactors is 0.1-1 MPa.

[0066] In all embodiments of the present disclosure, preferably, the feed gas temperature of the one or more reactors is 250-450°C, preferably 300-380°C.

[0067] The catalyst in step 3 of the present application is a conventional catalyst capable of reacting hydrogen chloride gas and oxygen gas via oxidation to generate chlorine gas and water. Suitable catalysts include a copper compound and/or a ruthenium compound, preferably a copper compound and/or a ruthenium compound loaded onto an alumina or titanium dioxide support, for example, alumina loaded with copper chloride or ruthenium chloride, preferably a ruthenium compound. The suitable catalysts according to the present application may also comprise other co-catalysts, for example, compounds of metals such as gold, palladium, platinum, osmium, iridium, nickel, or chromium, alkali metals, alkaline-earth metals, and rare earth metals. The suitable catalysts may have various shapes, for example, annular, cylindrical, spherical shapes, and it is preferred that the suitable catalysts have similar external dimensions.

[0068] The one or more reactors in step 3 of the present application are a conventional reactor, for example, a fixed bed or fluidized bed reactor, preferably a fixed bed reactor, which may be filled with a desired catalyst.

[0069] Reactors of any material that meets the requirements may be selected for the reactors according to the present application, and reactors made of pure nickel, nickel alloy, or quartz are preferred. If a plurality of reactors are selected, they may be connected in series or in parallel, preferably connected in series, such that the oxidation of hydrogen chloride may be performed in multiple stages. In the present application, preferably 2, 3, 4, 5, 6, 7, 8, 9, or 10, and more preferably 3 or 4 reactors are used. Advantageously, a person skilled in the art can understand that some raw material gases in the Deacon reaction are passed through the reactors in order, and then an additional gas stream containing hydrogen chloride and/or a gas stream containing oxygen for oxidation of hydrogen chloride is successively provided to the downstream reactors. In all embodiments of the present disclosure, preferably 2, 3, 4, 5, 6, 7, 8, 9, or 10, particularly preferably 3 or 4 adiabatic reactors connected in series are provided.

[0070] Particularly, reactors connected in series may also be combined with reactors connected in parallel. However, the method of the present disclosure particularly preferably has reactors that are only connected in series. If reactors connected in parallel are preferably used, then in particular, at most five, preferably three, particularly preferably at most two production lines (optionally comprising a reactor set consisting of reactors connected in series) are connected in parallel. Thus, the method of the present application may be operated with, for example, up to 60 reactors.

[0071] The method of the present application may be run in a batch or continuous mode, preferably in a continuous mode.

[0072] The "gas stream containing hydrogen chloride" according to the present application includes a fresh gas stream containing hydrogen chloride and a gas stream comprising the recovered hydrogen chloride by the method of the present disclosure or the recovered vaporized hydrochloric acid. The fresh gas stream containing hydrogen chloride may also be a gas stream containing hydrogen chloride as a by-product in related industries such as production of isocyanates, production of acid chlorides, or chlorination of aromatic compounds, preferably the gas stream containing hydrogen chloride as a by-product from steps 1 and 2 of the present disclosure. The gas streams containing hydrogen chloride as by-products may be gas streams containing hydrogen chloride as by-products that are preliminarily treated or gas streams containing hydrogen chloride as by-products directly from related industries that are not treated. The gas streams containing hydrogen chloride as by-products may contain little or no other impurity gases having no influence on the catalytic oxidation of hydrogen chloride and also resulting from the production processes in related industries, depending on the sources. The amounts of other impurity gases are determined by the nature of the production processes in related industries. A person skilled in the art can understand that the so-called waste hydrogen chloride generated in related industries may be a proper raw material for the present application.

[0073] The "unreacted gas stream containing hydrogen chloride" according to the present application refers to a gas stream containing hydrogen chloride that is not subjected to the catalytic oxidation through the reactors of the present application.

[0074] The "gas stream containing oxygen" according to the present application includes a fresh gas stream containing oxygen and a gas stream containing oxygen recovered by the method of the present disclosure. The fresh gas stream containing oxygen may be pure oxygen gas or other oxygen-containing gases (e.g. air).

[0075] The "product gas stream" according to the present application refers to a mixed gas comprising hydrogen chloride, oxygen gas, water vapor, and chlorine gas obtained from a reactor in which the catalytic oxidation is performed. Preferably, the returned product gas stream in the present disclosure is a mixed gas from the last reactor.

[0076] Step 4 (separation of the gas stream from step 3): separating the product gas steam from step 3 to obtain gas streams containing chlorine, containing oxygen, and/or containing hydrogen chloride.

[0077] The separation to obtain gas streams containing chlorine, containing oxygen, and/or containing hydrogen chloride in step 4 of the present disclosure comprises the steps of:

a. condensation: the product gas stream from step 3 is condensed; water in the product gas stream from step 3 along with a part of unreacted hydrogen chloride is condensed as an aqueous hydrochloric acid solution;
b. deep dehydration: the gas stream after being condensed in step a is subjected to deep dehydration, for example, through concentrated sulfuric acid, a molecular sieve, or by temperature swing adsorption, pressure swing adsorption, to remove residual moisture and reduce corrosiveness of the gas stream;
c. adsorption: the gas stream after being subjected to deep dehydration in step b is adsorbed by an adsorbent, to separate chlorine gas from oxygen gas.

[0078] On the one hand, the adsorption may use an adsorbent capable of adsorbing a large amount of oxygen gas and only a small amount of chlorine gas, such as a carbon molecular sieve and silica gels, to adsorb and remove oxygen gas; the treatment with the adsorbent generates a gas stream containing chlorine with chlorine gas as a main component, wherein a small amount of hydrogen chloride is optionally present. Oxygen gas adsorbed to the adsorbent after the treatment with the adsorbent is subjected to desorption, to obtain a separated gas stream containing oxygen; the adsorbent after the desorption may continue to be used in step c to adsorb and remove oxygen gas.

[0079] On the other hand, the adsorption may also use an adsorbent capable of adsorbing a large amount of chlorine gas and only a small amount of oxygen gas, such as fine-pored silica gel and activated carbon, to adsorb and remove chlorine gas, and the treatment with the adsorbent generates a gas stream containing oxygen with oxygen gas as a main component. Chlorine gas adsorbed to the adsorbent after the treatment with the adsorbent is subjected to desorption, to obtain a separated gas stream containing chlorine, wherein a small amount of hydrogen chloride is optionally present; the adsorbent after the desorption may continue to be used in step c to adsorb and remove chlorine gas.

[0080] And optionally, d. liquefaction: the gas stream containing chlorine obtained in step c is liquefied, to obtain a gas stream containing hydrogen chloride and a liquefied gas stream containing chlorine after separation thereof.

[0081] The condensation conditions in step a are: a temperature of -5-5°C and a pressure of 0.05-10 MPa.

[0082] The specific operation process of temperature swing adsorption drying and pressure swing adsorption drying to remove residual moisture in step b and the specific operation process of separation of chlorine gas and oxygen gas by the pressure and temperature swing adsorption technology in step c can be found in patent application publication No. CN103752270A, which are briefly described below: the drying in step b is preferably performed using temperature swing adsorption drying or pressure swing adsorption drying, and a composite adsorbent layer with two adsorbents in combination is preferably used in the temperature swing adsorption drying wherein the one adsorbent is an alumina adsorbent placed in an upper portion of an adsorber and the other adsorbent is an adsorbent for dehydration placed in a lower portion of the adsorber, and a volume ratio of the upper alumina adsorbent to the lower adsorbent for deep dehydration is 20-80%:80%-20%. A composite adsorbent layer with two adsorbents in combination is preferably used in the pressure swing adsorption drying wherein the one adsorbent is an alumina adsorbent placed in an upper portion of an adsorber and the other adsorbent is an adsorbent for dehydration placed in a lower portion of the adsorber, and a volume ratio of the upper alumina adsorbent to the lower adsorbent for dehydration is 20-80%:80%-20%.

[0083] The temperature swing adsorption drying process in step b is that: the gas stream condensed in step a is passed through the composite adsorbent layer from bottom to top, and the drying is accomplished when the gas stream exits the temperature swing adsorption drying apparatus; in the temperature swing adsorption drying, the adsorption pressure is 0.30-0.80 MPa and the adsorption temperature is 20-50°C. The temperature swing adsorption drying process comprises alternative processes of adsorption and regeneration, wherein the alternative processes of adsorption and regeneration are performed by conventional arrangements (including depressurization, replacement, heating up, and cooling down). The regeneration operation includes desorption and dehydration processes. The desorption pressure of the regeneration operation is 0.01-0.005 MPa and the desorption temperature of the regeneration operation is 110-180°C; the dehydration process of the regeneration operation uses a carrier gas at a temperature 50-180°C (feed gas or nitrogen gas), and when the feed gas is used as a carrier gas for regeneration, the feed gas is dried through a pre-drying tower, heated through a steam heater, and fed to an adsorption drying tower to be heated for regeneration and dehydration, wherein the water-bearing carrier gas out of the adsorption tower is cooled, condensed, separated to remove water, and sent back to the feed gas system for recycle.

[0084] The pressure swing adsorption drying process in step b comprises alternative processes of adsorption and desorption, wherein the adsorption pressure is 0.40-0.80 MPa, the desorption pressure is 0.02-0.07 MPa, and the adsorption temperature is ambient temperature; the alternative processes of adsorption and desorption processes are performed by conventional arrangements (including pressure equalization, flushing replacement, and vacuum aspiration); the pressure swing adsorption drying process generally is a conventional four-tower process, wherein the flushing replacement uses a dried product gas stream, and tail gases of the flushing replacement and the vacuum aspiration are cooled and dehydrated and then sent to a product gas stream system for hydrogen chloride removal for recycle.

[0085] The adsorbent for the molecular sieve drying in step b is a zeolitic molecular sieve or silica gel.

[0086] The adsorption in step c preferably adopts the pressure and temperature swing adsorption technology including adsorption and desorption processes, wherein the adsorption pressure is 0.20-0.7 MPa, and the temperature in the adsorption stage is gradually decreased from 40-70°C to 20-35°C; the desorption pressure under reduced pressure is -0.07 MPa and the desorption temperature is 40-70°C; in the adsorption, the gas stream as a feed gas at a temperature less than 40°C is charged, the adsorption is started, and the temperature is reduced; before desorption for regeneration, hot chlorine gas at a temperature greater than 50°C is charged to replace gas in the system, and the temperature is increased to facilitate desorption, and when the temperature reaches 40-70°C, the charging of hot chlorine gas is stopped and the vacuum desorption is started; after the desorption for regeneration is completed, oxygen is used to start the replacement before adsorption; both the tail gas replaced by hot chlorine gas and the tail gas replaced by oxygen gas are sent back to the feed gas system.

[0087] The "optionally step d" means that, when the ratio of hydrogen chloride to oxygen gas in the catalytic oxidation is appropriately controlled (for example, the ratio is 0.5:1-1:0.5 based on pure hydrogen chloride and pure oxygen), residual unreacted hydrogen chloride is substantially absorbed during the condensation by water generated in the reaction, and when the amount of hydrogen chloride in chlorine gas obtained in step c is comparatively small and does not affect the recycling of chlorine gas for the chlorination reaction, further liquefaction of chlorine gas to separate hydrogen chloride therefrom is not required; while when the ratio of hydrogen chloride to oxygen gas in the catalytic oxidation is at other values, some hydrogen chloride still remains after the treatments in steps a-c, and in this case, if necessary, the gas stream containing chlorine and hydrogen chloride may be liquefied in step d to separate out a gas stream containing hydrogen chloride.

[0088] The liquefaction conditions in step d are: a temperature of -20-20°C and a pressure of 0.05-10 MPa.

[0089] Step 5 (recycling of the separated substances): introducing the gas stream containing chlorine separated in step 4 as a raw material into the chlorination reaction including step 1; and introducing the gas streams containing hydrogen chloride and/or containing oxygen separated in step 4 as a raw material into the catalytic oxidation reaction of the by-product hydrogen chloride including step 3.

[0090] The gas stream containing chlorine separated in step 4 may also be introduced into other independent chlorination reactions.

[0091] The purity of chlorine gas in the gas stream containing chlorine obtained by the catalytic oxidation in step 3 of the present disclosure is up to above 99.6% (vol%), which can meet the quality requirements of chlorine feed gas in the photochlorination reaction.

[0092] The expression "closed circulation of chlorine resources (or chlorine element or chlorine atom)" in the present disclosure means that the by-product hydrogen chloride is suitably treated by the method of the present disclosure such that the chlorine element can be recycled in the method of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0093] The purity of the products, 1,3-bis-(trichloromethyl)-benzene, 1,4-bis-(trichloromethyl)-benzene, 1,3-bis-(chloroformyl)-benzene, 1,4-bis-(chloroformyl)-benzene, *p*-chloro-(trichloromethyl)benzene, and trichlorotoluene in the examples below was quantitatively determined by gas chromatography.

[0094] The purify of the product 1,3,5-tris(trichloromethyl)benzene in the examples below was determined by liquid chromatography.

Example 1

[0095] As shown in FIG. 1.

Step 1, chlorination reaction

[0096] In a continuous photochlorination apparatus consisting of 3 reaction columns connected in series, 1,3-dimethylbenzene was continuously added at a rate of 95 kg/h from the top of the first column, where the first column was controlled at a temperature of 80°C-120°C, with a central peak wavelength of incident light of 460 nm and an average illuminance of 20000-39000Lux, while chlorine gas was fed at a flow rate of 135 kg/h from the bottom for continuous chlorination reaction. The reaction solution in the first column overflowed from the bottom into the second column, where the second column had a central peak wavelength of incident light of 505 nm and an average illuminance of 40000-61000Lux. The second column was controlled at a temperature of 135-145°C, and chlorine gas was fed at a flow rate of 128 kg/h into the second column. The reaction solution in the second column overflowed from the bottom into the third column, where the third column had a central peak wavelength of incident light of 586 nm and an average illuminance of 60000-86000Lux. The third column was controlled at a temperature of 170-180°C, and chlorine gas was fed at a flow rate of 148 kg/h into the third column. The total amount of chlorine gas fed in the reaction system consisting of the three columns was 411 kg/h. The resulting reaction mixture at the outlet of the third column was 1,3-bis-(trichloromethyl)-benzene, which was purified by single rectification to obtain purified 1,3-bis-(trichloromethyl)-benzene. The by-product hydrogen chloride gas generated in the photochlorination reaction was collected.

Step 2, chloroacylation reaction

[0097] The purified 1,3-bis-(trichloromethyl)-benzene obtained in step 1 was added to a batching kettle equipped with a temperature measuring device, a condensation reflux device, and a stirring device, where two or more batching kettles may be provided to achieve continuous feeding.

[0098] 1,3-bis-(trichloromethyl)-benzene was heated to be completely melt.

[0099] *m*-phthalic acid with a purity of 99.50% was added in a molar ratio of 1:1.01 of 1,3-bis-(trichloromethyl)-benzene : *m*-phthalic acid, and then ferric chloride catalyst was added in a weight ratio of 1:0.003 of

[0100] 1,3-bis-(trichloromethyl)-benzene : ferric chloride.

[0101] 1,3-bis-(chloroformyl)-benzene with a purity of 99.0% was added as a reaction solvent in a weight ratio of 1:1 of 1,3-bis-(trichloromethyl)-benzene : 1,3-bis-(chloroformyl)-benzene. These raw materials for chloroacylation were heated and mixed in the batching kettle into a feedstock solution for chloroacylation, which was continuously added to two tandem chloroacylation reactors. The first-stage reactor was controlled at an inner temperature of 100°C, and the second-stage reactor had an inner temperature of 110°C. 1,3-bis-(chloroformyl)-benzene was obtained at the outlet of the second-stage reactor and was subjected to single rectification to obtain purified 1,3-bis-(chloroformyl)-benzene.

Step 3, catalytic oxidation of the by-product hydrogen chloride

[0102] The collected by-product hydrogen chloride in steps 1 and 2 was subjected to catalytic oxidation in the presence of a catalyst (the Deacon reaction) to prepare chlorine gas. The specific procedure was described below:

(1) firstly, the by-product hydrogen chloride gas was purified by adsorption to remove organic impurities. The gas stream containing hydrogen chloride and the gas stream containing oxygen entering the first-stage reactor were mixed, preheated, and then fed to the first-stage reactor;
(2) after passing through a heat exchanger, a gas stream from the first-stage reactor was mixed with other gas streams intended to enter the second-stage reactor (other gas streams refer to a returned product gas stream and a gas stream containing oxygen and/or a gas stream containing hydrogen chloride entering said reactor, the same hereinafter), and then entered the second-stage reactor; after passing through a heat exchanger, a gas stream from the second-stage reactor was mixed with other gas streams intended to enter the third-stage reactor, and then entered the third-stage reactor; and
(3) a product gas stream from the third-stage reactor was divided into two portions: one portion, returned product gas stream was equally distributed, returned to the inlets of the first-stage, second-stage, and third-stage reactors, mixed with a gas stream containing oxygen and/or a gas stream containing hydrogen chloride intended to enter each stage reactor, and then entered each stage reactor; and the other portion, remaining product gas stream was passed through a gas heat exchanger for heat exchange before separation thereof, where the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter the first reactor was used as a cooling medium.

Step 4, separation of the gas stream from step 3

[0103] The product gas steam from step 3 was separated to obtain gas streams containing chlorine, containing oxygen, or containing hydrogen chloride, which comprises the steps of:

a. condensation: the product gas stream from step 3 was condensed at a temperature of -5-5°C and at a pressure of 0.05-10 MPa, water along with a part of unreacted hydrogen chloride was condensed as an aqueous hydrochloric acid solution;
b. deep dehydration: the gas stream after being condensed in step a was subjected to deep dehydration by using concentrated sulfuric acid;
c. adsorption: the gas stream after being subjected to deep dehydration in step b was passed though silica gel as an adsorbent to remove oxygen gas by adsorption, using the pressure and temperature swing adsorption technology, wherein the adsorption pressure was 0.5 MPa, and the temperature in the adsorption stage was gradually decreased from 60°C to 25°C; the desorption pressure under reduced pressure was -0.07 MPa and the desorption temperature was 50°C, and the desorption generated a separated gas stream containing oxygen. The remaining gas after adsorption was a gas stream containing chlorine with chlorine gas as a main component; and
d. liquefaction: the gas stream containing chlorine obtained in step c was liquefied at a temperature of -20-20°C and a pressure of 0.05-10 MPa, to obtain a gas stream containing hydrogen chloride and a liquefied gas stream containing chlorine after separation thereof.

Step 5, recycling of the separated substances

[0104] The gas stream containing chlorine separated in step 4 was introduced as a raw material into the chlorination reaction including step 1. The gas streams containing oxygen and containing hydrogen chloride separated in step 4 were introduced again as raw materials into the catalytic oxidation of hydrogen chloride including step 3. Specific process conditions are shown in Table 2. The reaction results are shown in Table 1.
[0105] Example 2. The specific operation process is described below. Step 1, chlorination reaction
[0106] The operation process of the chlorination reaction was the same as step 1 in Example 1. The differences were that, 1,4-dimethylbenzene was used, the rate entering the first column was 100 kg/h, and the first column had a central peak wavelength of incident light of 460 nm and an average illuminance of 20000-39000Lux; the second column had a central peak wavelength of incident light of 505 nm and an average illuminance of 40000-61000Lux, and the second column was controlled at a temperature of 135-145°C; and the third column had a central peak wavelength of incident

light of 586 nm and an average illuminance of 60000-86000Lux, and the third column was controlled at a temperature of 170-180°C. The resulting reaction mixture at the outlet of the third column was 1,4-bis-(trichloromethyl)-benzene, which was purified by single rectification to obtain purified 1,4-bis-(trichloromethyl)-benzene. The by-product hydrogen chloride gas generated in the photochlorination reaction was collected.

Step 2, chloroacylation reaction

[0107] The operation process of the chloroacylation reaction was the same as step 2 in Example 1. 1,4-bis-(chloroformyl)-benzene was obtained at the outlet of the second-stage reactor and was subjected to single rectification to obtain purified 1,4-bis-(chloroformyl)-benzene.

Step 3, catalytic oxidation of the by-product hydrogen chloride

[0108] The collected by-product hydrogen chloride in steps 1 and 2 was subjected to catalytic oxidation in the presence of a catalyst to prepare chlorine gas. The specific oxidation process comprises the steps of:

(1) firstly, the by-product hydrogen chloride gas was purified by adsorption to remove organic impurities. The gas stream containing oxygen and the gas stream containing hydrogen chloride entering the first-stage reactor were mixed, preheated, and then fed to the first-stage reactor;
(2) after passing through a heat exchanger, a gas stream from the first-stage reactor was mixed with other gas streams intended to enter the second-stage reactor, and then entered the second-stage reactor; after passing through a heat exchanger, a gas stream from the second-stage reactor was mixed with other gas streams intended to enter the third-stage reactor, and then entered the third-stage reactor; and
(3) a product gas stream from the third-stage reactor was divided into two portions: one portion, returned product gas stream was equally distributed, returned to the inlets of the first-stage, second-stage, and third-stage reactors, mixed with a gas stream containing oxygen and/or a gas stream containing hydrogen chloride intended to enter each stage reactor, and then entered each stage reactor; and the other portion, remaining product gas stream was passed through a gas heat exchanger for heat exchange before separation thereof, where the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter the first reactor was used as a cooling medium.

Step 4, separation of the gas stream from step 3

[0109] The product gas steam from step 3 was separated to obtain gas streams containing chlorine, containing oxygen, and containing hydrogen chloride, which comprises the steps of:

a. condensation: the product gas stream from step 3 was condensed at a temperature of -5-5°C and at a pressure of 0.05-10 MPa, and water along with a part of unreacted hydrogen chloride was condensed as an aqueous hydrochloric acid solution;
b. deep dehydration: the gas stream after being condensed in step a was subjected to deep dehydration, wherein the drying was performed by the pressure swing adsorption technology using a composite adsorbent layer with two adsorbents in combination wherein the one adsorbent was an alumina adsorbent placed in an upper portion of an adsorber and the other adsorbent was a zeolitic molecular sieve adsorbent for deep dehydration placed in a lower portion of the adsorber, and a volume ratio of the upper alumina adsorbent to the lower adsorbent for deep dehydration was 40%:60%. In the pressure swing adsorption drying, the adsorption pressure was 0.40 MPa, the desorption pressure was 0.02 MPa, and the adsorption temperature was ambient temperature; and
c. adsorption: the gas stream after being subjected to deep dehydration in step b was passed though a carbon molecular sieve as an adsorbent to remove oxygen gas by adsorption, using the pressure and temperature swing adsorption technology including adsorption and desorption processes, wherein the adsorption pressure was 0.20 MPa, and the temperature in the adsorption stage was gradually decreased from 40°C to 20°C; the desorption pressure under vacuum was -0.07 MPa and the desorption temperature was 40°C, and the desorption generated a separated gas stream containing oxygen. The remaining gas after adsorption was a gas stream containing chlorine with chlorine gas as a main component.

Step 5, recycling of the separated substances

[0110] The gas stream containing chlorine separated in step 4 was introduced as a raw material into the chlorination reaction including step 1. The gas stream containing oxygen separated in step 4 was introduced again as a raw material into the catalytic oxidation of hydrogen chloride including step 3. Specific process conditions are shown in Table 2.

[0111] The reaction results are shown in Table 1.

[0112] Example 3. The operation was similar to the specific steps in Example 2, except the raw material methyl aromatic hydrocarbon was *p*-chlorotoluene, which was reacted with chlorine gas to obtain *p*-chloro-(trichloromethyl)benzene. The corresponding aromatic acid was *p*-chlorobenzoic acid.

[0113] Example 4. The operation was similar to the specific steps in Example 2, except the raw material methyl aromatic hydrocarbon was toluene, which was reacted with chlorine gas to obtain trichlorotoluene. The corresponding aromatic acid was benzoic acid.

[0114] Example 5. The operation was similar to the specific steps in Example 1, except the raw material methyl aromatic hydrocarbon was mesitylene, which was reacted with chlorine gas to obtain 1,3,5-tris(trichloromethyl)benzene. The corresponding aromatic acid was trimesic acid.

Example 6

Step 1, chlorination reaction

[0115] Into reaction columns, equipped with a temperature measuring device, a condensation reflux device, an illumination device of LED lamps, and a heating/cooling device, 100 kg of 1,3-dimethylbenzene was added and heated to 80°C. LED lamps were turned on for irradiation, with a central peak wavelength of incident light of 360 nm and an illuminance of 49000Lux. Then, chlorine gas was fed to initiate the reaction while the feeding rate of chlorine gas was controlled so that the system temperature was no more than 120°C. The amount of chlorine gas consumed was 135.8 kg and the first reaction stage took 4 h and 30 min. After the illuminance was adjusted to 60000Lux and the system temperature was increased to 140°C, chlorine gas continued to be fed. The amount of chlorine gas consumed was 136 kg and the second reaction stage took 3 h and 55 min. After the illuminance was maintained at 60000Lux and the system temperature was increased to 160°C, 155.2 kg of chlorine gas continued to be fed. The third reaction stage took 16 h and 35 min. The total amount of chlorine gas consumed in the reaction was 427 kg. The reaction mixture after the reaction was completed was a crude of 1,3-bis-(trichloromethyl)-benzene, which was purified by single rectification to obtain 255 kg of 1,3-bis-(trichloromethyl)-benzene with a purify of 99.42%. The gas generated in the chlorination reaction was collected to obtain 122m^3 of by-product hydrogen chloride.

Step 2, chloroacylation reaction

[0116] Into a reactor, equipped with a temperature measuring device, a condensation reflux device, and a stirring device, 255 kg of 1,3-bis-(trichloromethyl)-benzene with a purity of 99.42% obtained in step 1 was added and heated to be completely melt. 137.3 kg of m-phthalic acid with a purity of 99.50% was added in 1.01 times the mole number of 1,3-bis-(trichloromethyl)-benzene, and then 0.77 kg of ferric chloride catalyst was added in 0.30% of the weight of 1,3-bis-(trichloromethyl)-benzene. The temperature was raised to 110°C for 60 min, at which the reaction was completed. The resulting product was subjected to rectification to obtain purified 1,3-bis-(chloroformyl)-benzene with a purity of 99.97%. The gas generated in the chloroacylation reaction was collected to obtain 34m^3 of by-product hydrogen chloride.

Step 3, catalytic oxidation of the by-product hydrogen chloride

[0117] The two by-product hydrogen chloride gases generated in the present example were continuously compressed into the catalytic oxidation system. The operation process was the same as step 3 in Example 2.

Step 4, separation of the gas stream from step 3

[0118] The product gas steam from step 3 was separated to obtain gas streams containing chlorine and containing oxygen, which comprises the steps of:

a. condensation: the product gas stream from step 3 was condensed at a temperature of -5-5°C and at a pressure of 0.05-10 MPa, water along with a part of unreacted hydrogen chloride was condensed as an aqueous hydrochloric acid solution;

b. deep dehydration: the gas stream after being condensed in step a was subjected to deep dehydration, wherein the drying was performed by the temperature swing adsorption technology using a composite adsorbent layer with two adsorbents in combination wherein the one adsorbent was an alumina adsorbent placed in an upper portion of an adsorber and the other adsorbent was a zeolitic molecular sieve adsorbent for deep dehydration placed in a lower portion of the adsorber, and a volume ratio of the upper alumina adsorbent to the lower adsorbent for deep dehydration was 30%:70%. In the temperature swing adsorption drying, the adsorption pressure was 0.70 MPa and the adsorption temperature was 30°C; the regeneration operation included desorption and dehydration processes. The desorption pressure of the regeneration operation was 0.009 MPa and the desorption temperature of the regeneration operation was 160°C; the dehydration process of the regeneration operation used a carrier gas at a temperature of 180°C;

c. adsorption: the gas stream after being subjected to deep dehydration in step b was passed though a carbon molecular sieve as an adsorbent to remove oxygen gas by adsorption, using the pressure and temperature swing adsorption technology including adsorption and desorption processes, wherein the adsorption pressure was 0.5 MPa, and the temperature in the adsorption stage was gradually decreased from 60°C to 25°C; the desorption pressure under reduced pressure was -0.07 MPa and the desorption temperature was 50°C, and the desorption generated a separated gas stream containing oxygen. The remaining gas after adsorption was a gas stream containing chlorine with chlorine gas as a main component; and

d. liquefaction: the gas stream containing chlorine obtained in step c was liquefied at a temperature of -20-20°C and a pressure of 0.05-10 MPa, to obtain a gas stream containing hydrogen chloride and a liquefied gas stream containing chlorine after separation thereof.

[0119] The amount of chlorine gas obtained after separation thereof in step 4 was determined to be 195Kg, with a purity of 99.97(v.%), and the amount of recovered hydrogen chloride obtained after separation thereof was 18m^3; and the amount of recovered oxygen gas obtained after separation thereof was 30m^3. Step 5, recycling of the separated substances

[0120] The gas stream containing chlorine separated in step 4 was introduced as a raw material into the chlorination reaction including step 1, and the resulting crude was purified by single rectification to obtain 1,3-bis-(trichloromethyl)-benzene with a purity of 99.4%. Further, the purified 1,3-bis-(trichloromethyl)-benzene was introduced into the chloroacylation reaction including step 2, to obtain 1,3-bis-(chloroformyl)-benzene with a purity of 99.96%. The reaction results are shown in Table 1.

[0121] Table 1 below shows input and output amounts of main materials in Examples 1-5; and table 2 shows operation conditions for the oxidation unit in step 2 of the respective Examples.

Table 1

Input and output amounts of main materials in the clean process													
	Chlorination reaction						Chloroacylation reaction		Catalytic oxidation reaction	Separation of product gas stream			
	Methyl aromatic hydrocarbon		Chlorine gas (Kg/h)	HCl amount (m^3/h)	Trichloromethyl-substituted benzene Purity (%)	Trichloromethyl-substituted benzene yield (Kg/h)	HCl yield (m^3/h)	Chloroformyl-substituted benzene Purity (%)	Amount of O_2 used (m^3/h)	Amount of HCl recovered (m^3/h)	Amount of O_2 recovered (m^3/h)	**Chlorine gas recovered**	
	Species	Amount used (Kg/h)										Yield	Purity (v.%)
Example 1	1,3-dimethylbenzene	95	411	117	99.12	252	33	99.97	49.9	17	18	186 Kg/h	99.98
Example 2	1,4-dimethylbenzene	100	435	122	99.23	245	32	99.96	309.3	/	267	73 m^3/h	99.97
Example 3	*p*-chloro toluene	85.5	156	43	99.86	143	12	99.95	55.2	/	40	25 m^3/h	99.97
Example 4	toluene	125	312	89	99.9	250	26	99.98	141	/	111	54 m^3/h	99.96
Example 5	Mesitylene	92.6	530	153	99.43	312	47	99.96	40	46	13	156 Kg/h	99.98
Notes: Chlorine gas consumed in the chlorination step may comprise recovered gas streams containing chlorine separated in steps 4 and 5;													

[0122] Hydrogen chloride used in step 3 of the examples of the present disclosure is the total amount of hydrogen chloride generated by the chlorination in step 1 and the chloroacylation in step 2; those skilled in the art can understand that, a gas stream containing hydrogen chloride other than that generated in steps 1 and 2 of the present disclosure may also be introduced in actual production process.

[0123] Recovered hydrogen chloride and recovered oxygen gas from the catalytic oxidation of step 3 may be recycled through step 5 to participate in the catalytic oxidation of hydrogen chloride.

[0124] The trichloromethyl-substituted benzene purity (%) in the table refers to the purity of a sample obtained by introducing a separated, recovered gas stream containing chlorine into the chlorination reaction which includes step 1, thereby obtaining a trichloromethyl-substituted benzene crude product which is then purified via a single rectification to obtain the sample; the chloroformyl-substituted benzene purity (%) in the table refers to the purity of a sample obtained by introducing the resulting trichloromethyl-substituted benzene mentioned above into the chloroacylation reaction which includes step 2, thereby obtaining a chloroformyl-substituted benzene crude product which is then purified via a simple rectification to obtain the sample.

Table 2: the catalytic oxidation process of step 3

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Volume ratio of returned product gas stream and remaining product gas stream	0.5:0.5	0.3:0.7	0.5:0.5	0.3:0.7	0.3:0.7	0.4:0.6
Feeding mode of the gas stream containing hydrogen chloride	Totally entering the first reactor	Separately entering the reactors in a volume ratio of 0.5:1:1.5	Separately entering the reactors in a volume ratio of 1:1:1	Separately entering the reactors in a volume ratio of 0.5:1:1.5	Totally entering the first reactor	Separately entering the reactors in a volume ratio of 1:1:1
Feeding mode of the gas stream containing oxygen	Separately entering the reactors in a volume ratio of 1:1:1	Totally entering the first reactor	Totally entering the first reactor	Totally entering the first reactor	Separately entering the reactors in a volume ratio of 1:1:1	Totally entering the first reactor
Feed volume ratio of hydrogen chloride and oxygen gas	3:1	1:2	1:1	0.9:1.1	5:1	2.5:1
Gas stream containing hydrogen chloride (calculated based on pure hydrogen chloride) (m^3/h)	149.7	154.6	55.2	115.4	200	157.1
Gas stream containing oxygen (calculated based on pure oxygen) (m^3/h)	49.9	309.3	55.2	141	40	62.8
Feed temperature of the first reactor	310	325	360	313	313	325
Catalyst	Ruthenium-cop per composite catalyst 1	Ruthenium-copp er composite catalyst 2	Ruthenium-copp er composite catalyst 1	Ruthenium-coppe r composite catalyst 2	Ruthenium-copp er composite catalyst 2	Ruthenium-c opper composite catalyst 2

Claims

1. A process of preparing a chloroformyl-substituted benzene, comprising the steps of:

step 1: reacting a methyl aromatic hydrocarbon of formula $(X)_aC_6H_{6-a-b}(CH_3)_b$ or a pendant alkyl chloride thereof with chlorine gas under illumination conditions to prepare a trichloromethyl-substituted benzene and obtain a by-product hydrogen chloride, wherein X is a chlorine, bromine or fluorine atom, a is an integer selected from 0, 1, 2, 3, 4 and 5, b is an integer selected from 1, 2, 3 and 4, and a+b≤6, and the pendant alkyl chloride thereof refers to a compound where hydrogen atoms of a pendant alkyl group in the methyl aromatic compound are not completely substituted by chlorine atoms,
wherein the representative reaction in step 1 is represented by the following equation:
$(X)_aC_6H_{6-a-b}(CH_3)_b + 3bCl_2 = (X)_aC_6H_{6-a-b}(CCl_3)_b + 3bHCl$;
step 2: further reacting the resulting trichloromethyl-substituted benzene in step 1 with water or the corresponding aromatic acid of formula $(X)_aC_6H_{6-a-b}(COOH)_b$ to prepare the chloroformyl-substituted benzene and to obtain a by-product hydrogen chloride, wherein the corresponding aromatic acid means that a substituent on a parent nucleus of the aromatic acid and a substituent on a parent nucleus of the methyl aromatic hydrocarbon or pendant alkyl chloride thereof are located at the same substitution position or corresponding substitution positions, and wherein X is a chlorine, bromine or fluorine atom, a is an integer selected from 0, 1, 2, 3, 4 and 5, b is an integer selected from 1, 2, 3 and 4, and a+b≤6,
wherein the representative reaction in step 2 is represented by the following equation:
$(X)_aC_6H_{6-a-b}(CCl_3)_b + (X)_aC_6H_{6-a-b}(COOH)_b = 2(X)_aC_6H_{6-a-b}(COCl)_b + bHCl$ or $(X)_aC_6H_{6-a-b}(CCl_3)_b + bH_2O = (X)_aC_6H_{6-a-b}(COCl)_b + 2bHCl$;
step 3: subjecting a gas stream containing the hydrogen chloride from steps 1 and 2 to catalytic oxidation,
wherein the representative reaction in step 3 is represented by the following equation:
$4bHCl + bO_2 = 2bCl_2 + 2bH_2O$;
step 4: separating a product gas steam from step 3 to obtain gas streams containing chlorine, containing oxygen, and/or containing hydrogen chloride;
step 5: introducing the gas stream containing chlorine separated in step 4 as a raw material into the chlorination in step 1; and
wherein in the chlorination in step 1, the methyl aromatic hydrocarbon is reacted with chlorine gas under illumination conditions to prepare the trichloromethyl-substituted benzene, where the illumination has a light source wavelength of about 350 nm-700 nm and a light amplitude of no more than about 200 nm, and where chlorine gas feeding is initiated under conditions of a reaction temperature of about 0°C-85°C and an illuminance of about 2000 Lux-about 55000 Lux, for a first reaction stage where the reaction temperature is no more than about 120°C at the illuminance; and then the remaining amount of chlorine gas is fed at a higher reaction temperature until the reaction is completed; preferably, wherein the light source is an LED lamp;
optionally, wherein separating the product gas steam from step 3 in step 4 comprises the steps of:

a. condensation: the product gas stream from step 3 is condensed, wherein water generated by the reaction in step 3 along with a part of unreacted hydrogen chloride is condensed as an aqueous hydrochloric acid solution;
b. deep dehydration: the product gas stream after being condensed in step a is subjected to deep dehydration, for example, through concentrated sulfuric acid, a molecular sieve, or by temperature swing adsorption, pressure swing adsorption, to remove residual moisture;
c. adsorption: the gas stream after being subjected to deep dehydration in step b is adsorbed by an adsorbent, to separate chlorine gas from oxygen gas; and

optionally, d. liquefaction: the gas stream containing chlorine obtained in step c is liquefied, to obtain a gas stream containing hydrogen chloride and a liquefied gas stream containing chlorine after separation thereof;
or optionally, wherein the chloroacylation in step 2 preferably comprises the steps of:

i) fully melting the trichloromethyl-substituted benzene at an elevated temperature, adding water or the corresponding aromatic acid and a catalyst, and stirring thoroughly; and
ii) heating the reaction system to maintain the reaction.

2. The process according to claim 1, wherein step 5 comprises introducing the gas streams containing hydrogen chloride and/or containing oxygen separated in step 4 as a raw material again into the catalytic oxidation of the hydrogen chloride in step 3.

3. The process according to any one of claims 1-2, wherein the oxidation of the by-product hydrogen chloride in step 3 comprises the steps of:

1) providing one or more reactors, preferably adiabatic reactors, filled with a catalyst that are connected in series or in parallel;
2) providing a gas stream containing hydrogen chloride and a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a first reactor of the one or more reactors, and providing a gas stream containing hydrogen chloride and/or a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a downstream reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
3) directly returning a part of a product gas stream from a last reactor of the one or more reactors from the catalytic oxidation to any of the one or more reactors without separation thereof; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof;

optionally, wherein a feed volume ratio of the gas stream containing hydrogen chloride, calculated based on pure hydrogen chloride, to the gas stream containing oxygen, calculated based on pure oxygen, is 1:2-5:1, preferably 1:1.2-3.5:1, more preferably 1:1-3:1;
or optionally, wherein a feed volume ratio of the gas stream containing hydrogen chloride, calculated based on pure hydrogen chloride, to the gas stream containing oxygen, calculated based on pure oxygen, is 2:1-5:1;
or optionally, wherein a feed volume ratio of the gas stream containing hydrogen chloride, calculated based on pure hydrogen chloride, to the gas stream containing oxygen, calculated based on pure oxygen, is 1:2-2:1, preferably 1.1:0.9-0.9:1.1.

4. The process according to claim 3, wherein before returning a part of a product gas stream from a last reactor of the one or more reactors to a feed inlet of any of the one or more reactors without separation thereof in step 3), mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation.

5. The process according to any one of claims 3 and 4, wherein in step 3), the part of the product gas stream from the last reactor of the one or more reactors is returned to each of the provided one or more reactors without separation thereof.

6. The process according to claim 5, wherein in returning the part of the product gas stream from the last reactor of the one or more reactors to each of the provided one or more reactors without separation thereof, the returned product gas stream is distributed among the one or more reactors in any ratio; wherein preferably, the returned product gas stream is equally distributed into corresponding parts according to the number of the one or more reactors, for respectively being returned to the one or more reactors.

7. The process according to any one of claims 3-6, wherein the gas stream containing hydrogen chloride and the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride are provided to the first reactor of the one or more reactors, and the gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride is provided to the downstream reactor of the one or more reactors.

8. The process according to claim 7, wherein the gas streams containing oxygen for oxidation of a gas stream containing hydrogen chloride provided to the one or more reactors are portions of a desired amount of a gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride that are distributed among the one or more reactors in any ratio as desired, preferably equally distributed into corresponding parts according to the number of the one or more reactors.

9. The process according to any one of claims 3-6, wherein the gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride and the gas stream containing hydrogen chloride are provided to the first reactor of the one or more reactors, and the gas stream containing hydrogen chloride is provided to the downstream reactor of the one or more reactors; wherein preferably, an oxygen content in the gas stream containing oxygen entering each of the one or more reactors is greater than a theoretical oxygen consumption required for oxidation of the gas stream containing hydrogen chloride entering said reactor.

10. The process according to claim 9, wherein the gas streams containing hydrogen chloride provided to the one or more reactors are portions of a gas stream containing hydrogen chloride to be oxidated that are distributed among the one or more reactors in any ratio as desired, preferably equally distributed into corresponding parts according to the number of the one or more reactors.

11. The process according to any one of claims 1-10, wherein the oxidation of the by-product hydrogen chloride in step 3 comprises the steps of:

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2a) providing a gas stream containing hydrogen chloride and a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to a first reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
2b) providing a product gas stream from the first reactor of the one or more reactors to a downstream reactor of the one or more reactors through a heat exchanger, providing a gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride to the downstream reactor of the one or more reactors, and successively providing a product gas stream from the previous reactor and a gas stream containing oxygen for oxidation of a gas stream containing hydrogen chloride to a remaining downstream reactor of the one or more reactors;
3) before returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, preferably to a feed inlet of any of the one or more reactors, mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

12. The process according to any one of claims 1-10, wherein the oxidation of the by-product hydrogen chloride in step 3 comprises the steps of:

1) providing one or more reactors filled with a catalyst that are connected in series or in parallel;
2a) providing a gas stream containing oxygen for oxidation of hydrogen chloride and a gas stream containing hydrogen chloride to a first reactor of the one or more reactors, for the catalytic oxidation of hydrogen chloride;
2b) providing a product gas stream from the first reactor of the one or more reactors to a downstream reactor of the one or more reactors through a heat exchanger, providing a gas stream containing hydrogen chloride to the downstream reactor of the one or more reactors, and successively providing a product gas stream from the previous reactor and a gas stream containing hydrogen chloride to a remaining downstream reactor of the one or more reactors;
3) before returning a part of a product gas stream from the last reactor of the one or more reactors to any of the one or more reactors without separation thereof, preferably to a feed inlet of any of the one or more reactors, mixing the part of the product gas stream from the last reactor of the one or more reactors with the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter any of the one or more reactors, which then is fed to said reactor for the catalytic oxidation; and
4) providing a remainder of the product gas stream from the last reactor of the one or more reactors for separation thereof.

13. The process according to any one of claims 3-12, wherein each of the one or more reactors optionally has a heat exchanger disposed thereafter for removing reaction heat, the heat exchanger located after said reactor being a heat exchanger, preferably a tube bundle heat exchanger, plate heat exchanger, gas heat exchanger, or the like; wherein preferably, a gas heat exchanger is disposed after the last reactor of the one or more reactors.

14. The process according to claim 13, wherein the remainder of the product gas stream from the last reactor of the one or more reactors from the catalytic oxidation is passed through the gas heat exchanger before separation thereof, wherein the heat exchange is preferably performed in the gas heat exchanger using the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride intended to enter the first reactor as a cooling medium; preferably, the gas stream containing hydrogen chloride and/or the gas stream containing oxygen for oxidation of the gas stream containing hydrogen chloride after being heat exchanged is mixed with a part of the returned product gas stream out of the third-stage reactor before being provided to the first reactor, and then is fed to the first reactor for the catalytic oxidation of hydrogen chloride.

15. The process according to any one of claims 3-14, wherein a volume ratio of the part of the product gas stream from the last reactor of the one or more reactors directly returned to the one or more reactors without separation thereof to the remainder of the product gas stream from the last reactor of the one or more reactors is 0.25:0.75-0.75:0.25, preferably 0.35:0.65-0.45:0.55.

Patentansprüche

1. Verfahren zur Herstellung eines Chlorformyl-substituierten Benzols, umfassend die Schritte:

Schritt 1: Umsetzen eines methylaromatischen Kohlenwasserstoffs der Formel $(X)_aC_6H_{6\text{-}a\text{-}b}(CH_3)_b$ oder eines anhängenden Alkylchlorids davon mit Chlorgas unter Beleuchtungsbedingungen, um ein Trichlormethyl-substituiertes Benzol herzustellen und ein Chlorwasserstoff Nebenprodukt zu erhalten, wobei X ein Chlor-, Brom- oder Fluoratom ist, a eine ganze Zahl ausgewählt aus 0, 1, 2, 3, 4 und 5 ist, b eine ganze Zahl ausgewählt aus 1, 2, 3 und 4 ist und $a+b \leq 6$ ist, und das anhängende Alkylchlorid davon sich auf eine Verbindung bezieht, bei der Wasserstoffatome einer anhängenden Alkylgruppe in der methylaromatischen Verbindung nicht vollständig durch Chloratome substituiert sind,
wobei die repräsentative Reaktion in Schritt 1 durch die folgende Gleichung dargestellt ist:
$(X)_aC_6H_{6\text{-}a\text{-}b}(CH_3)_b + 3bCl_2 = (X)_aC_6H_{6\text{-}a\text{-}b}(CCl_3)_b + 3bHCl$;
Schritt 2: weiteres Umsetzen des resultierenden Trichlormethyl-substituierten Benzols in Schritt 1 mit Wasser oder der korrespondierenden aromatischen Säure der Formel $(X)_aC_6H_{6\text{-}a\text{-}b}(COOH)_b$, um das Chlorformyl-substituierte Benzol herzustellen und ein Chlorwasserstoff Nebenprodukt zu erhalten, wobei die korrespondierende aromatische Säure bedeutet, dass ein Substituent an einem Stammkern der aromatischen Säure und ein Substituent an einem Stammkern des methylaromatischen Kohlenwasserstoffs oder anhängigen Alkylchlorids davon an derselben Substitutionsposition oder korrespondierenden Substitutionspositionen angeordnet sind, und wobei X ein Chlor-, Brom- oder Fluoratom ist, a eine ganze Zahl ausgewählt aus 0, 1, 2, 3, 4 und 5 ist, b eine ganze Zahl ausgewählt aus 1, 2, 3 und 4 ist und $a+b \leq 6$ ist;
wobei die repräsentative Reaktion in Schritt 2 durch die folgende Gleichung dargestellt ist:
$(X)_aCeH_{6\text{-}a\text{-}b}(CCl_3)_b + (X)_aC_6H_{6\text{-}a\text{-}b}(COOH)_b = 2(X)_aC_6H_{6\text{-}a\text{-}b}(COCl)_b + bHCl$ oder $(X)_aC_6H_{6\text{-}a\text{-}b}(CCl_3)_b + bH_2O = (X)_aC_6H_{6\text{-}a\text{-}b}(COCl)_b + 2bHCl$;
Schritt 3: Unterziehen eines Gasstroms, der den Chlorwasserstoff aus den Schritten 1 und 2 enthält, einer katalytischen Oxidation,

wobei die repräsentative Reaktion in Schritt 3 durch die folgende Gleichung dargestellt ist:
$4bHCl + bO_2 = 2bCl_2 + 2bH_2O$;
Schritt 4: Trennen eines Produktgasdampfes aus Schritt 3, um Gasströme zu erhalten, die Chlor enthalten, Sauerstoff enthalten und/oder Chlorwasserstoff enthalten;
Schritt 5: Einleiten des in Schritt 4 abgetrennten chlorhaltigen Gasstroms als Rohmaterial in die Chlorierung in Schritt 1; und
wobei in der Chlorierung in Schritt 1 der methylaromatische Kohlenwasserstoff mit Chlorgas unter Beleuchtungsbedingungen umgesetzt wird, um das Trichlormethylsubstituierte Benzol herzustellen, wobei die Beleuchtung eine Lichtquellenwellenlänge von etwa 350 nm - 700 nm und eine Lichtamplitude von nicht mehr als etwa 200 nm aufweist, und wobei die Chlorgaszufuhr unter Bedingungen einer Reaktionstemperatur von etwa 0°C - 85°C und einer Beleuchtungsstärke von etwa 2000 Lux - etwa 55000 Lux für eine erste Reaktionsstufe initiiert wird, bei der die Reaktionstemperatur bei der Beleuchtungsstärke nicht mehr als etwa 120°C beträgt; und dann die restliche Chlorgasmenge bei einer höheren Reaktionstemperatur zugeführt wird, bis die Reaktion beendet ist; bevorzugt wobei die Lichtquelle eine LED Lampe ist;
gegebenenfalls, wobei Trennen des Produktgasstroms von Schritt 3 in Schritt 4 die Schritte umfasst:

a. Kondensation: der Produktgasstrom aus Schritt 3 wird kondensiert, wobei durch die Reaktion in Schritt 3 erzeugtes Wasser zusammen mit einem Teil von nicht umgesetztem Chlorwasserstoff als eine wässrige Salzsäurelösung kondensiert wird;
b. Tiefentrocknung: der Produktgasstrom wird nach der Kondensation in Schritt a einer Tiefentrocknung unterzogen, beispielsweise durch konzentrierte Schwefelsäure, ein Molekularsieb oder durch Temperaturwechseladsorption, Druckwechseladsorption, um Restfeuchte zu entfernen;

c. Adsorption: der Gasstrom wird, nachdem er in Schritt b einer Tiefentrocknung unterzogen wurde, durch ein Adsorptionsmittel adsorbiert, um Chlorgas von Sauerstoffgas zu trennen; und

gegebenenfalls d. Verflüssigung: der in Schritt c erhaltene chlorhaltige Gasstrom wird verflüssigt, um einen Chlorwasserstoff enthaltenden Gasstrom und einen verflüssigten, Chlor enthaltenden Gasstrom nach dessen Trennung zu erhalten;
oder gegebenenfalls, wobei die Chloracylierung in Schritt 2 vorzugsweise die Schritte umfasst:

i) vollständiges Schmelzen des Trichlormethyl-substituierten Benzols bei erhöhter Temperatur, Zugabe von Wasser oder der korrespondierenden aromatischen Säure und eines Katalysators und gründliches Rühren; und
ii) Erhitzen des Reaktionssystems, um die Reaktion aufrechtzuerhalten.

2. Verfahren nach Anspruch 1, wobei Schritt 5 umfasst, die in Schritt 4 getrennten Gasströme enthaltend Chlorwasserstoff und/oder enthaltend Sauerstoff als Rohstoff wieder in die katalytische Oxidation des Chlorwasserstoffs in Schritt 3 einzuleiten.

3. Verfahren nach einem der Ansprüche 1 bis 2, wobei die Oxidation des Nebenprodukts Chlorwasserstoff in Schritt 3 die Schritte umfasst:

1) Bereitstellen eines oder mehrerer Reaktoren, vorzugsweise adiabatischer Reaktoren, gefüllt mit einem Katalysator, die in Reihe oder parallel geschaltet sind;
2) Bereitstellen eines Chlorwasserstoff enthaltenden Gasstroms und eines Sauerstoff enthaltenden Gasstroms zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms in einem ersten Reaktor des einen oder der mehreren Reaktoren und Bereitstellen eines Chlorwasserstoff enthaltenden Gasstroms und/oder eines Sauerstoff enthaltenden Gasstroms zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms für einen nachgeschalteten Reaktor des einen oder der mehreren Reaktoren zur katalytischen Oxidation von Chlorwasserstoff;
3) direktes Zurückführen eines Teils eines Produktgasstroms aus einem letzten Reaktor des einen oder der mehreren Reaktoren aus der katalytischen Oxidation zu einem des einen oder der mehreren Reaktoren ohne dessen Trennung; und
4) Bereitstellen eines Rests des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu dessen Trennung;

gegebenenfalls, wobei ein Zufuhrvolumenverhältnis des Chlorwasserstoff enthaltenden Gasstroms, berechnet auf Basis von reinem Chlorwasserstoff, zu dem Sauerstoff enthaltenden Gasstrom, berechnet auf Basis von reinem Sauerstoff, 1:2 - 5:1, vorzugsweise 1:1,2 - 3,5:1, stärker bevorzugt 1:1 - 3:1 beträgt;
oder gegebenenfalls wobei ein Zufuhrvolumenverhältnis des Chlorwasserstoff enthaltenden Gasstroms, berechnet auf Basis von reinem Chlorwasserstoff, zu dem Sauerstoff enthaltenden Gasstrom, berechnet auf Basis von reinem Sauerstoff, 2:1 - 5:1 beträgt;
oder gegebenenfalls wobei ein Zufuhrvolumenverhältnis des Chlorwasserstoff enthaltenden Gasstroms, berechnet auf Basis von reinem Chlorwasserstoff, zu dem Sauerstoff enthaltenden Gasstrom, berechnet auf Basis von reinem Sauerstoff, 1:2 -2:1, bevorzugt 1,1:0,9-0,9:1,1 beträgt.

4. Verfahren nach Anspruch 3, wobei, vor einem Zurückführen eines Teils eines Produktgasstroms aus einem letzten Reaktor des einen oder der mehreren Reaktoren zu einem Zufuhreinlass eines des einen oder der mehreren Reaktoren ohne dessen Trennung in Schritt 3), der Teil des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren mit dem Chlorwasserstoff enthaltenden Gasstrom und/oder dem Sauerstoff enthaltenden Gasstrom zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms, der/die in einen der einen oder mehreren Reaktoren eintreten soll(en), gemischt wird, der dann dem Reaktor zur katalytischen Oxidation zugeführt wird.

5. Verfahren nach einem der Ansprüche 3 und 4, wobei in Schritt 3) der Teil des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren ohne dessen Trennung in jeden der bereitgestellten einen oder mehreren Reaktoren zurückgeführt wird.

6. Verfahren nach Anspruch 5, wobei beim Zurückführen des Teils des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu jedem der bereitgestellten einen oder mehreren Reaktoren ohne dessen Trennung der zurückgeführte Produktgasstrom auf den einen oder die mehreren Reaktoren in einem beliebigen

Verhältnis aufgeteilt wird; wobei vorzugsweise der zurückgeführte Produktgasstrom entsprechend der Anzahl des einen oder der mehreren Reaktoren gleichmäßig in korrespondierende Teile verteilt wird, um jeweils in den einen oder die mehreren Reaktoren zurückgeführt zu werden.

7. Verfahren nach einem der Ansprüche 3 bis 6, wobei der Chlorwasserstoff enthaltende Gasstrom und der Sauerstoff enthaltende Gasstrom zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms dem ersten Reaktor des einen oder der mehreren Reaktoren bereitgestellt werden, und der Sauerstoff enthaltende Gasstrom zur Oxidation eines Chlorwasserstoff enthaltenden Gasstroms dem nachgeschalteten Reaktor des einen oder der mehreren Reaktoren bereitgestellt wird.

8. Verfahren nach Anspruch 7, wobei die Sauerstoff enthaltenden Gasströme zur Oxidation eines Chlorwasserstoff enthaltenden Gasstroms, die dem einen oder den mehreren Reaktoren bereitgestellt werden, Teile einer gewünschten Menge eines Sauerstoff enthaltenden Gasstroms zur Oxidation eines Chlorwasserstoff enthaltenden Gasstroms sind, die in einem beliebigen gewünschten Verhältnis auf den einen oder die mehreren Reaktoren verteilt werden, vorzugsweise gleichmäßig in korrespondierende Teile entsprechend der Anzahl des einen oder der mehreren Reaktoren verteilt werden.

9. Verfahren nach einem der Ansprüche 3 bis 6, wobei der Sauerstoff enthaltende Gasstrom zur Oxidation eines Chlorwasserstoff enthaltenden Gasstroms und der Chlorwasserstoff enthaltende Gasstrom dem ersten Reaktor des einen oder der mehreren Reaktoren bereitgestellt werden, und der Chlorwasserstoff enthaltende Gasstrom dem nachgeschalteten Reaktor des einen oder der mehreren Reaktoren bereitgestellt wird; wobei vorzugsweise ein Sauerstoffgehalt in dem Sauerstoff enthaltenden Gasstrom, der in jeden des einen oder der mehreren Reaktoren eintritt, größer ist als ein theoretischer Sauerstoffverbrauch, der für eine Oxidation des Chlorwasserstoff enthaltenden Gasstroms erforderlich ist, der in den Reaktor eintritt.

10. Verfahren nach Anspruch 9, wobei die Chlorwasserstoff enthaltenden Gasströme, die dem einen oder den mehreren Reaktoren bereitgestellt werden, Teile eines zu oxidierenden, Chlorwasserstoff enthaltenden Gasstroms sind, die in einem beliebigen, gewünschten Verhältnis auf den einen oder die mehreren Reaktoren verteilt werden, vorzugsweise gleichmäßig in korrespondierende Teile entsprechend der Anzahl des einen oder der mehreren Reaktoren verteilt werden.

11. Verfahren nach einem der Ansprüche 1 bis 10, wobei die Oxidation des Nebenprodukts Chlorwasserstoff in Schritt 3 die Schritte umfasst:

1) Bereitstellen eines oder mehrerer mit einem Katalysator gefüllter Reaktoren, die in Reihe oder parallel geschaltet sind;
2a) Bereitstellen eines Chlorwasserstoff enthaltenden Gasstroms und eines Sauerstoff enthaltenden Gasstroms zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms für einen ersten Reaktor des einen oder der mehreren Reaktoren zur katalytischen Oxidation von Chlorwasserstoff;
2b) Bereitstellen eines Produktgasstroms aus dem ersten Reaktor des einen oder der mehreren Reaktoren für einen nachgeschalteten Reaktor des einen oder der mehreren Reaktoren durch einen Wärmetauscher, Bereitstellen eines Sauerstoff enthaltenden Gasstroms zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms für den nachgeschalteten Reaktor des einen oder der mehreren Reaktoren und sukzessives Bereitstellen eines Produktgasstroms aus dem vorherigen Reaktor und eines Sauerstoff enthaltenden Gasstroms zur Oxidation eines Chlorwasserstoff enthaltenden Gasstroms für einen verbleibenden nachgeschalteten Reaktor des einen oder der mehreren Reaktoren;
3) vor einer Rückführung eines Teils eines Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu einem beliebigen des einen oder der mehreren Reaktoren ohne dessen Trennung, vorzugsweise zu einem Zufuhreinlass eines beliebigen des einen oder der mehreren Reaktoren, Mischen des Teils des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren mit dem Chlorwasserstoff enthaltenden Gasstrom und/oder dem Sauerstoff enthaltenden Gasstrom zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms, der/die in einen des einen oder der mehreren Reaktoren eintreten soll(en), der dann dem Reaktor für die katalytische Oxidation zugeführt wird; und
4) Bereitstellen eines Rests des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu dessen Trennung.

12. Verfahren nach einem der Ansprüche 1 bis 10, wobei die Oxidation des Nebenprodukts Chlorwasserstoff in Schritt 3 die Schritte umfasst:

1) Bereitstellen eines oder mehrerer mit einem Katalysator gefüllter Reaktoren, die in Reihe oder parallel geschaltet sind;
2a) Bereitstellen eines Sauerstoff enthaltenden Gasstroms zur Oxidation von Chlorwasserstoff und eines Chlorwasserstoff enthaltenden Gasstroms für einen ersten Reaktor des einen oder der mehreren Reaktoren zur katalytischen Oxidation von Chlorwasserstoff;
2b) Bereitstellen eines Produktgasstroms aus dem ersten Reaktor des einen oder der mehreren Reaktoren für einen nachgeschalteten Reaktor des einen oder der mehreren Reaktoren durch einen Wärmetauscher, Bereitstellen eines Chlorwasserstoff enthaltenden Gasstroms für den nachgeschalteten Reaktor des einen oder der mehreren Reaktoren, und sukzessives Bereitstellen eines Produktgasstroms aus dem vorherigen Reaktor und eines Chlorwasserstoff enthaltenden Gasstroms für einen verbleibenden nachgeschalteten Reaktor des einen oder der mehreren Reaktoren;
3) vor einer Rückführung eines Teils eines Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu einem beliebigen des einen oder der mehreren Reaktoren ohne dessen Trennung, vorzugsweise zu einem Zufuhreinlass eines beliebigen des einen oder der mehreren Reaktoren, Mischen des Teils des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren mit dem Chlorwasserstoff enthaltenden Gasstrom und/oder dem Sauerstoff enthaltenden Gasstrom zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms, der/die in einen des einen oder der mehreren Reaktoren eintreten soll(en), der dann dem Reaktor für die katalytische Oxidation zugeführt wird; und
4) Bereitstellen eines Rests des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren zu dessen Trennung.

13. Verfahren nach einem der Ansprüche 3 bis 12, wobei jeder des einen oder der mehreren Reaktoren gegebenenfalls einen dahinter angeordneten Wärmetauscher zum Entfernen von Reaktionswärme aufweist, wobei der Wärmetauscher, der sich hinter dem Reaktor befindet, ein Wärmetauscher ist, bevorzugt ein Rohrbündelwärmetauscher, Plattenwärmetauscher, Gaswärmetauscher oder dergleichen; wobei vorzugsweise nach dem letzten Reaktor des einen oder der mehreren Reaktoren ein Gaswärmetauscher angeordnet ist.

14. Verfahren nach Anspruch 13, wobei der Rest des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren aus der katalytischen Oxidation vor dessen Trennung durch den Gaswärmetauscher geleitet wird, wobei der Wärmetausch vorzugsweise in dem Gaswärmetauscher unter Verwendung des Chlorwasserstoff enthaltenden Gasstroms und/oder des Sauerstoff enthaltenden Gasstroms zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms, der/die in den ersten Reaktor als ein Kühlmedium eintreten soll(en), durchgeführt wird; vorzugsweise wobei der Chlorwasserstoff enthaltende Gasstrom und/oder der Sauerstoff enthaltende Gasstrom zur Oxidation des Chlorwasserstoff enthaltenden Gasstroms nach dem Wärmeaustausch mit einem Teil des rückgeführten Produktgasstroms aus dem Reaktor der dritten Stufe gemischt wird, bevor er dem ersten Reaktor bereitgestellt wird, und dann dem ersten Reaktor zur katalytischen Oxidation von Chlorwasserstoff zugeführt wird.

15. Verfahren nach einem der Ansprüche 3 bis 14, wobei ein Volumenverhältnis des Teils des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren, der direkt in den einen oder die mehreren Reaktoren zurückgeführt wird ohne dessen Trennung, zum Rest des Produktgasstroms aus dem letzten Reaktor des einen oder der mehreren Reaktoren 0,25:0,75 - 0,75:0,25, vorzugsweise 0,35:0,65 - 0,45:0,55 beträgt.

Revendications

1. Procédé de préparation d'un benzène à substituant chloroformyle, comprenant les étapes suivantes :

étape 1 : la réaction d'un hydrocarbure aromatique méthylé de formule $(X)_aC_6H_{6-a-b}(CH_3)_b$ ou d'un chlorure d'alkyle pendant de celui-ci avec du chlore gazeux dans des conditions d'éclairage pour préparer un benzène à substituant trichlorométhyle et obtenir du chlorure d'hydrogène en tant que sous-produit, dans lequel X est un atome de chlore, de brome ou de fluor, a est un nombre entier sélectionné parmi 0, 1, 2, 3, 4 et 5, b est un nombre entier sélectionné parmi 1, 2, 3 et 4, et $a+b \leq 6$, et le chlorure d'alkyle pendant de celui-ci fait référence à un composé où les atomes d'hydrogène d'un groupe alkyle pendant dans le composé aromatique méthylé ne sont pas complètement remplacés par des atomes de chlore,
dans lequel la réaction représentative dans l'étape 1 est représentée par l'équation suivante :
$(X)_aC_6H_{6-a-b}(CH_3)_b + 3bCl_2 = (X)_aC_6H_{6-a-b}(CCl_3)_b + 3bHCl$;
étape 2 : la réaction en outre du benzène à substituant trichlorométhyle résultant dans l'étape 1 avec de l'eau ou l'acide aromatique correspondant de formule $(X)_aC_6H_{6-a-b}(COOH)_b$ pour préparer le benzène à substituant

chloroformyle et pour obtenir du chlorure d'hydrogène en tant que sous-produit, dans lequel l'acide aromatique correspondant signifie qu'un substituant sur un noyau parent de l'acide aromatique et un substituant sur un noyau parent de l'hydrocarbure aromatique méthylé ou du chlorure d'alkyle pendant de celui-ci sont situés à la même position de substitution ou à des positions de substitution correspondantes, et dans lequel X est un atome de chlore, de brome ou de fluor, a est un nombre entier sélectionné parmi 0, 1, 2, 3, 4 et 5, b est un nombre entier sélectionné parmi 1, 2, 3 et 4, et $a+b \leq 6$;
dans lequel la réaction représentative dans l'étape 2 est représentée par l'équation suivante :
$(X)_aC_6H_{6\text{-}a\text{-}b}(CCl_3)_b + (X)_aC_6H_{6\text{-}a\text{-}b}(COOH)_b = 2(X)_aC_6H_{6\text{-}a\text{-}b}(COCl)_b + bHCl$ ou $(X)_aC_6H_{6\text{-}a\text{-}b}(CCl_3)_b + bH_2O = (X)_aC_6H_{6\text{-}a\text{-}b}(COCl)_b + 2bHCl$;
étape 3 : la soumission d'un courant gazeux contenant le chlorure d'hydrogène provenant des étapes 1 et 2 à une oxydation catalytique ;
dans lequel la réaction représentative dans l'étape 3 est représentée par l'équation suivante :
$4bHCl + bO_2 = 2bCl_2 + 2bH_2O$;
étape 4 : la séparation d'une vapeur de produit gazeux provenant de l'étape 3 pour obtenir des courants gazeux contenant du chlore, contenant de l'oxygène et/ou contenant du chlorure d'hydrogène ;
étape 5 : l'introduction du courant gazeux contenant du chlore séparé dans l'étape 4 en tant que matière première dans la chloration de l'étape 1 ; et
dans lequel dans la chloration de l'étape 1, l'hydrocarbure aromatique méthylé est mis à réagir avec du chlore gazeux dans des conditions d'éclairage pour préparer le benzène à substituant trichlorométhyle, où l'éclairage présente une longueur d'onde de source de lumière d'environ 350 nm à 700 nm et une amplitude de lumière de pas plus d'environ 200 nm, et où l'alimentation en chlore gazeux est initiée dans des conditions d'une température réactionnelle d'environ 0 °C à 85 °C et d'un éclairage d'environ 2000 Lux à environ 55 000 Lux, pour un premier stade réactionnel où la température réactionnelle n'est pas supérieure à environ 120 °C à l'éclairage ; et ensuite la quantité restante de chlore gazeux est introduite à une température réactionnelle plus élevée jusqu'à ce que la réaction soit terminée ; de préférence, dans lequel la source de lumière est une lampe à DEL ;
facultativement, dans lequel la séparation de la vapeur de produit gazeux provenant de l'étape 3 dans l'étape 4 comprend les étapes suivantes :

a. une condensation : le courant de produit gazeux provenant de l'étape 3 est condensé, dans lequel l'eau générée par la réaction dans l'étape 3 avec une partie du chlorure d'hydrogène n'ayant pas réagi est condensée sous la forme d'une solution aqueuse d'acide chlorhydrique ;
b. une déshydratation profonde : le courant de produit gazeux après avoir été condensé dans l'étape a est soumis à une déshydratation profonde, par exemple, au moyen d'acide sulfurique concentré, d'un tamis moléculaire, ou par adsorption modulée en température, adsorption modulée en pression, pour éliminer l'humidité résiduelle ;
c. une adsorption : le courant gazeux après avoir été soumis à une déshydratation profonde dans l'étape b est adsorbé par un adsorbant, pour séparer le chlore gazeux de l'oxygène gazeux ; et

facultativement, d. une liquéfaction : le courant gazeux contenant du chlore obtenu dans l'étape c est liquéfié, pour obtenir un courant gazeux contenant du chlorure d'hydrogène et un courant gazeux liquéfié contenant du chlore après séparation de ceux-ci ;
ou facultativement, dans lequel la chloroacylation dans l'étape 2 comprend de préférence les étapes suivantes :

i) la fusion totale du benzène à substituant trichlorométhyle à une température élevée, l'ajout d'eau ou de l'acide aromatique correspondant et d'un catalyseur, et une agitation parfaite ; et
ii) le chauffage du système réactionnel pour maintenir la réaction

2. Procédé selon la revendication 1, dans lequel l'étape 5 comprend l'introduction des courants gazeux contenant du chlorure d'hydrogène et/ou contenant de l'oxygène séparés dans l'étape 4 en tant que matière première à nouveau dans l'oxydation catalytique du chlorure d'hydrogène dans l'étape 3.

3. Procédé selon l'une quelconque des revendications 1 à 2, dans lequel l'oxydation du sous-produit chlorure d'hydrogène dans l'étape 3 comprend les étapes suivantes :

1) la fourniture d'un ou de plusieurs réacteurs, de préférence des réacteurs adiabatiques, remplis avec un catalyseur qui sont connectés en série ou en parallèle ;
2) la fourniture d'un courant gazeux contenant du chlorure d'hydrogène et d'un courant gazeux contenant de

l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène à un premier réacteur des un ou plusieurs réacteurs, et la fourniture d'un courant gazeux contenant du chlorure d'hydrogène et/ou d'un courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène à un réacteur en aval des un ou plusieurs réacteurs, pour l'oxydation catalytique du chlorure d'hydrogène ;
3) le retour direct d'une partie d'un courant de produit gazeux à partir d'un dernier réacteur des un ou plusieurs réacteurs de l'oxydation catalytique vers l'un quelconque des un ou plusieurs réacteurs sans séparation de celui-ci ; et
4) la fourniture d'un reste du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs pour la séparation de celui-ci ;

facultativement, dans lequel un rapport volumique d'alimentation entre le courant gazeux contenant du chlorure d'hydrogène, calculé sur la base du chlorure d'hydrogène pur, et le courant gazeux contenant de l'oxygène, calculé sur la base de l'oxygène pur, est de 1:2 à 5:1, de préférence de 1:1,2 à 3,5:1, de manière davantage préférée de 1:1 à 3:1 ;
ou facultativement, dans lequel un rapport volumique d'alimentation entre le courant gazeux contenant du chlorure d'hydrogène, calculé sur la base du chlorure d'hydrogène pur, et le courant gazeux contenant de l'oxygène, calculé sur la base de l'oxygène pur, est de 2:1 à 5:1 ;
ou facultativement, dans lequel un rapport volumique d'alimentation entre le courant gazeux contenant du chlorure d'hydrogène, calculé sur la base du chlorure d'hydrogène pur, et le courant gazeux contenant de l'oxygène, calculé sur la base de l'oxygène pur, est de 1:2 à 2:1, de préférence de 1,1:0,9 à 0,9:1,1.

4. Procédé selon la revendication 3, dans lequel avant de renvoyer une partie d'un courant de produit gazeux à partir d'un dernier réacteur des un ou plusieurs réacteurs vers une entrée d'alimentation de l'un quelconque des un ou plusieurs réacteurs sans séparation de celui-ci dans l'étape 3), mélanger la partie du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs avec le courant gazeux contenant du chlorure d'hydrogène et/ou le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène destiné à entrer dans l'un quelconque des un ou plusieurs réacteurs, qui est ensuite introduit dans ledit réacteur pour l'oxydation catalytique.

5. Procédé selon l'une quelconque des revendications 3 et 4, dans lequel dans l'étape 3), la partie du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs est renvoyée vers chacun des un ou plusieurs réacteurs fournis sans séparation de celui-ci.

6. Procédé selon la revendication 5, dans lequel lors du renvoi de la partie du courant de produit gazeux à partir du dernier réacteur des un ou plusieurs réacteurs vers chacun des un ou plusieurs réacteurs fournis sans séparation de celui-ci, le courant de produit gazeux renvoyé est réparti entre les un ou plusieurs réacteurs dans n'importe quel rapport ; dans lequel, de préférence, le courant de produit gazeux renvoyé est réparti de manière égale en parties correspondantes en fonction du nombre des un ou plusieurs réacteurs, pour être respectivement renvoyé vers les un ou plusieurs réacteurs.

7. Procédé selon l'une quelconque des revendications 3 à 6, dans lequel le courant gazeux contenant du chlorure d'hydrogène et le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène sont fournis au premier réacteur des un ou plusieurs réacteurs, et le courant gazeux contenant de l'oxygène pour l'oxydation d'un courant gazeux contenant du chlorure d'hydrogène est fourni au réacteur en aval des un ou plusieurs réacteurs.

8. Procédé selon la revendication 7, dans lequel les courants gazeux contenant de l'oxygène pour l'oxydation d'un courant gazeux contenant du chlorure d'hydrogène fournis aux un ou plusieurs réacteurs sont des portions d'une quantité souhaitée d'un courant gazeux contenant de l'oxygène pour l'oxydation d'un courant gazeux contenant du chlorure d'hydrogène qui sont réparties entre les un ou plusieurs réacteurs dans n'importe quel rapport comme souhaité, de préférence réparties de manière égale en parties correspondantes en fonction du nombre des un ou plusieurs réacteurs.

9. Procédé selon l'une quelconque des revendications 3 à 6, dans lequel le courant gazeux contenant de l'oxygène pour l'oxydation d'un courant gazeux contenant du chlorure d'hydrogène et le courant gazeux contenant du chlorure d'hydrogène sont fournis au premier réacteur des un ou plusieurs réacteurs, et le courant gazeux contenant du chlorure d'hydrogène est fourni au réacteur en aval des un ou plusieurs réacteurs ; dans lequel de préférence, une teneur en oxygène dans le courant gazeux contenant de l'oxygène entrant dans chacun des un ou plusieurs réacteurs

est supérieure à une consommation d'oxygène théorique requise pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène entrant dans ledit réacteur.

10. Procédé selon la revendication 9, dans lequel les courant gazeux contenant du chlorure d'hydrogène fournis aux un ou plusieurs réacteurs sont des portions d'un courant gazeux contenant du chlorure d'hydrogène à oxyder qui sont réparties entre les un ou plusieurs réacteurs dans n'importe quel rapport comme souhaité, de préférence répartis de manière égale en parties correspondantes en fonction du nombre des un ou plusieurs réacteurs.

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'oxydation du sous-produit chlorure d'hydrogène dans l'étape 3 comprend les étapes suivantes :

1) la fourniture d'un ou de plusieurs réacteurs remplis avec un catalyseur qui sont connectés en série ou en parallèle ;
2a) la fourniture d'un courant gazeux contenant du chlorure d'hydrogène et d'un courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène à un premier réacteur des un ou plusieurs réacteurs, pour l'oxydation catalytique du chlorure d'hydrogène ;
2b) la fourniture d'un courant de produit gazeux provenant du premier réacteur des un ou plusieurs réacteurs à un réacteur en aval des un ou plusieurs réacteurs par l'intermédiaire d'un échangeur de chaleur, la fourniture d'un courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène au réacteur en aval des un ou plusieurs réacteurs, et successivement la fourniture d'un courant de produit gazeux provenant du réacteur précédent et d'un courant gazeux contenant de l'oxygène pour l'oxydation d'un courant gazeux contenant du chlorure d'hydrogène à un réacteur en aval restant des un ou plusieurs réacteurs ;
3) avant de renvoyer une partie d'un courant de produit gazeux à partir du dernier réacteur des un ou plusieurs réacteurs vers l'un quelconque des un ou plusieurs réacteurs sans séparation de celui-ci, de préférence vers une entrée d'alimentation de l'un quelconque des un ou plusieurs réacteurs, le mélange de la partie du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs avec le courant gazeux contenant du chlorure d'hydrogène et/ou le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène destiné à entrer dans l'un quelconque des un ou plusieurs réacteurs, qui est ensuite introduit dans ledit réacteur pour l'oxydation catalytique ; et
4) la fourniture d'un reste du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs pour la séparation de celui-ci.

12. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'oxydation du sous-produit chlorure d'hydrogène dans l'étape 3 comprend les étapes suivantes :

1) la fourniture d'un ou de plusieurs réacteurs remplis avec un catalyseur qui sont connectés en série ou en parallèle ;
2a) la fourniture d'un courant gazeux contenant de l'oxygène pour l'oxydation du chlorure d'hydrogène et d'un courant gazeux contenant du chlorure d'hydrogène à un premier réacteur des un ou plusieurs réacteurs, pour l'oxydation catalytique du chlorure d'hydrogène ;
2b) la fourniture d'un courant de produit gazeux provenant du premier réacteur des un ou plusieurs réacteurs à un réacteur en aval des un ou plusieurs réacteurs par l'intermédiaire d'un échangeur de chaleur, la fourniture d'un courant gazeux contenant du chlorure d'hydrogène au réacteur en aval des un ou plusieurs réacteurs, et successivement la fourniture d'un courant de produit gazeux provenant du réacteur précédent et d'un courant gazeux contenant du chlorure d'hydrogène à un réacteur en aval restant des un ou plusieurs réacteurs ;
3) avant de renvoyer une partie d'un courant de produit gazeux à partir du dernier réacteur des un ou plusieurs réacteurs vers l'un quelconque des un ou plusieurs réacteurs sans séparation de celui-ci, de préférence vers une entrée d'alimentation de l'un quelconque des un ou plusieurs réacteurs, le mélange de la partie du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs avec le courant gazeux contenant du chlorure d'hydrogène et/ou le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène destiné à entrer dans l'un quelconque des un ou plusieurs réacteurs, qui est ensuite introduit dans ledit réacteur pour l'oxydation catalytique ; et
4) la fourniture d'un reste du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs pour la séparation de celui-ci.

13. Procédé selon l'une quelconque des revendications 3 à 12, dans lequel chacun des un ou plusieurs réacteurs comporte facultativement un échangeur de chaleur disposé après pour éliminer la chaleur réactionnelle, l'échangeur de chaleur situé après ledit réacteur étant un échangeur de chaleur, de préférence un échangeur de chaleur à faisceau de tubes, un échangeur de chaleur à plaques, un échangeur de chaleur à gaz, ou équivalents ; dans lequel de préférence, un échangeur de chaleur à gaz est disposé après le dernier réacteur des un ou plusieurs réacteurs.

14. Procédé selon la revendication 13, dans lequel le reste du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs de l'oxydation catalytique est passé à travers l'échangeur de chaleur à gaz avant la séparation de celui-ci, dans lequel l'échange de chaleur est de préférence effectué dans l'échangeur de chaleur à gaz en utilisant le courant gazeux contenant du chlorure d'hydrogène et/ou le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène destiné à entrer dans le premier réacteur comme milieu de refroidissement ; de préférence, le courant gazeux contenant du chlorure d'hydrogène et/ou le courant gazeux contenant de l'oxygène pour l'oxydation du courant gazeux contenant du chlorure d'hydrogène après avoir été soumis à un échange de chaleur est mélangé avec une partie du courant de produit gazeux renvoyé hors du réacteur de troisième étage avant d'être fourni au premier réacteur, et ensuite est introduit dans le premier réacteur pour l'oxydation catalytique du chlorure d'hydrogène.

15. Procédé selon l'une quelconque des revendications 3 à 14, dans lequel un rapport volumique entre la partie du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs directement renvoyée vers les un ou plusieurs réacteurs sans séparation de celui-ci et le reste du courant de produit gazeux provenant du dernier réacteur des un ou plusieurs réacteurs est de 0,25:0,75 à 0,75:0,25, de préférence de 0,35:0,65 à 0,45:0,55.

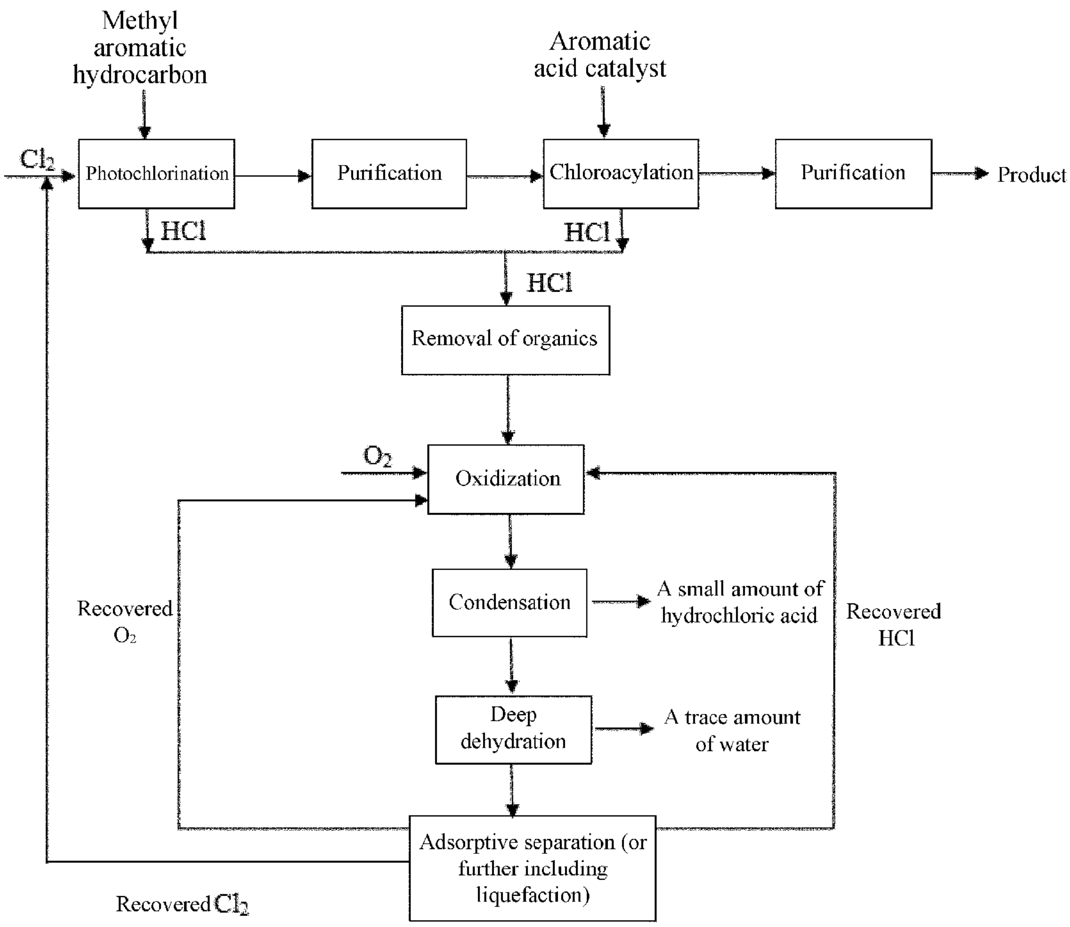
Methyl aromatic hydrocarbon
Aromatic acid catalyst
Cl_2
Photochlorination
Purification
Chloroacylation
Purification
Product
HCl
HCl
HCl
Removal of organics
O_2
Oxidization
Condensation
A small amount of hydrochloric acid
Recovered O_2
Recovered HCl
Deep dehydration
A trace amount of water
Adsorptive separation (or further including liquefaction)
Recovered Cl_2

FIG. 1

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- DE 3146868 **[0002]**
- JP 47130931 A **[0002]**
- CN 102516060 A **[0002]**
- CN 102344362 A **[0002]**
- US 4165337 A **[0003]**
- CN 102502498 A **[0005]**
- US 20080159948 A1 **[0005]**
- US 5514254 A **[0035]**
- CN 103752270 A **[0082]**

Non-patent literature cited in the description

- **NORMAN RABJOHN et al.** The Chloromethylation of Toluene and Conversion of p-xylyl chloride. *Journal of the American Chemical Society,* 01 November 1954, vol. 76 (21), 5479-5481 **[0003]**