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(54) Title: PROCESSES FOR SEPARATING ORGANIC IMPURITIES FROM AQUEOUS INORGANIC ACIDS

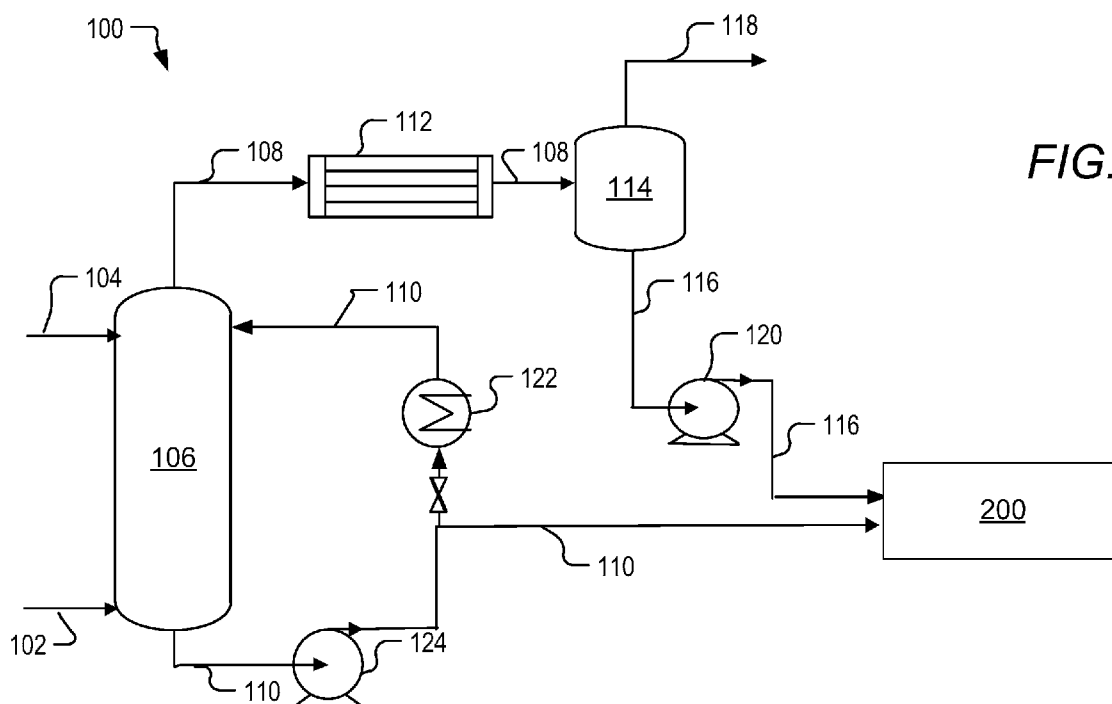


FIG. 1

(57) Abstract: Methods for removal of organic impurities from an aqueous acid stream obtained from an oxychlorination of methane reaction are described. A method includes heating an aqueous acid stream obtained from a quenching unit at a pressure of 1.4 MPa (200 psig) to 1.75 MPa (250 psig) to produce an aqueous acid product stream and an overhead stream. The aqueous acid product stream includes at least a minimal amount of, or substantially no, chlorinated hydrocarbons. The overhead stream can be recycled to the quenching unit or subjected to conditions suitable to remove water and chlorinated hydrocarbons from the overhead stream to produce a high purity hydrogen chloride stream.

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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**PROCESSES FOR SEPARATING ORGANIC IMPURITIES FROM AQUEOUS
INORGANIC ACIDS**

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Patent
5 Application No. 62/269,873, filed December 18, 2015, which is hereby incorporated by
reference in its entirety.

BACKGROUND OF THE INVENTION

A. Field of the Invention

[0002] The invention generally concerns the separation of organic impurities from an
10 aqueous inorganic acid. In particular, the invention concerns producing a high purity
hydrogen chloride stream from an aqueous stream that includes hydrogen chloride, light
hydrocarbons, chlorinated hydrocarbons, and inert gases at elevated pressures.

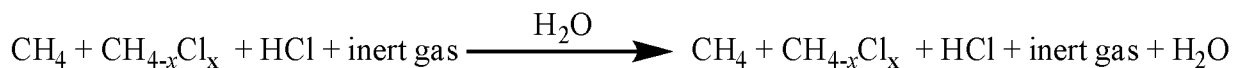
B. Description of Related Art

[0003] Monochloromethane can be made through a process termed "oxychlorination". By
15 way of example, an oxychlorination of methane reaction can include feeding methane, natural
gas or light hydrocarbon alkanes (*e.g.*, C₁-C₄ alkanes), an oxygen source, and a chlorine
source such as hydrogen chloride to a reactor containing a catalyst. The product stream can
include monochloromethane, heavy chlorinated hydrocarbons, and light components (*e.g.*,
methane, carbon oxides and inert gases) as shown in the general reaction scheme below.



Another process to make monochloromethane uses elemental chlorine (Cl₂) as the feed gas.
In this process, free chlorine, oxygen containing gas, and the hydrocarbon to be chlorinated
are contacted with a metal halide catalyst. The chlorine reacts with the hydrocarbon to
25 produce hydrogen chloride and a chlorinated product of the hydrocarbon. Hydrogen chloride
produced in this manner is then converted to elemental chlorine by a well-known series of
reactions, thereby providing additional chlorine for the chlorination of more hydrocarbon
feed.

[0004] The product mixture from the oxychlorination reaction is produced at a high temperature and is cooled (*e.g.*, quenched) by adding water to the solution to produce an aqueous mixture as shown below.



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There are many operational difficulties generally associated with the oxychlorination of methane reaction. For example, the recovery of the hydrogen chloride from the aqueous mixture can be difficult. The recovery of HCl can be complicated by the presence of the chlorinated hydrocarbons and/or be detrimental to process equipment. There have been various attempts to improve the separation process of hydrogen chloride from the quench mixture. Many of these processes use a stripping gas in an attempt to remove chlorinated hydrocarbons and light hydrocarbons from the quench mixture. By way of example, U.S. Patent No. 4,785,488 to Sticken describes the use of HCl gas as a stripper gas in a bubble column that is flooded with hydrochloric acid contaminated with chlorinated hydrocarbons at pressure of 1 to 4 bar (0.1 to 0.4 MPa). In yet another example, U.S. Patent No. 4,028,427 to Tsao describes stripping an aqueous hydrochloric acid stream contaminated with chlorinated hydrocarbons at a pressure of 20 psig to 200 psig (0.14 to 1.37 MPa) and a temperature of 50 to 150 °F (10 to 65 °C) with methane to remove chlorinated hydrocarbons from a dilute hydrochloric acid stream, which is then recycled to the oxychlorination reaction. This process suffers in that recycling of the chlorinated alkane back to the reactor can shorten the catalyst lifetime and reduce the selectivity for monochloromethane. U.S. Patent No. 4,263,269 to Little *et al.* describes removal of organic impurities (*e.g.*, chloral) from an aqueous hydrochloric acid stream by countercurrent stripping of the acidic stream with steam at pressures of 30 to 250 psig (0.2 to 1.7 MPa).

[0005] While many processes to remove some organic containments from a hydrochloric acid stream, they suffer in that they are inefficient (*e.g.*, HCl recovery rate is low) and produce low purity hydrogen chloride aqueous solutions. Production of low purity HCl solutions can negatively influence the production of chlorinated hydrocarbons when such streams are a source of HCl or chlorine in an oxychlorination of alkane reaction. While many processes remove some organic contaminants with light stripping gas, they suffer from high costs associated with recovery of the chlorinated methane.

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SUMMARY OF THE INVENTION

[0006] A solution that addresses the aforementioned inefficiencies and the problems associated with the production of low purity and/or dilute HCl streams from an oxychlorination of alkane reaction has been discovered. The solution provides a high purity HCl stream(s) that can be further used in an oxychlorination of alkane reaction without reducing the selectivity and/or shortening the life of the catalyst. The discovery is premised on the ability to separate the hydrogen chloride from the organic impurities under refluxing conditions (*e.g.*, pressures and temperatures sufficient to reflux the aqueous mixture) such that the need for a stripper gas is eliminated. The separation produces an overhead gas stream and an aqueous acid product stream that includes a minimal amount, trace amount, or substantially no chlorinated hydrocarbons and at least 9 wt.% HCl and only trace amount of HCl is present in the overhead gas stream. Notably, the HCl recovery rate is more than 99.9% so there is no need to recycle chlorinated alkanes back to the reactor. The overhead gas stream can include chlorinated hydrocarbons, trace amounts of hydrogen chloride, and optionally, a small amount of water, which can be recycled to the quench process, (thus lowering the need to add additional water to the quench tower) and/or further processed to produce a high purity HCl stream and a chlorinated hydrocarbon stream. The new design produces high purity and/or concentrated HCl stream(s) (*e.g.*, 90% to 99% purity and at least 9 wt.% HCl) in a cost effective and efficient manner. The high purity and/or concentrated HCl stream(s) have a trace amount (*e.g.*, less than 5 ppm) of organic impurities, namely, chlorinated hydrocarbons. The high purity HCl streams produced in this process can be used in an oxychlorination of alkane reaction without further processing. The use of high purity HCl streams in the oxychlorination reaction can extend catalyst life as a minimal amount or substantially no hydrocarbons are present in the stream. Furthermore, the absence of chlorinated hydrocarbons in the HCl reduces the amount of higher chlorinated compounds from being produced (*e.g.*, chloroform, methylene chloride, or the like). Said another way, the selectivity for the desired methyl chloride product of the oxychlorination reaction is not reduced when the high purity HCl stream is used. Furthermore, the process of the present invention does not require the use a stripper gas to separate the organic impurities from the HCl stream.

[0007] In a particular aspect, a process to purify an aqueous acid solution that includes HCl and organic hydrocarbons is described. The process can include (a) subjecting an acidic

feed stream (*e.g.*, an acid product stream from a methane oxychlorination reaction that includes HCl, chlorinated hydrocarbons, methane and inert gases) to aqueous quenching conditions suitable to produce a gaseous stream (*e.g.*, chlorinated hydrocarbons, light hydrocarbons and inert gases), and an aqueous acid stream that includes the HCl and organic hydrocarbons, and (b) heating the aqueous acid stream of step (a) at a pressure of 1.4 MPa (200 psig) to 1.75 MPa (250 psig), and to a temperature of 115 °C to 130 °C to produce an aqueous acid product stream and an overhead stream. Notably, a stripper gas is not required for the removal of the organic impurities from the aqueous acid stream. The organic hydrocarbons can include chlorinated hydrocarbons (*e.g.*, monochloromethane, methylene chloride, chloroform, carbon tetrachloride). The aqueous acid product stream can include at least a minimal amount of, or substantially no, chlorinated hydrocarbons. In some instances, the aqueous acid product stream includes at least 9 wt.% HCl. The overhead stream can include chlorinated hydrocarbons, water, and residual HCl, which can be recycled to step (a) and/or further processed. Further processing of the overhead stream can include (c) subjecting the overhead stream of step (b) to conditions suitable to remove water from the overhead stream and produce a water stream and a dried overhead stream. Still further, the method can include (d) distilling the dried overhead stream under conditions suitable to produce a second acid stream comprising HCl and a bottoms stream comprising chlorinated hydrocarbons. Distillation conditions can include a temperature of 50 °C to 70 °C and a pressure of 0.8 MPa (115 psig) to 0.9 MPa (130 psig). Drying of the overhead stream can remove water from the overhead stream in step (c) in an amount sufficient to inhibit hydrate formation during the low temperature distillation step (d). The second acid stream produced during the distillation step (d) can be a high purity HCl stream.

[0008] In some aspects, a system for the purification of an aqueous acid solution that includes HCl and organic impurities is described. The system can include: (a) a quench zone configured to receive an acidic feed stream (*e.g.*, a product stream from a methane oxychlorination reaction that includes HCl, chlorinated hydrocarbons, methane and inert gases) and produce a gaseous stream and an aqueous stream that includes the HCl and organic impurities (*e.g.*, chlorinated hydrocarbons); and (b) a first separation zone in fluid communication with the quench zone, the first separation zone configured to separate the aqueous acid stream of step (a) into an aqueous acid product stream and an overhead stream at a pressure of 1.4 MPa (200 psig) to 1.75 MPa (250 psig). Notably, a stripper gas is not required in the first separation zone to assist in the separation of the organic impurities from

the aqueous acid product stream. The aqueous acid product stream produced in the first separation zone includes a minimal amount of, or substantially no, chlorinated hydrocarbons. In some instances, the HCl content of the aqueous acid product stream is at least 9 wt.%. An average temperature of the first separation zone can range from 115 °C to 130 °C. The overhead stream of step (b) can include chlorinated hydrocarbons, water, and residual HCl. In some instances, the system can include a conduit in fluid communication with the quench zone and the separation zone. The conduit is configured to provide the overhead stream from the separation zone to the quench zone, and/or a drying zone in fluid communication with the first separation zone, the drying zone configured to remove water from the overhead stream and produce a dried overhead stream. The system can further include a second separation zone in fluid communication with the drying zone. The second separation zone can be configured to separate the dried overhead stream into an acid stream comprising the HCl and a bottoms stream comprising chlorinated hydrocarbons at a temperature of 50 °C to 70 °C and a pressure of 0.8 MPa (115 psig) to 0.9 MPa (130 psig). The acid stream can be collected at a temperature of -35 °C to -40 °C.

[0009] The following includes definitions of various terms and phrases used throughout this specification.

[0010] The phrase “chlorinated hydrocarbons” refers to chlorinated hydrocarbons having a general formula of $\text{CH}_{4-x}\text{Cl}_x$, where x is 1 to 4. Non-limiting examples of chlorinated hydrocarbons include monochloromethane, dichloromethane, chloroform, and carbon tetrachloride. “Heavy chlorinated hydrocarbons” are defined as $\text{CH}_{4-x}\text{Cl}_x$, where x is 2 to 4.

[0011] The term “hydrogen chloride” refers to the compound made up of hydrogen chloride (HCl) and may not be indicative of the phase (*e.g.*, gas or liquid) of the compound. “Hydrochloric acid” refers to aqueous hydrogen chloride.

[0012] The phrase “light components” or “light hydrocarbons” refer to compounds or hydrocarbons that are not condensable at standard temperature and pressure (25 °C and 1 atm). By way of example, hydrocarbons having from 1 to 4 carbon atoms (C_1 to C_4) are considered light hydrocarbons.

[0013] The term “inert” is defined as chemically inactive or substantially inactive under the reaction conditions. Non-limiting examples of inert chemical compounds in the context of this invention include helium, nitrogen, and argon.

[0014] The terms “about” or “approximately” are defined as being close to as understood by one of ordinary skill in the art. In one non-limiting embodiment, the terms are defined to be within 10%, preferably within 5%, more preferably within 1%, and most preferably within 0.5%.

5 [0015] The term “substantially” and its variations are defined to include ranges within 10%, within 5%, within 1%, or within 0.5%.

[0016] The terms “wt.%”, “vol.%”, or “mol.%” refers to a weight, volume, or molar percentage of a component, respectively, based on the total weight, the total volume of material, or total moles, that includes the component. A non-limiting example is that the acid
10 product stream includes at least 9 wt.% HCl, based on the total weight of the stream.

[0017] The terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, when used in the claims and/or the specification includes any measurable decrease or complete inhibition to achieve a desired result.

[0018] The term “effective,” as that term is used in the specification and/or claims, means
15 adequate to accomplish a desired, expected, or intended result.

[0019] The use of the words “a” or “an” when used in conjunction with any of the terms “comprising,” “including,” “containing,” or “having” in the claims, or the specification, may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.”

20 [0020] The words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

25 [0021] The methods of the present invention can “comprise,” “consist essentially of,” or “consist of” particular ingredients, components, compositions, etc. disclosed throughout the specification. With respect to the transitional phrase “consisting essentially of,” in one non-limiting aspect, a basic and novel characteristic of the methods of the present invention are

their abilities to separate organic impurities (*e.g.*, chlorinated hydrocarbons) from hydrogen chloride in an efficient and cost effective manner.

[0022] Other objects, features and advantages of the present invention will become apparent from the following figures, detailed description, and examples. It should be understood, however, that the figures, detailed description, and examples, while indicating specific embodiments of the invention, are given by way of illustration only and are not meant to be limiting. Additionally, it is contemplated that changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description. In further embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments. In further embodiments, additional features may be added to the specific embodiments described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings.

[0024] **FIG. 1** is a schematic of a quenching system to produce an aqueous acid stream that includes HCl and organic impurities connected to a separation system of the present invention.

[0025] **FIG. 2** is a schematic of a separation system of the present invention that includes recycling of an overhead gas stream that includes HCl to the quenching system of FIG. 1.

[0026] **FIG. 3** is a schematic of a separation system of the present invention where the overhead gas stream from separation system of FIG. 2 is further separated into a high purity HCl acid product stream.

[0027] **FIG. 4** is a schematic of a combination of recycling and purifying the overhead gas stream produced in the system of FIG. 2.

[0028] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale.

DETAILED DESCRIPTION OF THE INVENTION

5 [0029] A discovery has been made that provides an economical solution to the isolation of a high purity HCl stream from an aqueous acid stream contaminated with organic impurities. The solution is premised on refluxing the aqueous solution instead of stripping the solution using a stripper gas. Refluxing conditions at pressures of 1.4 MPa (200 psig) to 1.75 MPa (250 psig) promote the removal of the chlorinated hydrocarbons in presence of HCl at
10 concentrations of at least 9 wt.%. The present process is especially useful for recovering high purity and/or concentrated HCl streams formed from the oxychlorination reaction of methane. The high purity and/or concentrated HCl stream(s) can be recycled to the oxychlorination reaction without further purification. Due to the high purity of the HCl stream(s), there is little to no detrimental impact on the oxychlorination reaction. For example, catalyst life is
15 not shortened due to hydrocarbon impurities in the HCl stream and/or the monochloromethane selectivity is not reduced due to higher chlorinated hydrocarbons being produced (*e.g.*, methylene chloride and chloroform).

[0030] These and other non-limiting aspects of the present invention are discussed in further detail in the following sections with reference to the FIGS. 1 to 4. The systems and
20 methods of described in FIGS. 1 to 4 can also include various equipment that is not shown and is known to one of skill in the art of chemical processing. For example, some controllers, piping, computers, valves, pumps, heaters, thermocouples, pressure indicators may not be shown.

[0031] FIG. 1 depicts a schematic of a quench system that can be used to generate an
25 acidic aqueous stream that includes HCl and organic impurities connected to separation system 200. In system 100, gaseous feed stream 102 and water stream 104 can enter quenching unit 106 (quenching zone). In a particular embodiment, the quenching unit is a quench tower. Gaseous feed stream 102 can include chlorinated hydrocarbons and light components (*e.g.*, hydrogen chloride gas, light hydrocarbons, carbon oxides and inert gases).
30 Gaseous feed stream 102 can include 35 wt.% to 65 wt.% or 35 wt.%, 40 wt.%, 45 wt.%, 50 wt.%, 55 wt.%, 60 wt.%, 65 wt.% or any value or range there between of light hydrocarbons (*e.g.*, methane, ethane, or both, preferably methane), 35 wt.% to 65 wt.% or 35 wt.%, 40

wt.%, 45 wt.%, 50 wt.%, 55 wt.%, 60 wt.%, 65 wt.% or any value or range there between of chlorinated hydrocarbons, 0 wt.% to 60 wt.% or 0 wt.%, 1 wt.%, 5 wt.% 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.%, 30 wt.%, 35 wt.%, 40 wt.%, 45 wt.%, 50 wt.%, 55 wt.%, 60 wt.%, or any value or range there between of carbon oxides, hydrogen chloride, and the balance being inert gases, based on the total weight of the stream. The amount of hydrogen chloride in the gaseous feed stream can vary depending on the reaction conditions of the oxychlorination reaction. By way of example, the gaseous feed stream can include any amount of HCl. The gaseous feed stream can include 0.5 wt.% or more, 10 wt.% or more, 40 wt.% or more, 50 wt.% or more, 60 wt.% or more any range or value there between of HCl. The gaseous feed stream 102 entering quenching unit 106 can have an average temperature of 115 °C to 125 °C and an average pressure of 0.95 MPa to 1.0 MPa. Water stream 104 can enter the quenching unit 106 at a temperature of 45 °C to 50 °C and an average pressure of 0.95 MPa to 1.0 MPa. Direct contact of the water 104 with the gaseous feed stream 102 cools the gaseous feed stream and generates gaseous stream 108 and aqueous acid stream 110. Gaseous stream 108 can include chlorinated hydrocarbons, methane and inert gases. Contact of gaseous feed stream 102 with water stream 104 in quenching unit 106 can be performed using standard methods for effecting the contact of gases and liquids. The gaseous stream 102 can include less than 0.5 wt.%, 0.1 wt.% or less of hydrogen chloride and/or water. Aqueous acid stream 110 can include organic impurities (*e.g.*, chlorinated hydrocarbons), water, and hydrogen chloride.

[0032] Gaseous stream 108 can exit the quenching tower 106 and enter condenser 112. The average temperature of gaseous stream 108 can range from 85 °C to 95 °C, or 90 °C at operating pressures (*e.g.*, 0.85 MPa to 1.0 MPa or 0.93 MPa). Condenser 112 can cool the gaseous stream 108 to about 40 °C to 50 °C at operating pressures (*e.g.*, 0.90 MPa to 1.0 MPa or 0.89 MPa). Cooled gaseous product stream 108 can enter gas-liquid separation unit 114. Separation unit 114 can be any type of unit (*e.g.*, flash drum, settling unit, depressurizing vessel, *etc.*) capable of separating liquids from a gaseous mixture. In separation unit 114, any residual hydrogen chloride and/or water (*e.g.*, hydrochloric acid) in gaseous stream 108 can be separated from the gaseous stream to produce reflux stream 116 and second gaseous product stream 118. Reflux stream 116 can include the HCl and/or water, and can be provided to separation system 200 (shown in FIGS. 2 and 3) *via* fluid mover (*e.g.*, pump) 120. In some instances, a minimal amount of chlorinated hydrocarbons is present in reflux stream 116. Second gaseous stream 118 can include chlorinated hydrocarbons, methane and

inert gases. Second gaseous stream 118 can be transported to other processing units for further purification to obtain the desired chlorinated hydrocarbons (e.g., monochloromethane).

5 [0033] Aqueous acid stream 110 can be removed from quenching tower 106 and be provided to separation system 200 using fluid mover (e.g., pump) 124. The average temperature of aqueous acid stream 110 can be 120 °C to 130 °C, or 123 °C, or any value, or range there between, at operating pressures (e.g., 0.90 MPa to 1 MPa). In some embodiments, aqueous acid stream 110 includes at least 10 wt.%, 15 wt.%, or up to 20 wt.% of hydrogen chloride. A portion of aqueous acid stream 110 can pass through heat exchanger 10 122 and enter quench tower 106, where it is used as a quenching agent. Heat exchanger 122 can exchange heat with aqueous acid stream 110 to produce a cooled aqueous acid stream. For example, aqueous acid stream 110 can be cooled to a temperature of 55 °C to 65 °C at operating pressures (e.g., 0.85 MPa to 1.0 MPa or 0.93 MPa)

15 [0034] Separation of the organic impurities from the aqueous acid stream 110 to produce high purity and/or concentrated HCl streams can be accomplished using the methods and systems of the present invention. A first separation system can include a separating unit that generates an overhead stream that can be recycled to quench tower 106, thereby reducing the need for fresh purified water, which can be a scarce or costly commodity. FIG. 2 depicts a first separation system 200 effective for the separation of high purity hydrochloric acid 20 stream from aqueous acid stream 110 generated from quench system 100 (shown in dotted box and FIG. 1). Separation system 200 can include separation unit 202, condenser 204, gas/liquid separation unit 206, and fluid mover 208. As shown, aqueous acid stream 110 and reflux stream 116 can enter separation unit 202. In some embodiments, reflux stream 116 does not enter separation unit 202. Streams can be added to the separation unit 25 simultaneously, or at different time intervals. Separation unit 202 can be any unit capable of effecting separation of dissolved gas in a liquid. The separation can be effected, for example, in packed, unpacked, bubble cap, perforated plate, and other similar type columns used to effect the removal of a gas with a liquid. In particular, a packed column can be used. The column can be packed with for example, glass or polytetrafluoroethylene (TEFLON™, 30 Chemours, USA) Beryl saddles, or ceramic or metal Raschig (Raschig USA, Inc.) rings. The materials used in separation 202 can be made of material resistant to acids or chlorides. Separation unit 202 can include one or more heating and pressurizing systems (for example, a

reboiler system, heat exchangers and the like) to heat and pressurize the aqueous acid stream to a temperature and pressure sufficient to reflux the aqueous acid steam. The pressure of separation unit 202 can be 1.4 MPa (200 psig) to 1.75 MPa (250 psig), or 1.4 MPa, 1.45 MPa, 1.5 MPa, 1.55 MPa, 1.6 MPa, 1.65 MPa, 1.7 MPa, 1.75 MPa or any value or range there
5 between. An average temperature in separation unit 202 can be 115 °C to 130 °C, 120 °C to 125 °C, or 115 °C, 116 °C, 117 °C, 118 °C, 119 °C, 120 °C, 121 °C, 122 °C, 123 °C, 124 °C, 125 °C, 126 °C, 127 °C, 128 °C, 129 °C, 130 °C, or any value or range there between. Separation of aqueous acid stream 110 produces overhead stream 210 and acid product stream 212. Acid product stream 212 can include at least 9 wt.%, 15 wt.%, 20 wt.% or more
10 of hydrogen chloride and a trace amount (*e.g.*, 1000 ppm or less, 900 ppm or less, 500 ppm or less, 250 ppm or less, 150 ppm or less, 100 ppm or less or 50 ppm or less) of chlorinated hydrocarbons. Acid product stream 212 can be stored, transported, or sent to other processing units to recover the hydrogen chloride from the water.

[0035] Overhead stream 210 can include chlorinated hydrocarbons and hydrogen chloride,
15 and, in some instances, a small amount of water vapor or steam. In some instances, overhead stream 210 can undergo heat exchange in condenser 204 and enter gas/liquid separation unit 206 at a temperature of 105 °C to 110 °C at operating pressures (*e.g.*, 1.4 MPa (200 psig) to 1.75 MPa (250 psig) or 1.5 MPa (220 psig)). In gas/liquid separation unit 206, overhead stream 210 can be separated into overhead gas stream 214 and recycle bottoms liquid stream
20 216. Overhead gas stream 214 can include hydrogen chloride, chlorinated hydrocarbons, and small amounts water (*e.g.*, water, steam or water vapor). By way of example, overhead gas stream 214 can include 80 wt.% or less, 50 wt.%, 30 wt.% or 10 wt.% or less of hydrogen chloride, a residual amount of chlorinated hydrocarbons (*e.g.*, less than 1 wt.% of chlorinated hydrocarbons) with the balance being small amounts of water. Overhead gas stream 214 can
25 be provided to quench tower 106 *via* conduit coupled to the quench tower and the separation unit 206. In some instances, condenser 204 and gas/liquid separation unit 206 are not used and overhead stream 214 is sent directly to quench tower 106 *via* piping coupled to the separation unit 202 and the quench tower 106. In other embodiments, a portion of the overhead stream 214 can be sent to separation unit 202 and quench tower 106. Bottoms
30 liquid stream 216 can be refluxed back to separation unit 202 using fluid mover 208 to recover more hydrogen chloride from the stream. Since the overhead stream includes water, the amount of water in the overhead stream will determine the amount of quench water added to the quench tower 106.

[0036] In some embodiments, the overhead stream 214 some or the entire overhead stream is further processed to produce a high purity hydrogen chloride stream and a chlorinated hydrocarbon stream. FIG. 3 depicts a schematic of a second separation system 300 effective for producing high purity hydrogen chloride stream(s). Separation system 300 can include the components of separation system 200 (shown inside the dotted line), drying unit 302, heat exchanger 304, distillation unit 306, condenser, 308, gas/liquid separation unit 310, and fluid mover 312. As shown, the overhead stream is not returned to the quench tower 106 in quench system 100 (See, FIG. 1), thus the thermodynamic limitation of the final HCl concentration at the bottom of separation unit 202 can be used to determine the amount of quench water added to quench tower 106.

[0037] Overhead stream 214 produced from separation unit 202 can enter drying unit (drying zone) 302. Non-limiting examples of a drying unit include adsorbing units, membrane units, and/or drying unit can include CaSO_4 , H_2SO_4 , P_4O_{10} , MgSO_4 , and/or CaCl_2 as drying agents. In drying unit 302, water can be removed from the overhead stream in an amount sufficient to inhibit production of hydrates at the temperatures used in distillation unit 306. In some embodiments, the drying temperature can be the temperature of the inlet stream without any heating or cooling. By way of example, a water content of the overhead stream can be less than 0.1 wt.%, and less than 0.01 wt.%, less than 0.001 wt.%, less than 0.0001 wt.% or 0 wt.%. Dried overhead stream 314 can exit drying unit 302, undergo heat exchange in heat exchanger 304 and enter distillation unit 306. Heat exchanger 304 can cool the dried overhead stream 314 to about 10 °C or less at operating temperatures (e.g., 0.90 MPa, 130 psig). Distillation unit 306 can be any unit capable of separating two compounds having different boiling points. Non-limiting examples of distillation units include a thin film distillation unit, a flash distillation unit, plate distillation units, fractional distillation units, and the like. Conditions to effect separation in distillation unit include an average temperature of 50 °C to 75 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C, -34 °C, or any value or range there between and operating conditions (e.g., 0.8 MPa (115 psig) to 0.9 MPa (130 psig), or 0.87 MPa (126 psig)). Separation unit 306 can include one or more heating and pressurizing systems (for example, a reboiler system, heat exchangers, and the like) to heat and pressurize the overhead stream to effect separation of the organic impurities (e.g., chlorinated hydrocarbons) from the dried overhead stream and produce second overhead stream 316 and bottoms stream 322. Bottoms stream 322 can include the organic impurities such as chlorinated hydrocarbons, and can be collected, transported, stored or further

processed. Overhead stream 316 can include hydrogen chloride, water, and, in some instances, chlorinated hydrocarbons. Overhead stream 316 can pass through condenser 308 and enter gas/liquid separation unit 310. Condenser 308 can cool the overhead stream to -40 °C to -35 °C at operating pressures (*e.g.*, 0.8 MPa (115 psig) to 0.9 MPa (130 psig), or 5 0.87 MPa (126 psig)). Gas/liquid separation unit 310 can be a decanter or a vertical tank with demister or the like. In gas/liquid separation unit 310, overhead stream 316 can be subjected to temperature and pressures suitable to separate any remaining chlorinated hydrocarbons and HCl from the overhead stream to produce dry HCl product stream 318 (second acid stream) and chlorinated methane bottoms stream 320. Dry HCl product stream 318 includes high 10 purity hydrogen chloride. By way of example, dry HCl product stream 318 can include 90 wt.% HCl, 95 wt.% HCl, 99 wt.% HCl or 100 wt.% HCl, with the balance being trace amounts of light inert compounds. In some instances, a trace amount of chlorinated hydrocarbons (*e.g.*, less than 10 ppm) is present in the HCl product stream 318. Bottoms stream 320 can include chlorinated hydrocarbons, and, in some instances, HCl, and can be 15 returned to distillation unit 306 as a reflux stream and/or stored, transported or sent to other processing units.

[0038] In some embodiments, a portion of first overhead stream 214 can be sent to separation unit 302 for further processing and a portion of the overhead stream can be recycled to quench tower 106. FIG. 4 depicts a schematic of a system that includes recycling 20 a portion of the overhead stream 214 and separating a portion of the overhead stream to form second acid stream 318. As shown in FIG. 4, system 400 includes quench system 100, separation system 200, and separation system 300. In system 400, a portion of overhead stream 214 can enter distillation unit 302 and be further processed as described in FIG. 3 to produce the second acid product stream (*e.g.*, product stream 318) and/or be recycled to 25 quench tower 106. Valves 402, 404, and 406 can be used to regulate the flow of fluids to the quench tower (*e.g.*, valves 402 and 404) and/or distillation unit 302 (*e.g.*, valve 406). The balance of this operation can be determined by process economics.

EXAMPLES

[0039] The present invention will be described in greater detail by way of specific 30 examples. The following examples are offered for illustrative purposes only, and are not intended to limit the invention in any manner. Those of skill in the art will readily recognize

a variety of noncritical parameters, which can be changed or modified to yield essentially the same results.

[0040] Tables 1 and 2 list the weight fractions of the components of the streams in FIG. 2 and FIG. 3, respectively as determined through computer calculations using Aspen Plus®
5 (Aspen Technology, USA).

Table 1

Case I (streams)	102	110	116	118	210	216	214	212
wt. fraction								
CH ₄	0.3177	0.0001	0.0001	0.3811	0.0002	0.0000	0.0057	0.0000
O ₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCl	0.0321	0.0910	0.0017	0.0000	0.1034	0.1050	0.0428	0.0914
CO ₂	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000
CH ₃ Cl	0.2297	0.0060	0.0122	0.2755	0.1167	0.1090	0.4085	0.0000
CH ₂ Cl ₂	0.0772	0.0063	0.0098	0.0926	0.5855	0.5898	0.4250	0.0000
H ₂ O	0.1400	0.8950	0.9729	0.0069	0.1310	0.1342	0.0080	0.9086
CHCl ₃	0.0060	0.0007	0.0014	0.0073	0.0604	0.0608	0.0475	0.0000
CO	0.1602	0.0009	0.0019	0.1922	0.0028	0.0012	0.0622	0.0000
N ₂	0.0369	0.0000	0.0000	0.0442	0.0000	0.0000	0.0003	0.0000
Total Flow Kg/hr	1,218,536	432,349	1,713	1,015,839	249,869	243,425	6,444	427,618

Table 2

Case II	102	110	118	116	210	216	214	212	314	318	322
wt. fraction											
CH ₄	0.3351	0.0001	0.4119	0.0002	0.0001	0.0000	0.0010	0.0000	0.0010	0.0012	0.0000
O ₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HCl	0.0529	0.2125	0.0002	0.1693	0.2349	0.1396	0.8036	0.1079	0.8036	0.9913	0.0011
CO ₂	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CH ₃ Cl	0.2245	0.0094	0.2719	0.0345	0.1106	0.1140	0.0902	0.0000	0.0902	0.0000	0.4757
CH ₂ Cl ₂	0.0738	0.0100	0.0864	0.0397	0.6402	0.7310	0.0987	0.0000	0.0987	0.0000	0.5209
H ₂ O	0.1302	0.7670	0.0045	0.7548	0.0085	0.0099	0.0000	0.8920	0.0000	0.0000	0.0000
CHCl ₃	0.0003	0.0001	0.0004	0.0001	0.0047	0.0054	0.0004	0.0000	0.0004	0.0000	0.0023
CO	0.1463	0.0008	0.1795	0.0012	0.0010	0.0001	0.0061	0.0000	0.0061	0.0075	0.0000
N ₂	0.0362	0.0000	0.0445	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Mass Flow Kg/hr	1,180,291	260,484	960,283	40,507	297,742	255,002	42,741	258,253	42,740	34,638	8,103

CLAIMS

1. A process to purify an aqueous acid solution comprising HCl and organic hydrocarbons, the process comprising:
 - (a) subjecting an acidic feed stream to aqueous quenching conditions suitable to produce a gaseous stream and an aqueous acid stream comprising HCl and organic hydrocarbons, wherein the organic hydrocarbons comprise chlorinated hydrocarbons; and
 - (b) heating the aqueous acid stream of step (a) at a pressure of 1.4 MPa (200 psig) to 1.75 MPa (250 psig) to produce an aqueous acid product stream and an overhead stream, wherein the aqueous acid product stream comprises at least a minimal amount of, or substantially no, chlorinated hydrocarbons.
2. The process of claim 1, wherein heating in step (b) comprises heating the aqueous acid stream to a temperature of 115 °C to 130 °C.
3. The process of any one of claims 1 to 3, wherein the overhead stream comprises chlorinated hydrocarbons, water, and residual HCl.
4. The process of any one of claims 1 to 3, further comprising recycling the overhead stream of step (b) to step (a).
5. The process of any one of claims 1 to 3, further comprising:
 - (c) subjecting the overhead stream of step (b) to conditions suitable to remove water from the overhead stream and produce a water stream and a dried overhead stream; and
 - (d) distilling the dried overhead stream under conditions suitable to produce a second acid stream comprising HCl and a bottoms stream comprising chlorinated hydrocarbons.
6. The process of claim 5, wherein the step (d) distillation is performed at a temperature of 50 °C to 70 °C and a pressure of 0.8 MPa (115 psig) to 0.9 MPa (130 psig).

7. The process of any one of claims 5 to 6, wherein the removal of water from the overhead stream in step (c) is in an amount sufficient to inhibit hydrate formation during distillation.
8. The process of any one of claims 5 to 7, wherein the second acid stream is a high purity HCl stream.
9. The process of any one of claims 1 to 8, wherein the step (a) gaseous stream comprises chlorinated hydrocarbons, light hydrocarbons and inert gases.
10. The process of any one of claims 1 to 9, wherein aqueous acid product stream comprises greater than 9 wt.% HCl.
11. The process of any one of claims 1 to 10, wherein a stripper gas is not used in step (b).
12. The process of any one of claims 1 to 11, wherein the acidic feed stream is from a methane oxychlorination reaction, and wherein the acidic feed stream comprises HCl, chlorinated hydrocarbons, methane and inert gases.
13. A system for the purification of an aqueous acid solution comprising hydrogen chloride and organic impurities, the system comprising:
 - (e) a quench zone configured to receive an acidic feed stream and produce a gaseous stream and an aqueous stream comprising hydrogen chloride and organic impurities, wherein the organic impurities comprise chlorinated hydrocarbons; and
 - (f) a first separation zone in fluid communication with the quench zone, the first separation zone configured to separate the aqueous acid stream of step (a) into an aqueous acid product stream and an overhead stream at a pressure of 1.4 MPa (200 psig) to 1.75 MPa (250 psig), wherein the aqueous acid product stream comprises a minimal amount of, or substantially no, chlorinated hydrocarbons.
14. The system of claim 13 wherein an average temperature of the first separation zone ranges from 115 °C to 130 °C.

15. The system of any one of claims 13 to 14, wherein the overhead stream of step (b) comprises light hydrocarbons, chlorinated hydrocarbons, water, and residual HCl.
16. The system of any one of claims 13 to 15, further comprising a conduit in fluid communication with the quench zone and the separation zone, the conduit configured to provide the overhead stream from the separation zone to the quench zone.
17. The system of any one of claims 13 to 15, further comprising:
 - (c) a drying zone in fluid communication with the first separation zone, the drying zone configured to remove water from the overhead stream and produce a dried overhead stream; and
 - (d) a second separation zone in fluid communication with the drying zone, the second separation zone configured separate the dried overhead stream at a temperature of 50 °C to 70 °C and a pressure of 0.8 MPa (115 psig) to 0.9 MPa (130 psig) into an acid stream comprising the HCl and a bottoms stream comprising chlorinated hydrocarbons.
18. The system any one of claims 13 to 17, wherein the HCl content of the aqueous acid product stream is at least 9 wt.% HCl.
19. The system of any one of claims 13 to 18, wherein a stripper gas is not used in step (b).
20. The system of any one of claims 13 to 19, wherein the acidic feed stream of step (a) is from a methane oxychlorination reaction, and wherein the acidic feed stream comprises HCl, chlorinated hydrocarbons, methane and inert gases.

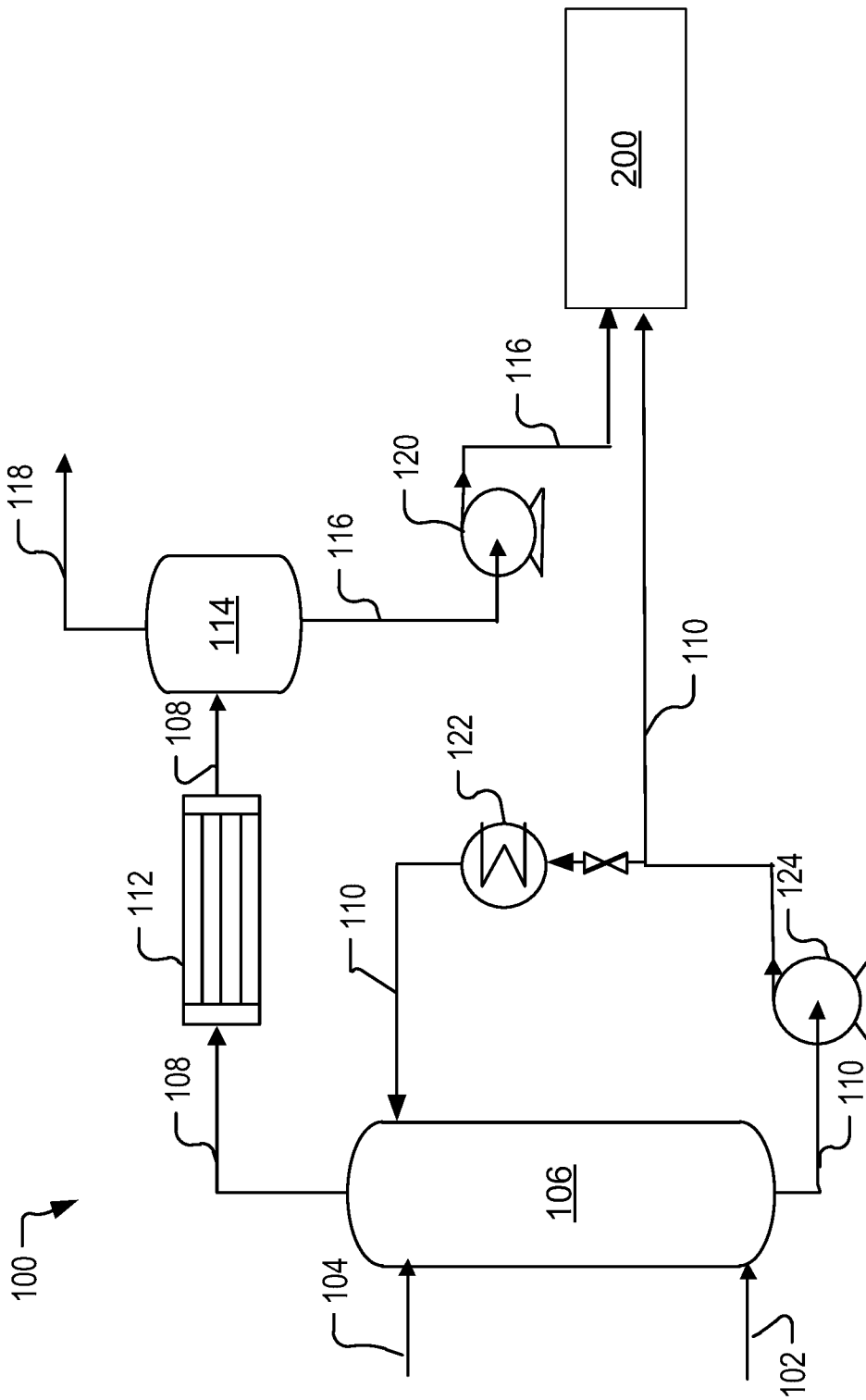


FIG. 1

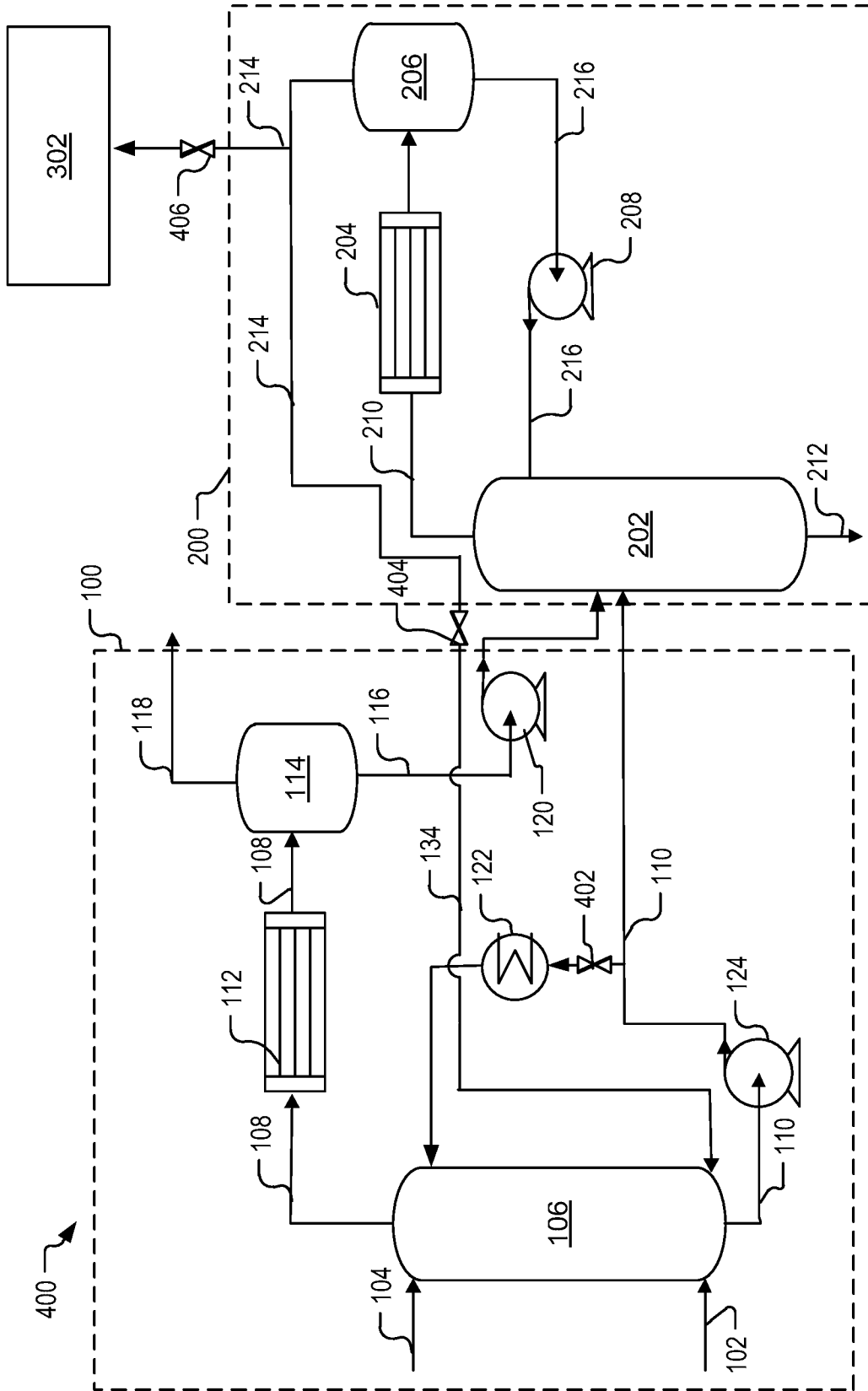


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2017/052603**A. CLASSIFICATION OF SUBJECT MATTER****C01B 7/07(2006.01)i, C07C 17/154(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
C01B 7/07; C07C 17/10; B01D 53/02; B01D 1/16; B01D 53/047; C07C 17/154Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: purification, hydrochloric acid, quenching, heating**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2730194 A (WOHLERS, HERBERT C. et al.) 10 January 1956 See column 1, lines 27-37; column 2, lines 1-3, 43-58; column 3, lines 47-52; column 4, lines 44-65; claim 2; and figure 1.	1-3,13-15
A	US 3968178 A (OBRECHT, ROBERT P. et al.) 06 July 1976 See column 3, line 45-column 4, line 8.	1-3,13-15
A	WO 01-25144 A1 (MERCK PATENT GMBH) 12 April 2001 See claim 1; and figure 1.	1-3,13-15
A	US 2003-0196764 A1 (BRADY JR., BILL L. et al.) 23 October 2003 See paragraph [0020]; and claim 1.	1-3,13-15
A	US 2008-0264253 A1 (BRETTSCHEIDER, OLE et al.) 30 October 2008 See paragraphs [0046]-[0053]; and figure 1.	1-3,13-15

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

07 August 2017 (07.08.2017)

Date of mailing of the international search report

07 August 2017 (07.08.2017)

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 6
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 6 is not clear because it refers to claim 5 which does not comply with PCT Rule 6.4(a).

3. Claims Nos.: 4,5,7-12,16-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2017/052603

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2730194 A		None	
US 3968178 A	06/07/1976	BE 723595 A CA 943145 A CA 950478 A CS 152460 B2 CS 174872 B2 DE 1806988 A1 DE 1806988 B2 FR 1590889 A GB 1256707 A GB 1256708 A	08/05/1969 05/03/1974 02/07/1974 19/12/1973 29/04/1977 11/12/1969 02/11/1978 20/04/1970 15/12/1971 15/12/1971
WO 01-25144 A1	12/04/2001	AU 7524800 A1 CA 2387584 A1 CN 100473600 C CN 1377323 A DE 19948206 A1 EP 1218291 A1 JP 2003-511329 A JP 4718077 B2 MY 128168 A TW 539646 B US 6793905 B1	10/05/2001 12/04/2001 01/04/2009 30/10/2002 12/04/2001 03/07/2002 25/03/2003 06/07/2011 31/01/2007 01/07/2003 21/09/2004
US 2003-0196764 A1	23/10/2003	AU 2003-221872 A1 CA 2482595 A1 CN 1328154 C CN 1662443 A CN 1662443 C DE 10392517 B4 DE 10392517 T5 HU 0500353 A2 HU 0500353 A3 HU 230333 B1 JP 2005-523226 A JP 4523288 B2 KR 10-0970035 B1 KR 10-2004-0101496 A MX PA04010223 A US 2004-0163411 A1 US 6719957 B2 US 7555917 B2 WO 03-089370 A1	03/11/2003 30/10/2003 25/07/2007 31/08/2005 25/07/2007 06/07/2006 06/10/2005 28/07/2005 28/12/2010 29/02/2016 04/08/2005 11/08/2010 16/07/2010 02/12/2004 03/02/2005 26/08/2004 13/04/2004 07/07/2009 30/10/2003
US 2008-0264253 A1	30/10/2008	CN 101663234 A CN 101663234 B DE 102007020144 A1 EP 2142470 A1	03/03/2010 19/06/2013 30/10/2008 13/01/2010

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2017/052603

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		EP 2142470 B1	21/06/2017
		JP 2010-524829 A	22/07/2010
		JP 5537415 B2	02/07/2014
		KR 10-1563012 B1	23/10/2015
		KR 10-2010-0015860 A	12/02/2010
		US 7837767 B2	23/11/2010
		WO 2008-131873 A1	06/11/2008