



PROCESS FOR THE PRODUCTION OF CHLORINATED PROPANES AND/OR  
PROPENES

FIELD

[0001] The present invention relates to processes for the production of chlorinated propanes and/or propenes.

BACKGROUND

[0002] Hydrofluorocarbon (HFC) products are widely utilized in many applications, including refrigeration, air conditioning, foam expansion, and as propellants for aerosol products including medical aerosol devices. Although HFC's have proven to be more climate friendly than the chlorofluorocarbon and hydrochlorofluorocarbon products that they replaced, it has now been discovered that they exhibit an appreciable global warming potential (GWP).

[0003] The search for more acceptable alternatives to current fluorocarbon products has led to the emergence of hydrofluoroolefin (HFO) products. Relative to their predecessors, HFOs are expected to exert less impact on the atmosphere in the form of a lesser detrimental impact on the ozone layer and their generally lower GWP. Advantageously, HFO's also exhibit low flammability and low toxicity.

[0004] As the environmental, and thus, economic importance of HFO's has developed, so has the demand for precursors utilized in their production. Many desirable HFO compounds, e.g., such as 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene, may typically be produced utilizing feedstocks of chlorocarbons, and in particular, chlorinated propenes, which may also find use as feedstocks for the manufacture of polyurethane blowing agents, biocides and polymers.

[0005] Unfortunately, many chlorinated propenes may have limited commercial availability, and/or may only be available at prohibitively high cost, due at least in part to the complicated, multi-step processes typically utilized in their manufacture. For example, in methods that utilize allyl chloride or 1,2,3-trichloropropane (TCP) as starting materials, successive dehydrochlorinations and chlorinations with elemental chlorine may be done until the desired number of chlorine atoms has been added. Or, some conventional methods call

for the chlorination of chlorinated alkanes having fewer chlorine atoms than desired in the final product.

[0006] Such multistep reactions are typically carried out as batch and/or semi-batch processes, and thus can suffer from low production capacity. In addition to the multiple reaction steps, each of which typically being carried out in a different reactor, such processes may also require purification steps to be carried out either between or after the reaction steps making these multistep processes very capital intensive.

[0007] It would thus be desirable to provide improved processes for the large capacity and/or continuous production of chlorocarbon precursors useful as feedstocks in the synthesis of refrigerants and other commercial products. More particularly, such processes would provide an improvement over the current state of the art if they were less costly not only in processing time, but capital costs required to implement and maintain the process.

#### BRIEF DESCRIPTION

[0008] The present invention provides efficient processes for the production of chlorinated propenes. Advantageously, the processes make use of 1,2-dichloropropane, a by-product in the production of chlorohydrin, as a low cost starting material, alone or in combination with 1,2,3-trichloropropane. Even though the use of 1,2-dichloropropane can require at least one additional chlorination and/or dehydrochlorination step in order to provide the desired chlorinated propane and/or propene in some embodiments, the process nonetheless provides substantial time and cost savings by requiring fewer reactors in which to conduct the process. Finally, in some embodiments, the processes start with a dehydrochlorination step, and as a result, the first chlorination occurs across a double bond. As a result, catalysts may not be required for this step, and further cost savings can be seen.

[0009] In one aspect, the present invention provides a process for the production of chlorinated propanes and/or propenes from 1,2-dichloropropane wherein at least two reactions are carried out in the same reactor, e.g., at least two chlorination reactions occur in the same reactor and/or at least two dehydrochlorination reactions are carried out in the same reactor. In some embodiments, all of the chlorination reactions are desirably carried out in one chlorination reactor and/or all of the dehydrochlorination reactions are desirably carried out in one dehydrochlorination reactor. The process is capable of operating continuously,

and in some embodiments, continuous operation may be preferred. The chlorination agent may comprise chlorine,  $\text{SO}_2\text{Cl}_2$ , or combinations of these. The chlorinated propane and/or chlorinated propene produced desirably comprises from 3 to 5, or 3 to 4, chlorine atoms, respectively, and in some embodiments, may be a pentachloropropane, or a tetrachloropropene, such as, e.g., 1,1,2,3-tetrachloropropene.

[0010] The advantages provided by the present processes may be carried forward by utilizing the chlorinated propenes to produce further downstream products, such as, e.g., 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene.

[0011] DESCRIPTION OF THE FIGURES

[0012] FIG. 1 shows a schematic (not to scale) representation of a process according to another exemplary embodiment; and

[0013] FIG. 2 shows a schematic (not to scale) representation of a process according to yet another exemplary embodiment.

[0014] DETAILED DESCRIPTION

[0015] The present specification provides certain definitions and methods to better define the present invention and to guide those of ordinary skill in the art in the practice of the present invention. Provision, or lack of the provision, of a definition for a particular term or phrase is not meant to imply any particular importance, or lack thereof. Rather, and unless otherwise noted, terms are to be understood according to conventional usage by those of ordinary skill in the relevant art.

[0016] The terms “first”, “second”, and the like, as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. Also, the terms “a” and “an” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item, and the terms “front”, “back”, “bottom”, and/or “top”, unless otherwise noted, are merely used for convenience of description, and are not limited to any one position or spatial orientation.

[0017] If ranges are disclosed, the endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of “up to 25 wt.%, or,

more specifically, 5 wt.% to 20 wt.%,” is inclusive of the endpoints and all intermediate values of the ranges of “5 wt.% to 25 wt.%,” etc.). As used herein, percent (%) conversion is meant to indicate change in molar or mass flow of reactant in a reactor in ratio to the incoming flow, while percent (%) selectivity means the change in molar flow rate of product in a reactor in ratio to the change of molar flow rate of a reactant.

[0018] Reference throughout the specification to “one embodiment” or “an embodiment” means that a particular feature, structure, or characteristic described in connection with an embodiment is included in at least one embodiment. Thus, the appearance of the phrases “in one embodiment” or “in an embodiment” in various places throughout the specification is not necessarily referring to the same embodiment. Further, the particular features, structures or characteristics may be combined in any suitable manner in one or more embodiments.

[0019] “PDC” may be used from time to time herein as an abbreviation for 1,2-dichloropropane, “TCP” may be used herein as an abbreviation for 1,2,3-trichloropropane, “ACL” may be used as an abbreviation for allyl chloride or 3-chloropropene, and “TCPE” may be used as an abbreviation for 1,1,2,3-tetrachloropropene. The terms “cracking” and “dehydrochlorination” are used interchangeably to refer to the same type of reaction, i.e., one resulting in the creation of a double bond typically via the removal of a hydrogen and a chlorine atom from adjacent carbon atoms in chlorinated hydrocarbon reagents.

[0020] The present invention provides efficient processes for the continuous production of chlorinated propanes and/or propenes from a feed stream comprising 1,2-dichloropropane. The processes are not only advantageous in their ability to be run continuously, but also, since a dehydrochlorination step occurs first, the use of a catalyst is not required in at least the first chlorination step and some embodiments may not make use of the same in this, or later, chlorination steps. However, the invention is not so limited, and in some instances, e.g., wherein an increase in reaction kinetics and throughput is desirable, chlorination catalysts may be utilized.

[0021] The present processes are further advantageous in that, at least two of the reactions desirably take place in the same reactor, and so time and cost savings are provided. As used herein, the phrase “at least two reactions” is meant to indicate two chlorination or dehydrochlorination reactions, as the case may be, wherein, one chlorination or

dehydrochlorination reaction involves at least one different reagent than the at least one other chlorination reaction or dehydrochlorination reaction, respectively. That is, “at least two chlorination reactions” is meant to indicate, e.g., a chlorination reaction involving a dichloropropene and a chlorinating agent and a chlorination of a trichloropropene isomer with the same or a different chlorinating agent within the same physical reactor. As a further example, “at least two dehydrochlorination reactions” is meant to indicate, e.g., a dehydrochlorination reaction involving PDC and caustic and a dehydrochlorination reaction of trichloropropane isomer and the same, or a different, caustic solution within the same reactor.

[0022] In the present process, either two chlorination reactions may be conducted in the same chlorination reactor, or two dehydrochlorinations may be conducted in the same dehydrochlorination reactor, or both, or all of the chlorination reactions may take place in the same chlorination reactor and/or all dehydrochlorination reactions may take place in the same dehydrochlorination reactor, or both, or any combination there between. In some embodiments, the “at least two reactions” may occur substantially simultaneously, while in others, the “at least two reactions” may occur in succession. All the present invention requires is that at least two chlorination and/or dehydrochlorination reactions take place in the same reactor to provide the benefits of lower capital costs, processing time and hence higher capacity.

[0023] One or more of the dehydrochlorination steps of the present process may be conducted in the presence of a liquid caustic. Liquid phase reactions can provide cost savings since evaporation of reactants is not required. The lower reaction temperatures used in liquid phase reactions may also result in lower fouling rates than the higher temperatures used in connection with gas phase reactions, and so reactor lifetimes may also be optimized when at least one liquid phase dehydrochlorination is utilized. Desirably, at least the first dehydrochlorination step is conducted in the presence of liquid caustic.

[0024] Many chemical bases are known in the art to be useful for liquid caustic cracking, and any of these can be used. For example, suitable cracking bases include, but are not limited to, alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide, calcium hydroxide; alkali metal carbonates such as sodium carbonate; lithium, rubidium, and cesium or combinations of these. Phase transfer catalysts such as quaternary ammonium and

quaternary phosphonium salts (e.g. benzyltrimethylammonium chloride or hexadecyltributylphosphonium bromide) can also be added to improve the dehydrochlorination reaction rate with these chemical bases.

[0025] If additional dehydrochlorination steps are to be performed, they may be performed in the presence of liquid caustic, and in the same dehydrochlorination reactor as that used to conduct the first dehydrochlorination step. Or, any additional dehydrochlorination steps may be conducted in the vapor phase in an additional dehydrochlorination reactor suitable for vapor phase cracking reactions.

[0026] Any such vapor phase dehydrochlorination steps may be carried out in the presence of a catalyst so that the reaction rate and/or product selectivity is enhanced. If the use of catalysts is desired, suitable vapor phase dehydrochlorination catalysts include, but are not limited to, ferric chloride ( $\text{FeCl}_3$ ), activated carbon,  $\text{Cr}_2\text{O}_3$ , or a combination of these. Embodiments incorporating a catalytic vapor phase dehydrochlorination step provide the opportunity for reduced use of liquid caustic and for the recovery of anhydrous HCl, which is a higher value byproduct than aqueous HCl.

[0027] Catalysts are not required for the chlorination steps of the present process, but can be used, if desired, in order to increase the reaction kinetics of these steps. Suitable free radical chlorination catalysts include, but are not limited to, compounds comprising one or more azo- groups ( $\text{R-N=N-R}'$ ) such as azobisisobutyronitrile (AIBN) or 1,1'-azobis(cyclohexanecarbonitrile (ABCN) and organic peroxides such as di-tert-butyl peroxide, benzoyl peroxide, methyl ethyl ketone peroxide, and acetone peroxide. UV or visible light may also be utilized to catalyze chlorinations that proceed via a free radical mechanism.

[0028] In some embodiments, ionic chlorination catalysts, may be utilized in one or more of the chlorination steps in the process. The use of ionic chlorination catalysts in the present process can be used to enhance the addition of two chlorines replacing the double bond to provide a higher chlorinated alkane. Ionic chlorination catalysts are well known to those of ordinary skill in the art and any of these may be used in the present process. Suitable ionic chlorination catalysts include e.g., but are not limited to, aluminum chloride, ferric chloride, iodine, sulfur, iron, etc.

[0029] Any or all of the chlorination catalysts can be provided either in bulk or in connection with a substrate, such as activated carbon, graphite, silica, alumina, zeolites, fluorinated graphite and fluorinated alumina. Whatever the desired catalyst, or format thereof, those of ordinary skill in the art are well aware of methods of determining the appropriate concentration and method of introduction thereof. For example, many catalysts are typically introduced into the reactor zone as a separate feed, or in solution with other reactants, e.g., TCP.

[0030] The amount of any chlorination catalyst utilized will depend upon the particular catalyst chosen as well as the other reaction conditions. Generally speaking, in those embodiments of the invention wherein the utilization of a catalyst is desired, enough of the catalyst should be utilized to provide some improvement to reaction process conditions (e.g., a reduction in required temperature) or realized products, but yet not be more than will provide any additional benefit, if only for reasons of economic practicality. For purposes of illustration only, then, it is expected in those embodiments wherein catalysts are utilized, that useful concentrations of each will range from 0.0001% to 10% by weight each with respect to the feedstream to be chlorinated, or from 0.001% to 5%, or from 0.01% to 1 wt.%, inclusive of all subranges there between.

[0031] The present process can make use of a feedstock comprising 1, 2-dichloropropane to produce the desired chlorinated propanes and/or propenes. The process feedstock may also comprise 1,2,3-trichloropropane, or other chlorinated alkanes, if desired. Whatever the composition of the feedstock, one or more of its components may be generated within the process, if desired, by any methods known to those of ordinary skill in the art.

[0032] Any chlorinated propane and/or chlorinated propene may be produced using the present method, although chlorinated propanes with 3-5 chlorine atoms and chlorinated propenes with 3-4 chlorine atoms are more commercially attractive, and production of the same may thus be preferred in some embodiments. In some embodiments, the process may be used in the production of 1,1,2,3-tetrachloropropene, which may be a preferred feedstock for refrigerants, polymers, biocides, etc.

[0033] In additional embodiments, one or more reaction conditions of the process may be optimized, in order to provide even further advantages, i.e., improvements in selectivity,



conversion or production of reaction by-products. In certain embodiments, multiple reaction conditions are optimized and even further improvements in selectivity, conversion and production of reaction by-products produced can be seen.

[0034] Reaction conditions of the process that may be optimized include any reaction condition conveniently adjusted, e.g., that may be adjusted via utilization of equipment and/or materials already present in the manufacturing footprint, or that may be obtained at low resource cost. Examples of such conditions may include, but are not limited to, adjustments to temperature, pressure, flow rates, molar ratios of reactants, etc.

[0035] That being said, the particular conditions employed at each step described herein are not critical, and are readily determined by those of ordinary skill in the art. What is important is that the initial feedstream comprises 1,2-dichloropropane and that at least two reactions are carried out in the same vessel, i.e., two chlorination reactions, and/or two dehydrochlorination reactions are carried out in a single chlorination or dehydrochlorination reactor, as the case may be. Those of ordinary skill in the art will readily be able to determine suitable equipment for each step, as well as the particular conditions at which the distillation/fractionation, drying, chlorination, dehydrochlorination and isomerization steps described herein are carried out.

[0036] In the present process, a feed stream comprising fresh 1,2-dichloropropane, either alone, or in some embodiments, in combination with fresh 1,2,3-trichloropropane, and/or recycled PDC, TCP, tetrachloropropanes and/or pentachloropropanes, is converted to pentachloropropanes, and/or to TCPE using a series of consecutive dehydrochlorination and chlorination reactions, at least two of which occur in the same reactor.

[0037] In one exemplary embodiment, PDC is first fed to a liquid phase dehydrochlorination reactor, e.g., such as a shell and multitube exchanger with a coolant contained in the shell to maintain the desired temperature, a fixed bed reactor followed by a separation unit, or a batch or continuous stirred tank type of reactor with cooling coil to maintain reactor temperature. For reasons of process efficiency, the use of a reactor capable of accommodating a continuous process is preferred.

[0038] Conditions of a caustic cracking reactor that will provide for the cracking of PDC are either well-known, or readily determined, by those of ordinary skill in the art. Generally

speaking, a caustic dehydrochlorination reactor may be co-fed with a stream comprising caustic soda to achieve 20-50wt% overall concentration with a slight molar excess of caustic compared to the di-, tri- and tetrachlorinated propane(s) and operated at pressures of from ambient to 400kPA, temperatures of from 40°C to 150°C, or from 60°C to 120°C and with residence times of less than 3 hours. Caustic dehydrochlorinations may be carried out with or without the use of phase transfer agent catalysts.

[0039] The product stream from the liquid phase dehydrochlorination reactor is typically composed of an aqueous and organic phase, which may be separated by any means known in the art. The dried stream, comprising 1,1,2,3-TCPE, 2,3,3,3-TCPE, and mono, di-, tri- and other tetrachloroolefins, is then provided to a distillation column operated at conditions sufficient to separate the mono-, di- and trichloroolefins from the tetrachloroolefins. The mono-, di- and trichloroolefins may then be fed to a chlorination reactor to produce tri-, tetra- and pentachloropropanes, while the tetrachloroolefins may be fed to a reactor to isomerize any 2,3,3,3-tetrachloropropene to 1,1,2,3-tetrachloropropene under the appropriate conditions.

[0040] For example, catalysts may be utilized to assist in the isomerization, in which case, suitable catalysts include, but are not limited to (i) siliceous granules having a polar surface including kaolinite, bentonite, and attapulgite; (ii) other mineral salts of silica such as saponite, quartz, (iii) siliceous non-mineral substance such as silica gel, fumed silica, and glass, or combinations of any of these. Suitable conditions for drying columns for such reaction streams are also known to those of ordinary skill in the art, as evidenced by US Patent No. 3,926,758.

[0041] The product stream from the isomerization reactor is then provided to a refining column operable to provide a stream of refined 1,1,2,3-TCPE as an overhead stream. The remainder of the stream of tetrachloroolefins, comprising unreacted 1,1,2,3-tetrachloropropane, pentachloropropanes and heavier byproducts, is disposed of as waste or fed to a further distillation column to recover the tetrachloropropane and pentachloropropane in the overhead stream and to dispose of the heavier unwanted byproducts in the bottom stream. The recovered tetra- and pentachloropropanes can then be recycled back to the dehydrochlorination reactor.

[0042] The liquid phase chlorination reactor can be a batch or continuous stirred tank reactor with an internal cooling coil. A shell and multitube exchanger followed by vapor liquid disengagement tank or vessel can also be used. The suitable reaction conditions for liquid phase chlorinations include, e.g., temperatures of from ambient temperature (e.g., 20°C) to 200°C, or from 30°C to 150°C, or from 40°C to 120°C or from 50°C to 100°C. Ambient pressure, or pressures of from 100 kPa to 1000 kPa, or from 100 kPa to 500 kPa, or from 100kPa to 300 kPa may be used. In some embodiments, one or more catalysts, e.g., one or more free radical catalysts such as AIBN, ACBN, and/or dibenzoyl peroxide, or one or more ionic chlorination catalysts such as  $\text{FeCl}_3$  or  $\text{AlCl}_3$  may be used in the chlorination reactor, while in others, their use is either not necessary, or without benefit.

[0043] In liquid phase chlorinations, one or more solvents may be provided to the chlorination reactor, and may be provided as feedstock, or, recycled from one or more purification columns operably disposed to receive streams from the chlorination reactor. For example, monochloropropene intermediates may be recycled back to the chlorination reactor from one purification column, tri- and tetrachloropropene intermediates may be recycled from another purification column and/or the chlorination reactor may be provided with a feedstock of any appropriate solvent for chlorination reactions, such as, e.g., carbon tetrachloride, sulfuryl chloride, 1,1,2,3,3-pentachloropropane, 1,1,2,2,3,3-hexachloropropane, other hexachloropropane isomers, or a combination of these.

[0044] At such conditions, monochloropropene is chlorinated to trichloropropane, dichloropropene is converted to tetrachloropropane, and trichloropropenes are chlorinated to pentachlorinated propanes at conversions of greater than 60%, or 70%, or 80%, or 85%, or 90% or 95%, or even up to 100% can be seen. The entire liquid product stream from this chlorination reactor is then recycled back to the dehydrochlorination reactor.

[0045] In some embodiments, the liquid product stream from the chlorination reactor may be fed to a separation column prior to being recycled to the dehydrochlorination reactor, while in those wherein a refining step is carried out prior to the chlorination reactor, the liquid product stream may simply be directly recycled to the dehydrochlorination reactor. In the case of the former, the separation column is desirably operated at conditions effective to separate the tri- and tetrachlorinated propanes from the pentachlorinated propanes. The overhead stream from this separation column, comprising tri- and tetrachlorinated propanes

and unreacted PDC, may be recycled back to the dehydrochlorination reactor to produce chlorinated propene intermediates, while the bottom stream, expected to comprise pentachloropropanes, e.g., 1,1,2,2,3-pentachloropropane, 1,1,1,2,2-pentachloropropane, and heavier by-products is then sent to a further vapor phase dehydrochlorination reactor operated at conditions effective to produce a product stream comprising 1,1,2,3-TCPE and 2,3,3,3-tetrachloropropene. This embodiment, while employing an additional dehydrochlorination reactor and thus requiring a greater capital expenditure, also offers the option of recovering anhydrous HCl as a byproduct, which may then be recovered and repurposed.

[0046] The reaction stream from the second vapor phase dehydrochlorination reactor, comprising 1,1,2,3-TCPE, may optionally be provided to a distillation column to remove HCl and other lighter byproduct than tetrachloropropenes, and the stream therefrom provided to a further reactor to isomerize any 2,3,3,3-tetrachloropropene to 1,1,2,3-tetrachloropropene.

[0047] A schematic illustration of another embodiment of the process is shown in Figure 1. Process 100 makes use of liquid phase dehydrochlorination reactor 102, chlorination reactor 130, isomerization reactor 140, drying unit 110, separation units 150, 160 and 180, and vapor phase dehydrochlorination reactor 170. The provision of the second, vapor phase dehydrochlorination reactor 170 provides process 100 with the ability to provide for the optional recovery of anhydrous HCl.

[0048] In operation, the feed to dehydrochlorination reactor 102 comprises fresh PDC, and recycled PDC, tri-, tetra-, and pentachloropropanes together with 50wt% caustic soda solution. Dehydrochlorination reactor 102 is desirably operated at conditions sufficient to produce the corresponding mono-, di-, tri- and tetrachloropropenes.

[0049] The crude product, along with any unconverted PDC and recycled chloropropanes, is sent to drying unit 110 to remove water and sodium chloride. In some embodiments, multiple columns (not shown) could be utilized in place of drying unit 110, e.g., a heterogeneous azeotropic distillation could be carried out by using a drying column and a water removal column. In such embodiments, the overhead streams of both columns would be combined in a decanter (not shown), with the water phase fed to the water column (not shown) and the organic phase fed to the drying column (not shown).

[0050] The overhead stream from drying unit 110 is then fed to liquid phase chlorination reactor 130 to convert the mono, di, and trichloropropenes to tri, tetra, and pentachloropropanes, respectively.

[0051] The product stream of liquid phase chlorination reactor 130 is fed to separation unit 160. Separation unit 160 is operated at conditions effective to provide PDC and trichloropropane in the overhead stream thereof. This overhead stream is then recycled to caustic dehydrochlorination reactor 102.

[0052] The bottom stream of separation unit 160, comprising pentachloropropane, is fed to vapor dehydrochlorination reactor 170 to produce TCPE, 2,3,3,3-tetrachloropropene, and anhydrous HCl. This product stream is fed to separation unit 180 to recover HCl in the overhead stream, while the bottom stream from separation unit 180, comprising TCPE, its isomer, and unreacted pentachloropropane, is fed to isomerization reactor 140 and purification unit 150 where TCPE is recovered in the overhead stream. The bottom stream, comprising unreacted pentachloropropane and other heavier byproducts, can then be further purified to recover pentachloropropane and recycled to separation unit 160.

[0053] A schematic illustration of another embodiment of the process is shown in Figure 2. Process 200 makes use of liquid phase dehydrochlorination reactor 202, chlorination reactor 230, drying unit 220, and separation units 260 and 280. Process 200 is exemplary of those processes wherein chlorinated propanes are desirably produced.

[0054] In operation, the feed to dehydrochlorination reactor 202 contains fresh PDC, and recycled PDC, tri-, and tetrachloropropanes together with 50wt% caustic soda solution. Dehydrochlorination reactor 202 is desirably operated at conditions sufficient to produce the corresponding mono-, di-, and trichloropropenes. The crude product, along with any unconverted PDC and recycled chloropropanes, is fed to drying unit 220 for the removal of water and salt byproduct, and then, fed directly to the liquid phase chlorination reactor 230. The overhead product stream from chlorination reactor 230, comprising di-, tri-, tetra- and pentachloropropanes, is then provided to separation unit 260.

[0055] Separation unit 260 is operated at conditions effective to provide an overhead stream comprising PDC, trichloropropane, and tetrachloropropane that is recycled back to reactor 202. The bottom stream of separation unit 260, comprising pentachloropropane and

heavier byproducts, is fed to separation unit 280. Separation unit 280, in turn, is operated at conditions effective to provide for the recovery of the desired pentachloropropane products, e.g., 1,1,1,2,3-pentachloropropane and/or 1,1,2,2,3-pentachloropropane, in the overhead stream thereof.

[0056] The chlorinated propanes and/or propenes produced by the present process may typically be processed to provide further downstream products including hydrofluoroolefins, such as, for example, 1,3,3,3-tetrafluoroprop-1-ene (HFO-1234ze). Since the present invention provides an improved process for the production of chlorinated propanes and/or propenes, it is contemplated that the improvements provided will carry forward to provide improvements to these downstream processes and/or products. Improved methods for the production of hydrofluoroolefins, e.g., such as 2,3,3,3-tetrafluoroprop-1-ene (HFO-1234yf), are thus also provided herein.

[0057] The conversion of chlorinated propanes and/or propenes to provide hydrofluoroolefins may broadly comprise a single reaction or two or more reactions involving fluorination of a compound of the formula  $C(X)_mCCl(Y)_n(C)(X)_m$  to at least one compound of the formula  $CF_3CF=CHZ$ , where each X, Y and Z is independently H, F, Cl, I or Br, and each m is independently 1, 2 or 3 and n is 0 or 1. A more specific example might involve a multi-step process wherein a feedstock of a chlorinated propene is fluorinated in a catalyzed, gas phase reaction to form a compound such as 1-chloro-3,3,3-trifluoropropene (1233zd). The 1-chloro-2,3,3,3-tetrafluoropropane is then dehydrochlorinated to 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene via a catalyzed, gas phase reaction.

[0058] Some embodiments of the invention will not be described in detail in the following Examples.

[0059] **Example 1: Caustic Cracking of 1,2 PDC**

[0060] An aqueous basic solution is prepared by mixing 8% sodium hydroxide, 14.7% sodium chloride, and 25% of a surfactant. At ambient pressure, 1,2 PDC is pumped into a 500 ml reactor at 1.16 g/min, and the basic solution fed to the reactor at 6.55 g/min. When heated, the reactor contents begin to boil at 81°C, and the product is removed in an overhead stream at a temperature of 40°C. The level is held constant by semi continuous operation of a bottoms valve. The reactor contains 2 phases, but the overhead stream is a single phase.

PCD conversion is 17%. The overhead stream composition is 30 % 2-chloropropene, 30.8 % cis-1-chloropropene, 31.6% trans-1-chloropropene, 0.11% 3-chloropropene, and 7.45% PDC.

[0061] This example shows that cracking reactions of chloropropanes competes with the removal of the chloropropanes by distillation, which limits chloropropane conversion. The conversion can be increased by operating a fixed bed reactor before an azeotropic product separation step so that the reactant chloropropane(s) is/are not removed by distillation during the reaction step.

[0062] **Example 2: Cracking of 1,2,2,3 tetrachloropropane**

[0063] 1,2,2,3 tetrachloropropane containing 1 wt.% of a surfactant is added to a 5 liter vessel equipped with a 15 tray column and heated to 120°C. Caustic feed at 20 wt.% is pumped in at a rate of 0.1 mole caustic per hour per mole of tetrachloropropane charged.

[0064] The overhead product is condensed and returned to the reactor for 1 hour. The overhead vapor temperature dropped from 97°C to 93.5°C. The bottom layer of the product azeotrope was removed at a rate such that the overhead temperature remained between 93.5°C and 94.5° C.

[0065] The crude product was refined in a 15 tray column at a 5:1 reflux ratio. The fraction that boiled between 73°C and 88°C at 120 mm Hg pressure was collected as product. Conversion of tetrachloropropane to 1,2,3 trichloropropene was 60-66%.

[0066] **Example 3: Cracking of 1,2 PDC concurrently with 1,2,2,3 tetrachloropropane**

[0067] 1,2,2,3 tetrachloropropane containing 1 wt.% surfactant and 1,2 PDC are added to a 5 liter vessel equipped with a 15 tray column and heated to 120°C. Caustic feed at 20 wt.% is pumped in at a rate of 1 mole caustic per hour per mole of tetrachloropropane charged.

[0068] When heated, the reactor contents begin to boil at 81°C, and the lighter product stream is taken overhead at a temperature of 70°C and returned to the reactor for one hour. PDC conversion is 10%. Conversion of tetrachloropropane to 1,2,3 trichloropropene is 60%.

## CLAIMS:

1. A continuous process for the production of chlorinated propanes and/or propenes from a feed comprising 1,2-dichloropropane, wherein at least two reactions occur in the same reactor.
2. The process of claim 1, wherein a dehydrochlorination step occurs first.
3. The process of claim 1, wherein at least two chlorination reactions occur in the same reactor.
4. The process of claim 1 or 3, wherein at least two dehydrochlorination reactions occur in the same reactor.
5. The process of claim 1, wherein at least one chlorination reaction is conducted in the liquid phase.
6. The process of claim 5, wherein the chlorination reaction is conducted in the presence of a catalyst.
7. The process of claim 6, wherein wherein the catalyst comprises one or more free radical catalysts comprising AIBN or dibenzoyl peroxide or a combination of these.
8. The process of claim 7, wherein the catalyst comprises an ionic chlorination catalyst comprising  $\text{AlCl}_3$ ,  $\text{I}_2$ ,  $\text{FeCl}_3$ , sulphur, iron, or combinations of these.
9. The process of claim 1, wherein the feed further comprises 1,2,3-trichloropropane.
10. The process of claim 1 or 9, wherein at least one component of the feed stream is generated within, or upstream of, the process.
11. The process of claim 1, wherein at least one dehydrochlorination reaction occurs in the liquid phase.



12. The process of claim 1, wherein the chlorination agent comprises chlorine or  $\text{SO}_2\text{Cl}_2$ , or combinations of these.
13. The process of claim 1, wherein the chlorinated propane comprises 3-5 chlorine atoms and/or the chlorinated propene comprises 3-4 chlorine atoms.
14. The process of claim 13, wherein the chlorinated propene comprises 1,1,2,3-tetrachloropropene.
15. A process for preparing 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene comprising converting a chlorinated propene prepared by the process of claim 1 into 2,3,3,3-tetrafluoroprop-1-ene or 1,3,3,3-tetrafluoroprop-1-ene.

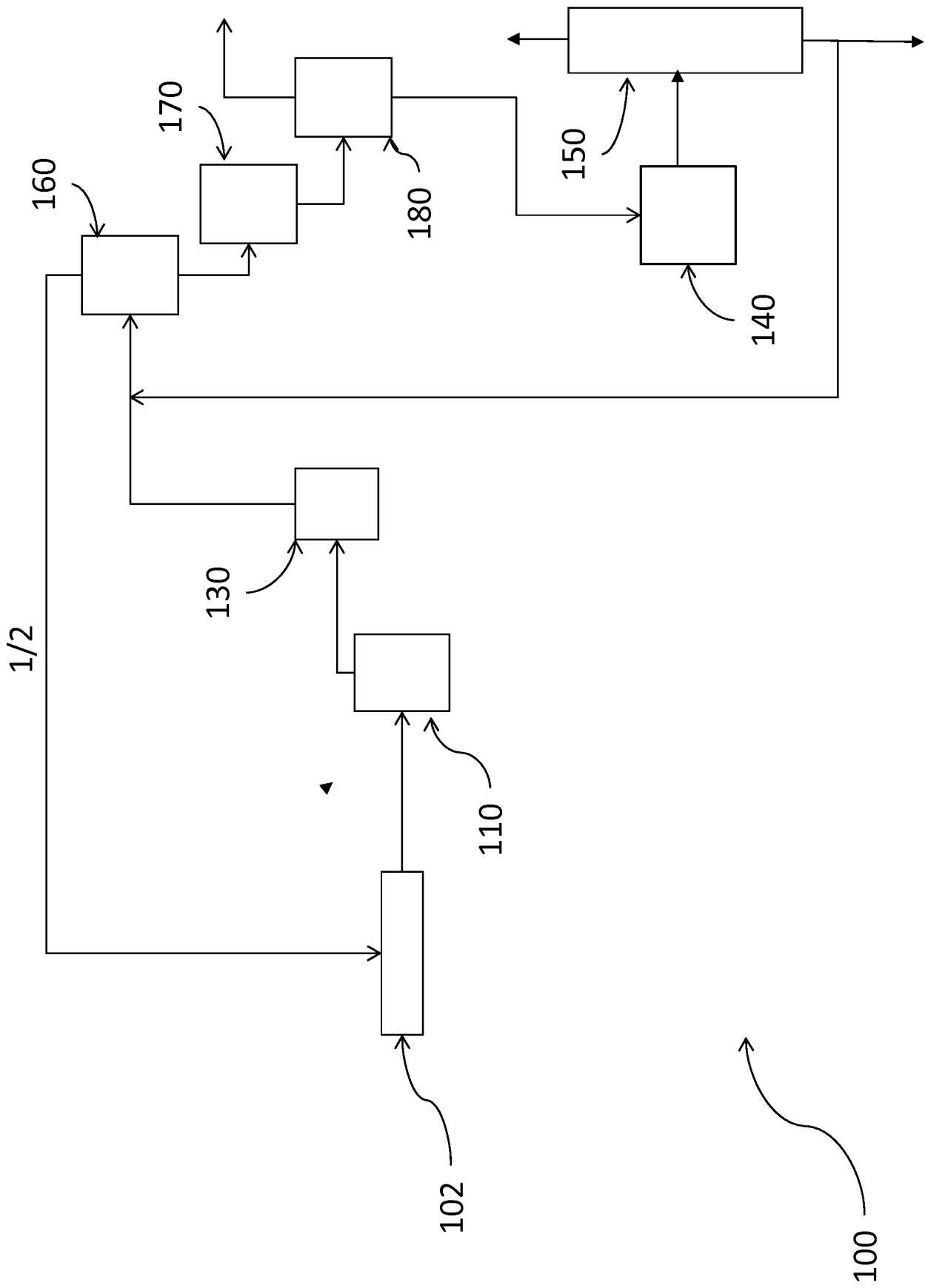


FIGURE 1

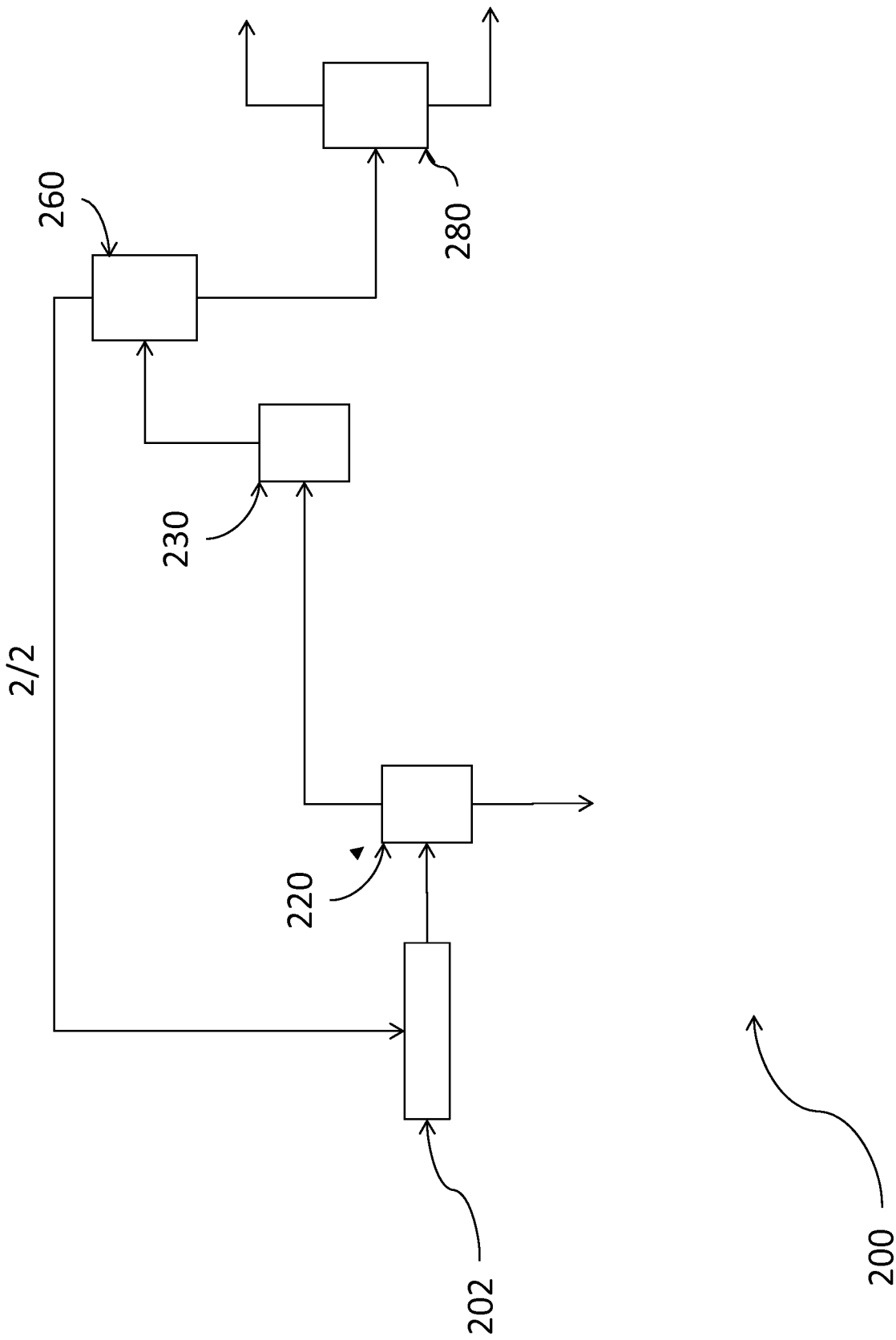


FIGURE 2

# INTERNATIONAL SEARCH REPORT

|   |
|---|
| International application No<br>PCT/US2012/064417 |
|---|

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C07C17/25 C07C21/04  
 ADD.

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

**B. FIELDS SEARCHED**

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                           | Relevant to claim No.               |
|-----------|--|-------------------------------------|
| X<br>A    | US 2 449 286 A (FAIRBAIRN ALASDAIR W)<br>14 September 1948 (1948-09-14)<br>Example<br><br>-----              | 1,3,4,<br>12,13<br>2,5-11,<br>14,15 |
| X<br>A    | US 4 051 182 A (PITT HAROLD M)<br>27 September 1977 (1977-09-27)<br>Claim 1, example<br><br>-----            | 5-8,10,<br>11<br>9,14,15            |
| E         | WO 2012/166393 A1 (DOW GLOBAL TECHNOLOGIES<br>LLC) 6 December 2012 (2012-12-06)<br>Example II<br><br>-----   | 1-15                                |
| A         | DD 209 184 A1 (BUNA CHEM WERKE VEB [DD])<br>25 April 1984 (1984-04-25)<br>claim 1; examples 2-4<br><br>----- | 1-15                                |
|           | -/--   |                                     |

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

18 January 2013

Date of mailing of the international search report

28/01/2013

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International application No  
PCT/US2012/064417

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                     | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | DD 235 631 A1 (BUNA CHEM WERKE VEB [DD])<br>14 May 1986 (1986-05-14)<br>claim 1; examples 1-2<br>----- | 1-15                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
PCT/US2012/064417

| Patent document cited in search report |    | Publication date | Patent family member(s) | Publication date |
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| US 2449286                             | A  | 14-09-1948       | NONE                    |                  |
| -----                                  |    |                  |                         |                  |
| US 4051182                             | A  | 27-09-1977       | NONE                    |                  |
| -----                                  |    |                  |                         |                  |
| WO 2012166393                          | A1 | 06-12-2012       | NONE                    |                  |
| -----                                  |    |                  |                         |                  |
| DD 209184                              | A1 | 25-04-1984       | NONE                    |                  |
| -----                                  |    |                  |                         |                  |
| DD 235631                              | A1 | 14-05-1986       | NONE                    |                  |
| -----                                  |    |                  |                         |                  |