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(54) **Title**: PROCESS FOR THE MANUFACTURE OF AT LEAST ONE ETHYLENE DERIVATIVE COMPOUND

(57) **Abstract**: Process for the manufacture of at least one ethylene derivative compound starting from a low value residual gas, preferably a ROG, according to which : a) the low value residual gas is subjected to a series of treatment steps in a low value residual gas recovery unit in order to remove the undesirable components present therein and to obtain a mixture of products containing ethylene and other constituents; b) the said mixture of products is fractionated in one fractionation step into one fraction containing almost all the ethylene (fraction A), optionally into one individual fraction of ethane and into one heavy fraction (fraction C); and c) fraction A is conveyed to the manufacture of at least one ethylene derivative compound.

Process for the manufacture of at least one ethylene derivative compound

The present invention relates to a process for the manufacture of at least one ethylene derivative compound, in particular to a process for the manufacture of 1,2-dichloroethane (DCE) and optionally also of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE.

To date, ethylene which is more than 99.8 % pure is usually used for the manufacture of ethylene derivative compounds, in particular of DCE. This ethylene of very high purity is obtained via the cracking of various petroleum products, followed by numerous complex and expensive separation operations in order to isolate the ethylene from the other products of cracking and to obtain a product of very high purity.

Given the high costs linked to the production of ethylene of such high purity, various processes for the manufacture of ethylene derivative compounds, in particular DCE, using ethylene having a purity of less than 99.8 % have been developed. These processes have the advantage of reducing the costs by simplifying the course of separating the products resulting from the cracking and by thus abandoning complex separations which are of no benefit for the manufacture of ethylene derivative compounds, in particular DCE.

For example, patent application WO 00/26164 describes a process for the manufacture of DCE by simplified cracking of ethane coupled with chlorination of ethylene. To this effect, an ethylene chlorination step takes place in the presence of the impurities obtained during the cracking of the ethane.

Patent application WO 03/048088 describes the production of low-concentration ethylene for the chemical reaction with chlorine by means of ethane dehydrogenation. The ethane-loaded gas stream contains not only hydrogen and methane, but also high amounts of unconverted ethane. For the economic design of the process, the unconverted ethane must be fed back to ethane dehydrogenation after complicated cleaning processes. This process can only use ethane as feedstock. A significant disadvantage is the very low concentration of ethylene – less than 60 % - as well as the fact that further components of the gas stream such as hydrogen, propylene, butadiene only allow to use the ethylene in very special processes.

Further, patent applications WO 2006/067188, WO 2006/067190, WO 2006/067191, WO 2006/067192, WO 2006/067193 and WO 2007/147870 describe processes for the manufacture of DCE starting from a hydrocarbon source, in particular naphtha, gas oil, natural gas liquid, ethane, propane, butane, isobutane or mixtures thereof, which is first subjected to a simplified cracking. Two different factions containing ethylene are afterwards separated from the gas mixture issued from the simplified cracking before being conveyed independently to a chlorination reactor and to an oxychlorination reactor in order to produce DCE. Those processes, the aim of which is to produce and use ethylene having a purity of less than 99.8 %, present however the disadvantages of requiring a first step of cracking which needs an important investment causing an increase in the production costs and further of involving the use of expensive hydrocarbon sources. Moreover, those processes present the disadvantages of requiring several steps of fractionation in order to obtain the two fractions containing ethylene which complicate them and increase their costs.

Patent applications WO2008/000705, WO2008/000702 and WO2008/000693 describe, for their part, processes for the manufacture of DCE starting from a stream of ethane which is first subjected to a catalytic oxydehydrogenation. The processes described in the above-mentioned patent applications, the aim of which is to produce and use ethylene having a purity of less than 99.8 %, present however the disadvantages of requiring a first step of catalytic oxydehydrogenation which needs an important investment causing an increase in the production costs and further of involving the use of expensive hydrocarbon source.

Low value residual gases such as the refinery off-gases (also called petrochemical off-gases) produced in oil refineries (in fluid catalytic cracking (FCC) units, coker units, etc of the oil refineries) are usually burnt and used as fuel, for example within the refinery, without any recovery of the olefins contained therewith because the olefins content is relatively small and the costs linked to such recovery process are too high.

The aim of the present invention, for its part, is to provide a process for the manufacture of at least one ethylene derivative compound, in particular of at least DCE, using ethylene with a purity of less than 99.8 % which does not present the disadvantages of the above-mentioned processes using ethylene having a purity of less than 99.8 % and which allows the valorization of low value residual gases such as the refinery off-gases which are usually burnt and used as fuel.

To this effect, the invention relates to a process for the manufacture of at least one ethylene derivative compound starting from a low value residual gas according to which :

a) the low value residual gas is subjected to a series of treatment steps in a low value residual gas recovery unit in order to remove the undesirable components present therein and to obtain a mixture of products containing ethylene and other constituents ;
b) the said mixture of products is fractionated in one fractionation step into one fraction containing almost all the ethylene (fraction A), optionally into one individual fraction of ethane and into one heavy fraction (fraction C) ;
c) fraction A is conveyed to the manufacture of at least one ethylene derivative compound.

The expression “at least one ethylene derivative compound” is understood to mean, for the purpose of the present invention, that one or more than one ethylene derivative compounds may be manufactured by the process according to the present invention.

The expression “ethylene derivative compound”, used hereafter in the singular or in the plural, is understood to mean, for the purpose of the present invention, any ethylene derivative compound manufactured directly starting with ethylene as well as any compound derived there from.

The expression “ethylene derivative compound manufactured directly starting with ethylene”, used hereafter in the singular or in the plural, is understood to mean, for the purpose of the present invention, any compound manufactured directly from ethylene.

The expression “compound derived there from”, used hereafter in the singular or in the plural, is understood to mean, for the purpose of the present invention, any compound manufactured from one compound itself manufactured from ethylene as well as any compound derived there from.

As examples of such ethylene derivative compounds manufactured directly starting with ethylene, may be cited among others, ethylene oxide, linear alpha-olefines, linear primary alcohols, homopolymers and copolymers of ethylene, ethylbenzene, vinyl acetate, acetaldehyde, ethyl alcohol, propionaldehyde and DCE.

As examples of such compound derived there from, may be cited among others,

- glycols and ethers manufactured from ethylene oxide,
- styrene manufactured from ethylbenzene and polymers of styrene derived from styrene,
- vinyl chloride (VC) manufactured from DCE,
- vinylidene chloride, fluorinated hydrocarbons and polyvinyl chloride (PVC) derived from VC and fluorinated polymers derived from fluorinated hydrocarbons, as well as
- polyvinylidene chloride and fluorinated hydrocarbons (and fluorinated polymers) derived from vinylidene chloride.

The process according to the invention is a process starting from a low value residual gas.

The expression “a low value residual gas” (LVRG), used hereafter in the singular, is understood to mean, for the purpose of the present invention, one gas or a mixture of several gases containing ethylene and/or precursor(s) thereof, which are off-gases produced as by-product in units the aim of which is to produce at least one combustible liquid ; the LVRG being constituted of more than 10 % by weight of permanent gas.

The expression “gas” is to be understood, for the purpose of the present invention, in the sense of the definition given by the NFPA69 Standard on Explosion Prevention Systems, 1997 Edition, i.e. the state of matter characterized by complete molecular mobility and unlimited expansion.

The expression “precursor” is understood to mean, for the purpose of the present invention, any hydrocarbon compounds containing two carbon atoms other than ethylene, in particular ethane, ethanol and acetylene, more particularly ethane and acetylene.

The expression “combustible liquid” is understood to mean, for the purpose of the present invention, any hydrocarbon fraction containing carbon, hydrogen and possibly oxygen, that is at least partially liquid at 21°C under its charged pressure and that is capable of undergoing combustion.

The expression “combustion” is to be understood, for the purpose of the present invention, in the sense of the definition given by the NFPA69 Standard on Explosion Prevention Systems, 1997 Edition, i.e. a chemical process of oxidation that occurs at a rate fast enough to produce heat and usually light, in the form of either a glow or flames.

The expression “permanent gas” is understood to mean, for the purpose of the present invention, any gas the critical temperature of which is less that 0°C and which can not be liquefied by simple compression. Examples of permanent gases are hydrogen, oxygen, nitrogen, argon, carbon monoxide and methane.

LVRG can be produced in at least one kind of units processing hydrocarbon sources in order to produce combustible liquids. Such units could be hydrocarbon sources pyrolysis, hydro-pyrolysis, catalytic pyrolysis, electrical arc pyrolysis, Fischer-Tropsch synthesis or oil-refinery units. Hydrocarbon sources could be solid sources like coal, lignite and wood, liquid sources like oil (petroleum) and naphta or gaseous sources like synthesis gas or residual gas from oil and/or gas fields. Such LVRG are usually burnt as fuel or flared.

The expression “at least one kind of units processing hydrocarbon sources” is understood to mean, for the purpose of the present invention, that LVRG can be produced in one kind of units processing hydrocarbon sources or in several kinds of units processing hydrocarbon sources. Preferably, LVRG is produced in one kind of units processing hydrocarbon sources.

LVRG is advantageously at a pressure above the atmospheric pressure and preferably at a pressure comprised between the atmospheric pressure and the pressure of the unit where it is generated.

LVRG which is particularly preferred for the process according to the present invention is LVRG produced in oil refineries, usually called refinery off-gas (also called petrochemical off-gas) and designated hereafter as ROG.

The process according to the invention is therefore preferably a process starting from a ROG.

ROG can be produced in one or more of the units present in oil refineries. ROG are preferably produced in at least one of the following units present in oil refineries : fluid catalytic cracking (FCC), coker (delayed coker, fluid coker, flexicoker), gas plant, reformer, hydrocracker, hydrotreater and hydrodesulfuration (HDS). ROG is more preferably produced in at least one FCC unit.

ROG can be produced in one or in several oil refineries.

Most preferably, ROG is produced in one oil refinery and with a particular preference, in one FCC unit.

LVRG, preferably ROG, usually notably comprises :

- hydrogen, methane, ethane, ethylene, propane, propylene, hydrocarbons containing 4, 5 or 6 carbon atoms, heavier C6+ and hydrogen sulfide ;

- nitrogen, argon, carbon dioxide and water ;
- oxygen, carbon monoxide and nitrogen oxides ;
- hydrogen chloride, hydrogen cyanide, ammonia, nitrides, nitriles, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides, organic compounds containing more than one atom of sulfur like disulfides, sulfur oxides, acetylene, propadiene, methylacetylene, butadiene, diethanolamine, methanol, phosphines, other inorganic compounds containing chlorine and organic compounds containing nitrogen ; and
- arsenic (like arsines), mercury, vanadium, bromine, fluorine, silicon, aluminium and metal carbonyls.

All the above-mentioned components except ethylene can be designated as undesirable components. The expression “undesirable components” is understood to mean, for the purpose of the present invention, all the components to be at least partially removed if they are harmful for at least one of the following steps of the process.

These undesirable components can be classified notably as :

- combustible gases like hydrogen, methane, ethane, propane, hydrocarbons containing 4, 5 or 6 carbon atoms, heavier C6+ ;
- inert gases like nitrogen and argon ;
- oxygenated compounds like oxygen and nitrogen oxides ;
- corrosive compounds like carbon dioxide, hydrogen sulfide, water, hydrogen chloride, hydrogen cyanide, ammonia, nitrides, nitriles, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides as well as sulfur oxides ;
- reactive compounds like propylene, acetylene, propadiene, methylacetylene, butadiene, diethanolamine, methanol, phosphines, other inorganic compounds containing chlorine, organic compounds containing nitrogen, organic compounds containing more than one atom of sulfur per molecule like disulfides as well as carbon monoxide ; and
- catalyst poisoning compounds like arsenic (like arsines), mercury, vanadium, bromine, fluorine, silicon, aluminium and metal carbonyls.

These undesirable components can also be classified notably as :

1. the undesirable components which can be harmful for at least step b) and which are advantageously substantially removed during step a) i.e.

  - corrosive compounds like carbon dioxide, hydrogen sulfide, water, hydrogen chloride, hydrogen cyanide, ammonia, nitrides, nitriles, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides as well as sulfur oxides ; and
  - catalyst poisoning compounds like arsenic (like arsines), mercury, vanadium, bromine, fluorine, silicon, aluminium and metal carbonyls.

2. the undesirable components which can be acceptable within step b) but which can be harmful for at least one of the steps of the process following step b) and which can possibly be at least partially removed during step a) i.e.
  - combustible gases like hydrogen, methane, ethane, propane, hydrocarbons containing 4, 5 or 6 carbon atoms, heavier C6+ ;
  - inert gases like nitrogen and argon ;
  - oxygenated compounds like oxygen and nitrogen oxides ; and
  - reactive compounds like propylene, acetylene, propadiene, methylacetylene, butadiene, diethanolamine, methanol, phosphines, other inorganic compounds containing chlorine, organic compounds containing nitrogen, organic compounds containing more than one atom of sulfur per molecule like disulfides as well as carbon monoxide.

The expression “at least partially removed” is understood to mean, for the purpose of the present invention, that advantageously at least 25 % , preferably at least 40 %, more preferably at least 50 % of the quantity of each undesirable component present in the LVRG, preferably ROG, fed to step a) and/or formed during step a), is removed. Advantageously, at most 90 % of the quantity of such each undesirable component present in the LVRG, preferably ROG, fed to step a) and/or formed during step a), is removed.

The expression “substantially removed” is understood to mean, for the purpose of the present invention, that advantageously at least 95 % , preferably at least 98 %, more preferably at least 99 % of the quantity of each undesirable component present in the LVRG, preferably ROG, fed to step a) and/or formed during step a), is removed.

The compositions which are given hereafter for the LVRG, preferably ROG, are expressed on dry gas basis (water not included). As mentioned above, the LVRG, preferably ROG, can be one gas or a mixture of several gases (combined LVRG) containing ethylene and/or precursor(s) thereof. The compositions which are given hereafter when referring to individual LVRG, preferably ROG, correspond to the case when the LVRG, preferably ROG, is one gas containing ethylene and/or precursor(s) thereof. When referring to combined LVRG, preferably ROG, the compositions correspond to the case when the LVRG, preferably ROG, is a mixture of several gases containing ethylene and/or precursor(s) thereof.

Individual LVRG, preferably ROG, comprises advantageously from 0.25 to 60 % by weight of ethylene. LVRG, preferably ROG, comprises advantageously at least 0.25, preferably at least 2, more preferably at least 5, most preferably at least 8 and with a particular preference at least 10 % by weight of ethylene. LVRG, preferably ROG, comprises advantageously at most 60, preferably at most 55, more preferably at most 50 and most preferably at most 48 % by weight of ethylene.

Combined LVRG, preferably ROG, comprises advantageously from 10 to 60 % by weight of ethylene. LVRG, preferably ROG, comprises advantageously at least 10, preferably at least 15, more preferably at least 18 and most preferably at least 20 % by weight of ethylene. LVRG, preferably ROG, comprises advantageously at most 60, preferably at most 55, more preferably at most 50 and most preferably at most 48 % by weight of ethylene.

Individual LVRG, preferably ROG, comprises advantageously from 3 to 60 % by weight of ethylene plus its precursor(s). LVRG, preferably ROG, comprises advantageously at least 3, preferably at least 5, more preferably at least 8 and most preferably at least 10 % by weight of ethylene plus precursor(s). LVRG, preferably ROG, comprises advantageously at most 60, preferably at most 55, more preferably at most 50 and most preferably at most 48 % by weight of ethylene plus precursor(s).

Combined LVRG, preferably ROG, comprises advantageously from 10 to 60 % by weight of ethylene plus its precursor(s). LVRG, preferably ROG, comprises advantageously at least 10, preferably at least 15, more preferably at least 20, most preferably at least 22 and still most preferably at least 22.5 % by weight of ethylene plus precursor(s). LVRG, preferably ROG, comprises advantageously at most 60, preferably at most 55, more preferably at most 50 and most preferably at most 48 % by weight of ethylene plus precursor(s).

Individual LVRG, preferably ROG, is characterized by a lower heating value advantageously comprised between 10 and 90 MJ/kg of the dry gas. LVRG, preferably ROG, is characterized by a lower heating value advantageously of at least 10, preferably of at least 12 and more preferably of at least 15 MJ/kg of the dry gas. LVRG, preferably ROG, is characterized by a lower heating value advantageously of at most 90, preferably of at most 85 and more preferably of at most 80 MJ/kg of the dry gas.

Combined LVRG, preferably ROG, is characterized by a lower heating value advantageously comprised between 20 and 75 MJ/kg of the dry gas. LVRG, preferably ROG, is characterized by a lower heating value advantageously of at least 20, preferably of at least 25, more preferably of at least 30 and most preferably of at least 35 MJ/kg of the dry gas. LVRG, preferably ROG, is characterized by a lower heating value advantageously of at most 75, preferably of at most 70, more preferably of at most 60 and most preferably of at most 55 MJ/kg of the dry gas.

Individual LVRG, preferably ROG, comprises advantageously at most 90, preferably at most 85, more preferably at most 80 and most preferably at most 75 % by volume of inert gases.

Combined LVRG, preferably ROG, comprises advantageously at most 25, preferably at most 20, more preferably at most 18 and most preferably at most 15 % by volume of inert gases.

Combined LVRG, preferably ROG, comprises advantageously at most 25, preferably at most 20, more preferably at most 18 and most preferably at most 15 % by volume of nitrogen.

Individual LVRG, preferably ROG, comprises oxygenated compounds in a total amount advantageously lower or higher than the level needed to make the gaseous mixture flammable (so outside the flammable domain), preferably of at most 21, more preferably of at most 18 and most preferably of at most 15 % by volume.

Combined LVRG, preferably ROG, comprises oxygenated compounds in a total amount advantageously lower than the level needed to make the gaseous mixture flammable, preferably of at most 10, more preferably of at most 7 and most preferably of at most 5 % by volume.

Combined LVRG, preferably ROG, comprises oxygen in an amount advantageously of at most 9, preferably of at most 7 and more preferably of at most 5 % by volume.

Individual LVRG, preferably ROG, comprises corrosive compounds in a total amount advantageously of at most 50, preferably of at most 40 and more preferably of at most 35 % by volume.

Combined LVRG, preferably ROG, comprises corrosive compounds in a total amount advantageously of at most 20, preferably of at most 15 and more preferably of at most 10 % by volume.

Combined LVRG, preferably ROG, comprises each corrosive compound in an individual amount advantageously of at most 10, preferably of at most 8 and more preferably of at most 5% by volume.

Individual LVRG, preferably ROG, comprises reactive compounds in a total amount advantageously of at most 40, preferably of at most 35 and more preferably of at most 33 % by volume.

Combined LVRG, preferably ROG, comprises reactive compounds in a total amount advantageously of at most 20, preferably of at most 18 and more preferably of at most 15% by volume.

Combined LVRG, preferably ROG, comprises each reactive compound in an individual amount advantageously of at most 15, preferably of at most 12 and more preferably of at most 10% by volume.

Combined LVRG, preferably ROG, comprises carbon monoxide in an amount advantageously of at most 5, preferably of at most 3 and more preferably of at most 2 % by volume.

Individual LVRG, preferably ROG, comprises catalyst poisoning compounds in a total amount advantageously of at most 200, preferably of at most 100 and more preferably of at most 50 ppm by volume.

Combined LVRG, preferably ROG, comprises catalyst poisoning compounds in a total amount advantageously of at most 5, preferably of at most 2 and more preferably of at most 1 ppm by volume.

Combined LVRG, preferably ROG, comprises catalyst poisoning compounds in an individual volume advantageously of at most 500, preferably of at most 300 and more preferably of at most 200 ppb by volume.

In the process for the manufacture of at least one ethylene derivative compound, in particular the process for the manufacture of DCE and of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE, starting from a LVRG, preferably a ROG, according to the present invention, the LVRG, preferably the ROG, is subjected to a series of treatment steps (step a)) in a LVRG, preferably ROG, recovery unit in order to remove the undesirable components present therein and to obtain a mixture of products containing ethylene and other constituents that will be subjected to step b).

When LVRG, preferably ROG, is a mixture of several gases, the different gases may be all subjected to the same series of treatment steps in step a), each of them may be subjected to a dedicated series of treatment steps in step a) or each of them may be subjected to a combination of dedicated series of treatment steps and common series of treatment steps in step a). Preferably each of them is subjected to a combination of dedicated series of treatment steps and common series of treatment steps in step a).

The series of treatment steps in the LVRG, preferably ROG, recovery unit in step a) is advantageously composed of the following steps, not necessary performed in the order they are recited :

a1) optionally a compression step,
a1bis) optionally one or several dedusting step(s),
a2) corrosive compounds removal,
a3) catalyst poisoning compounds removal,
a4) optionally cooling,
a5) optionally at least a partial removal of some of the combustible gases,
a6) optionally at least a partial removal of some of the inert gases,
a7) optionally at least a partial removal of some of the oxygenated compounds ; and
a8) optionally at least a partial removal of some of the reactive compounds.

A compression step (step a1)) is optionally performed.

When present, the compression step of the LVRG, preferably ROG, increases advantageously the pressure to at least 8, preferably to at least 10, more preferably to at least 12 and most preferably to at least 14 kg/cm^2.g and advantageously to at most 60, preferably to at most 55, more preferably to at most 50 and most preferably to at most 45 kg/cm^2.g.

The step a1) is preferably performed in several stages, either in a multi-stage gas compressor or in several compressors. A droplets separation is preferably performed before the compression step a1).

The compression ratio at each compression stage is such that the temperature at the exit of the compression stage is advantageously of at most 150, preferably of at most 120 and more preferably of at most 100°C. The gas which exits the stage is afterwards advantageously cooled down by indirect cooling with a cooling media. The cooling media is advantageously chosen among cooling tower water, cold water, atmospheric air and colder gas issued from the process. The cooling media is preferably chosen among cooling tower water and atmospheric air. The cooling fluid is more preferably cooling tower water.

The gas is advantageously cooled down under 50, preferably under 48 and more preferably under 45°C but advantageously not under 0, preferably not under 5 and more preferably not under 10°C.

At the end of the cool down, some condensates could be produced. If some condensates are produced, they can be separated or not. They are preferably separated. The condensates are advantageously degassed by pressure release, preferably pressure release at the pressure of the upstream stage. A stripping of the separated liquids can be performed in order to recover the volatile fractions. The produced gas is more preferably recycled with the gases of the upstream stage.

The solid particles present in the gas or generated by any of the pretreatment steps can optionally be eliminated by a suitable operation i.e. one or several dedusting step(s) (dedusting step(s) a1bis)). Among the suitable operations may be cited for examples gravity settling, impingement, use of a cyclone, filtering, electrofiltering and/or electrical precipitation. Use of a cyclone, filtering and electrofiltering are preferred.

The corrosive compounds removal (step a2)) may be performed in one or several group of steps, each comprising one or several steps.

A first group of steps (steps a2a)) comprises advantageously one or several steps of absorption.

The absorption is advantageously an absorption with a regenerable solution like an amine (preferably alkanolamine) solution, a physical absorption with a suitable solvent like methanol or dimethyletherpolyethylene glycol, or an absorption with chemical reaction performed by scrubbing in an alkaline solution.

The alkali is preferably a hydroxide, an oxide or a carbonate. Examples of alkalis are sodium hydroxide, potassium hydroxide, calcium oxide, magnesium oxide, sodium carbonate and potassium carbonate.

The corrosive compounds removal by absorption (steps a2a)) comprises preferably a first step which is an absorption with a regenerable solution of an amine, preferably alkanolamine, followed by an absorption with an alkaline solution (caustic/water wash tower), preferably sodium hydroxide solution.

The regenerable solution may be regenerated or not. If regeneration takes place, it occurs advantageously in one or several stages, in particular in order to separate carbon dioxide and hydrogen sulfide. The regenerable solution is preferably regenerated and more preferably in two stages.

The corrosive compounds removal by absorption (steps a2a)) comprises more preferably a first step which is an absorption with a regenerable solution of an amine, preferably alkanolamine, which is regenerated in two stages, followed by an absorption with an alkaline solution (caustic/water wash tower), preferably sodium hydroxide solution.

The corrosive compounds which can be at least partially removed by such steps a2a) are advantageously hydrogen sulfide, hydrogen chloride, carbonyl sulfide, hydrogen cyanide, carbon dioxide, ammonia and organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides.

Alternatively, the organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides, ammonia as well as sulfur oxides can be at least partially hydrolyzed during steps a2a).

Water can also be at least partially removed by such steps a2a) if a physical sorbent like methanol is used.

A second group of steps (steps a2b)) comprises advantageously one or several steps of hydrogenation.

The hydrogenation of corrosive compounds such as, for example, hydrogen cyanide, nitrides, nitriles, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides as well as sulfur oxides, is advantageously performed in a hydrogenation reactor by using a hydrogenation catalyst. After steps a2b), hydrogen cyanide, nitrides, nitriles, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides as well as sulfur oxides are advantageously at least partially hydrogenated.

Suitable catalytic species include advantageously metals of group VIII, metals of group Ib and metals of group VIb. Catalysts based on palladium, on nickel or on gold are preferred. Catalysts based on palladium or on nickel are more preferred. Nickel based catalysts are most preferred with a particular preference for sulphided nickel catalysts. The hydrogenation catalysts may be supported or not. They are preferably supported. Catalysts such as those defined for step a7) may also be used.

Carbonyl sulfide, if still present in the hydrogenation feed, is advantageously at least partially converted into mercaptans during hydrogenation steps a2b), preferably with a palladium or nickel based catalyst, more preferably with a sulphided nickel catalyst.

Nitriles present in the hydrogenation feed are also advantageously at least partially converted, preferably with a palladium or nickel based catalyst, more preferably with a sulphided nickel catalyst, into amines during hydrogenation steps a2b).

Hydrogen cyanide, if still present in the hydrogenation feed, is advantageously at least partially removed during hydrogenation steps a2b), preferably with a palladium or nickel based catalyst, more preferably with a sulphided nickel catalyst.

Steps a2b) are advantageously performed at a temperature between 25 and 100°C.

A third group of steps (steps a2c)) comprises advantageously one or several cooling steps.

The cooling is advantageously performed by direct or indirect cooling with a cooling media. By direct cooling, one means the physical contact of the process stream with a cooling media. Example of suitable cooling media for direct contact cooling are water, methanol, hydrocarbon or mixture of thereof. Other example of suitable cooling media is aqueous solution of alkanolamine, metal carbonate or bicarbonate, inorganic acid like sulfuric acid or nitric acid. Other example of suitable media is methanolic solution of alkanolamine or metal carbonate or bicarbonate. Preferably, the cooling media is at a temperature lower then the stream temperature. The cooling is preferably performed by indirect cooling with a cooling media. The cooling media is advantageously chosen among cooling tower water, cold water, atmospheric air and colder gas issued from the process. The cooling media is preferably chosen among cooling tower water and atmospheric air. The cooling fluid is more preferably cooling tower water.

The gas is advantageously cooled down under 50, preferably under 48 and more preferably under 45°C but advantageously not under 0, preferably not under 5 and more preferably not under 10°C. Alternatively, a freezed drying step can be used to dry.

The condensates can be separated or not. They are preferably separated.

A fourth group of steps (steps a2d)) comprises advantageously one or several steps of adsorption.

The adsorption is advantageously an adsorption on a suitable solid like activated carbon, charcoal, molecular sieve, zeolithe, silica gel or alumina.

Water adsorption is advantageously realized at least partially by an adsorption step on molecular sieve, silica gel or alumina.

Preferably, water removal is at least partially performed by a combination of cooling (steps a2c)) and adsorption (steps a2d)).

Mercaptans derived from carbonyl sulfide, carbonyl sulfide as well as sulfides are advantageously at least partially removed via adsorption in a bed of a suitable material. Suitable adsorbents include advantageously carboneous material such as activated carbon and particularly activated carbon having a specific surface between 500 and 2500 m^2/g, molecular sieve 3, 4A or 13X, a zeolithe, a mesoporous adsorbent including activated alumina such as a mesoporous activated alumina with a specific BET surface between 150 m^2/g and 800 m^2/g, silica gel, a mesoporous silica gel adsorbent with a specific BET surface between 150 m^2/g and 800 m^2/g, a type A zeolithe, a type 5A zeolithe, a type X faujasite zeolithe, a type Y faujasite zeolithe and a MFI zeolithe. Preferred are activated carbon, molecular sieve 3 or 4A and activated alumina.

Amines derived from nitriles as well as residual nitriles, are advantageously at least partially removed via adsorption with the same kind of adsorbents as for removing mercaptans. Nitrides may also be at least partially adsorbed during steps a2d).

Ammonia is also advantageously at least partially removed by adsorption with the same kind of adsorbents as for removing mercaptans, if not removed already.

Carbon dioxide, if not removed during steps a2a), can also advantageously be at least partially removed by adsorption on a suitable adsorbent. Suitable adsorbents include activated copper, mineral clays, silica gel and activated alumina.

The catalyst poisoning compounds removal (step a3)) may be performed in one or several group of steps, each comprising one or several steps.

A first group of steps (steps a3a)) comprises advantageously one or several steps of adsorption.

The adsorption is advantageously a chemical or a physical adsorption on a suitable solid like activated carbon, charcoal, molecular sieve, zeolithe or alumina which is activated or not.

Preferably, the catalyst poisoning compounds are at least partially removed by a chemical or a physical adsorption on alumina, preferably activated, or on activated carbon.

Advantageously at least 1, preferably at least 2 adsorbents are used for the adsorption. Advantageously at most 6, preferably at most 5, more preferably at most 4 adsorbents are used for the adsorption. Most preferably 3 adsorbents are used.

The gas stream can contacted with the solid adsorbents in any suitable devices. Pneumatic conveying moving beds and fixed beds can be cited as suitable devices. Fixed beds are preferred.

The adsorbents can be arranged in mixed beds or in dedicated beds. They can be arranged in a single vessel or in separated vessels. The adsorbents are preferably arranged in dedicated beds, more preferably in 3 dedicated beds, and preferably in separated vessels.

Each adsorption step can be realized in one or several parallel beds. Each adsorption step is preferably realized in several parallel beds, more preferably in at least 2 separated beds.

Regeneration can be realised in the apparatus itself or outside the apparatus. Regeneration is preferably realized in the apparatus itself.

A second group of steps (steps a3b)) comprises advantageously one or several steps of absorption.

The absorption is advantageously a physical absorption, for example with a suitable solvent like dimethyletherpolyethylene glycol or methanol, or a chemical absorption, for example with an alkaline aqueous solution as described for steps a2a).

Step a3) is advantageously performed at a temperature between 25 and 100°C.

In addition to a steps a2c), a cooling step (step a4)) is optionally performed by indirect cooling with a cooling media. The cooling media is advantageously chosen among cooling tower water, cold water, hydrocarbon such as ethylene, ethane, propylene, propane or mixture or two or more of thereof, CO_2, hydrofluoro carbon refrigerant, atmospheric air and colder gas issued from the process. The cooling media is preferably chosen among cooling tower water, hydrocarbon such as ethylene, ethane, propylene, propane or mixture of two or more of thereof or colder gas issued from the process or atmospheric air. The cooling fluid is more preferably cooling tower water or hydrocarbon such as ethylene, ethane, propylene, propane or mixture or two or more of thereof or colder gas issued from the process.

The gas is advantageously cooled down under 0, preferably under -10 and more preferably under -20°C but advantageously not under -150, preferably not under -120 and more preferably not under -100°C.

The condensates can be separated or not. They are preferably separated.

At least a partial removal of some of the combustible gases is optionally performed (step a5)).

At least part of hydrogen and/or methane may be at least partially removed (step a5a)). This removal is optionally performed during step a) of the process according to the invention. Such step for removing at least part of hydrogen and/or methane may also be performed during step b) of the process according to the invention, for example during fractionation of the mixture of products derived from step a) or on fraction A. Preferably, when performed, removal of at least part of hydrogen and/or methane is performed during step a) (step a5a)) of the process according to the invention.

Suitable separation steps for hydrogen and/or methane during step a) or on fraction A, are advantageously membrane permeation and pressure swing adsorption (PSA). PSA is preferred.

At least part of ethane, propane and/or hydrocarbons containing 4, 5 or 6 carbon atoms or heavier C6+ may be at least partially removed (step a5b)), advantageously in several steps.

This removal is optionally performed during step a) of the process according to the invention. Such step for removing at least part of ethane, propane and/or hydrocarbons containing 4, 5 or 6 carbon atoms or heavier C6+ may also be performed during step b) of the process according to the invention, for example during fractionation of the mixture of products derived from step a).

Suitable separation step for ethane, propane and/or hydrocarbons containing 4, 5 or 6 carbon atoms or heavier C6+ during step a) is advantageously condensation. Advantageously step a5b) is combined with the compression step a1) and/or the cooling steps a2c) and/or a4).

At least a partial removal of some of the inert gases is optionally performed (step a6)).

This removal is optionally performed during step a) of the process according to the invention. Such step for removing at least part of inert gases may also be performed during step b) of the process according to the invention, for example during fractionation of the mixture of products derived from step a) or on fraction A. Preferably, when performed, removal of at least part of inert gases is performed during step a) (step a6)) of the process according to the invention.

Suitable separation steps for inert gases during step a) or on fraction A, are advantageously membrane permeation and pressure swing adsorption (PSA). PSA is preferred.

At least a partial removal of some of the oxygenated compounds is optionally performed (step a7)).

At least part of the oxygen can be at least partially removed (step a7a)) by a chemical step or by a physical step.

A suitable chemical step is advantageously performed by using a reduced bed of copper or a sulphided nickel catalyst, preferably by using a sulphided nickel catalyst (step a7a1)).

Another suitable chemical step is advantageously a hydrogenation step which can be catalyzed or not, preferably is catalyzed (step a7a2)).

The hydrogenation step may be performed by means of any known hydrogenation catalyst such as, for example, catalysts based on palladium, platinum, rhodium, ruthenium, iridium, gold, silver or mixture of these elements deposited on a support such as alumina, silica, silica/alumina, carbon, calcium carbonate or barium sulphate, but also catalysts based on nickel and those based on the cobalt-molybdenum complex. Preferably, the hydrogenation step is performed by means of a catalyst based on palladium or platinum deposited on alumina or carbon, on a catalyst based on nickel or on a catalyst based on the cobalt-molybdenum complex. In a particularly preferred manner, it is performed by means of a catalyst based on nickel.

The hydrogenation step uses advantageously part of the hydrogen available in the LVRG, preferably ROG.

A suitable physical process is advantageously performed by adsorption (step a7a3)), for example via a PSA (pressure swing adsorption), by absorption (step a7a4)) or via a membrane process (step a7a5)).

Step a7a2) is more particularly preferred.

Step a7a) is advantageously performed at a temperature between 25 and 100°C.

At least part of the nitrogen oxides (step a7b)) can be at least partially removed by a chemical step or by a physical step.

A suitable chemical step is advantageously performed by denox with ammonia or urea, preferably with urea (step a7b1)).

Another suitable chemical step is advantageously a hydrogenation step which can be catalyzed or not, preferably is catalyzed (step a7b2)). Suitable catalysts are advantageously palladium or nickel based catalysts, more preferably sulphided nickel catalysts.

The hydrogenation step may be performed by means of the same catalysts as those defined for the hydrogenation of oxygen, with the same preferences. The hydrogenation step uses advantageously part of the hydrogen available in the LVRG, preferably ROG.

Hydrogenation is preferred over denox.

A suitable physical process is advantageously performed by adsorption (step a7b3)), for example via a PSA (pressure swing adsorption), by absorption (step a7b4)) or via a membrane process (step a7b5)). Suitable adsorbents include activated copper, mineral clays, silica gel and activated alumina.

Step a7b2) and a7b3) are more particularly preferred.

Step a7b) is advantageously performed at a temperature between 25 and 100°C.

At least a partial removal of some of the reactive compounds is optionally performed (step a8)).

The reactive compounds removal (step a8)) may be performed in one or several group of steps, each comprising one or several steps.

A first group of steps (steps a8a)) comprises advantageously one or several steps of hydrogenation.

The partial hydrogenation of acetylene is advantageously performed in an acetylene converter by using a hydrogenation catalyst. After steps a8a), acetylene is advantageously at least partially hydrogenated. Suitable catalytic species include advantageously metals of group VIII, metals of group Ib and metals of group VIb. Catalysts based on palladium, on nickel or on gold are preferred. Catalysts based on palladium or on nickel are more preferred. Nickel based catalysts are most preferred with a particular preference for sulphided nickel catalysts. The hydrogenation catalysts may be supported or not. They are preferably supported. In other words, catalysts such as those defined for step a2b) may be used.

Organic compounds containing nitrogen present in the hydrogenation feed, are advantageously at least partially removed during hydrogenation steps a8a), preferably with a palladium or nickel based catalyst, more preferably with a sulphided nickel catalyst.

The organic compounds containing more that one atom of sulfur like disulfides can be partially hydrogenated during steps a8a).

Higher acetylenic compounds present in the hydrogenation feed including methylacetylene, propadiene and butadiene are advantageously at least partially hydrogenated during steps a8a), preferably with a palladium or nickel based catalyst, more preferably with a sulphided nickel catalyst.

Steps a8a) is advantageously performed at a temperature between 25 and 100°C.

A second group of steps (steps a8b)) comprises advantageously one or several steps of adsorption.

The adsorption is advantageously performed on chemically specific adsorbents in order to at least partially remove the other undesirable components.

The organic compounds containing more that one atom of sulfur like disulfides are advantageously at least partially removed via adsorption in a bed of a suitable material. Suitable adsorbents include advantageously carboneous material such as activated carbon and particularly activated carbon having a specific surface between 500 and 2500 m^2/g, molecular sieve 3, 4A or 13X, a zeolithe, a mesoporous adsorbent including activated alumina such as a mesoporous activated alumina with a specific BET surface between 150 m^2/g and 800 m^2/g, silica gel, a mesoporous silica gel adsorbent with a specific BET surface between 150 m^2/g and 800 m^2/g, a type A zeolithe, a type 5A zeolithe, a type X faujasite zeolithe, a type Y faujasite zeolithe and a MFI zeolithe. Preferred are activated carbon, molecular sieve 3 or 4A and activated alumina.

Phosphines, methanol and inorganic compounds containing chlorine may also be at least partially adsorbed during steps a8b).

Advantageously at least 1, preferably at least 2 adsorbents are used for the adsorption steps a8b). Advantageously at most 6, preferably at most 5, more preferably at most 4 adsorbents are used for the adsorption steps a8b). Most preferably 3 adsorbents are used. If realized, steps a8b) could be combined or not with steps a3).

The gas stream can contacted with the solid adsorbents in any suitable devices. Pneumatic conveying moving beds and fixed beds can be cited as suitable devices. Fixed beds are preferred.

The adsorbents can be arranged in mixed beds or in dedicated beds. They can be arranged in a single vessel or in separated vessels. The adsorbents are preferably arranged in dedicated beds, more preferably in 3 dedicated beds, and preferably in separated vessels.

Each adsorption step can be realized in one or several parallel beds. Each adsorption step is preferably realized in several parallel beds, more preferably in at least 2 separated beds.

Regeneration can be realized in the apparatus itself or outside the apparatus. Regeneration is preferably realized in the apparatus itself.

Steps a8b) are advantageously performed at a temperature between 25 and 100°C.

A third group of steps (steps a8c)) comprises advantageously one or several steps of absorption.

The absorption is advantageously performed with a suitable solvent, for example with dimethyletherpolyethylene glycol, in order to at least partially remove among others, organic compounds containing more than one atom of sulfur per molecule like disulfides

Diethanolamine and methanol can advantageously be at least partially removed during steps a8c).

The different steps mentioned before are not necessary performed in the order they are recited. They can be realized in any other order.

Step a4) is however advantageously the last step of the treatment steps.

All or some of the hydrogenation steps a2b), a7a2), a7b2) and a8a) can be advantageously combined. All or some of the adsorption steps a3a), a7a3), a7b3) and a8b) can be advantageously combined. All or some of the absorption steps a2a), a3b), a7a4), a7b4) and a8c) can be advantageously combined.

A preferred order according to which the treatment steps a2) and a3) take place is :

1. steps a3a),
2. steps a3b),
3. steps a2b),
4. steps a2a),
5. steps a2c), and

6. steps a2d).

When optional compression step a1) takes place, steps a3a), a3b), a2b) and a2c) are preferably intercalated before the last compression stage. When optional dedusting step(s) a1bis) takes place, it is preferably after steps a2d).

When optional cooling step a4) takes place, it is preferably the last step.

When step a5a) takes place, it is advantageously intercalated in the cooling steps a2c).

When step a5b) takes place, it is advantageously performed in several steps located in the cooling steps a2c) and/or step a4).

When step a6) takes place, it is advantageously intercalated in the cooling steps a2c).

When step a5a) and step a6) take place, they are advantageously combined.

When step a7a2) takes place, it is advantageously combined with steps a2b).

When step a7b2) takes place, it is preferably combined with steps a2b).

When step a7b3) takes place, it is preferably combined with steps a3a).

When steps a8a), a8b) and a8c) take place, they are advantageously combined respectively with steps a2b), a3a) and a3b).

A more preferred order according to which the treatment steps take place is :

1. first stage(s) of step a1) with the following steps intercalated before the last or unique compression stage,
2. steps a3a) combined with steps a8b) and step a7b3),
3. steps a3b) combined with steps a8c),
4. steps a2b) combined with step a7a2), steps a8a) and step a7b2),
5. steps a2a),
6. last compression stage of step a1),
7. steps a2c) combined with part of step a5b),
8. steps a2d),
9. step(s) a1bis), and
10. step a4) combined with part of step a5b).

A most preferred order according to which the treatment steps take place is :

1. first stage(s) of step a1) with the following steps intercalated before the last or unique compression stage,
2. steps a3a) combined with steps a8b) and step a7b3),

3. steps a3b) combined with steps a8c),
4. steps a2b) combined with step a7a2), steps a8a) and step a7b2),
5. steps a2a),
6. last compression stage of step a1),
7. steps a2c) combined with step a5a), step a6) and part of step a5b),
8. steps a2d),
9. step(s) a1bis), and
10. step a4) combined with part of step a5b).

Advantageously, in the process according to the invention, the mixture of products containing ethylene and other constituents derived from step a) comprises hydrogen, methane, ethane, ethylene, propane, hydrocarbons containing 4, 5 or 6 carbon atoms and heaviers C6+, inert gases, oxygenated compounds, reactive compounds and substantially reduced amount of corrosive compounds and of catalyst poisoning compounds.

Optionally, the content of inert gases is at least partially reduced versus their inlet content.

Optionally, the content of some of the reactive compounds is at least partially reduced versus their inlet content. Preferably, the content of some of the reactive compounds is at least partially reduced versus their inlet content.

Optionally, the content of the combustible gases (other than ethylene) is at least partially reduced versus their inlet content. Preferably, the content of some of the combustible gases having a normal boiling point higher than the normal boiling point of ethylene is at least partially reduced versus their inlet content. Advantageously, the content of some of the combustible gases having a normal boiling point lower than the normal boiling point of ethylene is at least partially reduced versus their inlet content. More preferably, the content of some of the combustible gases having a normal boiling point lower than the normal boiling point of ethylene and the content of some of the combustible gases having a normal boiling point higher than the normal boiling point of ethylene are at least partially reduced versus their inlet content.

The compositions which are given hereafter for the mixture of products containing ethylene and other constituents derived from step a), are expressed on dry gas basis (water not included).

The mixture of products containing ethylene and other constituents derived from step a) advantageously comprises at least 10, preferably at least 15, more preferably at least 20 % by volume of ethylene. It advantageously comprises at most 60, preferably at most 55, more preferably at most 50 % by volume of ethylene.

The mixture of products containing ethylene and other constituents derived from step a) is advantageously characterized by a lower heating value advantageously of at least 30, preferably of at least 33, more preferably of at least 35 and most preferably of at least 37 MJ/kg of the dry gas. The mixture of products containing ethylene and other constituents derived from step a) is advantageously characterized by a lower heating value advantageously of at most 75, preferably of at most 70, more preferably of at most 65 and most preferably of at most 60 MJ/kg of the dry gas.

The partial pressure of water comprised in the mixture of products containing ethylene and other constituents derived from step a) is advantageously lower than 55, preferably lower than 25, more preferably lower than 15 and most preferably lower than 10 mm of mercury.

The mixture of products containing ethylene and other constituents derived from step a) comprises each of the following constituent i.e. carbon dioxide, hydrogen sulfide, carbonyl sulfide, organic compounds containing one atom of sulfur per molecule like mercaptans and sulfides, sulfur oxides, ammonia, nitrides, nitriles, hydrogen chloride, hydrogen cyanide, mercury, arsenic (like arsines), vanadium, bromine, fluorine, silicon, aluminium and metal carbonyls, in a quantity which is advantageously of at most 5 %, preferably at most 2 % and more preferably at most 1 % of the quantity of the same constituent in the LVRG, preferably ROG, fed to step a) and/or formed during step a).

After step a) defined above, according to step b), the mixture of products containing ethylene and other constituents is fractionated in one fractionation step into one fraction containing almost all the ethylene (fraction A), optionally into one individual fraction of ethane and into one heavy fraction (fraction C).

Preferably, according to step b), the mixture of products containing ethylene and other constituents is separated into fraction A and into fraction C.

The expression "one fractionation step" is understood to mean, for the purpose of the present invention, that one and only one fractionation step is considered.

The term "fractionated" or "fractionation" in the expression "the mixture of products containing ethylene and other constituents is fractionated in one fractionation step", is understood to mean, for the purpose of the invention, the splitting of the mixture of products containing ethylene and other constituents in two or more sub-mixtures by a single separation (fractionation) step in such a way that at least one of the sub-mixture is characterized, at the specified pressure range, by a composition which is outside of the range defined by the composition of the mixture of products containing ethylene and other constituents at the bubble point and by the composition of the same mixture at the dew point.

The expression "fractionation step" in intended to mean any part of potentially multiple-step process which can be considered to have a single function. The fractionation step can be made in one or several interconnected apparatus.

The expression "bubble point" is understood to mean, for the purpose of the invention, the point such that, during the heating of the mixture of products containing ethylene and other constituents at constant pressure from a starting temperature, the mixture is at the liquid state where the first bubble of vapor is formed ; the bubble point composition being the composition of this first vapor bubble.

The expression "dew point" is understood to mean, for the purpose of the invention, the point such that, during the cooling of the mixture of products containing ethylene and other constituents at constant pressure from a starting temperature, the mixture is at the vapor state where the first bubble of liquid is formed, the dew point composition being the composition of this first liquid bubble.

The fractionation step advantageously involves a fractionation operation.

Examples of fractionation operations are distillation, extractive distillation, liquid-liquid extraction, pervaporation, gas-permeation, adsorption, pressure swing adsorption (PSA), absorption, chromatography, reverse osmosis and molecular filtration. Distillation, gas-permeation, pervaporation and PSA are preferred. Distillation is more preferred.

This fractionation step therefore more preferably consists in the fractionation of the mixture of products derived from step a) inside a main column (called column C) into two different fractions, namely fraction A which leaves at the top of column C and fraction C which leaves at the bottom of column C.

Prior to its introduction into column C, the mixture of products derived from step a) may be subjected to a heat conditioning step. The expression heat conditioning step is understood to mean a succession of heat exchanges optimizing the use of energy, for example the gradual cooling of the mixture of products in a train of exchangers first cooled with cooling water, and then with ice-cold water and then with increasingly cooled fluids plus cross exchangers recovering the sensible heat of the streams produced.

The said mixture of products may be introduced into the column C during step b) as a single fraction or as several subfractions. It is preferably introduced as several subfractions.

The main column C is advantageously a column comprising a stripping section and/or a rectifying section. If the two sections are present, the rectifying section preferably surmounts the stripping section.

The column C is advantageously chosen from distillation columns comprising the abovementioned two sections and the columns containing only one of the two sections. Preferably, the column C is a distillation column.

Step b) is therefore preferably a distillation step.

The column C is advantageously provided with the associated auxiliary equipment such as for example at least one reboiler and at least one condenser. Devices allowing intermediate drawing off and an intermediate heat exchange may be added to the main column.

Fraction A containing almost all the ethylene advantageously leaves at the top of column C whereas fraction C enriched with the least volatile compounds advantageously leaves at the bottom of column C.

The abovementioned step b) is advantageously performed at a pressure of at least 8, preferably of at least 10, more preferably of at least 12, most preferably of at least 20 and very most preferably of at least 27 bar. Step b) is advantageously performed at a pressure of at most 50, preferably of at most 45 and in a particularly preferred manner of at most 40 bar.

The temperature at which step b) is performed is advantageously at least -140, preferably at least -120, more preferably at least -110, most preferably at least -100°C at the top of column C1. It is advantageously at most -20, preferably at most -30, more preferably at most -50, most preferably at most -65 and very most preferably at most -80°C at the top of column C1.

The temperature at which step b) is performed is advantageously at least 0, preferably at least 10, more preferably at least 20°C at the bottom of column C1. It is advantageously at most 100, preferably at most 80, more preferably at most 70, most preferably at most 60°C at the bottom of column C1.

Pressure and temperature at which step b) is performed are advantageously selected so that one fraction containing almost all the ethylene (fraction A) is obtained after step b).

Particularly preferred pressure range is 20-50 bar with a preference for 27-38 bar.

Particularly preferred temperature range at the top of column C1 is -110 to -50°C with a preference for -100 to -80°C.

Particularly preferred temperature range at the bottom of column C1 is 0 to 100°C with a preference for 20 to -60°C.

Fraction A at the top of the column is advantageously partially condensed to supply the reflux ; the cooling power is advantageously supplied by an external low temperature cycle, an internal low temperature cycle by pressure release of part of the condensed matter or a mixture thereof, preferably by a mixture thereof. An energy recovery by turboexpension of the gas product is optionally used.

The phrase "one fraction containing almost all the ethylene" is understood to mean, for the purpose of the invention, that one and only one fraction containing almost all the ethylene is obtained after step b).

The phrase "fraction containing almost all the ethylene", is understood to mean, for the purpose of the invention, this fraction contains at least 90 % of the ethylene quantity which is contained in the mixture of products subjected to step b).

Preferably, fraction A contains at least 95 and more preferably at least 98 % of the ethylene quantity which is contained in the mixture of products subjected to step b).

The phrase "one heavy fraction" is understood to mean, for the purpose of the invention, that one and only one heavy fraction is obtained after step b).

The quantities defined below to characterize fraction A and fraction C are those for these fractions leaving the step b).

Fraction A is advantageously enriched with compounds which are lighter than ethylene. These compounds are generally methane, nitrogen, oxygen, hydrogen and carbon monoxide. Advantageously, fraction A contains at least 80 %, preferably at least 90 % and in a particularly preferred manner at least 95 % of compounds lighter than ethylene which are contained in the mixture of products subjected to step b).

Fraction A is advantageously characterized by a volume content of inert gases lower than 30, preferably lower than 25 and more preferably lower than 20 %.

Fraction A is advantageously characterized by a total amount of oxygenated compounds lower than the level needed to make the gaseous mixture flammable, preferably by a volume content lower than 15, preferably lower than 12 and more preferably lower than 10 %.

Fraction A is advantageously characterized by a volume content of oxygen lower than 9 %, preferably lower than 8 % and more preferably lower than 7 %.

Fraction A is advantageously characterized by a volume content of nitrogen oxides lower than 0.00025 %, preferably lower than 0.0002 % and more preferably lower than 0.00015 %.

Fraction A is advantageously characterized by a volume content of corrosive compounds lower than 0.2 %, preferably lower than 0.1 % and more preferably lower than 0.08 %.

Fraction A is advantageously characterized by a volume content of hydrogen sulfide lower than 0.005 %, preferably lower than 0.001 % and more preferably lower than 0.0005 %.

Fraction A is advantageously characterized by a volume content of reactive compounds lower than 2 %, preferably lower than 1 % and more preferably lower than 0.8 %.

Fraction A is advantageously characterized by a volume content of reactive compounds other than carbon monoxide lower than 0.02 %, preferably lower than 0.01 % and more preferably lower than 0.005 %.

Fraction A is advantageously characterized by a volume content of acetylene lower than 0.2 %, preferably lower than 0.1 %, more preferably lower than 0.05 % and most preferably lower than 0.02 %.

Fraction A is characterized by a content of compounds containing at least 3 carbon atoms, advantageously less than or equal to 0.1 %, preferably less than or equal to 0.05 % and in a particularly preferred manner less than or equal to 0.01 % by volume relative to the total volume of fraction A.

Fraction A is advantageously characterized by a volume content of catalyst poisoning compounds lower than 0.001 %, preferably lower than 0.0005 % and more preferably lower than 0.0002 %.

Fraction C advantageously contains compounds comprising at least 3 carbon atoms. Advantageously, these compounds comprising at least 3 carbon atoms result from the mixture of products containing ethylene and other constituents derived from step a) or are generated by side reactions during step b). Among the compounds comprising at least 3 carbon atoms, there may be mentioned propane, propylene, butanes and their unsaturated derivatives as well as all the saturated or unsaturated heavier compounds.

Fraction C advantageously contains at least 95 %, preferably at least 98 % and particularly preferably at least 99 % of compounds comprising at least 3 carbon atoms contained in the mixture of products subjected to step b).

Fraction C advantageously contains at most 1 %, preferably at most 0.8 % and particularly preferably at most 0.5 % by weight of ethylene relative to the total weight of fraction C.

Fraction C is advantageously enriched in components heavier than ethylene. Preferably, fraction C is burnt as fuel or valorised chemically. More preferably, fraction C is valorised chemically.

In the case the LVRG, preferably ROG, is very rich in ethane, it can be interesting to isolate the ethane in order to valorize it. In these circumstances, the process according to the invention can be adapted so that ethane is directed to fraction A, to fraction C or be isolated as an individual fraction.

In the case ethane is directed to fraction C, ethane can be separated by fractionation from the heavier hydrocarbons present in fraction C by the use of a further distillation column. Ethane can also be recovered by drawing it off from the side of the distillation column used to isolate fraction C (drawn at the bottom) from fraction A, or by using a dividing wall column instead of a conventional distillation column when isolating fraction C.

In the case ethane is directed to the fraction directed to chlorination, ethane can be recovered from the gaseous effluent of the chlorination, preferably by an intermediate step of gas-permeation, pervaporation or pressure swing adsorption.

In the case ethane is isolated as an individual fraction, it can be separated fractionated from the other fractions during step b).

After having been recovered, ethane can be burnt as fuel or valorized chemically. Ethane is preferably valorized chemically. Ethane is therefore more preferably subjected to an oxydehydrogenation (ODH) as described in patent applications WO2008/000705, WO2008/000702 and WO2008/000693 in order to generate ethylene afterwards subjected to oxychlorination.

After step b) defined above, according to step c), fraction A is conveyed to the manufacture of at least one ethylene derivative compound.

Before step c), fraction A is optionally subjected to an acetylene hydrogenation step followed optionally by a drying step, in particular when directed to the manufacture of DCE and optionally of any compound derived there from. Preferably, fraction A directed to the manufacture of DCE and optionally of any compound derived there from is subjected to an acetylene hydrogenation. More preferably, fraction A directed to the manufacture of DCE by direct chlorination is subjected to an acetylene hydrogenation step followed by a drying step. More preferably, fraction A directed to the manufacture of DCE by oxychlorination is subjected to an acetylene hydrogenation without a drying step.

The hydrogenation of acetylene is advantageously performed as described previously for step a8a).

Advantageously, in case of such acetylene hydrogenation of fraction A, treated fraction A is advantageously characterized by a acetylene volume content lower than 0.01 %, preferably lower than 0.005 %, more preferably lower than 0.002 % and most preferably lower than 0.001%.

According to a first embodiment of the process according to the invention, fraction A is advantageoulsy conveyed in one fraction to the manufacture of one ethylene derivative compound.

According to this first embodiment, the process is advantageously such that, after steps a) and b), c) fraction A is conveyed in one fraction to the manufacture of one ethylene derivative compound, preferably to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation.

According to a first variant of the first embodiment, the process is advantageously such that, after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of DCE, optionally after having been subjected to an acetylene hydrogenation, in a chlorination reactor in which most of the ethylene present in fraction A is converted to DCE by reaction with molecular chlorine ;
d) the DCE obtained is separated from the stream of products derived from the chlorination reactor ;
e) the separated DCE is subjected to a DCE cracking step thus producing VC and hydrogen chloride ; and
f) the VC and hydrogen chloride obtained are separated from the stream of products derived from the DCE cracking step.

The chlorination reaction (usually called direct chlorination) is advantageously carried out in a liquid phase (preferably mainly DCE) containing a dissolved catalyst such as $FeCl_3$ or another Lewis acid. It is possible to advantageously combine this catalyst with cocatalysts such as alkali metal chlorides. A pair which has given good results is the complex of $FeCl_3$ with LiCl (lithium tetrachloroferrate – as described in Patent Application NL 6901398).

The amounts of $FeCl_3$ advantageously used are around 1 to 30 g of $FeCl_3$ per kg of liquid stock. The molar ratio of $FeCl_3$ to LiCl is advantageously of the order of 0.5 to 2.

In addition, the chlorination reaction is preferably performed in a chlorinated organic liquid medium. More preferably, this chlorinated organic liquid medium, also called liquid stock, mainly consists of DCE.

The chlorination reaction according to the invention is advantageously performed at temperatures between 30 and 150°C. Good results were obtained regardless of the pressure both at a temperature below the boiling point (chlorination process under subcooled conditions) and at the boiling point itself (process for chlorination at boiling point).

When the chlorination process according to the invention is a chlorination process under subcooled conditions, it gave good results by operating at a temperature which was advantageously greater than or equal to 50°C and preferably greater than or equal to 60°C, but advantageously less than or equal to 80°C and preferably less than or equal to 70°C, and with a pressure in the gaseous phase advantageously greater than or equal to 1 and preferably greater than or equal to 1.1 bar absolute, but advantageously less than or equal to 20, preferably less than or equal to 10 and particularly preferably less than or equal to 6 bar absolute.

A process for chlorination at boiling point may be preferred to usefully recover the heat of reaction. In this case, the reaction advantageously takes place at a temperature greater than or equal to 60°C, preferably greater than or equal to 70°C and particularly preferably greater than or equal to 85°C, but advantageously less than or equal to 150°C and preferably less than or equal to 135°C, and with a pressure in the gaseous phase advantageously greater than or equal to 0.2, preferably greater than or equal to 0.5, particularly preferably greater than or equal to 1.1 and more particularly preferably greater than or equal to 1.3 bar absolute, but advantageously less than or equal to 10 and preferably less than or equal to 6 bar absolute.

The chlorination process may also be a hybrid loop-cooled process for chlorination at boiling point. The expression "hybrid loop-cooled process for chlorination at boiling point" is understood to mean a process in which cooling of the reaction medium is carried out, for example, by means of an exchanger immersed in the reaction medium or by a loop circulating in an exchanger, while producing in the gaseous phase at least the amount of DCE formed. Advantageously, the reaction temperature and pressure are adjusted for the DCE produced to leave in the gaseous phase and for the remainder of the heat from the reaction medium to be removed by means of the exchange surface area.

Fraction submitted to the chlorination and also the molecular chlorine (itself pure or diluted) may be introduced, together or separately, into the reaction medium by any known device. A separate introduction of the fraction submitted to the chlorination may be advantageous in order to increase its partial pressure and facilitate its dissolution which often constitutes a limiting step of the process.

The molecular chlorine is added in a sufficient amount to convert most of the ethylene and without requiring the addition of an excess of unconverted chlorine. The chlorine/ethylene ratio used is preferably between 1.2 and 0.8 and particularly preferably between 1.05 and 0.95 mol/mol.

The chlorinated products obtained contain mainly DCE and also small amounts of by-products such as 1,1,2-trichloroethane or small amounts of ethane or methane chlorination products.

The separation of the DCE obtained from the stream of products derived from the chlorination reactor is carried out according to known modes and in general makes it possible to exploit the heat of the chlorination reaction. It is then preferably carried out by condensation and gas/liquid separation.

The unconverted products (methane, ethane, carbon monoxide, nitrogen, oxygen and hydrogen) are then advantageously subjected to an easier separation than what would have been necessary to separate pure ethylene starting from the initial mixture.

Hydrogen in particular can be extracted from the unconverted products and be valorized as for example for the hydrogenation of working solution in hydrogen peroxide manufacture or for the direct synthesis of hydrogen peroxide.

The conditions under which the DCE cracking step may be carried out are known to persons skilled in the art. The DCE cracking can be performed in the presence or in the absence of third compounds among which can be cited the catalysts ; the DCE cracking is in this case a catalytic DCE cracking. The DCE cracking is however preferably performed in the absence of third compounds and under the action of heat only ; the DCE cracking is in this case often called pyrolysis.

This pyrolysis is advantageously obtained by a reaction in the gaseous phase in a tubular oven. The usual pyrolysis temperatures are between 400 and 600°C with a preference for the range between 480°C and 540°C. The residence time is advantageously between 1 and 60 seconds with a preference for the range from 5 to 25 seconds. The rate of conversion of the DCE is advantageously limited to 45 to 75 % in order to limit the formation of by-products and the fouling of the tubes of the oven.

The separation of the VC and hydrogen chloride obtained from the stream of products derived from the pyrolysis is carried out according to known modes, using any known device, in order to collect the purified VC and the hydrogen chloride. Following purification, the unconverted DCE is advantageously conveyed to the pyrolysis oven.

According to the first variant of the first embodiment, VC is afterwards preferably polymerized to produce PVC.

The manufacture of PVC may be a mass, solution or aqueous dispersion polymerization process, preferably it is an aqueous dispersion polymerization process.

The expression aqueous dispersion polymerization is understood to mean free radical polymerization in aqueous suspension as well as free radical polymerization in aqueous emulsion and polymerization in aqueous microsuspension.

The expression free radical polymerization in aqueous suspension is understood to mean any free radical polymerization process performed in aqueous medium in the presence of dispersing agents and oil-soluble free radical initiators.

The expression free radical polymerization in aqueous emulsion is understood to mean any free radical polymerization process performed in aqueous medium in the presence of emulsifying agents and water-soluble free radical initiators.

The expression aqueous microsuspension polymerization, also called polymerization in homogenized aqueous dispersion, is understood to mean any free radical polymerization process in which oil-soluble initiators are used and an emulsion of droplets of monomers is prepared by virtue of a powerful mechanical stirring and the presence of emulsifying agents.

After separation, hydrogen chloride may be used for any purpose. It can for example be conveyed to the synthesis of compounds like calcium chloride, chloro(s) alcohol(s) among which chloro(s) propanol(s) by reaction with 1,2-propanediol, 1,3-propanediol or 1,2,3-propanetriol (glycerin or glycerol leading to the synthesis of epichlorhydrin), chloro(s) alcane(s) among which chloro(s) methane by reaction with methanol, aqueous hydrochloric acid, ferric chloride, aluminium chloride, chlorosilanes, titanium chloride, zinc chloride, other inorganic chlorides like ammonium chloride but also to oxychlorination processes for example of aromatic compounds, hydrochlorination of alkynes (for example hydrochlorination of acetylene into VC) or of alkenes or be oxidized to molecular chlorine.

After separation according to step f) of the first variant of the first embodiment of the process according to the invention, g) hydrogen chloride is preferably subjected to an oxidation into molecular chlorine which is afterwards more preferably recycled to the chlorination reactor.

A particular preferred process is therefore such that, after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of DCE, optionally after having been subjected to an acetylene hydrogenation, in a chlorination reactor in which most of the ethylene present in fraction A is converted to DCE by reaction with molecular chlorine ;
d) the DCE obtained is separated from the stream of products derived from the chlorination reactor ;
e) the separated DCE is subjected to a DCE cracking step thus producing VC and hydrogen chloride ;
f) the VC and hydrogen chloride obtained are separated from the stream of products derived from the DCE cracking step ; and
g) hydrogen chloride is subjected to an oxidation into molecular chlorine which is afterwards recycled to the chlorination reactor.

The oxidation of the separated hydrogen chloride into molecular chlorine can be made according to any known process.

Among those known processes may be cited the electrolysis of hydrochloric acid, the catalytic oxidation processes of hydrogen chloride by oxygen like the KEL chlorine process called Kellogg (using concentrated sulfuric acid and nitrosylsulfuric acid as catalyst), the Shell-Deacon process (using a mixture of copper(II) chloride and other metallic chlorides on a silicate carrier as catalyst) and modified Deacon processes like the Mitsui-Toatsu (MT-Chlorine) process (using a chromium(III) oxide on a silicate carrier as catalyst) as well as the oxidation of hydrogen chloride by nitric acid.

Catalytic oxidation of hydrogen chloride by oxygen is preferred for the process according to the invention. This oxidation is advantageously performed with a gas containing oxygen.

As the gas containing oxygen, molecular oxygen or air can be used. Oxygen may be produced by usual industrial methods such as pressure-swing method of air or deep-cooling separation of air.

While the theoretical molar amount of oxygen necessary for oxidizing one mole of hydrogen chloride is 0.25 mole, it is preferable to use oxygen in an amount exceeding the theoretical amount, and more preferably, 0.25 to 2 moles of oxygen is used per one mole of hydrogen chloride.

The catalyst used in the oxidation reaction according to the present invention may be any known catalyst that is used in the production of chlorine through the oxidation of hydrogen chloride.

Examples of catalysts are copper-based catalysts as in the Deacon process, chromium oxide, ruthenium oxide or mixture of ruthenium oxide and titanium oxide. Deacon catalysts comprises advantageously copper chloride, potassium chloride and various kinds of compounds a third components.

The shape of the catalyst may be any of conventionally used shapes such as a spherical particle, a cylindrical pellet, an extruded form, a ring form, a honeycomb form, or a granule having a suitable size which is produced by milling of a molded material followed by sieving. The size of the catalyst is preferably 10 mm or less. Although the lower limit of the size of the catalyst may not be limited, the size of the catalyst is advantageously at least 0.1 mm. Herein, the size of the catalyst means a diameter of a sphere in the case of the spherical particle, a diameter of a cross section in the case of the cylindrical pellet or the largest size of the cross section in the case of other forms.

It can be interesting to divide the gas containing oxygen into portions and introduced it in at least two reaction zones.

The oxidation reaction is advantageously carried out in at least two reaction zones each comprising a catalyst-packed layer, preferable arranged in series.

The reaction pressure is advantageously from 0.1 to 5 MPa. The reaction temperature is advantageously from 200 to 650°C, more preferably from 200 to 500°C.

The reactors are advantageously tubular reactors, the inner diameter of which are preferably from 10 to 50 mm, more preferably from 10 to 40 mm.

The molecular chlorine is more preferably recycled to the chlorination reactor. The recycling can be made according to any known process. The molecular chlorine is advantageously first dried and then put at the required pressure for entering chlorination. The drying is advantageously performed either by a compression with a condensation at the outlet or with the use of a column with sulfuric acid or with an adsorbent compatible with chlorine, preferably with a column with sulfuric acid.

According to a second variant of the first embodiment, the process is preferably such that, after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of DCE, optionally after having been subjected to an acetylene hydrogenation, in a chlorination reactor in which at most 90 % of the ethylene present in fraction A is converted to DCE by reaction with molecular chlorine ;

d) the DCE formed in the chlorination reactor is optionally isolated from the stream of products derived from the chlorination reactor ;

e) the stream of products derived from the chlorination reactor, from which the DCE has optionally been extracted, is conveyed to an oxychlorination reactor in which the majority of the balance of ethylene is converted to DCE, after optionally having subjected the latter to an absorption/desorption step e'), during which the DCE formed in the chlorination reactor is optionally extracted if it has not previously been extracted ; and

f) the DCE formed in the oxychlorination reactor is isolated from the stream of products derived from the oxychlorination reactor and is optionally added to the DCE formed in the chlorination reactor.

According to this second variant of the first embodiment, DCE is advantageously further subjected to a DCE cracking step to produce VC and VC is afterwards preferably polymerized to produce PVC.

Reference is made to the first variant of the first embodiment for the details about the chlorination reaction in the particular case of the second variant of the first embodiment except for the flow of chlorine detailed here after.

The flow of chlorine is such that advantageously at least 10 %, preferably at least 20 % and particularly preferably at least 30 % of the ethylene is converted to DCE. The flow of chlorine is such that advantageously at most 90 %, preferably at most 80 % and particularly preferably at most 70 % of the ethylene is converted to DCE.

According to step d) of the second variant of the first embodiment, the DCE formed in the chlorination reactor is optionally isolated from the stream of products derived from the chlorination reactor. In certain cases it may be advantageous not to isolate the DCE formed in the chlorination reactor from the stream of products derived from the chlorination reactor. Preferably however, the DCE formed in the chlorination reactor is isolated from the stream of products derived from the chlorination reactor.

When it takes place, the separation of the DCE obtained from the stream of products derived from the chlorination reactor is carried out according to known methods and in general makes it possible to exploit the heat of the chlorination reaction. It is then preferably carried out by condensation and gas/liquid separation.

According to step e) of the second variant of the first embodiment, the stream of products derived from the chlorination reactor, from which the DCE has optionally been extracted, is conveyed to an oxychlorination reactor in which the majority of the balance of ethylene is converted to DCE, after optionally having subjected the latter to an absorption/desorption step e'), during which the DCE formed in the chlorination reactor is optionally extracted if it has not previously been extracted ;

The oxychlorination reaction is advantageously performed in the presence of a catalyst comprising active elements including copper deposited on an inert support. The inert support is advantageously chosen from alumina, silica gels, mixed oxides, clays and other supports of natural origin. Alumina constitutes a preferred inert support.

Catalysts comprising active elements which are advantageously at least two in number, one of which is copper, are preferred. Among the active elements other than copper, mention may be made of alkali metals, alkaline-earth metals, rare-earth metals and metals from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum and gold. The catalysts containing the following active elements are particularly advantageous : copper/magnesium/potassium, copper/magnesium/sodium ; copper/magnesium/ lithium, copper/magnesium/caesium, copper/magnesium/sodium/lithium, copper/ magnesium/potassium/lithium and copper/magnesium/caesium/lithium, copper/ magnesium/sodium/potassium, copper/magnesium/sodium/caesium and copper/ magnesium/potassium/caesium. The catalysts described in Patent Applications EP-A 255 156, EP-A 494 474, EP-A-657 212 and EP-A 657 213, incorporated by reference, are most particularly preferred.

The copper content, calculated in metal form, is advantageously between 30 and 90 g/kg, preferably between 40 and 80 g/kg and particularly preferably between 50 and 70 g/kg of catalyst.

The magnesium content, calculated in metal form, is advantageously between 10 and 30 g/kg, preferably between 12 and 25 g/kg and particularly preferably between 15 and 20 g/kg of catalyst.

The alkali metal content, calculated in metal form, is advantageously between 0.1 and 30 g/kg, preferably between 0.5 and 20 g/kg and particularly preferably between 1 and 15 g/kg of catalyst.

The Cu:Mg:alkali metal(s) atomic ratios are advantageously 1:0.1-2:0.05-2, preferably 1:0.2-1.5:0.1-1.5 and particularly preferably 1:0.5-1:0.15-1.

Catalysts having a specific surface area, measured according to the BET method with nitrogen that is advantageously between 25 m^2/g and 300 m^2/g, preferably between 50 and 200 m^2/g and particularly preferably between 75 and 175 m^2/g, are particularly advantageous.

The catalyst may be used in a fixed bed or in a fluidized bed. This second option is preferred. The oxychlorination process is operated under the range of the conditions usually recommended for this reaction. The temperature is advantageously between 150 and 300°C, preferably between 200 and 275°C and most preferably from 215 to 255°C. The pressure is advantageously above atmospheric pressure. Values of between 2 and 10 bar absolute gave good results. The range between 4 and 7 bar absolute is preferred. This pressure may be usefully adjusted in order to attain an optimum residence time in the reactor and to maintain a constant rate of passage for various operating speeds. The usual residence times range from 1 to 60 s and preferably from 10 to 40 s.

The source of oxygen for this oxychlorination may be air, pure oxygen or a mixture thereof, preferably pure oxygen. The latter solution, which allows easy recycling of the unconverted reactants, is preferred.

The reactants may be introduced into the bed by any known device. It is generally advantageous to introduce the oxygen separately from the other reactants for safety reasons. These safety reasons also require the gaseous mixture leaving the reactor or recycled thereto to be kept outside the limits of inflammability at the pressures and temperatures in question. It is preferable to maintain a so-called rich mixture, that is to say containing too little oxygen relative to the fuel to ignite. In this regard, the abundant presence (> 2 vol %, preferably > 5 vol %) of hydrogen would constitute a disadvantage given the wide range of inflammability of this compound.

The hydrogen chloride/oxygen ratio used is advantageously between 3 and 6 mol/mol. The ethylene/hydrogen chloride ratio is advantageously between 0.4 and 0.6 mol/mol.

The chlorinated products obtained contain mainly DCE and also small amounts of by-products such as 1,1,2-trichloroethane.

In certain cases, it may be advantageous, before entering into the oxychlorination reactor, to subject the stream of products derived from the chlorination reactor, from which the DCE has optionally been extracted, to the absorption/desorption step e'), during which the DCE formed in the chlorination reactor is optionally extracted if it has not previously been extracted.

The expression "step e'), during which the DCE formed in the chlorination reactor is optionally extracted if it has not previously been extracted" is understood to mean that the DCE formed in the chlorination reactor may be extracted during step e') if this step takes place and if it has not previously been extracted. Preferably, the DCE formed in the chlorination reactor is extracted during step e') if this step takes place and if it has not previously been extracted.

Thus, the stream of products derived from the chlorination reactor, from which the DCE has optionally been extracted, (known hereinafter as chlorination stream) is advantageously subjected to an absorption step and to a desorption step in which said stream is preferably brought into contact with a washing agent containing a solvent.

The expression "washing agent containing a solvent" or more simply "washing agent" is understood to mean a composition in which the solvent is present in the liquid state.

The washing agent that can be used according to the present invention therefore advantageously contains a solvent in the liquid state. The presence, in said washing agent, of other compounds is not at all excluded from the scope of the invention. However, it is preferred that the washing agent contain at least 50 % by volume of the solvent, more particularly at least 65 % by volume and most particularly preferably at least 70 % by volume.

The solvent is advantageously chosen among the alcohols, glycols, polyols, ethers, mixtures of glycol(s) and ether(s), mineral oils as well as DCE. The solvent is preferably chosen among the alcohols, the mineral oils and DCE and more preferably among azeotropic ethanol (aqueous ethanol with advantageously at least 70, preferably at least 80 and more preferably at least 85 % by volume of ethanol) and DCE. The solvent is most preferably DCE.

The washing agent used for the absorption step may be composed of fresh washing agent of any origin, for example crude azeotropic ethanol or crude DCE exiting the chlorination unit, crude DCE exiting the oxychlorination unit or a mixture of the two which has not been purified. It may also be composed of said DCE that has been previously purified or all or part of the washing agent recovered during the desorption step explained below optionally containing the DCE formed in the chlorination reactor and extracted in the desorption step, after an optional treatment making it possible to reduce the concentration, in the DCE, of the compounds that are heavier than ethane, as explained below, optionally with the addition of fresh washing agent.

Preferably, the washing agent used for the absorption step is composed of all or part of the washing agent recovered during the desorption step optionally containing the DCE formed in the chlorination reactor and extracted in the desorption step, after the abovementioned optional treatment, optionally with the addition of fresh washing agent. In the case where the DCE formed in the chlorination reaction is isolated from the stream of products derived from the chlorination reactor at the chlorination outlet, in a particularly preferred manner, the washing agent used for the absorption step is composed of all or part of the washing agent recovered during the desorption step, after the aforementioned optional treatment, with the addition of fresh washing agent (to compensate for losses of washing agent during the absorption and desorption steps).

The abovementioned optional treatment making it possible to reduce the concentration, in the washing agent, of the compounds that are heavier than ethane, preferably of the compounds comprising at least 3 carbon atoms, may be a step of desorbing the compounds that are heavier than ethane and lighter than the washing agent or a step of distilling the washing agent. Preferably, it consists of desorbing the compounds that are heavier than ethane and lighter than the washing agent. Preferably, this treatment of the washing agent takes place.

An essential advantage of the most preferred case when DCE is the washing agent, lies in the fact that the presence of this DCE is not at all troublesome, as it is the compound mainly formed during the oxychlorination or chlorination.

The ratio between the respective throughputs of washing agent and the chlorination stream is not critical and can vary to a large extent. It is in practice limited only by the cost of regenerating the washing agent. In general, the throughput of washing agent is at least 1, preferably at least 5 and particularly preferably at least 10 tonnes per tonne of chlorination stream. In general, the throughput of washing agent is at most 100, preferably at most 50 and particularly preferably at most 25 tonnes per tonne of the ethylene and ethane mixture to be extracted from the chlorination stream.

The absorption step is advantageously carried out by means of an absorber such as, for example, a climbing film or falling film absorber or an absorption column chosen from plate columns, columns with random packing, columns with structured packing, columns combining one or more of the aforementioned internals and spray columns. The absorption step is preferably carried out by means of an absorption column and particularly preferably by means of a plate absorption column.

The absorption column is advantageously equipped with associated accessories such as, for example, at least one condenser or chiller that is internal or external to the column.

The abovementioned absorption step is advantageously carried out at a pressure of at least 15, preferably of at least 20 and particularly preferably of at least 25 bar absolute. The absorption step is advantageously carried out at a pressure of at most 40, preferably at most 35 and particularly preferably at most 30 bar absolute.

The temperature at which the absorption step is carried out is advantageously at least -10, preferably at least 0 and particularly preferably at least 10°C at the top of the absorber or absorption column. It is advantageously at most 60, preferably at most 50 and particularly preferably at most 40°C at the top of the absorber or absorption column.

The temperature at the bottom of the absorber or absorption column is at least 0, preferably at least 10 and particularly preferably at least 20°C. It is advantageously at most 70, preferably at most 60 and particularly preferably at most 50°C.

The stream resulting from the absorption step, which is the chlorination stream purified of compounds that are lighter than ethylene and enriched in washing agent is advantageously subjected to the desorption step.

The washing agent recovered after the desorption step optionally containing the DCE formed in the chlorination reactor then extracted may be removed, completely or partly conveyed to the oxychlorination sector where the DCE comes together with the DCE formed in the oxychlorination reactor, or completely or partly reconveyed to the absorption step, optionally after the abovementioned treatment, with the optional addition of fresh washing agent. Preferably, the washing agent recovered after the desorption step is completely or partly reconveyed to the absorption step, after the abovementioned optional treatment, with optional addition of fresh washing agent, or to the oxychlorination sector. In the case where the DCE formed in the chlorination reactor is isolated from the stream of products derived from the chlorination reactor at the chlorination outlet, in a particularly preferred manner, the washing agent recovered after the desorption step is completely or partly reconveyed to the absorption step, after the abovementioned optional treatment, with addition of fresh washing agent.

The desorption step is advantageously carried out by means of a desorber such as, for example, a climbing film or falling film desorber, a reboiler or a desorption column chosen from plate columns, columns with random packing, columns with structured packing, columns combining one or more of the aforementioned internals and spray columns. The desorption can also be performed by direct injection of vapour in order to collect DCE. The desorption step is preferably carried out by means of a desorption column and particularly preferably by means of a plate desorption column.

The desorption column is advantageously equipped with associated accessories such as, for example, at least one condenser or one chiller that is internal or external to the column and at least one reboiler.

The desorption pressure is advantageously chosen so that the content of compounds having at least 3 carbon atoms in the desorbed gas is less than 100 ppm, preferably less than or equal to 50 ppm and particularly preferably less than or equal to 20 ppm by volume.

The abovementioned desorption step is advantageously carried out at a pressure of at least 1, preferably at least 2 and particularly preferably at least 3 bar absolute. The desorption step is advantageously carried out at a pressure of at most 20, preferably at most 15 and particularly preferably at most 10 bar absolute.

The temperature at which the desorption step is carried out is advantageously at least -10, preferably at least 0 and particularly preferably at least 10°C at the top of the desorber or desorption column. It is advantageously at most 60, preferably at most 50 and particularly preferably at most 45°C at the top of the desorber or desorption column.

The temperature at the bottom of the desorber or desorption column is at least 60, preferably at least 80 and particularly preferably at least 100°C. It is advantageously at most 200, preferably at most 160 and particularly preferably at most 150°C.

A most particular preference is attached to the case where the absorption step is carried out in an absorption column and the desorption step in a desorption column.

The hydrogen recovered following the absorption step is advantageously developed as a fuel or as a reactant, optionally after a purification step. Thus, the hydrogen may be developed as a fuel in the DCE cracking step. It may also be developed as a reactant for a hydrogenation reaction for example.

According to step f) of the second variant of the first embodiment, the DCE formed in the oxychlorination reactor is isolated from the stream of products derived from the oxychlorination reactor and is optionally added to the DCE formed in the chlorination reactor.

The separation of the DCE obtained from the stream of products derived from the oxychlorination reactor is carried out according to known methods. It is preferably carried out first by condensation. The heat of the oxychlorination reactor is generally recovered in the vapour state which may be used for the separations or for any other use.

After exiting from the oxychlorination reactor, the stream of products derived from the reactor is also advantageously washed to recover the unconverted HCl. This washing operation is advantageously an alkaline washing step. It is preferably followed by a gas/liquid separation step which makes it possible to recover the DCE formed in liquid form and finally to dry the DCE.

The expression "is optionally added to the DCE formed in the chlorination reactor" is understood to mean that if the DCE formed in the chlorination reactor is isolated from the stream of products derived from this reactor, on exiting the chlorination reactor or after step e'), the DCE formed in the oxychlorination reactor may or may not be added thereto. Preferably, it is added thereto. If on the other hand, this first DCE is not isolated, the DCE isolated from the stream of products derived from the oxychlorination reactor is advantageously the only stream of DCE recovered. Another alternative is advantageously to mix the DCE isolated from the stream of products derived from the oxychlorination reactor with a part of the DCE isolated from the stream of products derived from the chlorination reactor and to send the other part of this latter directly to the DCE cracking step.

Reference is made to the first variant of the first embodiment for more details about the DCE cracking step and about the separation of the VC obtained from the stream of products derived from the DCE cracking step.

According to this second variant of the first embodiment, VC is afterwards preferably polymerized to produce PVC. Reference is made to the first variant of the first embodiment for more details about the manufacture of PVC.

According to a second embodiment of the process according to the invention, fraction A is advantageoulsy divided into at least two fractions of the same composition or of different composition, preferably into fraction A1 and fraction A2 of the same composition or of different composition.

According to this second embodiment, the process is advantageously such that, after steps a) and b), c) fraction A is divided into at least two fractions, preferably into fraction A1 and fraction A2, of the same composition or of different composition before being conveyed to the manufacture of at least one ethylene derivative compound.

The term “divided” (or “division”) in the expression “fraction A is divided into at least two fractions” is understood to mean, for the purpose of the invention, the splitting of fraction A into two or more sub-mixtures in such a way that all the sub-mixtures are characterized, at the specified pressure range, by a composition which is comprised in the range defined by the composition of fraction A at the bubble point and by the composition of fraction A at the dew point.

The division of fraction A into at least two fractions, preferably into fraction A1 and fraction A2, is advantageously operated by divided fraction A into several, preferably two, fractions of the same composition or of different composition by means of any known means.

The division step can be made in one or several apparatus. The division step advantageously involves a division operation. Examples of division operations are division of a mixture in sub-mixtures having identical composition, partial condensation of a gaseous mixture, partial vaporization of a liquid mixture, partial solidification of a liquid mixture.

The case when fraction A is divided into at least two, preferably into fraction A1 and fraction A2, of the same composition is particularly interesting when the mixture of products containing ethylene and other constituents leaving step a) can simply be divided, preferably by two, preferably when the mixture of products leaving step a) is poor in hydrogen and/or rich in compounds reacting with hydrogen during hydrogenation steps or when step a8) is performed.

The case when fraction A is divided into at least two fractions, preferably into fraction A1 and fraction A2, of different composition is particularly interesting when fractions of different composition are required for step c). Fraction A is therefore advantageously divided into at least two fractions, preferably into fraction A1 and fraction A2, of different composition so that each fraction can be conveyed to the respective manufacture of ethylene derivative compound.

The division of fraction A into at least two fractions, preferably into fraction A1 and fraction A2 of different composition, can be made by any known means. Preferably, fraction A is cooled down by indirect cooling in a heat exchanger where fraction A2 is vaporized after expansion to a suitable pressure and overcooled by indirect contact in an heat exchanger cooled with a suitable cooling media up to a defined lowering of its temperature. The liquid vapor is preferably divided to produce the vapor fraction A1 and the liquid fraction A2. The temperature lowering is advantageously greater than 5, preferably greater than 7 and more preferably greater than 8°C. The temperature lowering is advantageously lower than 30, preferably lower than 25 and more preferably lower than 22°C.

Fraction A1 advantageously contains more than 10, preferably more than 20 and more preferably more than 25 % the ethylene quantity which is contained in fraction A. Fraction A1 advantageously contains less than 90, preferably less than 80 and more preferably less than 75 % the ethylene quantity which is contained in fraction A.

Fraction A1 advantageously contains more than 80, preferably more than 85 and more preferably more than 90 % the hydrogen quantity which is contained in fraction A.

Fraction A1 advantageously contains more than 70, preferably more than 75 and more preferably more than 80 % the methane quantity which is contained in fraction A.

Fraction A1 advantageously contains less than 40, preferably less than 30 and more preferably less than 25 % of the ethane quantity which is contained in fraction A.

According to a first variant of the second embodiment, the process is advantageously such that, after steps a) and b),

c) fraction A is divided into fraction A1 and fraction A2 of the same composition or of different composition, fraction A1 and fraction A2 being conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation.

The process according to this first variant of the second embodiment is preferably such that, after steps a), b) and c),

d) fraction A1 is conveyed to a chlorination reactor and fraction A2 to an oxychlorination reactor, optionally after having been subjected to an acetylene hydrogenation, in which reactors most of the ethylene present in fractions A1 and A2 is converted to DCE ; and
e) the DCE obtained is separated from the streams of products derived from the chlorination and oxychlorination reactors.

According to a second variant of the second embodiment, the process is advantageously such that, after steps a) and b),

c) fraction A is divided into fraction A1 and fraction A2 of the same composition or of different composition, one of which being conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, while the other is conveyed to the manufacture of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE and optionally of any compound derived there from.

The process according to this second variant of the second embodiment is preferably such that, after steps a) and b),

c) fraction A is divided into fraction A1 and fraction A2 of the same composition or of different composition, fraction A1 being conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, while fraction A2 is conveyed to the manufacture of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE and optionally of any compound derived there from.

The three variants detailed for the first embodiment of the process according to the invention in order to obtain DCE and afterwards VC and PVC from fraction A apply also for the second variant of the second embodiment of the process according to the invention in order to obtain DCE and afterwards VC and PVC from fraction A1.

According to the second variant of the second embodiment, fraction A2 is advantageously conveyed to the manufacture of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE and optionally of any compound derived there from.

As examples of ethylene derivative compounds manufactured directly starting with ethylene which are different from DCE which can be manufactured from fraction A may be cited among others, ethylene oxide, linear alpha-olefines, linear primary alcohols, homopolymers and copolymers of ethylene, ethylbenzene, vinyl acetate, acetaldehyde, ethyl alcohol and propionaldehyde.

As examples of the optional compound derived there from, may be cited among others, glycols manufactured from ethylene oxide, styrene manufactured from ethylbenzene and polymers of styrene derived from styrene.

Fraction A2 can be conveyed to the manufacture of one or of several ethylene derivative compounds manufactured directly starting with ethylene which are different from DCE.

In order to be sent to the manufacture of several ethylene derivative compounds manufactured directly starting with ethylene which are different from DCE, fraction A2 is advantageously divided into as many fractions of the same composition as necessary.

Preferably, fraction A2 is conveyed to the manufacture of one ethylene derivative compound manufactured directly starting with ethylene which is different from DCE.

Fraction A2 is more preferably conveyed to the manufacture of ethylbenzene and most preferably to the manufacture of ethylbenzene itself conveyed to the manufacture of styrene afterwards polymerized in order to obtain polymers of styrene.

According to the second embodiment, DCE is more preferably further subjected to a DCE cracking step to produce VC and VC is afterwards most preferably polymerized to produce PVC.

The DCE separated from the streams of products derived from the chlorination reactor can be mixed or not with the DCE separated from the streams of products derived from the oxychlorination reactor before the DCE cracking step. When both DCE are mixed, they can be mixed totally or partially. A preferred case is when DCE isolated from the stream of products derived from the oxychlorination reactor is mixed with a part of the DCE isolated from the stream of products derived from the chlorination reactor and the other part of this latter is sent directly to the DCE cracking step.

Reference is made to the first variant of the first embodiment for the details about the chlorination reaction and the separation of the DCE obtained from the stream of products derived from the chlorination reactor. Reference is also made to the same first variant for the details about the DCE cracking step and the separation of the VC obtained from the stream of products derived from the DCE cracking step. Reference is made to the second variant of the first embodiment for the details about the oxychlorination reaction and the separation of the DCE obtained from the stream of products derived from the oxychlorination reactor.

According to this second embodiment, VC is afterwards preferably polymerized to produce PVC. Reference is made to the first variant of the first embodiment for more details about the manufacture of PVC.

An advantage of the process according to the invention is that it recovers and converts a gas stream containing significant amounts of ethylene and/or precursor(s) thereof which was until the invention characterized by a low valorization (low value residual gas).

Another advantage of the process according to the invention is that it does neither comprise cracking steps followed by organic and aqueous quenching steps nor catalytic oxydehydrogenation steps which need important investment which causes an increase in the production costs and which involve the use of expensive hydrocarbon sources.

An advantage of the process according to the invention is that it allows one fractionation step b) which, being a fractionation of the mixture or products containing ethylene and other constituents in one step, is simplified compared with corresponding fractionation steps described in the previous patent applications WO 2006/067188, WO 2006/067190, WO 2006/067191, WO 2006/067192, WO 2006/067193 and WO 2007/147870 including advantageously several steps of fractionation. The process according to the invention allows therefore a lower energy demand.

An advantage of the process according to the invention is also that almost all the ethylene is present in one fraction while in the previous patent applications WO 2006/067188, WO 2006/067190, WO 2006/067191, WO 2006/067192, WO 2006/067193 and WO 2007/147870, the ethylene is advantageously divided between two different fractions, one containing part of the ethylene which is enriched with compounds lighter than ethylene and the other which is enriched with ethylene and characterized by a low hydrogen content.

An advantage of the second variant of the second embodiment of the process according to the invention is that it allows the integration of the DCE manufacture with the manufacture of at least one ethylene derivative compound different from DCE.

This integration allows a reduction of the total cost thanks to the sharing of the costs linked to the common steps.

An advantage of the process according to the invention is that it makes it possible to have, on the same industrial site, a completely integrated process.

CLAIMS

1 – Process for the manufacture of at least one ethylene derivative compound starting from a low value residual gas according to which :

a) the low value residual gas is subjected to a series of treatment steps in a low value residual gas recovery unit in order to remove the undesirable components present therein and to obtain a mixture of products containing ethylene and other constituents ;

b) the said mixture of products is fractionated in one fractionation step into one fraction containing almost all the ethylene (fraction A), optionally into one individual fraction of ethane and into one heavy fraction (fraction C) ; and

c) fraction A is conveyed to the manufacture of at least one ethylene derivative compound.

2 – Process according to Claim 1 according to which after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of 1,2-dichloroethane and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation.

3 – Process according to Claim 2, according to which after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of 1,2-dichloroethane, optionally after having been subjected to an acetylene hydrogenation, in a chlorination reactor in which most of the ethylene present in fraction A is converted to 1,2-dichloroethane by reaction with molecular chlorine ;

d) the 1,2-dichloroethane obtained is separated from the stream of products derived from the chlorination reactor ;

e) the separated 1,2-dichloroethane is subjected to a 1,2-dichloroethane cracking step thus producing vinyl chloride and hydrogen chloride ;

f) the vinyl chloride and hydrogen chloride obtained are separated from the stream of products derived from a 1,2-dichloroethane cracking step ; and

g) hydrogen chloride is subjected to an oxidation into molecular chlorine which is afterwards recycled to the chlorination reactor.

4 – Process according to Claim 3, according to which vinyl chloride is polymerized to produce polyvinyl chloride.

5 – Process according to Claim 2, according to which after steps a) and b),

c) fraction A is conveyed in one fraction to the manufacture of 1,2-dichloroethane, optionally after having been subjected to an acetylene hydrogenation, in a chlorination reactor in which at most 90 % of the ethylene present in fraction A is converted to 1,2-dichloroethane by reaction with molecular chlorine ;

d) the 1,2-dichloroethane formed in the chlorination reactor is optionally isolated from the stream of products derived from the chlorination reactor ;

e) the stream of products derived from the chlorination reactor, from which the 1,2-dichloroethane has optionally been extracted, is conveyed to an oxychlorination reactor in which the majority of the balance of ethylene is converted to 1,2-dichloroethane, after optionally having subjected the latter to an absorption/desorption step e'), during which the 1,2-dichloroethane formed in the chlorination reactor is optionally extracted if it has not previously been extracted ; and

f) the 1,2-dichloroethane formed in the oxychlorination reactor is isolated from the stream of products derived from the oxychlorination reactor and is optionally added to the 1,2-dichloroethane formed in the chlorination reactor.

6 – Process according to Claim 5, according to which 1,2-dichloroethane is subjected to a 1,2-dichloroethane cracking step to produce vinyl chloride and vinyl chloride is afterwards polymerized to produce polyvinyl chloride.

7 – Process according to Claim 1 according to which after steps a) and b),

c) fraction A is divided into at least two fractions, preferably into fraction A1 and fraction A2, of the same composition or of different composition before being conveyed to the manufacture of at least one ethylene derivative compound.

8 – Process according to Claim 7, according to which after steps a) and b),

c) fraction A is divided into fraction A1 and fraction A2 of the same composition or of different composition, fraction A1 and fraction A2 being conveyed to the manufacture of 1,2-dichloroethane and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation.

9 – Process according to Claim 7, according to which after steps a) and b),

c) fraction A is divided into fraction A1 and fraction A2 of the same composition or of different composition, one of which being conveyed to the manufacture of 1,2-dichloroethane and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, while the other is conveyed to the manufacture of at least one ethylene derivative compound manufactured directly starting with ethylene which is different from 1,2-dichloroethane and optionally of any compound derived there from.

10 – Process according to any one of Claims 1 to 9, characterized in that the low value residual gas is a refinery off-gas produced in at least one fluid catalytic cracking unit.

11 – Process according to any one of Claims 1 to 10, characterized in that the low value residual gas is a mixture of several gases containing ethylene and/or precursor(s) thereof and comprises from 10 to 60 % by weight of ethylene.

12 – Process according to any one of Claims 1 to 11, characterized in that fraction A contains at least 95 % of the ethylene quantity which is contained in the mixture of products subjected to step b).

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/056640

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/02 C07C17/156 C07C17/25 C07C19/045 C07C21/06

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 practical, 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	WO 2006/067192 A (SOLVAY [BE]; STREBELLE MICHEL [BE]; BALTHASART DOMINIQUE [BE]) 29 June 2006 (2006-06-29) cited in the application the whole document	1,2,7-12
Y		3-6

Y	DE 102 52 859 A1 (BASF AG [DE]) 27 May 2004 (2004-05-27) claim 1	3,4

Y	WO 2008/000705 A (SOLVAY [BE]; STREBELLE MICHEL [BE]; BALTHASART DOMINIQUE [BE]) 3 January 2008 (2008-01-03) cited in the application claim 1	5,6

☐ 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 document 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 5 August 2009	Date of mailing of the international search report 18/08/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Cooper, Simon

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/056640

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
WO 2006067192	A	29-06-2006	AR	052834	A1	04-04-2007
			AR	052835	A1	04-04-2007
			AU	2005318153	A1	29-06-2006
			AU	2005318154	A1	29-06-2006
			BR	PI0518657	A2	02-12-2008
			BR	PI0519701	A2	14-07-2009
			CA	2590663	A1	29-06-2006
			CA	2592329	A1	29-06-2006
			EA	200701353	A1	28-02-2008
			EP	1831140	A1	12-09-2007
			EP	1831137	A1	12-09-2007
			WO	2006067193	A1	29-06-2006
			JP	2008525379	T	17-07-2008
			JP	2008525380	T	17-07-2008
			KR	20070094934	A	27-09-2007
			KR	20070094935	A	27-09-2007
			US	2008207965	A1	28-08-2008
			US	2008207967	A1	28-08-2008
DE 10252859	A1	27-05-2004	NONE			
WO 2008000705	A	03-01-2008	AR	061631	A1	10-09-2008
			AU	2007263778	A1	03-01-2008
			CA	2655145	A1	03-01-2008
			EP	2035358	A1	18-03-2009
			FR	2902785	A1	28-12-2007
			KR	20090025356	A	10-03-2009