Abstract: Process for the manufacture of at least one ethylene derivative compound starting a hydrocarbon source according to which a) the hydrocarbon source, optionally containing fraction E1 recycled from step d), is subjected to a simplified cracking which produces a mixture of products containing ethylene and other constituents; b) the said mixture of products is subjected to a first separation step S1 which consists of separating said products containing ethylene and other constituents into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 and into a fraction F2; c) fraction F1 is sent to an ethylene recovery unit in which it is separated into a fraction enriched with ethylene called fraction E1 and into a fraction enriched with the compounds which are lighter than ethylene called light fraction; d) fraction E1 is recycled to step a) or is conveyed to the manufacture of at least one ethylene derivative compound; e) fraction F2 is subjected to a second separation step S2 which consists of separating fraction F2 into one fraction enriched with ethylene called fraction E2 or into two fractions enriched with ethylene called fractions E2a and E2b, and into a fraction enriched with ethane and hydrogen containing at least 3 carbon atoms called heavy fraction; f) fraction E2 or fractions E2a and E2b are then 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 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.
Patent applications WO 2008/000705, WO 2008/000702 and WO 2008/000693 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 disadvantage of requiring a first step of catalytic oxydehydrogenation which needs an important investment causing an increase in the production costs.

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. The processes, the aim of which is to produce and use ethylene having a purity of less than 99.8%, are such that two factions of different composition of ethylene are afterwards separated from the gas mixture issued from the simplified cracking, a first one containing part of the ethylene which is enriched with the compound lighter than ethylene and a second one which is enriched with ethylene and characterized by a low hydrogen content, being respectively conveyed independently to a chlorination reactor and to an oxychlorination reactor in order to produce DCE.

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.

One process the aim of which is to produce and use ethylene having a purity of less than 99.8% as well as to valorise such low value residual gases is described in patent application WO 2009/106479. The concerned process is a process for the manufacture of at least one ethylene derivative compound starting from such gases which is subjected to a separation into two fractions containing ethylene of different composition, afterwards separately conveyed to the manufacture of at least one ethylene derivative compound. Such process starting from low value residual gases however suffer from a very limited availability of
such gases and of a straight coupling with a manufacture which may have contradictory aims and constraints.

The process described in this last patent application as well as the ones described in the patent applications WO 2006/067188, WO 2006/067190, WO 2006/067191, WO 2006/067192, WO 2006/067193 and WO 2007/147870 present however the disadvantage of requiring a separation into two fractions of ethylene which are of different composition. Another disadvantage is that the conditions of use of these two fractions are different what can disrupt the processes in which they are afterwards used. Moreover, certain uses are not acceptable for the two qualities of ethylene considering the reactive impurities they contain; for example hydrogen which is not acceptable in the oxychlorination process of ethylene. Another disadvantage is that a very high content of compounds which are lighter than ethylene in the ethylene fraction implies to increase the dimension of the apparatus to be used and contributes to increase the losses by stripping which renders the process less efficient. Finally, the valorisation of the ethylene fraction containing the compounds lighter than ethylene is more difficult because it depends on the pressure and the temperature at the outlet of the units in which it is used.

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 %, which further allows a valorization of the compounds which are lighter than ethylene, a higher flexibility in the operation of the downstream units as well as an economy in these downstream units.

To this effect, the invention relates to a process for the manufacture of at least one ethylene derivative compound starting with a hydrocarbon source according to which:

a) the hydrocarbon source, optionally containing fraction E1 recycled from step d), is subjected to a simplified cracking which produces a mixture of products containing ethylene and other constituents;
b) the said mixture of products is subjected to a first separation step S1 which consists of separating said products containing ethylene and other constituents into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 and into a fraction F2;
c) fraction F1 is sent to an ethylene recovery unit in which it is separated into a fraction enriched with ethylene called fraction E1 and into a fraction enriched with the compounds which are lighter than ethylene called light fraction;

d) fraction E1 is recycled to step a) or is conveyed to the manufacture of at least one ethylene derivative compound;

e) fraction F2 is subjected to a second separation step S2 which consists of separating fraction F2 into one fraction enriched with ethylene called fraction E2 or into two fractions enriched with ethylene called fractions E2a and E2b, and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms called heavy fraction;

f) fraction E2 or fractions E2a and E2b are then 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 with a hydrocarbon source.

The hydrocarbon source considered may be any known hydrocarbon source. Preferably, the hydrocarbon source subjected to cracking (step a)) is chosen from the group consisting of naphtha, gas oil, natural gas liquid, ethane, propane, butane, isobutane and mixtures thereof. In a particularly preferred manner, the hydrocarbon source is chosen from the group consisting of ethane, propane, butane and propane/butane mixtures. In a more particularly preferred manner, the hydrocarbon source is chosen from the group consisting of propane, butane and propane/butane mixtures. The propane/butane mixtures may exist as such or may consist of mixtures of propane and butane.

The expression ethane, propane, butane and propane/butane mixtures is understood to mean, for the purposes of the present invention, products that are commercially available, namely that consist mainly of the pure product (ethane, propane, butane or propane/butane as a mixture) and secondarily of other saturated or unsaturated hydrocarbons, which are lighter or heavier than the pure product itself.

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 hydrocarbon source, according to the present invention, the hydrocarbon source, optionally containing fraction E1 recycled from step d), is subjected to a simplified cracking (step a)) which produces a mixture of products containing ethylene and other constituents that will be subjected to step b).

The expression simplified cracking (step a)) is understood to mean, for the purposes of the present invention, all the steps for treating the hydrocarbon
source which lead to the formation of a mixture of products containing ethylene and other constituents which will be separated afterwards.

Such a cracking may be carried out according to any known technique as long as it allows the production of a mixture of products containing ethylene and other constituents. Advantageously, the cracking comprises a first cracking step of pyrolysis (that is to say a conversion under the action of heat) of the hydrocarbon source in the presence or absence of third compounds such as water, oxygen, a sulphur derivative and/or a catalyst. This first cracking step of pyrolysis is advantageously carried out in at least one cracking furnace to give rise to the formation of a mixture of cracking products.

This mixture of cracking products advantageously comprises hydrogen, carbon monoxide, carbon dioxide, nitrogen, oxygen, hydrogen sulphide, organic compounds comprising at least one carbon atom and water.

First cracking step of pyrolysis is preferably carried out in at least two cracking furnaces and particularly preferably in at least three cracking furnaces.

First cracking step of pyrolysis is preferably carried out in at most five cracking furnaces and particularly preferably in at most four cracking furnaces. With a more particular advantage, an additional cracking furnace is available to replace one of the furnaces in service when that furnace must undergo a decoking operation.

In a more particularly preferred manner, first cracking step of pyrolysis is carried out in three cracking furnaces. In a most particularly preferred manner, first cracking step of pyrolysis is carried out in three different cracking furnaces, the mixtures of cracking products derived from each of them being gathered together. With a more particular advantage, a fourth cracking furnace is available to replace one of the three furnaces in service when that furnace must undergo a decoking operation.

It is therefore particularly advantageous to carry out first cracking step of pyrolysis in three different cracking furnaces, the mixtures of cracking products derived from each of them being gathered together afterwards and to make a fourth cracking furnace available to replace one of the three furnaces in service.

After this first cracking step of pyrolysis, said mixture of cracking products is subjected to a series of treatment steps making it possible to obtain a mixture of products containing ethylene and other constituents which is advantageously composed of the following steps, not necessary performed in the order they are recited:
- step of thermal recovery of the heat of the cracked gases,
- optionally organic quenching step (optionally including heat recovery across a network of exchangers with intermediate liquids),
- aqueous quenching step,

5 - compression step;
- drying step comprising advantageously an outlet,
- removal step of most of the carbon dioxide and most of the sulphur compounds that are present or added (for example, by means of an alkaline wash),
- optionally hydrogenation step of the undesirable derivatives such as, for example, acetylene, and
- optionally elimination step of hydrogen and/or methane, for example via a PSA (pressure swing adsorption) process or via a membrane process.

The simplified cracking step a) comprises therefore advantageously a first cracking step of pyrolysis followed by a series of treatment steps (detailed above) among which a compression step and a drying step.

Advantageously, in the process according to the invention, the mixture of products containing ethylene and other constituents derived from step a) comprises hydrogen, methane, compounds comprising from 2 to 7 carbon atoms, carbon monoxide, nitrogen and oxygen. Hydrogen, methane and compounds comprising from 2 to 7 carbon atoms other than acetylene are preferably present in an amount of at least 200 ppm by volume relative to the total volume of said mixture of products. Carbon monoxide, nitrogen, oxygen and acetylene may be present in an amount of less than 200 ppm by volume or in an amount of at least 200 ppm by volume relative to the total volume of said mixture of products. Compounds containing more than 7 carbon atoms, carbon dioxide, hydrogen sulphide and the other sulphur compounds and also water may also be present in the abovementioned mixture of products in an amount of less than 200 ppm by volume relative to the total volume of said mixture of products.

The compression and drying of the gases may be advantageously performed under particular conditions so that the passage of the compounds comprising at least 6 carbon atoms is minimized. The cooling fluid which may be used is advantageously at a temperature lower than the temperature of the water from an atmospheric cooling tower. The cooling fluid is preferably at a temperature of at least -5°C, more preferably at least 0°C. The cooling fluid is most preferably iced water.
After step a) defined above, the mixture of products containing ethylene and other constituents is subjected to step b) which is a first separation step S1 which consists of separating said products containing ethylene and other constituents into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 and into a fraction F2.

Prior to its separation, the mixture of products containing ethylene and other constituents may be subjected to a heat conditioning step.

The term "heat conditioning step" is understood to mean a succession of heat exchanges in order to adjust the temperature of the mixture to requirements of the separation and/or to optimize the use of energy, preferably to adjust the temperature of the mixture to requirements of the separation and to optimize the use of energy.

When the heat conditioning step consists in a cooling, the cooling is advantageously a gradual cooling of the mixture of products in a train of exchangers first cooled with untreated water, then with ice-cold water, and then with increasingly cooled fluids plus cross exchangers recovering the sensible heat of the streams produced, optionally with latent heat when available. Advantageously, the condensates produced during the cooling step are physically separated from the gas stream and directed to an appropriate location in the following treatment. The heat conditioning included in step S1 is preferably a cooling and the separated condensate are preferably directed to an appropriate location in step S2.

The first separation step S1 advantageously consists in the fractionation of the mixture of products containing ethylene and other constituents into the two different fractions mentioned above.

The term "fractionation" is understood to mean, for the purpose of the present invention, 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.

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

Step S1 therefore preferably consists in the fractionation of the mixture of products containing ethylene and other constituents inside a distillation column.
(called column CI) into the two different fractions, namely fraction F1 which advantageously leaves from the rectifying section of column CI and fraction F2 which advantageously leaves from the stripping section of column CI.

By distillation column, it is meant according to the present invention, a column comprises any number of interconnected towers. By tower, it is meant a single envelope where the counter-current contact of liquid and gas is realised. Advantageously, column CI does not comprise more than two interconnected towers. Preferably, column CI consists of one single tower.

Column CI may be chosen from plate distillation columns, distillation columns with random packing, distillation columns with structured packing and distillation columns combining two or more of the abovementioned internals.

Column CI is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source. The heating source is preferably a reboiler. The cooling source can be direct or indirect cooling. Example of indirect cooling is a partial condenser. Example of direct cooling is the adiabatic flash of the liquid produced by a partial condenser. Direct cooling by the adiabatic flash of the liquid produced by a partial condenser is preferred. The gas subjected to partial condensation in the partial condenser can originated from column CI or from the mixture of products fed to column CI after possible heat conditioning step, preferably from column CI.

The stream originating from the column can be taken from the stripping section or from the rectifying section, preferably from the stripping section of column CI. It can be taken at any place in the stripping section, preferably in the upper third of the stripping section, more preferably at a place just under the place where the mixture of products is fed.

Said mixture of products can be introduced into the column CI as a single fraction or as several subtractions. It is preferably introduced as several subtractions.

The abovementioned step S1 is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly preferably at least 12 bar absolute. Step S1 is advantageously carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.

The temperature at which step S1 is carried out is advantageously at least -40, preferably at least -35 and particularly preferably at least -30°C at the bottom of the stripping section of column CI. It is advantageously at most 80,
preferably at most 60 and particularly preferably at most 40°C at the bottom of the stripping section of column CI.

The temperature at which step S1 is carried out is advantageously at least -140, preferably at least -130 and particularly preferably at least -125°C at the top of the rectifying section of column CI. It is advantageously at most 0, preferably at most -15 and particularly preferably at most -25°C at the top of the rectifying section of column CI.

After step b) defined above, fraction F1 is sent to an ethylene recovery unit in which it is separated into a fraction enriched with ethylene called fraction E1 and into a fraction enriched with the compounds which are lighter than ethylene called light fraction (step c)).

The separation in the ethylene recovery unit consists advantageously in the fractionation of fraction F1 into the two different fractions mentioned above. Reference is made to the definition of the term "fractionation" as well as to the examples of fractionation mentioned above for step b).

According to a first embodiment of step c), fraction F1 is advantageously subjected to an absorption step followed by a desorption step in which said fraction F1 is preferably brought into contact with a washing agent containing a solvent, in order to be separated into fraction E1 and into light fraction.

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.

A first group of solvents which can be used are the solvents advantageously characterized by a fusion temperature equal or less than -110°C, preferably equal and less than -105°C, more preferably equal and less than -100°C.

A second group of solvents which can be used are the solvents characterized by a fusion temperature higher than the fusion temperature of the solvents of the first group. In such last case however an appropriate thermal
conditioning step of fraction Fl is advantageously applied. Preferably, the thermal conditioning is a heat conditioning step as defined in step b).

As solvents according to the first group, one can cite for example the saturated hydrocarbons, the insaturated hydrocarbons and the mineral oils. The saturated or insaturated hydrocarbons may be used as pure hydrocarbon or as mixtures of hydrocarbons. Examples of saturated and insaturated hydrocarbons are propane/butane (LPG) mixtures, benzene, the heavy fraction produced by the process according to the invention, cyclopentane and derivatives, cyclopentene and derivatives in particular methylcyclopentene and ethylcyclopentene, cyclohexane and derivatives, in particular methylcyclohexane and ethylcyclohexane, cyclohexene and derivatives and C8-C9 isoparaffines. Methylcyclohexane, ethylcyclohexane and C8-C9 isoparaffines are preferred. Methylcyclohexane and ethylcyclohexane are particularly preferred.

As solvents according to the second group, one can cite for example the chlorinated solvents (like DCE), the alcohols, the glycols, the polyols, the ethers, the mixtures of glycol(s) and ether(s).

The solvents of the first group are preferred over the solvents of the second group.

The washing agent used for the absorption step may be composed of fresh washing agent or of all or part of the washing agent recovered during the desorption step explained below, after an optional treatment, optionally with the addition of fresh washing agent.

The ratio between the respective throughputs of washing agent and fraction Fl 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 0.1, preferably at least 0.2 and particularly preferably at least 0.25 tonnes per tonne of fraction Fl. 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 fraction Fl.

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 can be equipped or not with associated heat exchanger. When solvents of the first group are used, the absorption column is advantageously not equipped with associated heat exchanger. When solvents of the second group are used, the absorption column is advantageously equipped with associated heat exchanger.

When solvents of the first group are used, 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.

When solvents of the first group are used, the temperature at which the absorption step is carried out is advantageously at least -120, preferably at least -115 and particularly preferably at least -110°C at the top of the absorber or absorption column. It is advantageously at most -50, preferably at most -60 and particularly preferably at most -65°C at the top of the absorber or absorption column. Moreover, the temperature at which the absorption step is carried out is advantageously of 2, preferably of 5°C higher than the fusion temperature of the solvent.

When solvents of the first group are used, the temperature at the bottom of the absorber or absorption column is at least -120, preferably at least -115 and particularly preferably at least -110°C. It is advantageously at most -50, preferably at most -60 and particularly preferably at most -65°C.

When solvents of the second group are used, 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.

When solvents of the second group are used, 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.

When solvents of the second group are used, 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 fraction F1 purified of compounds that are lighter than ethylene and enriched in washing agent is advantageously subjected to the desorption step.

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.

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 abovementioned internals and spray columns. 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 ethylene in the regenerated solvent is less than or equal to 4, preferably less than or equal to 3.2 % by weight.

When solvents of the first group are used, 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 25, preferably at most 20 and particularly preferably at most 18 bar absolute.

When solvents of the first group are used, 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.

When solvents of the first group are used, the temperature at the bottom of the desorber or desorption column is at least 20, preferably at least 25 and particularly preferably at least 30°C. It is advantageously at most 200, preferably at most 160 and particularly preferably at most 150°C.
When solvents of the second group are used, 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.

When solvents of the second group are used, 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.

When solvents of the second group are used, 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.

The regenerated solvent is advantageously at least partially reused at the absorption after a heat conditioning step preferably including the cooling in a cross heat exchanger with the solvent leaving the absorption column.

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.

In the particular case when the process according to the invention is directed to the manufacture of DCE, it can be interesting to use a washing agent composed of DCE. In such case, the washing agent used for the absorption step may be composed of 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, after an optional treatment, optionally with the addition of fresh washing agent. The desorption can also be performed by direct injection of vapour in order to collect DCE.

An essential advantage of the 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.

According to a second embodiment of step c), fraction F1 is advantageously subjected to an adsorption step followed by a desorption step in order to be separated into fraction E1 and into light fraction.
The adsorption step advantageously comprises passing fraction F1 through an adsorbed bed charged with an adsorbent. The adsorbed bed can be a fluidized bed or a fixed bed. Any known adsorbent known in the art can be used. Examples of such adsorbents are those based on silver compounds or on copper compounds. Those silver or copper compounds are usually supported on a support having a sufficiently high surface area. Examples of supports are activated carbon, charcoal, activated alumina and zeolite. The adsorbents are usually solid in the form of pellets or beads.

The adsorption step is advantageously carried out at a pressure of at least 15, preferably at least 20 and particularly preferably at least 25 bar absolute. The adsorption 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 adsorption step is carried out is advantageously at least -10, preferably at least 0, more preferably at least 10 and most preferably at least 20°C. It is advantageously at most 70, preferably at most 60, more preferably at most 50 and most preferably at most 40°C.

The desorption step can be readily performed by lowering the pressure, by increasing the temperature or by lowering the pressure and increasing the temperature of the adsorber bed resulting in a regenerated adsorbent.

The 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 10, more preferably at least 20 and most preferably at least 60°C. It is advantageously at most 200, preferably at most 160, more preferably at most 100 and most preferably at most 60°C.

When a fluidized bed is used, the adsorbent advantageously continuously circulates from the adsorption bed to the desorption bed.

When a fixed bed is used, it is advantageous to work by cycle with preferably several beds in parallel, more preferably at least one in adsorption phase and at least one in desorption phase.

The first embodiment of step c) is preferred over the second embodiment.
The light fraction is enriched with the compounds which are lighter than ethylene. Those compounds are generally hydrogen, oxygen, nitrogen, helium, argon, carbon monoxide and methane.

Advantageously, the light fraction contains at least 75 %, preferably at least 80 % and more preferably at least 85 % of the methane which is contained in fraction F1 subjected to step c).

Advantageously, the light fraction contains at least 90 %, preferably at least 95 % and more preferably at least 97 % of the nitrogen, oxygen, hydrogen, carbon monoxide, argon and helium which are contained in fraction F1 subjected to step c).

Advantageously, the light fraction contains less than 2 %, preferably less than 1.5 % and more preferably less than 1 % by volume of ethylene.

After having been recovered, the light fraction can be burnt as fuel or valorized chemically, preferably valorized chemically.

The light fraction can be submitted to a chemical reaction like a partial oxidation or a steam reforming, in order to advantageously convert its hydrocarbon content into hydrogen, before being valorized chemically. When the light fraction is particularly rich in hydrogen, it can be used for any hydrogenation reaction as for example for the hydrogenation of the working solution in hydrogen peroxide manufacture by autoxydation or for the direct synthesis of hydrogen peroxide.

Alternatively, the light fraction can be valorized in synthesis gas after conversion of the hydrocarbon content by steam reforming or partial oxidation followed by water gas shift in order to produce derivatives such as methanol or in a Fischer Tropsch unit.

Alternatively, synthetic natural gas can be produced.

The energy of the light fraction can also be recuperated by turbo expansion.

Advantageously, fraction E1 contains at least 50 %, preferably at least 60 % and more preferably at least 66 % of the ethylene which is contained in fraction F1 subjected to step c).

After step c) defined above, fraction E1 is recycled to step a) or is conveyed to the manufacture of at least one ethylene derivative compound (step d)).

In the case when fraction E1 is recycled to step a), fraction E1 may be recycled anywhere in step a). Fraction E1 may be recycled at the entry of step a)
and/or in one or more than one of the treatment steps of the series of treatment steps following the first cracking step of pyrolysis of step a).

Fraction E1 is advantageously recycled to the compression step and/or to the drying step (in particular to the outlet of the drying step) and/or to the hydrogenation step and/or to the hydrogen and/or methane elimination step of step a). Preferably, fraction E1 is recycled to the compression step and/or to the drying step (in particular to the outlet of the drying step) of step a).

Fraction E1 may be recycled with or without adaptation of its pressure.

When an adaptation of its pressure is required, fraction E1 is advantageously submitted to a compression, possible combined with an upstream or downstream cooling either in the ethylene recovery unit itself or after having left this unit, before being recycled to step a). Compression can be made by any known process such as mechanical compressor, gas ejector, liquid ejector. Compression is preferably made by a mechanical compressor.

When fraction E1 is recycled without adaptation of its pressure, fraction E1 is advantageously recycled to one or the treatments steps of step a) where the pressure is appropriate, in other words, where the pressure is less than the pressure of fraction E1.

Fraction E1 may be recycled in one part or in several parts.

Advantageously, fraction E1 is recycled in one part.

More preferably, fraction E1 is recycled to the compression step and/or to the outlet of the drying step of step a).

When fraction E1 is recycled to the compression step of step a), it is advantageously recycled without adaptation of its pressure. Fraction E1 is then preferably recycled, either to one stage of the multi-stage gas compressor when only one compressor is used, or to the compressor of the train of compressors when several compressors are used, which are at the highest pressure which is lower than the pressure of fraction E1.

When fraction E1 is recycled to the outlet of the drying step of step a), it is advantageously recycled after its pressure has been adapted, preferably by submitting it to a compression.

Most preferably, fraction E1 is recycled to the compression step of step a) without adaptation of its pressure as described above.

Alternatively, fraction E1 can be conveyed to the manufacture of at least one ethylene derivative compound. Fraction E1 can be conveyed as such to such manufacture or can be mixed with fraction E2 or one of fractions E2a and E2b
obtained in step e) before being sent to such manufacture. When fraction E1 is conveyed to the manufacture of at least one ethylene derivative compound, it is preferably conveyed to the chlorination of ethylene into 1,2-dichloroethane.

The energy of fraction E1 can be recuperated by turbo expansion.

One part of fraction E1 can be recycled to step a) while another part is conveyed to the manufacture of at least one ethylene derivative compound.

Preferably, fraction E1 is recycled to step a). Preferably, the hydrocarbon source containing fraction E1 recycled from step d) is therefore subjected to the simplified cracking defined in step a).

According to step e), fraction F2 is subjected to a second separation step S2 which consists of separating fraction F2 into one fraction enriched with ethylene called fraction E2 or into two fractions enriched with ethylene called fractions E2a and E2b, and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms called heavy fraction.

Prior to its separation, fraction F2 may be subjected to a heat conditioning step.

The term "heat conditioning step" is understood to mean a succession of heat exchanges in order to adjust the temperature of fraction F2 to requirements of the separation and/or to optimize the use of energy, preferably to adjust the temperature of the fraction F2 to requirements of the separation and to optimize the use of energy. Optionally, fraction F2 is adiabatically flashed at the pressure of the vapor feed location in S2 and the condensates produced during the adiabatic flash are physically separated from the gas stream and directed to an appropriate location in S2.

The second separation step S2 advantageously consists in the fractionation of fraction F2 into the different fractions mentioned above.

The term "fractionation" is understood to mean, for the purpose of the present invention, 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.

Examples of fractionation are distillation, extractive distillation, liquid-liquid extraction, pervaporation, gas-permeation, adsorption, pressure swing adsorption (PSA), temperature swing adsorption (TSA), absorption, chromatography, reverse osmosis and molecular filtration. Distillation is preferred.
Step S2 therefore preferably consists in the fractionation of fraction F2 inside advantageously at least one distillation column, preferably one or two distillation columns, into the different fractions mentioned above.

By distillation column, it is meant according to the present invention, a column comprises any number of interconnected towers. By tower, it is meant a single envelope where the counter-current contact of liquid and gas is realised.

Preferably, each distillation column does not comprise more than two interconnected towers. More preferably, each distillation column consists of one single tower.

Each distillation column may be chosen from plate distillation columns, distillation columns with random packing, distillation columns with structured packing and distillation columns combining two or more of the abovementioned internals.

According to a first embodiment of step e), fraction F2 is advantageously subjected to a second separation step S2 which consists of separating fraction F2 into fraction E2 and into heavy fraction.

According to a first variant of the first embodiment of step e), the second separation step S2 preferably consists in the fractionation of fraction F2 inside one distillation column (called column C2) into two different fractions, namely fraction E2 which advantageously leaves from the rectifying section of column C2 and the heavy fraction which advantageously leaves from the stripping section of column C2.

Column C2 is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source. The heating source is preferably a reboiler. The cooling source could be direct or indirect cooling. Example of indirect cooling is a partial condenser. Example of direct cooling is the adiabatic flash of the liquid produced by a partial condenser. Direct cooling by the adiabatic flash of the liquid produced by a partial condenser is preferred. Optimisation of the energy requirements can be made by any techniques known in the art such as cross heat exchange with suitable fluids, heat integration of the column with vapour recompression, recompression cycle combined with cooling and adiabatic flash.

Fraction F2 may be introduced into the column C2 as a single fraction or as several subtractions. It is preferably introduced as a single fraction.

According to the first embodiment of step e), step S2 is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly
preferably at least 12 bar absolute. Step S2 is advantageously carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.

According to the first embodiment of step e), the temperature at which step S2 is carried out is advantageously at least -50, preferably at least -40 and particularly preferably at least -30°C at the bottom of the stripping section of column C2. It is advantageously at most 80, preferably at most 75°C at the bottom of the stripping section of column C2.

According to the first embodiment of step e), the temperature at which step S2 is carried out is advantageously at least -80, preferably at least -70 and particularly preferably at least -65°C at the top of the rectifying section of column C2. It is advantageously at most 5, preferably at most 0 and particularly preferably at most -3°C at the top of the rectifying section of column C2.

According to a second variant of the first embodiment of step e), the second separation step S2 advantageously consists in the separation of fraction F2 into two different separations, a first separation step called step S2' and a second separation step called step S2" in order to obtain fraction E2 and the heavy fraction.

According to this second variant of the first embodiment of step e), fraction F2 is subjected to
- a first separation step S2' which consists in the separation of fraction F2 into a first fraction enriched with ethylene called fraction E2' and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms containing part of the ethylene called fraction F2' ; and
- a second separation step S2" which consists in the separation of the fraction F2' into a second fraction enriched with ethylene called fraction E2" and into the heavy fraction.

Fraction E2' and fraction E2" are afterwards advantageously mixed. They can be mixed immediately after having been obtained, after having circulated in the installation for energy recovery and/or after having been integrated in a cooling cycle used in steps b) to e). Preferably, they are mixed after having circulated in the installation for energy recovery and/or after having been integrated in a cooling cycle used in steps b) to e). More preferably, they are mixed after having circulated in the installation for energy recovery and after having been integrated in a cooling cycle used in steps b) to e).
Step S2' preferably consists in the fractionation of fraction F2 in a first distillation column (called column C2') into two different fractions, namely fraction E2' which advantageously leaves from the rectifying section of column C2' and into fraction F2' which advantageously leaves from the stripping section of column C2'.

Step S2" preferably consists in the fractionation of fraction F2' in a second distillation column (called column C2") into two different fractions, namely fraction E2" which advantageously leaves from the rectifying section of column C2" and into the heavy fraction which advantageously leaves from the rectifying section of column C2".

Column C2' is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source. The heating source is preferably a reboiler. The cooling source could be direct or indirect cooling. Example of indirect cooling is a partial condenser. Example of direct cooling is the adiabatic flash of the liquid produced by a partial condenser. Direct cooling by the adiabatic flash of the liquid produced by a partial condenser is preferred.

Optimisation of the energy requirements can be made by any techniques known in the art such as cross heat exchange with suitable fluids; heat integration in one of the cooling cycles used in steps b), c) and e) (preferably in the cooling cycle used in steps b), c) and e)); heat integration of the column C2' with vapour recompression or recompression cycle combined with cooling and adiabatic flash; heat integration of the column C2' and the column C2" by a suitable choice of the columns pressure in such a way that the condenser of one of the columns is the reboiler of the other, preferably operating the column C2" at a higher pressure than the column C2' such that the condenser of the column C2" could be the reboiler of the column C2'. More preferably, optimisation of the energy requirements is made by heat integration in one of the cooling cycles used in steps b), c) and e) (preferably in the cooling cycle used in steps b), c) and e)).

Fraction F2 may be introduced into the column C2' during step S2' as a single fraction or as several subfractions. It is preferably introduced as a single fraction.

According to a second variant of the first embodiment of step e), step S2' is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly preferably at least 12 bar absolute. Step S2' is advantageously
carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.

According to the second variant of the first embodiment of step e), the temperature at which step S2' is carried out is advantageously at least -50, preferably at least -45 and particularly preferably at least -43°C at the bottom of the stripping section of column C2'. It is advantageously at most 30, preferably at most 20 and particularly preferably at most 10°C at the bottom of the stripping section of column C2'.

According to the second variant of the first embodiment of step e), the temperature at which step S2' is carried out is advantageously at least -70, preferably at least -65 and particularly preferably at least -63°C at the top of the rectifying section of column C2'. It is advantageously at most 0, preferably at most -15 and particularly preferably at most -25°C at the top of the rectifying section of column C2'.

Prior to its introduction into column C2'', fraction F2' may be subjected to a heat conditioning step, as defined for step SI, and a pressure conditioning step by pumping the liquid produced at the bottom of the stripping section of the column C2' to the column C2''.

Column C2'' is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source with the same characteristics as the ones defined for column C2' here above.

Fraction F2' may be introduced into the column C2'' during step S2'' as a single fraction or as several subtractions. It is preferably introduced as a single fraction.

According to the second variant of the first embodiment of step e), step S2'' is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly preferably at least 12 bar absolute. Step S2'' is advantageously carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.

According to a first sub-variant of the second variant of the first embodiment of step e), fractions E2' and E2'' are mixed immediately after having been obtained. In such sub-variant, step S2'' is advantageously carried out at a pressure equal to or different from the pressure at which S2' is carried out. Preferably, step S2'' is carried out at a pressure different from the pressure at which S2' is carried out. Step S2'' is advantageously carried out at a pressure slightly lower than the pressure at which step S2' is carried out.
According to a second sub-variant of the second variant of the first embodiment of step e), fractions E2' and E2'' are mixed after having circulated in the installation for energy recovery and/or after having been integrated in a cooling cycle used in steps b) to e). In such sub-variant, step S2'' is advantageously carried out at a pressure equal to or different from the pressure at which S2' is carried out. Preferably, step S2'' is carried out at a pressure different from the pressure at which S2' is carried out. Step S2'' is advantageously carried out at a pressure higher than the pressure at which step S2' is carried out. Step S2'' is carried out at a pressure which is preferably at least 2 bar, more preferably at least 4 bar, most preferably at least 5 bar higher than the pressure at which step S2' is carried out. Step S2'' is carried out at a pressure which is preferably at most 33 bar, more preferably at most 30 bar, most preferably at most 20 bar higher than the pressure at which step S2' is carried out.

According to second variant of the first embodiment of step e), the temperature at which step S2'' is carried out is advantageously at least -50, preferably at least -40 and particularly preferably at least -30°C at the bottom of the stripping section of column C2". It is advantageously at most 80, preferably at most 75 and particularly preferably at most 72°C at the bottom of the stripping section of column C2".

According to second variant of the first embodiment of step e), the temperature at which step S2'' is carried out is advantageously at least -70, preferably at least -65 and particularly preferably at least -63°C at the top of the rectifying section of column C2". It is advantageously at most 0, preferably at most -15 and particularly preferably at most -25°C at the top of the rectifying section of column C2"

According to a second embodiment of step e), fraction F2 is advantageously subjected to a second separation step S2 which consists of separating fraction F2 into fractions E2a and E2b, and into the heavy fraction.

According to this second embodiment of step e), the second separation step S2 advantageously consists in the separation of fraction F2 into two different separations, a first separation step called step S2'" and a second separation step called step S2"" in order to obtain fractions E2a and E2b and the heavy fraction.

According to this second embodiment of step e), fraction F2 is subjected to
- a first separation step S2'' which consists in the separation of fraction F2 into fraction E2a and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms containing part of the ethylene called fraction F2'' ; and

- a second separation step S2''' which consists in the separation of the fraction F2'' into fraction E2b and into the heavy fraction.

  Step S2'' preferably consists in the fractionation of fraction F2 in a first distillation column (called column C2'') into two different fractions, namely fraction E2a which advantageously leaves from the rectifying section of column C2'' and into fraction F2''' which advantageously leaves from the stripping section of column C2'''.

  Step S2''' preferably consists in the fractionation of fraction F2''' in a second distillation column (called column C2''') into two different fractions, namely fraction E2b which advantageously leaves from the rectifying section of column C2'''' and into the heavy fraction which advantageously leaves from the rectifying section of column C2''''.

  Column C2'' is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source. The heating source is preferably a reboiler. The cooling source could be direct or indirect cooling. Example of indirect cooling is a partial condenser. Example of direct cooling is the adiabatic flash of the liquid produced by a partial condenser. Direct cooling by the adiabatic flash of the liquid produced by a partial condenser is preferred.

  Optimisation of the energy requirements can be made by any techniques known in the art such as cross heat exchange with suitable fluids ; heat integration of the column with vapour recompression or recompression cycle combined with cooling and adiabatic flash ; material integration of one of the C2'' or C2''' columns (preferably C2'') in the cooling cycle used for steps b), c) and e) ; heat integration of one of the column and material integration of the other ; heat integration of the column C2'' and the column C2''' by a suitable choice of the columns pressure in such a way that the condenser of one of the columns is the reboiler of the other, preferably, operating the column C2''' at a higher pressure than the column C2'' such that the condenser of the column C2'''' could be the reboiler of the column C2''". More preferably, optimisation of the energy requirements is made by heat integration of the column C2'' and the column C2''' as explained above.
Fraction F2 may be introduced into the column C2'" during step S2'" as a single fraction or as several subfractions. It is preferably introduced as a single fraction.

According to the second embodiment of step e), step S2'" is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly preferably at least 12 bar absolute. Step S2'" is advantageously carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.

According to the second embodiment of step e), the temperature at which step S2'" is carried out is advantageously at least -50, preferably at least -40 and particularly preferably at least -30°C at the bottom of the stripping section of column C2'". It is advantageous at most 80, preferably at most 60 and particularly preferably at most 55°C at the bottom of the stripping section of column C2'".

According to the second embodiment of step e), the temperature at which step S2'" is carried out is advantageously at least -70, preferably at least -60 and particularly preferably at least -55°C at the top of the rectifying section of column C2'". It is advantageously at most 0, preferably at most -15 and particularly preferably at most -25°C at the top of the rectifying section of column C2'".

Prior to its introduction into column C2''", fraction F2'' may be subjected to a heat conditioning step as defined for step S1, and a pressure conditioning step by pumping the liquid produced at the bottom of the stripping section of the column C2'" to the column C2''".

Column C2''" is advantageously equipped with associated accessories such as, for example, at least a heating source and a cooling source with the same characteristics as the ones defined for column C2'" here above.

Fraction F2'' may be introduced into the column C2''" during step S2''" as a single fraction or as several subfractions. It is preferably introduced as a single fraction.

According to the second embodiment of step e), step S2''" is advantageously carried out at a pressure of at least 5, preferably at least 10 and particularly preferably at least 12 bar absolute. Step S2''" is advantageously carried out at a pressure of at most 40, preferably at most 38 and particularly preferably at most 36 bar absolute.
According to the second embodiment of step e), step S2'' is advantageously carried out at a pressure equal to or different from the pressure at which S2'' is carried out. Preferably, step S2''' is carried out at a pressure different from the pressure at which S2'' ' is carried out. Step S2'' is advantageously carried out at a pressure higher than the pressure at which step S2'' is carried out. Step S2'' is carried out at a pressure which is preferably at least 2 bar, more preferably at least 4 bar, most preferably at least 5 bar higher than the pressure at which step S2'' ' is carried out. Step S2''' is carried out at a pressure which is preferably at most 33 bar, more preferably at most 30 bar, most preferably at most 20 bar higher than the pressure at which step S2'' is carried out.

According to the second embodiment of step e), the temperature at which step S2'' is carried out is advantageously at least -50, preferably at least -40 and particularly preferably at least -30°C at the bottom of the stripping section of column C2'''. It is advantageously at most 80, preferably at most 60 and particularly preferably at most 55°C at the bottom of the stripping section of column C2'''.

According to the second embodiment of step e), the temperature at which step S2''' is carried out is advantageously at least -80, preferably at least -70 and particularly preferably at least -65°C at the top of the rectifying section of column C2''''. It is advantageously at most 0, preferably at most -15 and particularly preferably at most -25°C at the top of the rectifying section of column C2'''

According to the two embodiments of step e) defined above, the heavy fraction can be extracted in one unique fraction or in several fractions, preferably two fractions, more preferably one in the gaseous state enriched in ethane, preferably extracted in the lower third of the stripping section of the column, and one in the liquid state depleted in ethane, preferably extracted at the bottom of the stripping section of the column.

Second variant of the first embodiment is preferred over the second embodiment and over the first variant of the first embodiment. Second sub-variant of the second variant of the first embodiment is preferred over the first sub-variant of the second variant of the first embodiment. The second embodiment is preferred over the first variant of the first embodiment.

The quantities defined below to characterize fraction E2 are those at the outlet of separation step S2.
Fraction E2 is advantageously characterized by a hydrogen content of less than or equal to 2 %, preferably of less than or equal to 0.5 % and in a particularly preferred manner of less than or equal to 0.1 % by volume relative to the total volume of fraction E2.

Fraction E2 is advantageously characterized by a content of inert gases of less than or equal to 0.05 %, preferably of less than or equal to 0.04 % and in a particularly preferred manner of less than or equal to 0.03 % by volume relative to the total volume of fraction E2.

Fraction E2 is advantageously characterized by a volume content of oxygen lower than 0.05 %, preferably lower than 0.04 % and more preferably lower than 0.03 %.

Fraction E2 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 E2 is characterized by a content of compounds containing at least 3 carbon atoms, advantageously less than or equal to 0.01 %, preferably less than or equal to 0.005 % and in a particularly preferred manner less than or equal to 0.001 % by volume relative to the total volume of fraction E2.

Fraction E2 advantageously contains from 60 % to 99.5 % by volume of ethylene relative to the total volume of fraction E2. Fraction E2 advantageously contains at least 60 %, preferably at least 70 %, in a particularly preferred manner at least 80 % and a more particularly preferred manner at least 85 % by volume of ethylene relative to the total volume of fraction E2. Fraction E2 advantageously contains at most 99.5 %, preferably at most 98.5 %, in a particularly preferred manner at most 97.5 % and in a more particularly preferred manner at most 96 % by volume of ethylene relative to the total volume of fraction E2. Fraction E2 is therefore characterized in that it contains advantageously at least 4 %, preferably at least 2.5 %, more preferably at least 1.5 % and most preferably at least 0.5 % of compounds different from ethylene relative to the total volume of fraction E2.

The quantities defined below to characterize fractions E2a and E2b are those at the outlet of separation step S2.

Fraction E2a is advantageously characterized by a hydrogen content of less than or equal to 2 %, preferably of less than or equal to 0.5 % and in a particularly preferred manner of less than or equal to 0.1 % by volume relative to the total volume of fraction E2.
Fraction E2a is advantageously characterized by a content of inert gases of less than or equal to 0.05 %, preferably of less than or equal to 0.04 % and in a particularly preferred manner of less than or equal to 0.03 % by volume relative to the total volume of fraction E2.

Fraction E2a is advantageously characterized by a volume content of oxygen lower than 0.05 %, preferably lower than 0.04 % and more preferably lower than 0.03 %.

Fraction E2a 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 E2a is characterized by a content of compounds containing at least 3 carbon atoms, advantageously less than or equal to 0.001 %, preferably less than or equal to 0.0005 % and in a particularly preferred manner less than or equal to 0.0001 % by volume relative to the total volume of fraction E2.

Fraction E2a is advantageously characterized by an ethylene content which is similar to the content of fraction E2.

Fraction E2b is advantageously characterized by a hydrogen content of less than or equal to 0.2 %, preferably of less than or equal to 0.05 % and in a particularly preferred manner of less than or equal to 0.01 % by volume relative to the total volume of fraction E2.

Fraction E2b is advantageously characterized by a content of inert gases of less than or equal to 0.05 %, preferably of less than or equal to 0.04 % and in a particularly preferred manner of less than or equal to 0.03 % by volume relative to the total volume of fraction E2.

Fraction E2b is advantageously characterized by a volume content of oxygen lower than 0.05 %, preferably lower than 0.04 % and more preferably lower than 0.03 %.

Fraction E2b 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 E2b is characterized by a content of compounds containing at least 3 carbon atoms, advantageously less than or equal to 0.01 %, preferably less than or equal to 0.005 % and in a particularly preferred manner less than or equal to 0.001 % by volume relative to the total volume of fraction E2.

Fraction E2b is advantageously characterized by an ethylene content which is similar to the content of fraction E2.
The heavy fraction is enriched with ethane and hydrocarbon containing at least 3 carbon atom. The compounds comprising at least 3 carbon atoms result from the mixture of products containing ethylene and other constituents derived from step a). 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.

The heavy fraction advantageously contains at least 95 %, preferably at least 98 % and particularly preferably at least 99 % of and compounds comprising at least 3 carbon atoms contained in the mixture of products derived from step a).

The heavy fraction 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 the heavy fraction.

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

The heavy fraction can also be subjected to a separation step consisting of separating it, for example by distillation, into two different fractions respectively containing compounds comprising less than 5 carbon atoms for one of the fractions (fraction C1), and compounds comprising at least 5 carbon atoms for the other one (fraction C2). Fraction C1 is then preferably subjected to at least one hydrogenation step before recycling to step a) to be valorized chemically. Fraction C2, particularly enriched with benzene, is particularly preferably conveyed to the manufacture of ethylbenzene. It can therefore be interesting to adapt the process so that benzene is directed to the heavy fraction in order to maximize its recovery.

In some cases, it can be interesting to isolate ethane in order to valorize it. In these circumstances, the process according to the invention can be adapted so that ethane is isolated as an individual fraction.

After having been recovered, ethane can be burnt as fuel or valorized chemically. Ethane is preferably valorized chemically. Ethane is therefore more preferably either recycled to step a) or 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. Ethane is most preferably recycled to step a).
According to step f), fraction E2 or fractions E2a and E2b are then conveyed to the manufacture of at least 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, and 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, more preferably to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, most preferably either to a chlorination reactor and/or to an oxychlorination reactor, in which reactor most of the ethylene present in fractions E2 or E2a and/or E2b is converted to DCE.

The obtained DCE is thereafter advantageously, in step g) following step f), separated from the streams of products derived from the chlorination and/or oxychlorination reactor and preferably, in step h) following step g), subjected to a DCE cracking step to produce VC which is then still more preferably, in step i) following step h), polymerized to produce PVC.

Before step f), fractions E2 or E2a and/or E2b are 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, fractions E2 or E2a and/or E2b when directed to the manufacture of DCE and optionally of any compound derived there from are subjected to an acetylene hydrogenation. More preferably, fractions E2 or E2a and/or E2b when directed to the manufacture of DCE by direct chlorination are subjected to an acetylene hydrogenation step followed by a drying step. More preferably, fractions E2 or E2a and/or E2b when directed to the manufacture of DCE by oxychlorination are subjected to an acetylene hydrogenation without a drying step. In the last case, the hydrogenation of the fraction enriched in ethylene can be operated independently or simultaneously with the hydrogenation of the hydrogen chloride separated from the stream of products derived from the pyrolysis before it is sent back to the oxychlorination. Preferably, it is operated simultaneously with the hydrogenation of the hydrogen chloride.

The hydrogenation of acetylene is advantageously performed as described previously for step a8a). Advantageously, in case of such acetylene hydrogenation of fractions E2 or E2a and/or E2b, treated fractions are
advantageously characterized by an 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 step f), fraction E2 is advantageously conveyed to the manufacture of at least one ethylene derivative compound.

According to this first embodiment, the process according to the invention is advantageously such that, after steps a) to e), f) fraction E2 is then conveyed to the manufacture of at least 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, and 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, more 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 of step f), fraction E2 is advantageously conveyed in one fraction.

According to this first variant, the process according to the invention is advantageously such that, after steps a) to e), f) fraction E2 is conveyed in one fraction to the manufacture of at least one ethylene derivative compound, either to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, or 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.

Preferably, fraction E2 is conveyed in one fraction to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, either to a chlorination reactor or to an oxychlorination reactor, in which reactor most of the ethylene present in fraction E2 is converted to DCE.

The obtained DCE is thereafter more preferably, in step g) following step f), separated from the streams of products derived from the chlorination or oxychlorination reactor and most preferably, in step h) following step g), subjected to a DCE cracking step to produce VC which is then still most preferably, in step i) following step h), polymerized to produce PVC.
This case is particularly interesting when only one fraction is required for step f).

According to a second variant of the first embodiment of step f),
fraction E2 is advantageously divided into at least two fractions of the same
composition or of different composition, preferably into fraction E2d' and
fraction E2d" of the same composition or of different composition.

This last case is particularly interesting when different fractions, either of
the same or of different composition, are required for step f) to be conveyed to
the respective manufacture of ethylene derivative compound.

According to this second variant, the process according to the invention is
advantageously such that, after steps a') to e), f) fraction E2 is divided into at
least two fractions, preferably into fraction E2d' and fraction E2d", of the same
composition or of different composition, before being conveyed to the
manufacture of at least one ethylene derivative compound.

Preferably, one fraction among fractions E2d' and E2d" is 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.

More preferably, the two fractions are conveyed to the manufacture
of DCE and optionally of any compound derived there from, optionally after
having been subjected to an acetylene hydrogenation, one to a chlorination
reactor and the other to an oxychlorination reactor, in which reactors most of the
ethylene present in each fraction is converted to DCE.

The obtained DCE is thereafter advantageously, in step g) following
step f), separated from the streams of products derived from the chlorination and
oxychlorination reactors and preferably, in step h) following step g), subjected to
a DCE cracking step to produce VC which is then more preferably, in step i)
following step h), polymerized to produce PVC.

The term "divided" (or "division") in the expression "fraction E2 is divided
into at least two fractions" is understood to mean, for the purpose of the
invention, the splitting of fraction E2 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 E2 at the bubble point and by the composition of fraction E2 at the dew point.

The expression "bubble point" is understood to mean, for the purpose of the invention, the point such that, during the heating of fraction E2 at constant pressure from a starting temperature, fraction E2 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 fraction F2 at constant pressure from a starting temperature, fraction F2 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 division of fraction E2 into at least two fractions, preferably into fraction E2' and fraction E2", is advantageously operated by divided fraction E2 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 division of fraction E2 into at least two fractions, preferably into fraction E2d' and fraction E2d" of different composition, can be made by any known means. Advantageously, fraction E2 is cooled down by indirect cooling in a heat exchanger where fraction E2 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 mixture is preferably divided to produce the vapor fraction E2d' and the liquid fraction E2d". 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 E2d' advantageously contains more than 10, preferably more than 20 and more preferably more than 25 % the ethylene quantity which is contained in fraction E2. Fraction E2d' advantageously contains less than 90,
preferably less than 80 and more preferably less than 75% the ethylene quantity which is contained in fraction E2.

Fraction E2d’ is advantageously enriched in hydrogen in comparison with fraction E2. The ratio of the molar hydrogen concentration in fraction E2d’ versus the molar hydrogen concentration in fraction E2d” is advantageously higher than 25, preferably higher than 50 and more preferably higher than 60.

Fraction E2d’ is advantageously enriched in methane in comparison with fraction E2. The ratio of the molar methane concentration in fraction E2d’ versus the molar methane concentration in fraction E2d” is advantageously higher than 2.5, preferably higher than 4 and more preferably higher than 5.

Fraction E2d’ is advantageously depleted in ethane in comparison with fraction E2. The ratio of the molar ethane concentration in fraction E2d’ versus the molar ethane concentration in fraction E2d” is advantageously lower than 0.9, preferably lower than 0.85 and more preferably lower than 0.8.

According to a second embodiment of step f), fractions E2a and E2b are advantageously conveyed to the manufacture of at least one ethylene derivative compound.

According to this second embodiment, the process according to the invention is advantageously such that, after steps a) to e), f) fractions E2a and E2b are then conveyed to the manufacture of at least 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, and 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, more 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 second embodiment of step f), fractions E2a and E2b are conveyed separately.

According to this first variant, the process according to the invention is advantageously such that, after steps a) to e), f) fractions E2a and E2b are conveyed separately to the manufacture of at least one ethylene derivative compound.

Preferably, one fraction among fractions E2a and E2b is 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.

More preferably, the two fractions are conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, one, preferably fraction E2a, to a chlorination reactor and the other, preferably fraction E2b, to an oxychlorination reactor, in which reactors most of the ethylene present in each fraction is converted to DCE.

The obtained DCE is thereafter advantageously separated, in step g) following step f), from the streams of products derived from the chlorination and oxychlorination reactors and preferably, in step h) following step g), subjected to a DCE cracking step to produce VC which is then more preferably, in step i) following step h), polymerized to produce PVC.

This case is particularly interesting when different fractions are required for step f) to be conveyed to the respective manufacture of ethylene derivative compound.

According to a second variant of the second embodiment of step f), fractions E2a and E2b are mixed before being conveyed.

Fractions E2a and E2b can be mixed by any known means such as for example a mixing tee, a static mixer, a packed bed of inert particles, a succession of perforated plates or of orifices as well as a rotating machine (pump or compressor).

According to this second variant, the process according to the invention is advantageously such that, after steps a) to e), f) fractions E2a and E2b are mixed before being conveyed to the manufacture of at least one ethylene derivative compound, either to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, or 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.

Preferably fractions E2a and E2b are mixed before being conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, either to a chlorination reactor or to an oxychlorination reactor, in which reactor most of the ethylene present in fraction E2 is converted to DCE.
The obtained DCE is thereafter more preferably, in step g) following step f), separated from the streams of products derived from the chlorination or oxychlorination reactor and most preferably, in step h) following step g), subjected to a DCE cracking step to produce VC which is then still most preferably, in step i) following step h), polymerized to produce PVC.

This case is particularly interesting when only one fraction is required for step f).

As examples of ethylene derivative compounds manufactured directly starting with ethylene which are different from DCE which can be manufactured according to the embodiments described above, 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. A preference is given to the manufacture of ethylbenzene and a particular preference to the manufacture of ethylbenzene itself conveyed to the manufacture of styrene afterwards polymerized in order to obtain polymers of styrene.

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.

The chlorination reaction (usually called direct chlorination) is advantageously carried out in a liquid phase (preferably mainly DCE) containing a dissolved catalyst such as FeCl₃ 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 FeCl₃ with LiCl (lithium tetrachloroferrate - as described in Patent Application NL 6901398).

The amounts of FeCl₃ advantageously used are around 1 to 30 g of FeCl₃ per kg of liquid stock. The molar ratio of FeCl₃ 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 burnt as fuel or valorized chemically, for example for the hydrogenation of working solution in hydrogen peroxide manufacture or for the direct synthesis of hydrogen peroxide.

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

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 m²/g and 300 m²/g, preferably between 50 and 200 m²/g and particularly preferably between 75 and 175 m²/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 thereeto 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.

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.

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.

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.

5 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.

The first embodiment of step f) is preferred over the second one.

A preferred process according to the invention is a process for the manufacture of at least one ethylene derivative compound starting with a hydrocarbon source according to which:

a) the hydrocarbon source, containing fraction E1 recycled from step d), is subjected to a simplified cracking which produces a mixture of products containing ethylene and other constituents;

b) the said mixture of products is subjected to a first separation step S1 which consists of separating said products containing ethylene and other constituents into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 and into a fraction F2;

c) fraction F1 is sent to an ethylene recovery unit in which it is separated into a fraction enriched with ethylene called fraction E1 and into a fraction enriched with the compounds which are lighter than ethylene called light fraction;

d) fraction E1 is recycled to step a);

e) fraction F2 is subjected to a second separation step S2 which consists of separating, in one or in two separations, fraction F2 into one fraction enriched with ethylene called fraction E2 and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms called heavy fraction;
f) fraction E2 is then conveyed to the manufacture of at least one ethylene
derivative compound.

A particularly preferred process according to the invention is a process for
the manufacture of 1,2-dichloroethane starting with a hydrocarbon source
comprising steps a) to f) defined here above according to which the ethylene
derivative compound is 1,2-dichloroethane.

A first advantage of the process according to the invention is that it allows
the use of ethylene with a purity of less than 99.8 %.

Another advantage of the process according to the invention is that it does
not comprise catalytic oxydehydrogenation steps which need important
investment which causes an increase in the production costs.

An advantage of the process according to the invention compared with
processes described in the prior art is also that it does not require a separation
into two fractions of ethylene which are different in ethylene composition and
the conditions of use of which are different, what can disrupt the processes in
which they are afterwards used and which can limit the use thereof considering
the reactive impurities they contain; for example hydrogen which is not
acceptable in the oxychlorination process of ethylene.

Others advantages that can be attributed to the process according to the
invention are the advantages linked to the fact that the compounds which are
lighter than ethylene are separated from the ethylene fraction. Among them, one
can cite the advantage of operating the process in apparatus the dimension of
which are not to be increased and of avoiding losses by stripping which reduce
the efficiency of the process.

The process according to the invention by allowing the separation of the
fraction enriched with the compounds lighter than ethylene renders their
valorization easier.

Another advantage of this process is that it makes it possible to separate
the compounds comprising at least 3 carbon atoms via the heavy fraction, which
compounds are generally responsible for some undesirable side reactions leading
to formation of undesirable derivatives difficult to separate.

Finally, 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.

The preferred and particularly preferred processes according to the
invention will now be illustrated with references to the drawing accompanying
the present description. This drawing consists of the appended Figure 1, schematically representing the preferred process according to the invention for the manufacture of at least one ethylene derivative compound and the particularly preferred process according to the invention for the manufacture of 1,2-dichloroethane.

A hydrocarbon source (1), containing recycled fraction E1 (2), is subjected to a simplified cracking (3) which produces a mixture of products containing ethylene and other constituents (4). This mixture (4) is subjected to a first separation step SI (5) which consists of separating said mixture into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 (6) and into a fraction F2 (7). Fraction F1 (6) is then sent to an ethylene recovery unit (8) in which it is separated into a fraction enriched with ethylene called fraction E1 (2) which is recycled to the first step and into a fraction enriched with the compounds which are lighter than ethylene called light fraction (9). Fraction F2 (7) is subjected to a second separation step S2 (10) which consists of separating, in one or in two separations, fraction F2 (7) into one fraction enriched with ethylene called fraction E2 (11) and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms called heavy fraction (12). Fraction E2 (11) is then conveyed to the manufacture of at least one ethylene derivative compound and preferably, according to the particularly preferred process according to the invention, to the manufacture of 1,2-dichloroethane which can then be (not represented on the figure) subjected to a cracking to produce vinyl chloride which can then be polymerized to produce polyvinyl chloride.
CLAIMS

1 - Process for the manufacture of at least one ethylene derivative compound starting from a hydrocarbon source according to which

a) the hydrocarbon source, optionally containing fraction E1 recycled from step d), is subjected to a simplified cracking which produces a mixture of products containing ethylene and other constituents;

b) the said mixture of products is subjected to a first separation step SI which consists of separating said products containing ethylene and other constituents into a fraction containing the compounds which are lighter than ethylene and part of the ethylene called fraction F1 and into a fraction F2;

c) fraction F1 is sent to an ethylene recovery unit in which it is separated into a fraction enriched with ethylene called fraction E1 and into a fraction enriched with the compounds which are lighter than ethylene called light fraction;

d) fraction E1 is recycled to step a) or is conveyed to the manufacture of at least one ethylene derivative compound;

e) fraction F2 is subjected to a second separation step S2 which consists of separating fraction F2 into one fraction enriched with ethylene called fraction E2 or into two fractions enriched with ethylene called fractions E2a and E2b, and into a fraction enriched with ethane and hydrocarbon containing at least 3 carbon atoms called heavy fraction;

f) fraction E2 or fractions E2a and E2b are then conveyed to the manufacture of at least one ethylene derivative compound.

2 - Process according to Claim 1, characterized in that the hydrocarbon source is chosen from the group consisting of naphtha, gas oil, natural gas liquid, ethane, propane, butane, isobutane and mixtures thereof.

3 - Process according to Claim 2, characterized in that the hydrocarbon source is chosen from the group consisting of ethane, propane, butane and propane/butane mixtures.
4 - Process according to Claim 1, characterized in that step a) comprises a first cracking step of pyrolysis followed by a series of treatment steps among which a compression step and a drying step.

5 - Process according to Claim 1, characterized in that d) fraction E1 is recycled to step a).

6 - Process according to any one of Claims 1 to 5, characterized in that fraction E1 is recycled to the compression step and/or to the drying step of step a).

7 - Process according to Claim 1, characterized in that e) fraction F2 is subjected to a second separation step S2 which consists of separating fraction F2 into fraction E2 and into heavy fraction.

8 - Process according to Claim 1, characterized in that f) fraction E2 is conveyed to the manufacture of at least one ethylene derivative compound.

9 - Process according to Claim 1, characterized in that f) fraction E2 or fractions E2a and E2b are conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation, and 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.

10 - Process according to Claim 1, characterized in that f) fraction E2 or fractions E2a and E2b are conveyed to the manufacture of DCE and optionally of any compound derived there from, optionally after having been subjected to an acetylene hydrogenation.

11 - Process according to Claim 1, characterized in that fractions E2, E2a and E2b contain at most 99.5 % by volume of ethylene relative to their total volume.