

Process to produce a pyrolysis oil comprising liquid hydrocarbons from plastic material at high exergetic efficiency, and relative plant

Description

5 The present invention concerns a sustainable process for producing a pyrolysis oil which comprises liquid hydrocarbons from plastic material, preferably waste material.

 The field of application is the pyrolysis of plastic material to produce a pyrolysis oil comprising hydrocarbons.

10 This pyrolysis oil, after further treatment, can be converted into monomers useful for producing polymers, thus closing the loop.

 In the chemical industry, and more specifically polymers, it is increasingly strategic not only to recycle them, but also
15 to be able to do it in a sustainable way. In fact, a "closed loop" recycling process which is "closed" from the point of view of matter, but not of the required energy (i.e., it uses fossil fuels or anyway energy which ultimately derives mainly from that sources) is not truly closed, especially considering the very
20 high quantity of thermal energy required for pyrolysis process. As a result, the resulting carbon footprint can be so large that can jeopardize the effectiveness of the entire recycle loop, making the process no longer convenient.

 An integrated solution, such as the one now proposed,
25 allows not only the use of "green" energy, but also it maximizes its effectiveness. This efficiency improvement is significant, considering that the low solar irradiance and the required high concentration factor determines a high value of land surface per unit of pyrolysis oil produced.

The process, which would allow to close the plastic cycle and would therefore be highly desirable, however, requires large quantities of thermal energy at high temperatures. Conventionally, for this purpose the combustion of natural gas and/or electricity is used, which in turn is obtained largely by using the combustion of carbonaceous materials (gas, hydrocarbons, coal). The carbon footprint of the process is therefore high.

Technological solutions using solar rays as an energy source for gasification processes (therefore very similar to the pyrolysis of plastic materials) are known. Typically, in these processes, the solar rays are concentrated directly on an absorber placed in the reactor or on its external surface. In other processes (for example for the pyrolysis of biomass) a heat transfer fluid with molten salts is used, but obviously it must be brought at least to the highest temperature required for pyrolysis.

The use of solar radiation as an energy source could therefore be a known solution, however the solutions disclosed to date have severe limitations, including in particular the fact that heating a fluid to the temperature required by the pyrolysis process (or directly heating the reactor of pyrolysis) requires very high temperatures, that is, such as to require a very high concentration factor which is associated with a very low efficiency, the latter being linked, among other factors, to the dramatic increase in emissivity of the absorber tubes, for which a large part of the radiant energy is re-emitted towards the environment. This implies the use of a very high surface of mirrors, for a given fixed production of pyrolysis oil.

A pyrolysis process allowing the use of solar energy, but limiting the extension of the radiant surface required for a given production, is therefore desirable. The solution of the present invention makes it possible to achieve this goal.

5 Several patent applications disclose processes for thermal or catalytic pyrolysis of plastic materials. A few of them deals with the possibility to use solar energy.

Patent US 4,415,339 of the Department of Energy (DOE) teaches a method of producing with a solar reactor substantially
10 hydrocarbon free product gases (syngas) from a carbonaceous material feed, which method includes directing solar energy directly into the reactor. Solar energy is delivered directly, i.e. by means of a window where the solar rays can pass and heat the materials for gasification.

15 US 4,582,590 (National Aeronautics and Space Administration) discloses a method of pyrolyzing shale which includes the use of concentrated solar radiation. The solar radiation passes through a "solar window" reaching a ceramic honey-comb receiver, which is therefore heated at 350°C.

20 WO 2010/103520 discloses a solar-powered device for converting sludge by pyrolysis which includes a pyrolysis reactor operable by solar energy. Such solar energy is concentrated and redirected to the receiver located inside the pyrolytic reactor by focused mirrors. The reactor is shut down
25 when a sensor detects that the intensity of sunlight radiation falls below a threshold.

WO 2017/055652 (Department of Energy) describes a hybrid power plant based on the use of solar energy comprising a molten salt solar receiver configured to heat molten salts by solar

energy. There is a cold storage tank and a hot salt storage tank, a steam generator, a condenser, and a reactor-exchanger salts-biomass to exchange heat between a stream of salts and the biomass.

5 CN109207179 discloses a syngas production system through concentrated solar molten salt pyrolysis of carbonaceous material. The carbonaceous material can be, for instance, rice husk, cotton and corn straw residues, and urban domestic waste, and the temperature can be higher than 800°C, for instance
10 1000°C.

WO/2020/150244 (Sabic) discloses the use of renewable energy in olefin synthesis. In the claimed plant, at least one of the furnaces is an electrified furnace, wherein at least 90% of heating is produced without combusting a fuel.

15 None of the cited patents discloses a process to treat plastics material to produce a pyrolysis oil, by using a solar energy source. Moreover, in most cases the solar energy is used directly, e.g. by focusing the solar radiation directly to an absorbing surface which is located inside the reactor.

20 Some patent applications disclose the use of a molten salt as heat carrier medium to produce syngas from biomass (such as urban domestic waste, cotton and corn straw, rice husk). Biomasses are chemically quite different than plastic materials, and the product (syngas) is completely different from pyrolysis
25 oils. Therefore, the required operating conditions, such as temperature, is quite different (even over 1000°C). This process is typically unable to carry out the task of the present invention: for instance, as disclosed in cited CN109207179, the used molten salts melts at about 400°C. Generally, it is not

safe to use molten salts near their melting point to avoid solidification of the salt mixture in the apparatus, meaning that it would not be possible to use that process for pyrolysis of plastics, which requires a temperature of 400-520°C.

5 Pyrolysis of plastic materials is a highly desirable process as it allows to recycle mixed plastic waste materials, by breaking the polymeric chains into small organic molecules, which, after proper refining processes, can be used in the synthesis of polymers. Most of other recycle processes, such as
10 the so-called mechanical recycle (i.e. extrusion of waste plastics with virgin plastics so as to produce a blend) require the use of very pure plastic waste (that is, comprising only a specific polymer, for instance expanded polystyrene or linear low-density polyethylene or polyethylene terephthalate). In
15 fact, different polymers are incompatible to each other, and as a result the blend of such polymer mixture with a specific virgin polymer dramatically reduces its performance.

Other recycling processes, such as solvent dissolution and precipitation, can be used to specifically dissolve a specific
20 plastic material, so that it is possible to precipitate an almost pure polymer. However, extremely large quantities of solvent are required, and it is also needed to remove the plastics which do not dissolve as well as to purify the solvent from all dissolved and dispersed contaminants (such as short chain molecules,
25 inorganic additives which are used as fillers, and the like). Moreover, the process is available only for selected plastics, because for instance it is quite difficult to dissolve polyolefins.

Pyrolysis of plastic materials has the key advantage that

it is able to operate effectively with mixed plastic wastes, even in the presence of non-plastic waste materials such as paper; moreover, differently from other techniques, it has the capability to recycle mixed plastic waste unlimitedly, that is
5 there are unlimited loops of: plastic production from monomers, use of the plastics, collection of its waste after use, and monomers production by pyrolysis of its waste; thus closing the loop. For this reason, such process is frequently dubbed "closed loop recycling".

10 However, this is a strongly endothermic process and therefore it requires a huge amount of thermal energy. Moreover, as the required pyrolysis temperature is rather high ($>500^{\circ}\text{C}$), a high quality (i.e., at high exergy) heat is needed. As a result, only a few energy sources can be used to this scope.
15 Typically, this energy source is a gas heater (which burns natural gas and/or the incondensable gases produced by the pyrolysis process itself) or by direct electric heating via Joule effect. Electric energy has an extremely high exergetic content and it is not convenient to use it by Joule heating. Moreover,
20 both electric energy and gas heating considerably contribute to increase the carbon footprint, as the combustion of hydrocarbons produce large quantities of carbonic anhydride (CO_2) and in most countries electric energy is produced by gas, petroleum or carbon combustion. Moreover, due to the high temperature, the use of
25 heat pumps to pump heat from lower energy heat sources (such as steam or geothermal energy) is practically unfeasible.

As a result, there is the high risk that the unlimited recycle capability of pyrolysis ("closed loop recycling") is in fact limited by the fact that large quantities of precious and/or

not environmental-friendly energy sources have to be used.

As already reported, some patents disclose the direct use of sunlight, collected and concentrated by focusing mirrors, directly to a receiver located in the reactor chamber to produce
5 syngas. However, sunlight is an intermittent source and therefore the syngas production would stop shortly after sunlight decreases. Since these processes require high temperature and long period of time to stabilize, the use of direct sunlight is a serious limitation to its practical
10 implementation.

There is therefore the long-felt need for a process to produce pyrolysis oil from essentially plastic materials which use a heat source at almost zero impact on CO₂ production and which is able to use this energy source efficiently.

15 SUMMARY OF THE INVENTION

The Applicant has surprisingly found a process to produce at least a pyrolysis oil from essentially plastic materials which comprises the steps of:

- 20 a) Heating a first heat transfer fluid F1 to a temperature T1 comprised between 400°C and 520°C by means of solar radiation;
- b) Heating a second heat transfer fluid F2 to a temperature T2 higher than temperature T1 by means of solar radiation;
- c) Heating a first pyrolysis reactor R1 by means of the
25 heated first heat transfer fluid F1, which is therefore cooled in the operation;
- d) Heating a second pyrolysis reactor R2 by means of the heated second heat transfer fluid F2, which is therefore cooled in the operation;

- e) Feeding the first pyrolysis reactor R1 with at least an essentially plastic material M1;
- f) Keeping said essentially plastic material M1 in said first pyrolysis reactor for a residence time RT1 which is
5 at least 2 minutes and anyway sufficient to produce a fluid in the gaseous state M2 containing hydrocarbons;
- g) Feeding said fluid in the gaseous state M2 containing hydrocarbons produced in the first pyrolysis reactor R1 to a second pyrolysis reactor R2;
- 10 h) Keeping said fluid in the gaseous state M2 in said second pyrolysis reactor for a residence time RT2 which is at least 10 seconds;
- i) Condensing, totally or partially, the gas exiting said second pyrolysis reactor R2 so as to form at least a liquid
15 which comprises hydrocarbons having a standard boiling point not below 25°C.

The process disclosed and claimed in the present invention has the following advantages when compared to the processes known in the prior art:

- 20 - Closed loop recycling ready: The disclosed process is able to produce liquid hydrocarbons that, after further treating (e.g. by cracking and/or refining processes), can be used to produce polymers. After use, the articles made by such polymers can be fed again to the disclosed
25 process. The process can be repeated unlimitedly. As a result, the plastic materials can be recycled virtually an infinite number of times.
- GHG emissions free: the heat required to the pyrolysis process is obtained without direct and/or indirect

production of harmful greenhouse gases (such as carbon anhydride, CO₂).

- 5 - Efficient use of molten salt heat transfer fluid: the heat transfer fluid, which preferably consists of molten salts, is the same both in the solar system and in the pyrolysis system, so that the same fluid can flow in both systems. Therefore, there is no need of expensive heat exchangers.
- 10 - Maximized use of solar energy: solar energy is a precious source, especially when heat at high temperature is required. In fact, in this case a high concentration factor is required, which in turns means that a large area of incoming solar radiation has to be reflected to a relatively small heating area. The
15 special synergic process configuration disclosed in the present application is able to address this very specific issue, as the solution provided is able in fact to reduce the required average concentration factor, as it will be shown hereafter.
- 20 - Mixed plastics waste and Plasmix ready: Preferably the process is fed by mixed plastics waste materials, therefore little or no preprocessing is required, and there is no need to feed single-material sources such as essentially pure polyethylene. Even more preferably,
25 the process is fed by the residual plastics after the selection process has already selected and extracted the single-materials (especially polymers that can be reused as such when contaminations are low, such as polyethylene terephthalate (PET) and low-density

polyethylene (LDPE)). Such feed is sometimes called "Plasmix" (from plastic mix). The essentially plastics material that can be fed to the process can contain minor quantities of non-plastic materials such as wood, paper, concrete, metals and biomass. Plastics comprising inorganic fillers and halogens (such as polyvinyl chloride) can be fed and processed as well.

- Fouling free: The process is free from fouling and carbon build-up, clogging, even when the essentially plastic material which is fed is rich of high carbon-to-hydrogen plastics such as polystyrene or oxygen-rich polymers such as polyethylene terephthalate.

The present invention discloses and claims also a plant to produce at least a pyrolysis oil from essentially plastic materials which

comprises:

A) A first pyrolysis reactor (70) which has at least one inlet where an essentially plastic material is fed, an outlet where at least one gaseous effluent is removed, and a jacket and/or coil, provided with at least one inlet and one outlet for a heat transfer fluid;

B) A second pyrolysis reactor (71) which has at least one inlet where at least a gaseous stream from the first pyrolysis reactor (70) is fed, an outlet where at least one gaseous effluent is removed, and a jacket and/or coil, provided with at least one inlet and one outlet for a heat transfer fluid;

C) A first solar collector assembly (61) comprising a first solar receiver, preferably consisting of a tube receiver,

the first solar receiver comprising at least one inlet and one outlet for the heat transfer fluid, where said solar collector assembly is able to deliver concentrated solar radiation to said first solar receiver that in turns is configured to heat said heat transfer fluid;

D) A second solar collector assembly (62) comprising a second solar receiver, preferably consisting of a tube receiver, the second solar receiver comprising at least one inlet and one outlet for the heat transfer fluid, where said solar collector assembly is able to deliver concentrated solar radiation to said second solar receiver that in turns is configured to heat said heat transfer fluid;

E) A first tank (63, "cold reservoir") where the heat transfer fluid at low temperature is collected, the first tank (63) being fluidically connected to receive the heat transfer fluid from the first pyrolysis reactor (70) and send the heat transfer fluid to the first solar collector assembly (61);

F) A second tank (64, "warm reservoir") where the heat transfer fluid at medium temperature is collected, the second tank (64) being fluidically connected to receive the heat transfer fluid from the first solar collector assembly (61) and send the heat transfer fluid to the first pyrolysis reactor (70);

G) A third tank (65, "hot reservoir") where the heat transfer fluid at high temperature is collected, the third tank (65) being fluidically connected to receive the heat transfer fluid from second solar collector assembly (62)

and send it to the second pyrolysis reactor (71);

H) A condenser (72) with at least one inlet for the gaseous stream comprising hydrocarbons, and one outlet for the condensed liquid, which is able to at least partially

5 condense the gaseous stream comprising hydrocarbons;

 wherein said first solar collector (61) is fluidly connected to said first tank (63) at one end of the first solar receiver, and to said second tank (64) at the other end of the said first solar receiver; and wherein said second solar
10 collector (62) is fluidly connected to said second tank (64) at one end of the second solar receiver, and to said third tank (65) at the other end of the said second solar receiver; wherein said condenser (72) is fluidly connected to said second pyrolysis reactor (71), so as to be able to partly condense the pyrolysis
15 vapours produced by said first and second pyrolysis reactors.

DEFINITIONS

 In the description of the present invention, unless otherwise specified, the values of ranges (for example ranges of pressure, temperature, quantity, etc.) are to be considered to
20 include the extremes.

 In the description of the present invention, unless otherwise specified, percentages are by weight (i.e. by mass). The symbol "%" means percent, unless otherwise specified by weight (mass).

25 In the description of the present invention the term "comprising" also includes as a particular limiting case its meaning as "consisting of" and "essentially consisting of".

 In the description of the present invention the term "essentially consisting of" means that the composition or

formulation (i) necessarily includes the listed ingredients and (ii) is open to unlisted ingredients that do not materially affect the basic properties and innovative properties of the composition.

5 In the description of the present invention, unless otherwise specified, the act of maintaining a certain parameter (for example the pressure) within an indicated range means that operations are actively performed so that this parameter falls within the range, for example by checking that the measured value
10 falls within the indicated range, and/or by regulating the parameter by means of a feedback regulating system in which a value of this parameter is set within the indicated range.

 In the description of the present invention, by "essentially plastic material", a composition of one or more
15 plastics, optionally comprising up to 30 wt%, based on the weight of the essentially plastic material, of non-plastic materials, is meant.

 In the description of the present invention, by "plastic material" a generic polymeric material that may contain other
20 substances to improve performance and/or reduce costs is meant, as per the IUPAC definition (Pure Appl. Chem. Vol. 84 n.2, pp. 377-410, 2012).

 In the description of the present invention, "hydrocarbons having a standard boiling point not below 25°C" means that such
25 hydrocarbons have, individually, a standard boiling point, as defined by IUPAC, of at least 25°C (that is, equal to or greater than 25°C).

 In the description of the present invention, the act of condensing, totally or partially, the gas exiting said second

pyrolysis reactor R2 so as to form at least a liquid which comprises hydrocarbons having a standard boiling point not below 25°C does not exclude that such liquid can comprise also hydrocarbons having boiling point below 25°C, and non-
5 hydrocarbon compounds.

In the description of the present invention, by "pyrolysis vapours" the gaseous phase which is produced in the pyrolysis of the essentially plastic material is meant, such as the effluent in the gaseous state of the first pyrolysis reactor. This latter
10 contains the product of the pyrolysis, but also the compounds that are in the gaseous state at the pressure and temperature conditions of the pyrolysis, that were already present in the essentially plastic material subjected to the pyrolysis or added or already present in the first pyrolysis reactor (for instance,
15 in the inerting gas), such as nitrogen, water or low boiling point plasticizers. In the pyrolysis vapours, the content of hydrocarbons is typically more than 50 wt%.

In the description of the present invention, by pyrolysis oil the liquid formed by partial or total condensation of the
20 pyrolysis vapours, and which comprises hydrocarbons that have a standard boiling point not below 25°C, is meant. In the pyrolysis oil the content of hydrocarbons is typically more than 50 wt%.

In the description of the present invention, by pyrolysis residue (or equivalently, by char) the product which is in the
25 liquid, solid, or liquid and solid state (that is, semi-solid) in the first pyrolysis reactor, or which is in the liquid and/or solid state under the conditions of temperature, pressure and composition in the pyrolysis, is meant.

In the description of the present invention, unless

otherwise specified, by substantial absence of oxygen is meant that the oxygen (understood as molecular oxygen) in the pyrolysis vapours is less than 2% by weight, preferably less than 0.8% by weight, even more preferably between 20 and 4000 ppm by weight, with respect to the total weight of the composition of said vapours.

In the description of the present invention, by "heat transfer fluid" a solid, liquid, gaseous or also multiphase fluid that is used to transfer heat from one system to another, in particular from a heat source to other heat demands (heat duties), is meant. Preferably, heat transfer fluids are fluids specifically manufactured for the purpose of transmitting heat and that are stable (that is, do not degrade rapidly) in the used process conditions.

In the description of the present invention, the first heat transfer fluid does not need to be compositionally different from the second heat transfer fluid, however preferably they have different temperatures.

In the description of the present invention, by "SCA" the solar collector assembly is meant, which generally comprises reflectors (mirrors, such as the Fresnel reflectors, or parabolic mirrors in the case of parabolic troughs), the metal support structure, the receiver tube(s), and optionally the tracking system that includes the drive, sensors, and controls. The length of the receiver tubes does not need to be equal to the length of the reflector, as several receiver tubes can be connected in series to form a longer receiver tube (such that also a length of even more than 200 m can be obtained), which in turn can receive the sunlight radiation from multiple

mirrors/reflectors in series. Moreover, to optimize the mass flow rate of the heat transfer fluid in the receiver tubes, as well as to maximize the solar radiation, it is useful to split the flow of the heat transfer fluid to be heated into several
5 absorber tubes in parallel. For this reason, in the description of the present invention, the solar collector assembly generally comprises a plurality of mirrors/reflectors and relative absorber tubes, preferably combined in series, in parallel, and in series-parallel combinations.

10 In the description of the present invention, by "molten salt" (or, equivalently, molten salts) a salt which is solid at standard temperature and pressure but enters the liquid phase due to elevated temperature is meant. Molten salts can be composed by a single component (e.g. sodium nitrate alone) or a
15 mixture of salts (e.g. mixture of sodium and potassium nitrate).

In the description of the present invention, by "loaded device" any device that is heated by means of the heat transfer fluid is meant. Examples of "loaded device" are the first and second pyrolysis reactors, the coker, the preheater.

20 In the description of the present invention, by "fluid loop", "heat transfer fluid loop", "hot loop", "warm loop", the process by which the heat transfer fluid is substantially entirely recirculated in the process are meant.

By "substantially entirely recirculated" it is meant that
25 the heat transfer fluid is not generated or consumed in the process, so there are no net inlet or outlet streams; however, conveniently, the fluid may be spilled or slowly replaced, in particular because it is known that most heat transfer fluids degrades over time at high temperature. Preferably, a

substantially entirely recirculated fluid has a total inlet or outlet mass flow that is less than 1% of the recirculating mass flow, even more preferably less than 0.1%.

In the description of the present invention, unless
5 otherwise specified, for a value of a parameter that is equal to at most a determined value X, it is meant that the parameter is equal to X or less than X; and for a value of a parameter that is equal to at least a certain value X, it is meant that the parameter is equal to X or greater than X.

10 In the description of the present invention, unless otherwise specified, by yield in the production of a product the percentage by weight of that product with respect to the total of obtained products is meant.

Unless otherwise specified, in this document "part" and
15 "parts" mean respectively part by weight and parts by weight. Weight means mass, i.e. kg in SI units.

Unless otherwise specified, in this document the combination of an individual range from one list with another individual range emerging from a second list of ranges and
20 relating to a different feature should be considered to be disclosed in the application, even in the absence of a clear pointer to such combination.

BRIEF DESCRIPTION OF FIGURES

Figure 1 shows a process scheme illustrative of an
25 embodiment of the present invention, characterized by three heat transfer fluid reservoirs and two pyrolysis reactors.

Figure 2 shows a process scheme illustrative of an embodiment of the present invention, characterized by the addition of a plastic preheater (such as an extruder or screw

device).

Figure 3 shows a process scheme illustrative of an embodiment of the present invention, characterized by the addition of an additional device ("coker") which further treats
5 the liquid/solid/semi-solid residuum (char) effluent of the reactor.

Figure 4 shows a process scheme illustrative of an embodiment of the present invention, characterized by both the presence of said coker which further treats the
10 liquid/solid/semisolid residuum (char) effluent of the reactor, as well as the plastic preheater (such an extruder or screw device).

Figure 5 shows a process scheme illustrative of an embodiment of the present invention, characterized by the fact
15 that the condensation of the pyrolysis gas is carried out in more than one unit, and where in the first of such units said pyrolysis gas is cooled by the heat transfer fluid before entering the cold reservoir, thus realizing a heat recovery.

Figure 6 shows a process scheme illustrative of an embodiment of the present invention, characterized by the fact
20 that the heat transfer fluid coming from the warm reservoir is delivered to the first pyrolysis reactor and the preheater device in semi-series by means of a weir device 78 before returning to the cold reservoir.

25 Figure 7 shows a process scheme illustrative of an embodiment of the present invention, characterized by the fact that the heat transfer fluid coming from the hot reservoir is delivered to the coker device and the second pyrolysis reactor in semi-series by means of a weir device 79 before returning to

the cold reservoir.

Figure 8 shows a process scheme with a dual heat transfer fluid loop, corresponding to Example 1 (inventive).

Figure 9 shows a process scheme with a single heat transfer
5 fluid loop, corresponding to Example 2 (comparative).

Figure 10 shows a process scheme illustrative of an embodiment of the present invention, characterized by the fact that the first heat transfer fluid and relative heat transfer fluid loop is not fluidly in connection with the second heat
10 transfer fluid and relative heat transfer loop.

Figure 11 shows a process scheme illustrative of some embodiments of the present invention, characterized by the fact that it is shown the position of the additional power sources in three different positions (66A for parallel, 66B and 66C for
15 series arrangement)

Figure 12 shows a process scheme illustrative of an embodiment of the present invention, characterized by the use of three reservoirs, and which focuses to show the hot and warm loops and their distinction.

20 Figure 13 shows a process scheme illustrative of an embodiment of the present invention, characterized by the use of four reservoirs and two completely independent loops, which focuses to show the hot and warm loops and their distinction.

Figure 14 shows a process scheme illustrative of an
25 embodiment of the present invention, characterized by the three reservoirs and two completely independent or partly independent loops.

DETAILED DESCRIPTION OF THE INVENTION

According to one embodiment, the process to produce at

least a pyrolysis oil from essentially plastic materials is characterized by the fact that the fluids F1 and F2 are substantially entirely recirculated.

A first embodiment of the present invention is shown in
5 Figure 1. The scheme comprises:

- A first pyrolysis reactor (70) (at lower temperature), also referred to as primary pyrolysis reactor;
- A second pyrolysis reactor (71) (at higher temperature), also referred to as secondary pyrolysis reactor;
- 10 - A condenser (72) which condensate the effluent of the second pyrolysis reactor (71);
- A separator (73) which separates the gaseous (non condensed) phase from the liquid one;
- A medium temperature solar collector assembly or first solar
15 collector (61) (SCA);
- A high temperature solar collector assembly or second solar collector (62) (SCA);
- A cold reservoir of the heat transfer fluid (63);
- A warm reservoir of the heat transfer fluid (64);
- 20 - A hot reservoir of the heat transfer fluid (65);
- heat transfer fluid pumps 66 which deliver the heat transfer fluid to the heating system (solar receivers) and to the duties (pyrolysis reactors);
- Optional bypasses (B1) to (B4=.

25 In relation to the plant to produce at least a pyrolysis oil from essentially plastic materials, preferably the following operations are carried out:

- In said first solar collector assembly (61) comprising a first solar receiver, the first heat transfer fluid F1 is

heated to a temperature T1 comprised between 400°C and 520°C by means of solar radiation (process step a);

- In said second solar collector assembly (62) comprising a second solar receiver, the second heat transfer fluid F2 is heated to a temperature T2 higher than temperature T1 by means of solar radiation (process step b);
- A jacket and/or coil is provided with at least one inlet and one outlet for molten salts, comprised in said first pyrolysis reactor (70) (element "A"), and carries out the heating of said first pyrolysis reactor (70) (or R1) by means of the heated first heat transfer fluid F1;
- A jacket and/or coil is provided with at least one inlet and one outlet for molten salts, comprised in said second pyrolysis reactor (71) (element "B"), and carries out the heating of said second pyrolysis reactor (71) (or R2) by means of the heated second heat transfer fluid F2;
- in said first pyrolysis reactor (70) (element "A") are fed at least an essentially plastic material M1 (process step e) and the essentially plastic material M1 is kept in said first pyrolysis reactor for a residence time which is at least 2 minutes and anyway sufficient to produce a fluid in the gaseous state M2 that contains hydrocarbons (process step f);
- in said second pyrolysis reactor (71) (element "B") is fed said fluid in the gaseous state M2 that contains hydrocarbons produced in the first pyrolysis reactor (70) (or R1) (process step g) and said fluid in the gaseous state M2 is kept in said second pyrolysis reactor (71) (or R2)

for a residence time which is at least 10 seconds (process step h);

- in said condenser (72) (element "H") the gas exiting said second pyrolysis reactor (71) (or R2) is condensed so as to form at least a liquid which comprises hydrocarbons having a standard boiling point not below 25°C (process step i).
- In the context of the present invention, a fluid connection may comprise devices that are sandwiched or anyway positioned in between, such as, for instance, pumps and valves.

In the context of the present invention, an electronic connection includes any non-mechanical and non-thermal mean to transmit information, such as by a flow of electrons (electric current) or flow of photons (light transmission, such as by optical fibers) or electromagnetic waves (e.g. WiFi transmission).

The essentially plastic material is fed at (51) to the first pyrolysis reactor (70) which is heated by the heat transfer fluid at medium temperature (33) coming from the warm reservoir (64). The heat transfer fluid coming out of the first pyrolysis reactor (70) (therefore at lower temperature) is brought to the cold reservoir (63).

Pyrolysis gases developed in reactor (70) are delivered to the second pyrolysis reactor (71), which is at higher temperature than the first pyrolysis reactor (70), while the solid or semi-solid residuum (like char) is recovered at (53).

In some embodiments, also a part of the liquid comprised in the reactor (70) can be recovered from (53).

In the second pyrolysis reactor (71) the pyrolysis gas

coming from the first reactor (70) is further heated to a higher temperature by means of the heat transfer fluid (37) coming from the hot reservoir (65). In the second reactor (71), the gases are therefore further pyrolyzed. The effluent of the second reactor (71) is cooled and condensed by means of condenser (72). The gases that are not condensed are recovered at (55). The condensate forms the pyrolysis oil which is collected in reservoir (73) and recovered at (56). Reservoir (73) can be integrated in the condenser (72). The heat transfer fluid which exits from the second pyrolysis reactor is brought to the warm reservoir (64).

Optional bypasses (B1) to (B4) are useful to refill reservoirs one another, without the need to pass through the heating system and duties (for maintenance and/or to decouple flow rate from heat duty).

The medium temperature solar collector assembly (SCA) (61) heat up the heat transfer fluid (31) from the cold tank (63), while the high temperature solar collector assembly (62) heat up the heat transfer fluid (35) from the warm tank (64). From the medium temperature solar collector assembly (61) the heat transfer fluid is brought to the warm reservoir (64), while from the high temperature solar collector assembly (62) the heat transfer fluid is brought to the hot reservoir (65).

According to one preferred embodiment, the heat transfer fluid in one loop is heated by at least one solar collector assembly, and is cooled, releasing its heat, in at least one pyrolysis reactor, before returning to the solar collector assembly (possibly passing through a heat transfer fluid reservoir).

According to one preferred embodiment, in the process to produce at least a pyrolysis oil from essentially plastic materials, the fluids F1 and F2 are substantially entirely recirculated.

5 Preferably, the process of the present invention is a dual-loop process (or, alternatively, "two-loop process").

 This means that there are two substantially independent thermal loops: in the so-called "warm-temperature thermal loop" (or, more concisely, "warm loop"), the heat transfer fluid F1 is
10 heated from a low temperature to a "warm" temperature by means of a first (lower temperature) solar collector assembly. This fluid is used in the first pyrolysis reactor and optionally other devices as taught in the disclosure of the present invention.

 In the so-called "hot-temperature thermal loop" ("hot
15 loop"), the heat transfer fluid F2 is heated from a "warm" temperature to a "hot" temperature by means of a second solar collector assembly. This fluid is used in the second pyrolysis reactor and optionally other devices as taught in the disclosure of the present invention.

20 According to one preferred embodiment, the recirculation of fluid F1 forms a first heat transfer fluid loop ("warm loop"), and the recirculation of fluid F2 forms a second heat transfer fluid loop ("hot loop").

 In the dual-loop process, it is possible that the molten
25 salt fluids of the two loops mix at some point (typically, in the warm reservoir). However, the essential feature that characterizes the dual-loop process from the single-loop process is that the heat transfer fluid is at least partly withdrawn from at least two points of the solar collector assembly(ies)

(F1, F2) at different temperatures (T1, T2), and used at least in part separately to heat the pyrolysis devices (such as the reactors) at different temperatures.

By "used at least in part separately" it is meant that
5 there are at least two distinct circuits ("hot loop", "warm loop") where the heat transfer fluid flows and where the loaded devices (such as the pyrolysis reactors) are fluidly connected.

According to one embodiment, said first heat transfer fluid F1 and said second heat transfer fluid F2 are of the same
10 composition, but at a different temperature. According to one embodiment, fluids F1 and F2 can mix at a certain point, preferably when they have substantially the same temperature.

According to one embodiment, said first heat transfer fluid F1 and said second heat transfer fluid F2 are of the same
15 composition, but at different operating temperature (T1 and T2), and mix at a single point, preferably in a reservoir (such as the "warm reservoir").

A simplified view of this embodiment is shown in Figure 12, which is provided to clearly show the flow of the heat
20 transfer fluid in each loop. In Figure 12, it is seen that in the "warm" reservoir (64) the two loops mix together, however the two loops are kept substantially distinct as there is only one point of contact. In Figure 12 a dotted box has been placed around the coker (76) and the preheater (74), to show that they
25 are optional. The dashed lines in the reservoirs show the direction of the flow inside the reservoir.

The cold, hot and warm reservoirs optionally can comprise some mixing feature, such as an internal recirculation pump, or a stirrer, for instance an anchor stirrer, turbine stirrer, or

pitched blade impeller. Such mixing means improve homogenization of the temperature in the reservoir, and especially at start-up it can be particularly useful.

However, even without said mixing feature, the flow of the
5 heat transfer fluid from inlets to outlets and natural convection contribute to a certain degree of internal recirculation and mixing in the reservoirs. Therefore, said dashed lines, especially in the warm reservoir, are symbolic representations of the flow directions of the heat transfer fluid inside the
10 reservoirs, but they should not be intended as the only flows that can occur inside the reservoirs.

Therefore, with reference to the steps of the process of the present invention already disclosed, it is a subject of the present invention a process to produce at least a pyrolysis oil
15 from essentially plastic materials, where the first loop comprises said step a) and said step c) and the second loop comprises said step b) and d).

According to another embodiment, the process to produce at least a pyrolysis oil from essentially plastic materials
20 additionally comprises the steps of:

j) Storing the first heat transfer fluid F1 coming from step c) in a reservoir ("cold reservoir") before of its use in step a);

k) Storing the second heat transfer fluid F2 heated in
25 step b) in a reservoir ("hot reservoir") before of its use in step d).

According to another embodiment, in the process to produce at least a pyrolysis oil from essentially plastic materials, the heat transfer fluid F1 is compositionally the same as the heat

transfer fluid F2.

When the fluids F1 and F2 are compositionally the same, according to another embodiment, the process of the present invention to produce at least a pyrolysis oil from essentially plastic materials additionally comprises the step of:

1) Storing the first heat transfer fluid F1 heated in step a) before its use in step c), and the second heat transfer fluid F2 cooled in step d) before its use in step b), in a reservoir ("warm reservoir").

Another embodiment of the present invention, having "separate loops", is shown in Figure 10. The scheme comprises the same devices of Figure 1, except the warm reservoir 64 which is split into two separate reservoirs 64A and 64B:

- The first "warm" reservoir ("warm reservoir A", 64A) collects the heat transfer fluid coming from the first solar collector assembly (61).
- The first "warm" reservoir (64A) delivers the heat transfer fluid to the pyrolysis devices which require lower temperatures, such as the first pyrolysis reactor (70) and optionally the preheater or heat exchangers with organic heat transfer fluids.
- The second "warm" reservoir ("warm reservoir B", 64B) collects the heat transfer fluid coming from the devices which require higher temperatures, such as the second pyrolysis reactor or the coker.
- The second "warm" reservoir (64B) delivers the heat transfer fluid to the second solar collector assembly (62).

A simplified view of the same embodiment is shown in Figure 13, which is provided to clearly show the flow of the heat

transfer fluid in each loop.

It is therefore an embodiment of the present invention a process to produce at least a pyrolysis oil from essentially plastic materials, which additionally comprises the steps of:

- 5 m) Storing the first heat transfer fluid F1 heated in step a) before its use in step c) in a reservoir ("warm reservoir A");
- n) Storing the second heat transfer fluid F2 cooled in step d) before its use in step b), in a reservoir ("warm reservoir B").

10 According to said embodiment with separate loops, the heat transfer fluid loops can be fully separated, therefore it is possible to use different fluids for the hot loop and for the warm loop. For instance, it is possible to use molten salts having a lower melting temperature for such loop. It is generally advantageous to use low melting point molten salts as it means that it is possible to run the plant safely at lower temperatures (generally, it is advisable to run the plant so as that in the coldest point the molten salts have a temperature at least 50°C

15 higher than their melting point), and because restarts after prolonged stops take less time.

However, typically molten salts having lower melting point have also a lower thermal stability, so they cannot be used for the hot loop which requires very high temperature.

25 According to this embodiment, it is therefore advantageous to use a heat transfer fluid for the warm loop which is different from the heat transfer fluid of the hot loop. According to this embodiment, preferably the heat transfer fluid of the warm loop has a lower melting point than the heat transfer fluid of the

hot loop, more preferably the heat transfer fluid of the warm loop has a melting point that is at most 180°C, even more preferably at most 150°C.

For instance, it is possible to use as heat transfer fluid the so-called Hitec fused salts (sodium nitrate 7 wt%, potassium nitrate 53 wt%, sodium nitrite 40 wt%) or the ternary mixtures of lithium nitrate, sodium nitrate and potassium nitrate, for instance the eutectoid mixture having composition 25.9 wt% lithium nitrate + 20.6 wt% sodium nitrate + 54.1 wt% potassium nitrate.

For instance, it is possible to use the quaternary mixture of sodium nitrate, potassium nitrate, lithium nitrate and calcium nitrate, for example the mixture composed by 9.5 mol% sodium nitrate, 52.8 mol% potassium nitrate, 27.6 mol% lithium nitrate and 10.1 mol% calcium nitrate, having a melting point of only 98.3°C.

Another embodiment of the present invention, having "separate loops", is shown in Figure 14. According to this embodiment, the warm reservoir (64) is split into two reservoirs (64A) and (64B), as per the embodiment of Figure 13, however the two reservoirs (64A) and (64B) are inside the same container (such as a tank) and are separated by a weir (64C). In such a way, it is possible to reduce the number of units to be built, therefore reducing installation costs. Moreover, the weir (64C) let one heat transfer fluid to overflow in the other reservoir in the event the level becomes too high.

Optionally, the weir (64C) comprises at least one opening (64D), preferably in the bottom part of the weir, which allows to equilibrate the levels of the two reservoirs (64A) and (64B).

When such at least one opening is present, the separation of the fluids in the two reservoirs (64A) and (64B) is not complete. Therefore, when the opening is large, the scheme in Figure 14 corresponds to the scheme in Figure 12, as the contact surface
5 where the fluids of the two reservoirs are in touch is large. Oppositely, when the opening is small, the scheme in Figure 14 corresponds to the scheme of Figure 13, as the contact surface is minimal, or even zero.

It is therefore an embodiment of the present invention the
10 process to produce at least a pyrolysis oil from essentially plastic materials which additionally comprises the steps of m) and n) characterized in that said warm reservoir A and warm reservoir B are comprised in the same container and are preferably separated by a weir. According to another embodiment,
15 in said process said weir comprises at least one opening that allows the fluid in said warm reservoir A to flows in said warm reservoir B and vice versa.

Preferably, the essentially plastic material comprises compositions of different plastics. Still more preferably, said
20 compositions of different plastics comprise at least polymers with a high H/C ratio, such as for example polyethylene, polypropylene, polyamides, polymethyl methacrylate, and polymers with a low H/C ratio, such as polystyrene, polycarbonate, polyethylene terephthalate.

25 Alternatively, or in combination, said different plastics compositions include high carbon index polymers such as polyethylene (including LDPE, LLDPE, HDPE), polypropylene, polystyrene, elastomers and low carbon index polymers such as polyamides, polymethyl methacrylate, polyethylene

terephthalate, polyvinyl chloride and cellulose.

Preferably, said essentially plastic material is characterized by an H/C ratio (H/C index) equal to at least 70, preferably between 80 and 98, more preferably between 85 and 96.

5 Preferably, said essentially plastic material is characterized by a carbon index equal to at least 55, preferably between 65 and 95, more preferably between 75 and 90.

The H/C index is proportional to the ratio of the total mass of hydrogen atoms to the total mass of carbon atoms present
10 in the essentially plastic material, and is calculated using the following formula:

$$\text{H/C Index} = 100 \cdot \frac{12}{2} \cdot \frac{\text{Weight H atoms}}{\text{Weight C atoms}}$$

The carbon index is proportional to the ratio of the total mass of carbon atoms to the total mass of all atoms present in
15 the essentially plastic material, and is calculated using the following formula:

$$\text{Carbon Index} = 100 \cdot \frac{\text{Weight C atoms}}{\text{Weight ALL atoms}}$$

where "weight of ALL atoms" corresponds to the weight of the essentially plastic material.

20 Preferably said essentially plastic material contains at least one non-plastic material in an amount ranging from 0.01% to 10% by weight with respect to the weight of the essentially plastic material, more preferably in an amount ranging from 0.05% to 7.5%, even more preferably in an amount ranging from 0.2% and
25 5%. Said non-plastic material preferably comprises at least one of the following materials: paper, cardboard, wood, compost (as defined by IUPAC in "Terminology for biorelated polymers and applications (IUPAC Recommendations 2012)", Pure Appl. Chem.,

Vol. 84, No 2, pp. 377-410, 2012, DOI 10.1351/PAC-REC-10-12-04),
metallic materials such as aluminum and iron, and/or inert
materials.

Optionally, said essentially plastic material contains
5 inorganic fillers such as for example silica, titanium oxide,
talc, coke, graphite, carbon black, calcium carbonate.

Optionally, said essentially plastic material contains
brominated and chlorinated additives used to make the plastic
material fireproof or in any case to impart flame propagation
10 retardant properties. Examples of said additives are
hexabromocyclododecane, decabromodiphenyloxide, polybrominated
diphenyl ethers, and bromine-containing polymers such as
brominated styrene-butadiene copolymers or brominated
polystyrene.

15 Optionally, said essentially plastic material contains
non-halogenated additives used to make the plastic material
fireproof or in any case to impart flame propagation retardant
properties, such as compounds of phosphorus and nitrogen.

Preferably, said essentially plastic material is recycled
20 material, such as waste material or secondary raw material.

Preferably said essentially plastic material also contains
halogens (typically, from polyvinyl chloride) in an amount
ranging from 0.01% to 10% by weight of halogens with respect to
the weight of the essentially plastic material.

25 Preferably said essentially plastic material is obtained
from a plastic material sorting process. Still more preferably
said essentially plastic material is the essentially plastic
material residual material, i.e. the essentially plastic
material fraction which remains after having recovered some

plastics, or after having selectively extracted some plastics from the essentially plastic material fed to the selection process. Selective extraction consists in the essentially homomaterial extraction (i.e. as a monoplastic) of certain plastics. Typically, in a selection process (sorting) it is possible to extract streams of substantially pure plastic (i.e. as a monoplastic) of the polyethylene, polypropylene and polyethylene terephthalate components. In this preferred selection, the essentially plastic material residual material is therefore the material which results after the extraction of said substantially pure plastics. This fraction is known in Italy with the term "Plas Mix" or "Plasmix", which is defined as the "set of heterogeneous plastics included in post-consumer packaging and not recovered as individual polymers" (Article 1 of the draft bill of the Chamber of Deputies no. 4502 of 05/18/2017).

According to another embodiment of the present invention, shown in Figure 2, the essentially plastic material is preheated before being fed to the first pyrolysis reactor (70) in a preheat device (74). Advantageously, according to this embodiment, the heat transfer fluid (33) is fed from the warm reservoir to the heating jacket of the first pyrolysis reactor (70). The heat thermal fluid exiting the pyrolysis reactor jacket is sent to the jacket of said preheat device (74). The heat thermal fluid exiting the preheat device (34) is returned to the cold reservoir.

According to another embodiment of the present invention, shown in Figure 3, the solid, semi-solid or liquid material from the first pyrolysis reactor (70) is delivered to the "coker"

treatment device (76). A separator (77) (which can be integrated into the coker device) allows the gaseous phase (53E) to be recycled back into the process (for instance, in the first pyrolysis reactor as depicted in Figure 3), while the non-gaseous
5 phase is collected in flow (53D).

The char-feeder device (75) can be a pumping device, which moves the solid, semi-solid or liquid material from the first pyrolysis reactor to said coker device, allowing at the same time a physical separation between the two devices. An example
10 of such device is a gear pump. Alternatively, the char-feeder device (75) can be a valve, such as a rotary valve, gate valve or butterfly valve.

Advantageously, according to this embodiment, the heat thermal fluid coming from the hot reservoir (37) is delivered
15 first to said coker device (76) and then, at (53B), to the second pyrolysis reactor (71), before returning to the warm reservoir (38). Advantageously, said char-feeder device (75) can be heated by the heat transfer fluid (34A) exiting the heating jacket of the first pyrolysis reactor (70), before returning to the cold
20 reservoir.

According to another embodiment of the present invention, shown in Figure 4, both embodiments shown in Figure 2 and Figure 3 are combined together. As a result, the essentially plastic material is preheated in said preheater (74) and the solid, semi-
25 solid or liquid material from the first pyrolysis reactor (70) is delivered by means of the char-feeder device (75) to the "coker" (76). Advantageously, the heating of such devices is carried out by means of the heat transfer fluid coming from the hot and warm reservoirs as described before in the explanation

of the embodiments of Figure 2 and 3.

In the coker (76), said material is heated to a temperature from 500°C to 1200°C, preferably from 600°C to 1000°C, more preferably from 700°C to 900°C, for a time of at least 5 minutes, 5 preferably between 15 and 180 minutes, more preferably between 30 and 120 minutes. As a result of such heat treatment, the char is purified, in particular the more volatile components are separated and collected in the gaseous phase, and the char is further pyrolyzed, producing a solid product that has a lower 10 H/C ratio and higher carbon index, and with a better health safety environment (HSE) profile.

As the coker, any device that can carry out such operation is suitable. Preferably, such coker is a device comprising a rotating screw. More preferably, such rotating screw is 15 horizontal or at inclination of up to 30° to the horizontal axis.

The coker can be heated by means of a heat transfer fluid, and optionally also by a gas heater, by means of electric resistance (Joule effect) or combinations thereof. In case of use of the heat transfer fluid, it is preferred to use the heat 20 transfer fluid coming from the hot reservoir.

Therefore, according to one embodiment of the present invention, the process to produce at least a pyrolysis oil from essentially plastic materials additionally comprises the step of:

- 25 o) Heating the liquid, solid or semi-solid residue of the pyrolysis of step f) (the char) by means of the heated second heat transfer fluid F2 and optionally also by a gas heater, by means of electric resistance (Joule effect), or combinations thereof.

Preferably, in step o), said char is heated to a temperature from 500°C to 1200°C, preferably from 600°C to 1000°C, more preferably from 700°C to 900°C, for a time of at least 5 minutes, preferably between 15 and 180 minutes, more preferably between 30 and 120 minutes.

According to another embodiment of the present invention, shown in Figure 5, the condensation of the pyrolysis gas exiting the second pyrolysis reactor is split in more than one unit (e.g. unit (72A) and unit (72B)). More in detail, the pyrolysis gas (54) exiting the second pyrolysis reactor (71) passes through a first condenser (72A), at "high-temperature", and a first separator (73A), which separates the condensed liquid (56A) from the non-condensed vapours (55A). Said non-condensed vapours (55A) are then passed through a second condenser (72B) at "low temperature", and a second separator (73B), which separates the condensed liquid (56B) from the non-condensed vapours (55).

Advantageously, according to this embodiment, the cooling of the first condenser (72A) is carried out by means of the heat thermal fluid (33E) already used to heat the first pyrolysis reactor (70), before entering the cold reservoir (63). In this way, there is a heat recovery which allows to reduce the overall heat duty to condense the pyrolysis oil, and, at the same time, by heating the heat thermal fluid, to reduce the required heat duty of the solar collector assembly (61).

According to one embodiment, the heating of the first pyrolysis reactor (70), the char-feeder device (75) and the preheater (74), in the same range of temperature, can be carried out by using the heat transfer fluid (33) coming from the warm reservoir (64).

All the other ancillary and miscellaneous devices and parts that link such devices (for instance, the connecting pipes) can be heated as well with the same heat transfer fluid.

Preferably, the distribution of the heat transfer fluid to
5 such devices can be carried out in series, in parallel or in semi-series.

When in series, preferably the heat transfer fluid coming from the warm reservoir (64) is first fed to the pyrolysis reactor and then to the other devices, such as the preheater
10 (74) or the char-feeder device (75). More preferably, the order is: first pyrolysis reactor (70), then (if present) the preheater (74) and then (if present) the char-feeder device (75). According to a further embodiment, if the condensation is split into two or more steps, and the cooling fluid in the first condenser is
15 the heat transfer fluid, as depicted in Figure 5, such series includes also said first condenser, and preferably in said order the last element is said first condenser. As a result, more preferably, the order is: first pyrolysis reactor (70), then (if present) the preheater (74), then (if present) the char-feeder
20 device (75), and last (if present) the first condenser (72A).

Semi-series configurations are combination of series and parallel configurations which allows to get both the advantages of the series and of the parallel mode.

An embodiment of a semi-series configuration is depicted
25 in Figure 6 and Figure 7.

Figure 6 shows a weir device (78) which receives the heat transfer fluid coming from the warm reservoir (64) and delivers such fluid to the first pyrolysis reactor (70) and to the preheater (74), finally releasing such fluid to the cold

reservoir (63). According to such embodiment, the weir device comprises a first chamber, where the oil coming from said warm reservoir is sent. In such first chamber is located a first pump (66B) which delivers the heat transfer fluid to the first
5 pyrolysis reactor (70). The heat transfer fluid exiting the first pyrolysis reactor enters in the same chamber. A weir, which can be for instance a Bazin weir, ensures that there is enough head (net positive suction head) to avoid cavitation in the pumping of the heat transfer fluid to the first pyrolysis reactor (70),
10 as well as entrainment of the gaseous phase. This weir forms also the containment wall of said first chamber, so that the fluid inside the chamber is recirculated. This ensures uniformity in the fluid temperature inside the chamber, as well as high resilience to instabilities in the flow rate of the fluid
15 incoming from the warm reservoir.

The excess heat transfer fluid overflows from the weir, thus entering in the subsequent chamber. Similarly to the first chamber, in the subsequent chamber another pump (66B) is located, which delivers the heat transfer fluid to the preheater (74) and
20 collects its return. Similarly, another weir ensures that the pump (66B) which delivers the fluid to the preheater has enough NPSH and that no gas is entrained. Finally, the last chamber includes another pump to deliver the heat transfer fluid to the cold reservoir (63). Start and stop of such pump can be handled
25 automatically by means of a level switch, so that the pump starts only when the level of the last chamber is above a given height.

Differently from the series configuration, the weir device (78) makes it possible to deliver different flow rates of heat transfer fluid to each device. Differently from the parallel

configuration, where all the devices share the same source (the warm reservoir), the weir device makes it possible to deliver a heat transfer fluid at higher temperature to the device which requires higher temperature and higher relevance (i.e., in order to have a constant temperature on the heat transfer fluid if compared to the temperature of the successive chambers).

Therefore, the weir device allows greater flexibility and effectiveness if compared to standard parallel or series configurations.

In another embodiment, such device can be located inside the warm reservoir itself, so that the pump delivering the heat transfer fluid to the weir device is not required any longer. In another embodiment, the warm, cold and hot reservoirs can be located in the Solar field, while the pyrolysis plant can be located at a certain distance from the Solar field. In such cases, a buffer reservoir is required to avoid that any problem in the delivery of the heat transfer fluid determines a failure in the pyrolysis process.

In these cases, the weir devices can act also as a buffer reservoir.

It has to be understood that there are many different other customizations of the weir device, e.g. allowing more chambers for managing more devices to be heated by the heat transfer fluid.

Advantageously, all devices that receives the heat transfer fluid are placed at different height levels so that the minimum number of heat transfer pumps are required.

More precisely, according to this embodiment, the first device which receives the heat transfer fluid from the pumps

is located at the maximum height level, and the devices which receive the heat transfer fluid exiting the first device are located at a lower height level, so that the fluid can flow into the device by gravitational force. Doing so, there is no need of
5 additional pumps.

This is advantageous as any moving part on fluid at high temperature, which can show also high melting temperature, is particularly delicate and can requires special measures to start properly and to maintain in case of failure. Moreover, in this
10 way, the pressure of the heat transfer fluid in said devices can be atmospheric, simplifying the design and reducing the cost of the devices. Last but not least, being not in pressure, an accidental breakage of the heat jacket is much safer as the spill from the breakage is reduced.

15 According to a preferred embodiment, all heat transfer fluid reservoirs are located at the bottom level.

The preheater (74) can be any device where the essentially plastic material can be heated up and, preferably, partly or totally melted.

20 Example of such devices are mono-screw extruders, twin-screw extruders, or, more generally, screw devices that are able to deliver a plastic material and that have a jacket or equivalent means where the heat transfer fluid can flow.

Optionally, the heat transfer fluid flows also inside the
25 screw, thus improving the efficacy of the device.

Preferably, such device is able to be almost gas-tight so that the gases in the first pyrolysis reactor (70) do not exit the pyrolysis reactor (70). A means to obtain such result is to use the same plastics melt which flows between the screws and

the barrels as a mean to obtain gas tightness.

Said preheating equipment can be equipped with a degassing device for the evacuation of water vapour and any other gases produced, such as hydrogen chloride (HCl) in particular. For this purpose, it may be advantageous to feed said preheating apparatus, in addition to said essentially plastic material, also with additives able to favour the evolution of hydrochloric acid or to salify the same. These additives are preferably compounds of the elements of group IA and IIA. Even more preferably they are the oxides, hydroxides, carbonates, silicates and aluminosilicates of group IA and IIA. Even more preferably they are calcium oxide, calcium hydroxide, calcium carbonate, sodium oxide, sodium hydroxide, sodium carbonate, potassium oxide, potassium hydroxide, potassium carbonate, sodium aluminosilicate.

The preheating temperature can be between 120°C and 430°C, preferably between 150°C and 320°C, more preferably between 180°C and 220°C. The residence time in said preheating apparatus is preferably less than 20 minutes, more preferably less than 4 minutes, in particular less than one minute.

It is therefore an embodiment of the present invention a process to produce at least a pyrolysis oil from essentially plastic materials, which additionally comprises the step of:

p) Heating the essentially plastic material before step e) by means of the heated first heat transfer fluid (F1).

According to such embodiment, preferably in step p) the essentially plastic material is brought to a temperature between 120°C and 430°C, more preferably between 150°C and 320°C, even more preferably between 180°C and 220°C, and where the average

residence time of step p) is preferably less than 20 minutes, even more preferably less than 4 minutes, in particular less than one minute.

The first pyrolysis reactor (70) can be any reactor which
5 is able to receive an essentially plastic feed and to bring it to pyrolysis conditions (temperature and pressure).

Said first pyrolysis reactor for the pyrolysis of essentially plastic material can be operated both in batch mode, in continuous mode, and in semi-continuous mode. In the latter
10 mode, the essentially plastic material is loaded continuously, the vapours generated are extracted continuously, but any solid residue is kept inside the pyrolysis reactor.

When the amount of solid residue inside the reactor rises above a certain threshold, or at predefined time intervals, for
15 example with a frequency ranging from 2 to 10 days, the said solid material contained in the reactor is removed.

Preferably, the reactor is operated in continuous or semi-continuous mode, more preferably in semi-continuous mode.

The pyrolysis process of the present invention is not
20 limited by a particular type of reactor.

In particular, horizontal or vertical, stirred or non-stirred reactors, kiln reactors, or screw reactors can be used. Fluidized bed reactors are not preferred.

Among the stirred reactors, continuously stirred reactors
25 (CSTR) and multizone reactors can be used. Plug flow reactors (PFR) can also be used, preferably stirred so as to facilitate heat transfer.

Among the continuously stirred reactors (CSTR) it is possible to use totally filled reactors (meaning that there is

no essentially gaseous phase over the treated plastic melt and products of reaction such as char) and reactors with a separation of the gaseous phase from the phase, including the liquid and other possible phases such as the solid char produced, i.e. reactors in which there is a free surface.

Preferably the reactor is a stirred reactor with a free surface.

The residence time of the essentially plastic material (M1) in said first pyrolysis reactor is at least 2 minutes and anyway sufficient to produce a fluid in the gaseous state (M2) that contains hydrocarbons. This means that in any case the residence time shall be enough to produce a fluid in the gaseous state, and that this time can be more than 2 minutes. This time can be different depending on the composition of the essentially plastic material fed to the reactor, but in case no gases are produced, the expert of the art has no difficulty to increase the residence time so that this condition is met.

The temperature of the material in the pyrolysis reactors can be measured by any method known in the art. For example, the following devices can be used: thermocouples with a facing membrane aligned with the internal surface of the reactor, so as to reduce fouling; or thermowell thermocouples for a more precise measurement inside the reactor; or thermocouples that measure the temperature of the metal near the surface of the reactor wetted by the polymer; or non-contact measuring systems, for example infrared devices. Multiple systems can be used simultaneously for improved reliability.

The temperature can be regulated by acting on the thermal power introduced into the reactor. Thermal power is obtained by

the flow of said heat transfer fluid in the reactor.

The parts in contact with such heat transfer fluid are separated from the parts in contact with the process fluids (plastics inlet, liquified plastics, char, gas produced by
5 pyrolysis etc.).

Preferably, the heat transfer fluid flows in a jacket. Optionally, the heat transfer fluid flows also inside the stirrer, so as to heat the stirrer too.

Preferably, the heat transfer fluids F1 and/or F2 are
10 molten salts. Any molten salt can be used for the present invention.

The heat transfer fluid may be a low melting temperature alkaline metals of (III)A, (IV)A and (V)A-group (that is metal alloys where elements belongs from (III)A to (V)A groups of the
15 periodic table) and (III)A, (IV)A and (V)A-group based metal alloys. Alkaline metals include cesium (mp 28°C), lithium (180°C), potassium (63°C), rubidium (39°C), sodium (mp 98°C); (III)A, (IV)A and (V)A-group low melting temperature metals include Indium (m.p. 157°C), gallium (m.p. 30°C), bismuth (mp
20 271°C), lead (mp 327°C), tin (mp 232°C); (III)A, (IV)A and (V)A based metal alloys that are metal alloys where elements belonging from (III)A to (V)A groups of the periodic table sum up to at least 70% by weight, such as Wood's metal (50% bismuth, 26.7% lead, 13.3% tin, and 10% cadmium, mp 70°C), Field's metal (32.5%
25 Bi, 51% In, 16.5% Sn, mp 62°C), Rose's metal (50% bismuth, 25-28% lead and 22-25% tin, mp 98°C), Pewter metal (tin (85-99%), antimony (approximately 5-10%), copper (2%), bismuth, mp about 170-240°C), Cast metal (40% Bi, 60% Sn, mp 170°C), lead-antimony eutectic (12% Sb, 88% Pb, mp 252°C), lead-tin eutectic (61.9%

Sn, 38.1% Pb, mp 184°C), Galinstan (68.5% Ga, 21.5% In, and 10.0% Sn, mp -19°C).

Among low melting temperature alkaline metals, sodium and potassium are preferred; among (III)A, (IV)A and (V)A-group
5 metals, lead, bismuth, indium, gallium, tin are preferred; among (III)A, (IV)A and (V)A-group based metal alloys Wood's metal, Field's metal, Rose's metal, Pewter metal, Cast metal and Galinstan are preferred.

According to one embodiment, the molten salts are a molten
10 salt of group IA and IIA of the periodic table, preferably sodium nitrate, sodium nitrite, potassium nitrite, potassium nitrate, lithium nitrate, calcium nitrate, or mixtures thereof.

According to one embodiment, the molten salts that can be used are nitrate/nitrite mixtures, in particular mixtures of
15 potassium nitrate and sodium nitrate, optionally with the addition of sodium nitrite and calcium nitrate.

According to one embodiment, such nitrate/nitrite mixture is the eutectic mixture of 53 wt% potassium nitrate, 40 wt% of sodium nitrite and 7 wt% of sodium nitrate; alternatively,
20 according to another embodiment, such K/Na nitrate/nitrite mixtures are the eutectic mixture of 45.5 wt% potassium nitrate and 54.5 wt% of sodium nitrite.

According to one embodiment, such nitrate/nitrite mixture is the so-called "solar salt", characterized by 60 wt% of sodium
25 nitrate and 40 wt% of potassium nitrate.

According to one embodiment, such nitrate/nitrite mixture is the so-called "Hitec XL", characterized by 7 wt% of sodium nitrate, 45 wt% of potassium nitrate and 48 wt% of calcium nitrate.

According to one embodiment, the nitrate/nitrite mixture is 100 wt% of lithium nitrate.

According to one embodiment, the nitrate/nitrite mixture is lithium nitrate 25 wt%, sodium nitrate 25 wt% and potassium
5 nitrate 50 wt%.

According to one embodiment, the molten salts are mixture of chlorides, such as sodium chloride and mixtures of sodium and potassium chlorides, optionally with magnesium chloride.

According to a further embodiment, the heat transfer fluid
10 is a molten salt comprising group IA and IIA metal fluorides, preferably lithium, sodium, potassium and calcium fluoride. Even more preferably, the heat transfer fluid consists of a molten salt comprising sodium nitrite, sodium nitrate and potassium nitrate. Even more preferably, the heat transfer fluid consists
15 of a molten salt comprising sodium nitrate and potassium nitrate.

Preferably, this heat transfer fluid has a low melting temperature. More preferably, said melting temperature is at most 340°C, still more preferably at most 270°C, even more preferably at most 240°C.

20 Preferably, this heat transfer fluid has a high decomposition temperature. More preferably, said decomposition temperature is at least 400°C, still more preferably at least 450°C, even more preferably at least 490°C, mostly preferably at least 540°C.

25 According to one embodiment, the melting temperature of the heat transfer fluid is at least 60°C, preferably more than 80°C, more preferably more than 105°C.

Preferably, this heat transfer fluid has a low chloride content. Preferably, the chlorides content is less than 1000 ppm

by weight. More preferably, the chlorides content is lower than 100 ppm by weight.

According to one embodiment, any component of the process, such as for instance the reactor, the coker, the preheater, the valves and so on, intended to contain molten salts is drainable by gravity. For instance, the reservoirs (hot, cold, warm) can be located at the lowest point so that in case of failure (such as molten salt pumps failure, or sudden interruption of electrical energy source) the heat transfer fluid drains to the reservoirs by gravity. According to another embodiment, any component comprising molten salts which is characterized by the presence of moving parts (such as valves) or by large aspect ratios (e.g. pipes) has an electrical heat tracing which can be activated before starting the plant, so as to melt the heat transfer medium.

The solar collector assembly (SCA) can be of any type. According to one embodiment, the solar collector is a "single focal point", meaning that the Solar rays are reflected to a focal zone that is essentially limited in size. Examples of "single focal point" are the parabolic dish and the power tower. According to another embodiment, the solar collector is a "focal line", meaning that the Solar rays are reflected to a focal zone that is essentially a line. Example of such solar collectors are the parabolic trough and the linear Fresnel. There are several specific types of parabolic trough and linear Fresnel, such as the "compact linear Fresnel reflector" (CLFR) or the "enclosed trough system", that can be used in the present invention as well.

Preferably, the solar collector is a parabolic trough or

linear Fresnel, in the latter case, in particular the compact linear Fresnel.

Therefore, according to one embodiment of the process of the present invention, the heating of step a) and b) is carried out by means of at least one solar collector assembly comprising parabolic trough, linear Fresnel, or a combination thereof. According to one preferred embodiment of the process of the present invention, the heating of step a) and b) is carried out by means of at least one solar collector assembly consisting of parabolic trough, linear Fresnel, or a combination thereof.

The Solar rays that are collected by such collectors are reflected to the so-called Solar receivers. In one embodiment, such Solar receivers consist of a heat exchanger where the heat transfer fluid is heated. Typically, in such receivers the fluid flows in tubes which are heated by the solar rays.

In another embodiment, such Solar receivers consist of a tube where the Solar rays are directed to. The tube, typically a metallic tube, is called the "absorber". The tube is coated with a selective coating which maximizes sunlight absorption, while minimizing thermal losses by infrared emission. A glass tube which englobes said absorbing tube is transparent, so that the sunlight can pass through it. Between the two tubes, high vacuum is produced, so as to limit convection heat losses. Sometimes a degassing nozzle and/or a getter is added, so as to be able to maintain such vacuum over time.

The solar receiver ends with bellows to account for differential thermal expansion of the glass and metal materials.

Solar collectors and relative receivers can be assembled in parallel, in series, or in combination of parallel and series

configurations. The combination of parallel and series configurations is preferred.

In some cases, such as in particular for linear Fresnel (and compact linear Fresnel), a single receiver can receive the
5 concentrated solar radiation from several reflectors.

The concentration factor (sometimes called also "concentration ratio") is the ratio of the radiant power density at the receiver divided by the radiant power density of the sun without any concentration, therefore it is the factor by which
10 the incident energy flux is optically enhanced on the receiving surface. The concentration factor according to the present invention is from 8 to 1000, more preferably from 10 to 100, even more preferably from 15 to 80.

According to one embodiment of the present invention, the
15 concentration factor of the solar collector assembly 62 heating the hot reservoir 65 is higher than the concentration factor of the solar collector assembly 61 heating the warm reservoir 64.

Therefore, according to one embodiment of the process of the present invention, the concentration factor of the at least
20 one solar collector assembly of step b) is higher than the concentration factor of the at least one solar collector assembly of step a).

The hot, warm and cold reservoirs can be any container that can be filled with a heat transfer fluid, such as vertical
25 or horizontal tanks. Advantageously, these containers are thermally insulated to limit the heat losses.

According to one embodiment, the heat transfer fluid pump 66 is located inside the reservoir.

According to one embodiment, the level of the heat transfer

fluid in the reservoir is monitored, so as to limit the pyrolysis duty when the level of heat transfer fluid in the hot or warm reservoir becomes too low.

According to an embodiment of the present invention, there
5 is also a further reservoir of heat transfer fluid, so as to deliver heat transfer fluid at more than two temperatures to the pyrolysis devices.

According to one embodiment, such first pyrolysis reactor is a vertical vessel, preferably of essentially cylindrical
10 shape.

Preferably, the top and bottom ends of the first pyrolysis reactor are conical, ellipsoidal or semi-ellipsoidal. In this way both a better recirculation is carried out and less fouling is observed. Fouling is in fact critical in pyrolysis reactors.

15 Preferably, the first pyrolysis reactor 70 has at least a stirrer. Such stirrer should be of adequate size to ensure that at least the whole volume of the reactor filled with the liquid and solid phase is continuously or semi-continuously wiped (e.g., not necessarily the gaseous phase). Preferably, the
20 stirrer should also be able to periodically move the material near the wall of the reactor, so as to clean the surface and reduce fouling.

An example of such stirrers are anchor or ribbon stirrers, or in some cases turbine stirrers.

25 The speed of such stirrers is typically from 1 to 300 rpm, preferably from 5 to 120 rpm.

According to some embodiments, more than one stirrer can be used. In this case, advantageously, the stirrers have different stirrer speed. One simple way to accomplish this task

is to leave one stirrer free to rotate, so that it is entrained by the fluid to a rotational speed which is below the one of the stirrer actively run, but more than zero.

By "condenser" any equipment which receives a fluid in the gaseous state, and capable of removing sufficient heat from said fluid, so as to generate at least a part of the fluid in the liquid state, is meant.

Examples of this equipment are condensers comprising coils inside which a heat transfer fluid, capable of removing heat from the fluid in the gaseous state being processed, flows.

Other ways of removing heat can also be used, for example, alternatively or in combination, the condenser can be provided with a jacket in which said heat transfer fluid flows, in order to remove heat.

Flooded condensers can also advantageously be used, in which the condenser is partially flooded by the produced liquid phase, and whose condensing power is regulated by varying the height of said liquid phase, since only the coil which is not flooded is capable of absorbing calories from the vapour to be condensed. This therefore allows effective regulation of the power of the condenser.

Alternatively, the condenser can consist of a distillation column. In this case the condensed fluid originates in the condenser of the column and the condensed liquid flows back by gravity or by pumping in the column, condensing the vapours that are inside it. In this way, a better fractionation of the incoming vapours is also obtained, i.e. a better separation between higher boiling components which are condensed and lower boiling components which remain in the vapour phase is achieved,

since in each stage there is an enrichment of the liquid phase of heavy substances and an enrichment of the gaseous phase of light substances. Furthermore, the washing of the vapours operated by the column allows any solid particulate present in the incoming vapours to be separated and reunited in the liquid phase.

The condenser of the pyrolysis vapours can be a single condenser or many condensers in series or in parallel. Preferably, when more than one condenser is used, two to four condensers are used in series, even more preferably three condensers in series are used.

When the condensers are in series, each condenser receives the uncondensed gas leaving the previous condenser, while the first condenser receives the pyrolysis vapours.

In this preferred mode, the condenser which receives the pyrolysis vapours (the first condenser) operates at a higher temperature than the second condenser which receives the uncondensed vapours from the first condenser. If there are more condensers, the next one (e.g., the third one) receives the uncondensed vapours from the previous one and operates at a lower temperature.

According to a preferred method, part of the fluid in the liquid state condensed in at least one condenser is recycled to the first pyrolysis reactor. Preferably, the fluid recycled to the reactor is taken from the first condenser.

According to one embodiment, when more than one condenser is used, the heat is removed by the first condenser by means of the heat transfer fluid as already described in Figure 5 (condenser 72A).

The fluid comprising hydrocarbons which, after passing through said at least one condenser, has not been condensed, hereinafter defined as residual gas, advantageously contains at least 40% by weight of light hydrocarbons (C1-C5), and can advantageously be used as fuel gas. A part of this gas can be burned to supply additional thermal energy that may be useful for the pyrolysis process and related devices, especially the ones requiring higher temperature such as the second pyrolysis reactor and the coker. For this purpose, for example, a gas heater can be used, which gas heater regulates the temperature of the heat transfer fluid circulating in the reactor jacket. Alternatively or in combination, this residual gas can advantageously be used to feed refinery plants, such as for example a cracking plant.

According to the invention, the fluid which is in the liquid state after condensing in said at least one condenser is quantitatively at least 10% by mass, preferably between 20% and 92%, still more preferably between 30% and 85%, still more preferably between 40% and 75%, with respect to the mass of essentially plastic material fed. If several condensers are used, this quantity is calculated by adding the mass quantity of liquid produced by each condenser.

According to the invention, at least a fluid is formed after condensing in said at least one condenser, which fluid is in the liquid state and comprises hydrocarbons having a standard boiling point not below 25°C, preferably not below 40°C, more preferably between 80°C and 220°C.

Preferably, at least the first pyrolysis reactor is operated at a pressure that is atmospheric or supra-atmospheric

(that is, more than atmospheric pressure). According to one embodiment, the pressure is between 1.1 and 20 bara, more preferably between 2 and 10 bara, and even more preferably between 2.2 and 6 bara.

5 Preferably, the temperature to which the essentially plastic material is brought in said first pyrolysis reactor is from 330°C to 580°C, preferably from 340 to 540°C, more preferably from 360 to 500°C, still more preferably from 380 to 480°C, even more preferably from 410 to 450°C.

10 Any technique known in the art can be used to maintain the pressure in the first pyrolysis reactor at a defined value, wherein the maintained pressure may have different values as a function of the pyrolysis temperature. According to a first method, the pressure can be maintained at a defined value by
15 regulating the heat extracted from the condenser located downstream of the reactor and in fluid connection with it. In this mode, an increase of the heat removed from the condenser results in greater vapour condensation. This condensation, bringing the evaporated material from the gaseous state to the
20 liquid state, having a much greater density, leads to a reduction in pressure.

 Alternatively, pressure can be controlled by introducing a gas, like nitrogen, argon or water steam, and regulating the flow of such gas by means of a valve. According to one
25 embodiment, such gas is introduced in the first pyrolysis reactor and acts also as an inerting gas (that is, a gas that does not participate directly to the pyrolysis reactions and that can displace the oxygen present in the reactor when it is

open to atmosphere, e.g. during maintenance or before it is started).

According to a preferred embodiment, pressure can be controlled by regulating the flow of the gaseous stream that
5 is not condensed (in case of more than one condenser is used in series, the gaseous stream of the last condenser).

According to one embodiment, the pyrolysis of the essentially plastic material of the present invention is carried out in a substantial absence of oxygen, with the
10 meaning of "substantial absence of oxygen" defined before.

Therefore, according to this embodiment, the process to produce at least a pyrolysis oil from essentially plastic materials is also characterized by the fact that step f) and step h) are carried out in substantial absence of oxygen.

15 Heat power to the first pyrolysis reactor and the second pyrolysis reactor can be regulated by controlling the flow rate of the heat transfer fluid, or its temperature, or both.

Advantageously, the pyrolysis process of the present invention produces a product particularly useful for use as
20 jet fuel or as virgin naphtha, particularly suitable for steam cracking for the production of monomers of industrial interest, or suitable in the synthesis of polymers.

Preferably, the second pyrolysis reactor is operated at a temperature that is higher than the temperature of the first
25 pyrolysis reactor. More preferably, the temperature difference between the second pyrolysis reactor and the first pyrolysis reactor is at least 10°C, still more preferably between 30°C and 300°C, even more preferably between 60°C and 250°C.

According to another embodiment, the second pyrolysis reactor is always operated at a temperature that is at least 10°C more than the temperature of the first pyrolysis reactor, with the additional condition that such temperature is between
5 400°C and 650°C, preferably between 440°C and 550°C, more preferably between 460°C and 530°C; that means that when the minimum temperature of these ranges is lower than the temperature of the first pyrolysis reactor plus 10°C, the latter ($T_{\text{first pyrolysis reactor}} + 10^{\circ}\text{C}$) should be considered
10 as the lower range.

It is therefore included in the invention a process to produce at least a pyrolysis oil from essentially plastic material, where the gaseous effluent of the first pyrolysis reactor, before condensation, is brought to a second pyrolysis
15 reactor where the gaseous stream is heated to a temperature that is at least 10°C more than the temperature of the essentially plastic material in the first pyrolysis reactor.

Therefore, according to one embodiment of the present invention, it is provided a process to produce at least a
20 pyrolysis oil from essentially plastic materials, where the difference in temperature between temperature T2 of step b) and temperature T1 of step a) is at least 10°C, still more preferably between 30°C and 300°C, even more preferably between 60°C and 250°C.

25 Residence time of the pyrolysis vapours in said second pyrolysis reactor, computed dividing the volume occupied by vapours in the reactor and the volumetric flow rate, is at least 10 seconds, preferably between 30 seconds and 6 minutes, even more preferably between 1 and 4 minutes.

Preferably, the second pyrolysis reactor is catalytic. More preferably, said effluent in the gaseous state is in relative motion with respect to said solid catalyst in contact with said effluent in the gaseous state, and said relative
5 motion is at a speed of at least 0.5 m/s, more preferably from 2 to 50 m/s.

All pyrolysis catalysts known in the art can be used, including in particular zeolites.

The second pyrolysis reactor can be operated at the same
10 pressure of the first pyrolysis reactor 70 or at a lower pressure, preferably, the second pyrolysis reactor is operated at a pressure comprised between the atmospheric pressure and the pressure of the first pyrolysis reactor. Even more preferably, it is operated at a pressure comprised between the pressure of
15 the first pyrolysis reactor and the same pressure decreased by 10000 Pa.

Advantageously, the first pyrolysis reactor can be more than one unit, as well as the second pyrolysis reactor. In such way, it is possible to scale up the process easily.

20 Moreover, when the liquid/solid/semi-solid residuum (char) of the first reactor accumulates in one unit, it is possible to stop such unit, discharge the char, clean the unit and restart it. If the production plan of each first pyrolysis reactor is set programmatically, it is possible to set the stop of the
25 single units for maintenance regularly and one at a time, thus keeping the entire pyrolysis stable over time.

Advantageously, the second pyrolysis reactors can be fed by the outlet pyrolysis vapours coming from more than one first pyrolysis reactor units. Preferably, the gaseous vapours of from

2 to 20 first pyrolysis reactor units are fed to a single second pyrolysis reactor, even more preferably from 3 to 8 units.

Similarly, the char produced by more than one first pyrolysis reactor units is fed to a single char treatment device
5 (such as the "coker").

To sustain the pyrolysis process while the sunlight radiation power is too low to provide the required heat, for instance after sunset or in cloudy or rainy conditions, it is possible to use the heat transfer fluid accumulated in the hot
10 and warm reservoirs. Typically, the temperature of the reservoirs is not changed, so as to ensure a stable pyrolysis and not to affect the quality of the pyrolysis oil which is obtained.

On the contrary, it is possible to stop or reduce the flow
15 rate of the heat transfer fluid in the charge section (the solar collector assemblies) while keeping unchanged (or slowly reducing) the flow rate of the heat transfer fluids from the hot and the warm reservoir. In this way, the level of the heat transfer fluid in the hot reservoir decreases, possibly also the
20 level of the warm reservoir decreases (depending on the relative ratio of the mass flows), while the level of the cold reservoir increases.

The bigger the volume of the reservoirs, the longer the period of time when it is possible to operate the process in
25 such "discharging" additional power sources. Especially in these cases, the size of the reservoir can be very large, therefore it can be convenient to split the reservoirs in more units, that can be for instance operated in parallel.

It is also possible to increase the energy accumulation,

and therefore the hours of operation in full discharge, by let the heat transfer fluid exchange thermal energy with solid materials that can sustain the temperature of the heat transfer fluid, such as, for instance, concrete, sand, stones, etc.. A
5 simple means to carry out this embodiment is to put large masses of such materials in the reservoir or on its walls, or as its basement.

The additional power source is an energy source different from the concentrated solar power (CSP) that can be used for
10 instance for emergency shut down or for starting the plant. Alternatively or in combination, such additional power sources can be used for instance to stabilize the pyrolysis production or to boost it. Such sources can be for instance a so-called renewable source (such as wind, solar photovoltaic, tidal,
15 nuclear, hydroelectric, biomass) or fossil fuel (carbon, oil, shale, natural gas).

Preferred sources of such additional power sources are the photovoltaic, the biomass, the nuclear and the natural gas, particularly preferred the natural gas.

20 In the case of natural gas, particular preference is given to the gas heaters. Even more preferably, the gas that is burnt in the gas heater comprises the residual gas of the pyrolysis process (that is, as already described, the pyrolysis gas that is not condensed, e.g. stream 55 in Figure 11).

25 Such additional power source can be put in series or in parallel with respect of the heat transfer fluid to be heated.

Figure 11 shows some embodiments of the present invention, comprising such additional power source in parallel (68A) or in series (68B) and (68C).

In parallel configuration means that the power source, in parallel to the solar collector assembly, withdraws part of the heat transfer fluid from a colder reservoir (cold or warm ones), heats the fluid to the target temperature (usually, the temperature of the destination reservoir) and delivers the heat transfer fluid to said destination reservoir. The destination reservoir is the warm reservoir (64) or hot reservoir (65) in case the fluid is withdrawn from the cold reservoir (63) and the hot reservoir (65) in case the fluid is withdrawn from the warm reservoir (64).

When in series configuration, the inlet of such additional power source is the outlet of the solar collector assembly, and its outlet is the inlet of the receiving heat transfer fluid reservoir. With reference to Figure 11, an embodiment of this solution is the following: the heat transfer fluid from the warm reservoir (64) is sent to the hot solar collector assembly (62), then to the additional power source (68B), then to the hot reservoir (65).

Alternatively, always when in series configuration, the inlet of such additional power source is the outlet of the hot reservoir, and the outlet is the discharge circuit of the hot reservoir (the circuit supplying the second pyrolysis reactor and optionally the coker). This is the most preferred option.

With reference to Figure 11, an embodiment of this solution is the following: the heat transfer fluid from the hot reservoir (65) is sent to the additional power source (68C), then to the duties (second pyrolysis reactor 71).

Preferably, when such additional power source is present, its power is between 3% and 40%, more preferably between 6% and

20%, even more preferably between 8% and 15% of the power supplied by the hot and warm solar collector assemblies.

Examples

The present Examples report the simulation of a process using the dual heat transfer fluid driven process of the invention (dual loop) in comparison with the conventional single fluid driven process (single loop). For sake of clarity, they are prophetic Examples and therefore the present tense is used.

Example 1 (inventive)

10 Solar pyrolysis process driven by two fluids (dual heat transfer fluid loops) of the same composition.

The process corresponding to this Example is given in Figure 8.

The heat transfer fluid is the solar mixture of molten salts ("solar salt") having 60 wt% of sodium nitrate and 40 wt.% of potassium nitrate.

The solar collectors and receivers (61), (62) are composed by parabolic trough collectors (PTC) of type Luz (SEGS) LS-2 with 70 mm outer diameter evacuated tube solar receivers. This model has width W of 5.0 m and length L of 7.8 m. The detailed characteristics and characterization of such parabolic trough collector are reported in Dudley V, Kolb G, Sloan M, Kearney D., "SEGS LS2 solar collector-test results". 958 Report of Sandia National Laboratories, SAN94-1884, 1994, and are reported concisely in table 1 and 2 of Bellos, Evangelos & Tzivanidis, Christos "A detailed exergetic analysis of parabolic trough collectors", Energy Conversion and Management, (149) 275-292, 2017 doi: 10.1016/j.enconman.2017.07.035. This paper, which will be referred to as Bellos' paper in the following, is also used

for the detailed energetic and exergetic balance.

A code that reproduces the model developed in Bellos' paper was prepared and tested against validation Sandia National Laboratory test case 4 (table 4 at page 11 of Bello's paper).
5 Results corresponded very well to the ones shown in Table 4 and 5 of Bellos' paper for this test case, which in turn showed to be very close to the experimental values.

The flow rate of molten salts in the solar collector assembly (62) is 24.2 kg/s. The receivers of the solar collector
10 assembly are arranged in 20 lines in parallel, each one receiving $24.2/20 =$ about 1.21 kg/s of solar salts. Each line comprises 19 receivers. This is the number of receivers (each of 7.8 m length) required to increase the temperature from 485°C to 565°C. The computation is carried out as follows: the ambient conditions
15 (ambient temperature, sky temperature, sun temperature, incidence angle) are as per Table 3 of Bellos' paper, except that the specific air humidity (humidity ratio) was taken to be 0.01 (i.e., 10 g of water per kg of air). Moreover, the direct beam solar irradiation (G_b) is chosen to be 650 W/m², since the values
20 of about 900 W/m² reported in Table 4 of Bellos' paper are quite high and available only in selected regions of the Earth and for limited period of time. The PTC module characteristics and optical properties are as per Table 1 and 2 of Bellos' paper. The equations which are used are the ones described in the
25 Bellos' paper.

The physical properties of the "solar salt" heat transfer fluid are computed with the following expressions, taken from A. Bonk et al., "Solar Salt - thermal Property Analysis", Scientific Report DLR-FB-2021-19 31.08.2021, Deutsches Zentrum für Luft-

und Raumfahrt:

Property	Unit	Expression (T = fluid temperature, in [K])
Density	[kg/m ³]	2106 - 0.66795 * (T [K] - 273)
Viscosity	[Pa.s]	0.0000977 * exp(2030 / T [K])
Heat capacity	[J/kg.K]	1596
Heat transfer coefficient	[W/m.K]	0.55 + 0.00048 * (T [K] - (565 + 273))

The heat capacity is considered independent of temperature as there are large inconsistencies in the measurement of this parameter, so it is decided to use a constant value.

To carry out the computations, Bellos employed the software "Engineering Equation Solver", however it is found that they can be solved easily with an algorithm in any programming or script language, as the most difficult equation to be solved is a quartic equation (four degree polynomial) to compute the temperature at the cover ("Tc", in Kelvin), which has only two real roots, whose only one is positive (so only this root is meaningful and has to be selected), plus two iterative calculations (on outlet temperature and Tc), anyway converging very fast and without the existence of alternative solutions.

The simulation is carried out for each solar receiver, starting from the first one receiving the molten salts from the cold reservoir. The computed temperature of the molten salts at the outlet of the first receiver is set as the inlet temperature of the molten salts at the inlet of the second receiver. So it is possible to compute the temperature of the molten salts at the outlet of the second receiver, which becomes the inlet

temperature of the molten salts at the third receiver and so on. In this way it is possible to compute the number of receivers required to reach the target molten salt temperature (in this case, 19 receivers per line to reach 565°C).

5 The total energy and exergy flow is computed by adding the contributions of each receiver.

 The solar assembly (62) receives the solar salt from the warm reservoir (64), heats the solar salt to the target temperature, then send the hot solar salt to the hot reservoir
10 (65). From the hot reservoir, the solar salt is sent to the units that require the maximum operating temperature: the coker (76) and the secondary pyrolysis reactor (71).

 The molten salts are sent to the coker directly, i.e. without a weir device. The weir device would allow fine control
15 of the temperature and high flow rate (not required in the coker), but at the expenses of a reduced value of the same, whereas the coker benefits of high temperature of molten salts in the jacket.

 The molten salt feeding for both the first pyrolysis
20 reactor (70) and the second pyrolysis reactor (71) is carried out by means of the weir devices (78), (79). These weir devices have two chambers. The first one receives the hot molten salts and delivers them to the pyrolysis reactor jacket (for instance by means of a submersible pump). Differently from the weir
25 devices depicted in Figure 6 and Figure 7, the return of such molten salts from the reactor is sent to the second chamber. The flow rate of the molten salts that is circulated in the pyrolysis reactors is much higher than the flow rate of the hot molten salts delivered from the reservoir. This high flow rate is

desirable as it reduces the temperature difference inside the pyrolysis reactors, as well as it maximizes heat transfer. Therefore, part of the molten salts in the second chamber overflows the weir between the first and second chamber and falls
5 in the first chamber. This ensures that the pump in the first chamber is able to deliver the required flow rate while maximizing the temperature of the solar salts delivered to the pyrolysis reactors.

The molten salts from the coker are delivered to the weir
10 device (79) which feed the molten salts to the second pyrolysis reactor (71). The molten salts exiting the weir device (79) are sent to the warm reservoir (64), thus closing the "hot loop" of the heat transfer fluid.

The solar receiver (61) receives the solar salt from the
15 cold reservoir (63), heats the solar salt to the target temperature (485°C in this case), then send the warm solar salt to the warm reservoir (64). The solar receiver (61) is made by 75 parallel lines, each comprising 8 receiver tubes in series (each receiver tube being always 7.8 m in length). In this way,
20 the flow rate of each line is $91.6/75=1.22$ kg/s, therefore very similar to the flow rate of the hot receiver (62).

Ensuring enough high flow rate in the receiver tubes is required for a safe operation of the solar collector assembly, in particular to reduce the temperature difference between the
25 part of the tube exposed to different sunlight irradiation intensities and related bending of the tubes.

From the warm reservoir, the solar salt is sent to the first pyrolysis reactor (70) by means of the weir device (78).

Part of the solar salt exiting the first pyrolysis reactor

is sent to the hot oil exchanger (81). The hot oil exchanger is a heat exchanger which heats an organic heat transfer fluid (Marlotherm SH by Eastman), dubbed "oil", to about 320°C by means of molten salts at "low" temperature coming from the first
5 pyrolysis reactor.

The use of an organic heat transfer fluid for use at low temperature is advantageous as it has low melting temperature, thus eliminating the risk of freezing of solid salts in the zones where circulation is scarce or thermal insulation insufficient.
10 Moreover, electrical tracing is not required for oil-jacketed lines. As the required duty is far less than the duty of the first pyrolysis reactor, only a part of the fused salts exiting the first pyrolysis reactor is deviated to the hot oil exchanger.

The solar salt exiting the first pyrolysis reactor is
15 collected in the cold molten salt reservoir (63), closing the "warm loop" of molten salts.

The heat losses in the solar receiver (62) are computed in the aforementioned model of Bellos. Heat losses in the so-called headers and connecting pipes of the solar collector assembly is
20 neglected as considered negligible when compared with the heat losses in the receivers.

The heat losses in the molten salt circuit, comprising the coker and the second pyrolysis reactor and related connecting pipes, are lumped in a concentrated heat loss (83), named
25 "Enthalpy loss 2". The heat losses in the molten salt comprising the first pyrolysis reactor, the hot oil exchanger and related connecting pipes are lumped in a second concentrated heat loss (82), named "Enthalpy loss 1".

The exergy balance is carried out considering as the

control volume the inner walls wherein the fused salts circulates, except for the solar collector assembly (SCA), where the calculation is carried out following the aforementioned model and equations of Bellos. Therefore, for the SCA only (e.g. 5 for the exergy input) the boundary is on the incoming radiation coming from the Sun.

As there are no flows of matter through the chosen boundary, the only exergy streams are:

- the incoming Sun irradiance exergy (sign "+")
- 10 - the outcoming exergy associated to the thermal flow at:
 - o Pyrolysis reactors, coker, hot oil exchanger
 - o Thermal losses lumped in the "enthalpy loss" devices.

It can be assumed that the temperature at the boundary 15 changes linearly with the heat flow. This assumption is even more realistic considering that the temperature change along the heat flow boundary is low compared to its absolute value (in Kelvin). Therefore, the exergy flow at such boundaries can be computed with the following equation:

$$20 \quad \Delta\chi = \Delta Q \cdot \left[1 - \frac{T_0}{T_2 - T_1} \cdot \ln\left(\frac{T_2}{T_1}\right) \right]$$

where:

- T1 and T2 are the temperature at the beginning and at the end of the heat exchange boundary, in Kelvin.
- T0 is the reference temperature (here, 298 K)
- 25 - ΔQ is the heat flow
- $\Delta\chi$ is the exergy flow.

T1 and T2 correspond to the inlet and outlet temperatures except when a weir device is used. In fact, in this case the recirculation pump inside the weir device reduces the

temperature difference between inlet and outlet of the recirculated molten salt flow (in the limit of infinite flow rate, T_1 equals T_2).

The following table reports the detailed calculations, as well as the computation of the total heat and exergy flow obtained by summing up all the single contributions.

Item	Description	Mass flow [kg/s]	T in [°C]	T out [°C]	Heat flow [kW]	T1 [°C]	T2 [°C]	Exergy flow [kW]
65	HOT M.SALTS RESERVOIR		565	565				
62	SOLAR HOT CHARGER	24.2	485	565	3096	485	565	8966
76	COKER	24.2	565	555	-387	565	555	-327
79	REACTOR SECONDARY	24.2	555	495	-2322	520	495	-1937
83	ENTHALPY LOSS 2	24.2	495	485	-387	495	485	-321
64	WARM M.SALTS RESERVOIR		485	485				
61	SOLAR WARM CHARGER	91.6	438	485	6902	438	485	14158
78	REACTOR PRIMARY	91.6	485	455	-4386	475	455	-3617
82	ENTHALPY LOSS 1	91.6	455	451	-581	455	451	-477
80	HOT OIL EXCHANGER	11.4	451	345	-1935	345	335	-1527
63	COLD M.SALTS RESERVOIR	91.6	438	438				
	TOTAL SUM				0			14918

It can be seen that the balance of enthalpy ("Heat flow") is zero (meaning that all net energy received from the solar collector assemblies is delivered to duties or lost in said concentrated "enthalpy loss") while the sum of all exergy contributions is positive.

Such exergy imbalance accounts for exergy losses

(associated to heat losses), only for the SCA, plus exergy destruction (associated to irreversible loss of heat quality, i.e. when mixing two fluids at different temperature: the enthalpy before and after the mixing is the same, but on the contrary exergy is lost).

The present Example is applied to the pyrolysis of mixed plastics waste as follows:

- The essentially plastic material (mixed plastics waste) is fed to a screw heater whose jacket is heated by the organic heat transfer fluid (Marlotherm SH) that was heated by means of the hot oil exchanger, bringing its temperature to about 290°C.

- The heated essentially plastic material from the extruder is fed to the first pyrolysis reactor, heated by molten salts at "warm" temperature, where it is pyrolyzed, forming a gaseous phase and a semi-solid phase (char). The reactor is a substantially vertical cylinder with an anchor stirrer.

- The gaseous effluent of the first pyrolysis reactor is fed to a second pyrolysis reactor. This reactor is substantially a tubular heat exchanger, which can be optionally filled with a catalyst, where the pyrolysis vapours are heated and further pyrolyzed to smaller molecules.

- The gaseous effluent of the second pyrolysis reactor is fed to a condensing section, where at least one liquid stream, which is quantitatively more than 10 wt% of the initial weight of the plastic material fed, and which comprises hydrocarbons by a large fraction, is obtained.

- The char obtained in the first pyrolysis reactor is sent to a coker heated by hot fused salts, so as to produce a

solid material having better HSE profile (health, security, environment) and useful not only as an energy source, but also as a filler. The gases developed in such treatment are brought to the condensing section, thus increasing the yield of the
5 pyrolysis.

Comparative Example 2

Solar pyrolysis process driven by a single fluid (single heat transfer fluid loop).

The process corresponding to this Example is given in
10 Figure 9.

The heat transfer fluid is the same solar mixture of molten salts ("solar salt") of Example 1, and the same correlations of the physical properties were used.

The solar collector assembly (62) is of the same type of
15 Example 1.

The code used to compute the performance of the solar receivers is the same code used in Example 1, and with the same values of the geometric, optical, physical constants and ambient conditions.

20 The duties of the molten salts were the same as in Example 1, both in terms of heat flow power (in Watt), and inlet and outlet temperature of fused salts.

With these constraints, the required mass flow rate of fused salts through the solar receiver (63) is 42.6 kg/s. The
25 inlet temperature of the solar salts is 418°C and the outlet temperature is 565°C.

The hot receiver (64) receives the solar salt exiting the SCA (62). The hot solar salt coming from the hot reservoir is sent, in parallel, to the units that require the maximum

operating temperature (e.g. the coker 76 and the secondary pyrolysis reactor 71), and to the first pyrolysis reactor (70). In fact, the first pyrolysis reactor requires a larger heat flow at lower temperature. The setup shown in Figure 9 and herein
5 detailed is therefore specifically designed to maximize effectiveness in such configuration: the solar salt, after passing through the coker and the second pyrolysis reactor, is still sufficiently at high temperature to heat the first pyrolysis reactor, but its quantity is insufficient for the
10 required (large) heat to be supplied. Therefore, an additional stream of solar salt is fed directly from the hot reservoir to the first reactor.

The heating of both the first pyrolysis reactor (70) and the second pyrolysis reactor (71) is carried out by means of the
15 weir devices (78), (79). These weir devices were the same used in Example 1.

Part of the solar salt exiting the first pyrolysis reactor is sent to the hot oil exchanger (81). The hot oil exchanger is a heat exchanger which heats the organic heat transfer fluid by
20 means of molten salts at "low" temperature coming from the first pyrolysis reactor, in the same way of Example 1.

As the required duty is far less than the duty of the first pyrolysis reactor, only a part of the fused salts exiting the first pyrolysis reactor is deviated to the hot oil exchanger.

25 The solar salt exiting the first pyrolysis reactor is collected in the cold molten salt reservoir (63), closing the (single) molten salt loop.

As done in Example 1, the heat losses in the molten salt circuit comprising the coker and the second pyrolysis reactor

and related connecting pipes are lumped in a concentrated heat loss (83), named "Enthalpy loss 2". The heat losses in the molten salt comprising the first pyrolysis reactor, the hot oil exchanger and related connecting pipes are lumped in a second concentrated heat loss (82), named "Enthalpy loss 1".

The exergy balance is carried out in the same way as well.

The following table reports the detailed calculations, as well as the computation of the total heat and exergy flow obtained by summing up all the single contributions.

Item	Description	Mass flow [kg/s]	T in [°C]	T out [°C]	Heat flow [kW]	T1 [°C]	T2 [°C]	Exergy flow [kW]
64	HOT M. SALTS RESERVOIR	24.2	565	565				
62	SOLAR HOT CHARGER	42.6	418	565	9998	418	565	24776
76	COKER	24.2	565	555	-387	565	565	-327
79	REACTOR SECONDARY + WEIR	24.2	555	495	-2322	520	495	-1937
83	ENTHALPY LOSS 2	24.2	495	485	-387	495	485	-321
70	REACTOR PRIMARY + WEIR	42.6	519	455	-4386	475	455	-3617
82	ENTHALPY LOSS 1	42.6	455	446	-581	455	446	-477
80	HOT OIL EXCHANGER + BUFFER	11.9	446	345	-1935	345	335	-1527
63	COLD M.SALTS RESERVOIR	42.6	418	418				
	TOTAL SUM				0			16570

It can be seen that the balance of enthalpy ("Heat flow") is zero (like in Example 1) while the sum of all exergy contributions is positive.

Comparison of Example 1 with Comparative Example 2

The following table shows the duties of Example 1 in comparison with Comparative Example 2:

		EXAMPLE 1				COMPARATIVE EXAMPLE 2			
Item	Description	T in [°C]	T out [°C]	Heat flow [kW]	Exergy flow [kW]	T in [°C]	T out [°C]	Heat flow [kW]	Exergy flow [kW]
76	COKER	565	555	-387	-327	565	555	-387	-327
79	REACTOR SECONDARY	555	495	-2322	-1937	555	495	-2322	-1937
83	ENTHALPY LOSS 2	495	485	-387	-321	495	485	-387	-321
70	REACTOR PRIMARY	485	455	-4386	-3617	519	455	-4386	-3617
82	ENTHALPY LOSS 1	455	451	-581	-477	455	446	-581	-477
80	HOT OIL EXCHANGER	451	345	-1935	-1527	446	345	-1935	-1527
	SUM			-9998	-8206			-9998	-8206

In both cases, all the duties are the same, both in terms of heat flow and exergy flow. The latter is the same, despite different inlet temperature in the weir, as the internal circulation pump ensures the same temperature difference (T1 and T2 are the same in both Example 1 and Comparative Example 2).

As a result, it can be stated that both Example 1 and Comparative Example 2 deliver the same duties with the same temperatures towards the loads, therefore the pyrolysis process shows no differences. However, the exergetic balance is different: in fact, Example 1 has 14918 kW of imbalance, while Comparative Example 2 has 16570 kW, that is about 11% more.

This means that Comparative Example 2 is less efficient as it requires energy at the same quantity but at higher quality level (more energy at high temperature).

The reason is that whenever two streams at different temperature are mixed, energy is conserved but exergy is not. In fact, in such operation the stream at high temperature (so, at

higher quality) is irreversibly destroyed.

Ultimately, the better efficiency of the process of Example 1 results in a lower requirement of land and plant installation and operation costs, as shown in the following table:

5

Example	Charger	N.lines	Receivers per line	Total receivers	SCA area [m ²]	Occupied land [m ²]
Example 1	HOT CHARGER	20	19	380	14820	44460
	WARM CHARGER	75	8	600	23400	70200
	HOT+WARM CHARGER			980	38220	114660
C.Ex.2	SINGLE CHARGER	35	30	1050	40950	122850

By splitting the solar salt charger (the solar collector assembly, SCA) into two separate units, it is possible to generate a "hot energy" stream of molten salts, at high temperature but not high quantity, plus a "warm energy" stream of molten salts, at lower temperature but higher quantity. Solar collectors are more efficient when used to heat low temperature heat thermal fluids as the thermal losses are much lower, in particular because the evacuated tube allows a strong reduction of thermal conductivity, but it does not limit the radiative emissions, which increases with the 4th power of the temperature, not even considering that also the emissivity of the cermet material applied to the receiver tubes (to limit emissivity) increases considerably over 500°C.

The pyrolysis process of mixed plastic waste to produce a pyrolysis condensate comprising hydrocarbons requires a first

pyrolysis reactor (plus optionally a preheater) at relatively low temperature but high duty, and in addition a second pyrolysis reactor (plus optionally a coker) at higher temperature but lower duty. Therefore, it is possible to match the higher-temperature lower-quantity molten salt stream to the second pyrolysis reactor, and the lower-temperature higher-quantity molten salt stream to the first pyrolysis reactor, thus optimizing efficiency.

As a result, the number of total solar receivers in the Example using the dual circuit of molten salts, according to the present invention, is 980. Conversely, the number of solar receivers for the same duties, but using one single loop of molten salts is 1050, that is about 7% more. This not only implies larger installation and operation costs, but also (obviously) a larger occupied land.

CLAIMS

1. A process to produce at least a pyrolysis oil from essentially plastic materials which comprises the steps of:
- 5 a) Heating a first heat transfer fluid (F1) to a temperature (T1) comprised between 400°C and 520°C by means of solar radiation;
- b) Heating a second heat transfer fluid (F2) to a temperature (T2) higher than temperature (T1) by means of solar radiation;
- 10 c) Heating a first pyrolysis reactor (R1) by means of the heated first heat transfer fluid (F1);
- d) Heating a second pyrolysis reactor (R2) by means of the heated second heat transfer fluid (F2);
- 15 e) Feeding the first pyrolysis reactor (R1) with at least an essentially plastic material (M1);
- f) Keeping said essentially plastic material (M1) in said first pyrolysis reactor for a residence time which is at least 2 minutes and anyway sufficient to produce a fluid
- 20 in the gaseous state (M2) that contains hydrocarbons;
- g) Feeding said fluid in the gaseous state (M2) that contains hydrocarbons produced in the first pyrolysis reactor (R1) to a second pyrolysis reactor (R2);
- h) Keeping said fluid in the gaseous state (M2) in said
- 25 second pyrolysis reactor (R2) for a residence time which is at least 10 seconds;
- i) Condensing, totally or partially, the gas exiting said second pyrolysis reactor (R2) so as to form at least a liquid which comprises hydrocarbons having a standard
- 30 boiling point not below 25°C.

2. The process to produce at least a pyrolysis oil from essentially plastic materials according to claim 1, wherein the said first and second heat transfer fluids (F1, F2) are substantially entirely recirculated.

5 3. The process to produce at least a pyrolysis oil from essentially plastic materials according to claim 2, wherein the recirculation of the first heat transfer fluid (F1) forms a first heat transfer fluid loop ("warm loop"), and the recirculation of the second heat transfer fluid (F2)
10 forms a second heat transfer fluid loop ("hot loop").

4. The process to produce at least a pyrolysis oil from essentially plastic materials according to claim 3, wherein the first heat transfer fluid loop comprises said step a) and said step c) and the second heat transfer fluid loop
15 comprises said step b) and said step d).

5. The process to produce at least a pyrolysis oil from essentially plastic materials according to any one of claims from 1 to 4, which additionally comprises the steps of:

20 j) Storing the first heat transfer fluid (F1) coming from step c) in a reservoir ("cold reservoir") before of its use in step a);

k) Storing the second heat transfer fluid (F2) heated in step b) in a reservoir ("hot reservoir") before of its use in step d).

25 6. The process to produce at least a pyrolysis oil from essentially plastic materials according to any one of claims from 1 to 5, wherein the first heat transfer fluid (F1) is compositionally the same as the second heat transfer fluid (F2).

7. The process to produce at least a pyrolysis oil from essentially plastic materials according claim 6, which additionally comprises the step of:

5 1) Storing the first heat transfer fluid (F1) heated in step a) before its use in step c), and the second heat transfer fluid (F2) cooled in step d) before its use in step b), in a reservoir ("warm reservoir").

10 8. The process to produce at least a pyrolysis oil from essentially plastic materials according to any one of claims 1 to 6, which additionally comprises the steps of:

 m) Storing the first heat transfer fluid (F1) heated in step a) before its use in step c) in a reservoir ("warm reservoir A");

15 n) Storing the second heat transfer fluid (F2) cooled in step d) before its use in step b), in a reservoir ("warm reservoir B").

20 9. The process to produce at least a pyrolysis oil from essentially plastic materials according to any one of claims 1 to 8, which additionally comprises the step of:

 p) Heating the essentially plastic material before step e) by means of the heated first heat transfer fluid (F1).

25 10. The process to produce at least a pyrolysis oil from essentially plastic materials according to any one of claims 1 to 9, which additionally comprises the step of:

 o) Heating the liquid, solid or semi-solid residue of the pyrolysis of step f) (the char) by means of the heated second heat transfer fluid (F2) and

optionally also by a gas heater, by means of electric resistance (Joule effect), and combinations thereof.

11. The process according to claim 9, wherein in step p) the essentially plastic material is brought to a temperature
5 between 120 and 430°C, preferably between 150°C and 320°C, even more preferably between 180°C and 220°C, and wherein the average residence time of step p) is preferably less than 20 minutes, more preferably less than 4 minutes, in particular less than one minute.

10 12. The process according to claim 10, wherein in step o) said char is heated to a temperature from 500°C to 1200°C, preferably from 600°C to 1000°C, more preferably from 700°C to 900°C for a time of at least 5 minutes, preferably between 15 and 180 minutes, more preferably between 30 and
15 120 minutes.

13. The process according to any one of claims from 1 to 12, wherein the first and second heat transfer fluids (F1, F2) are molten salts, preferably with a melting temperature of at most 340°C, more preferably at most 270°C, still more
20 preferably at most 240°C.

14. The process according to claim 13, wherein said molten salts are a molten salt of group IA and IIA of the periodic table, preferably sodium nitrate, sodium nitrite, potassium nitrite, potassium nitrate, lithium nitrate, calcium
25 nitrate, or mixtures thereof.

15. The process according to claim 13, wherein said molten salts are nitrate/nitrite mixtures, in particular mixtures of potassium nitrate and sodium nitrate, preferably the "solar salt", optionally with the addition of sodium nitrite

and calcium nitrate.

16. The process according to claim 8, wherein the first heat transfer fluid (F1) is compositionally different from the second heat transfer fluid (F2).

5 17. The process according to claim 16, wherein the first heat transfer fluid (F1) has a lower melting point than the second heat transfer fluid (F2), and preferably the first heat transfer fluid (F1) has a melting point that is at most 180°C, even more preferably at most 150°C.

10 18. The process according to any one of claims 1 to 17, wherein the difference in temperature between temperature T2 of step b) and temperature T1 of step a) is at least 10°C, still more preferably between 30°C and 300°C, even more preferably between 60°C and 250°C.

15 19. The process according to any one of claims 1 to 18, wherein the heating of step a) and b) is carried out by means of at least one solar collector assembly comprising parabolic trough, linear Fresnel, or a combination thereof.

20 20. The process according to claims 19, wherein the concentration factor of the at least one solar collector assembly of step b) is higher than the concentration factor of the at least one solar collector assembly of step a).

25 21. The process according to any one of claims 1 to 20, wherein the temperature to which the essentially plastic material is brought in said first pyrolysis reactor (70) is from 330°C to 580°C, preferably from 340 to 540°C, more preferably from 360 to 500°C, still more preferably from 380 to 480°C, even more preferably from 410 to 450°C, and wherein the temperature difference between the second

pyrolysis reactor (71) and the first pyrolysis reactor (70) is at least 10°C , preferably between 30°C and 300°C, more preferably between 60°C and 250°C, with the additional condition that such temperature is between 400°C and 650°C, preferably between 440°C and 550°C, more preferably between 460°C and 530°C.

22. A plant to produce at least a pyrolysis oil from essentially plastic materials, which comprises:

A) A first pyrolysis reactor (70) which has at least one inlet where an essentially plastic material is fed, an outlet where at least one gaseous effluent is removed, and a jacket and/or coil, provided with at least one inlet and one outlet for a heat transfer fluid;

B) A second pyrolysis reactor (71) which has at least one inlet where at least a gaseous stream from the first pyrolysis reactor (70) is fed, an outlet where at least one gaseous effluent is removed, and a jacket and/or coil, provided with at least one inlet and one outlet for a heat transfer fluid;

C) A first solar collector assembly (61) comprising a first solar receiver, preferably consisting of a tube receiver, the first solar receiver comprising at least one inlet and one outlet for the heat transfer fluid, where said solar collector assembly is able to deliver concentrated solar radiation to said first solar receiver that in turns is configured to heat said heat transfer fluid;

D) A second solar collector assembly (62) comprising a second solar receiver, preferably consisting of a tube receiver, the second solar receiver comprising at least

one inlet and one outlet for the heat transfer fluid, where said solar collector assembly is able to deliver concentrated solar radiation to said second solar receiver that in turns is configured to heat said heat transfer fluid;

5

E) A first tank (63, "cold reservoir") where the heat transfer fluid at low temperature is collected, the first tank (63) being fluidically connected to receive the heat transfer fluid from the first pyrolysis reactor (70) and send the heat transfer fluid to the first solar collector assembly (61);

10

F) A second tank (64, "warm reservoir") where the heat transfer fluid at medium temperature is collected, the second tank (64) being fluidically connected to receive the heat transfer fluid from the first solar collector assembly (61) and send the heat transfer fluid to the first pyrolysis reactor (70);

15

G) A third tank (65, "hot reservoir") where the heat transfer fluid at high temperature is collected, the third tank (65) being fluidically connected to receive the heat transfer fluid from second solar collector assembly (62) and send it to the second pyrolysis reactor (71);

20

H) A condenser (72) with at least one inlet for the gaseous stream comprising hydrocarbons, and one outlet for the condensed liquid, which is able to at least partially condense the gaseous stream comprising hydrocarbons;

25

wherein said first solar collector (61) is fluidly connected to said first tank (63) at one end of the first solar receiver, and to said second tank (64) at the other end of the said first solar

receiver; and wherein said second solar collector (62) is fluidly connected to said second tank (64) at one end of the second solar receiver, and to said third tank (65) at the other end of the said second solar receiver; wherein said condenser (72) is
5 fluidly connected to said second pyrolysis reactor (71), so as to be able to partly condense the pyrolysis vapours produced by said first and second pyrolysis reactors.