

Process to produce a pyrolysis oil comprising liquid hydrocarbons from plastic material from an intermittent energy source, and relative plant

Description

5 Field of the invention

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
10 material to produce a pyrolysis oil comprising hydrocarbons. This pyrolysis oil, after further treatment, can be converted into monomers useful for producing polymers, thus closing the loop.

Background art

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

An integrated solution, such as the one now proposed, allows not only the use of "green" energy, but also it solves one of the biggest problems associated to the use of most

renewable energy sources (such as solar or wind energy), namely intermittency and variability in their intensity. Such intermittency and variability in turns determine large temporal variations in the available energy power.

5 Most chemical processes normally require very long running periods and steady process conditions to reach constant product quality and to become economically sustainable. This is particularly important for processes that, like the pyrolysis, require high temperatures and large flow rates, as it takes
10 longer to start, to stop and to reach steady process conditions.

Intermittency and variability of the energy source is therefore a very serious drawback for any pyrolysis process known in the art.

A pyrolysis process is therefore desirable that allows the
15 use of renewable energy sources, such as solar energy, but at the same time able to manage the intermittency and variability of the energy source, while preserving the quality of the produced pyrolysis oil.

Several patent applications disclose processes for thermal
20 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 a substantially hydrocarbon free product gases (syngas) with a solar reactor from a carbonaceous
25 material feed, which 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.

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.

5 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
10 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
15 energy. There is a cold hot 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.

CN109207179 discloses a syngas production system through
20 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 1000°C.

25 WO2020/150244 (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.

None of the cited patents discloses a process to treat

plastic 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.

5 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
10 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
15 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.

 Pyrolysis of plastic materials is a highly desirable
20 process as it allows to recycle mixed plastic waste materials, by breaking the polymeric chains into small organic molecules, which can be used, after proper refining processes, in the synthesis of polymers. Most of other recycle processes, such as the so-called mechanical recycle (i.e. extrusion of waste
25 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 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 process, such as solvent dissolution and precipitation, can be used to specifically dissolve a specific 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, inorganic additives which are used as fillers, and so on). 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 there are unlimited loops of: plastic production from monomers, use of the plastic, 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".

However, pyrolysis 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. 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, 5 both electric energy and gas heating considerably contribute to increase the carbon footprint, as the combustion of hydrocarbons produce large quantities of carbonic anhydride (CO₂) and in most countries electric energy is produced by gas, petroleum or carbon combustion. Moreover, due to the high temperature, the use of 10 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 15 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 syngas. However, sunlight is an intermittent source and 20 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 implementation.

25 It is possible to use energy storage means such as batteries or, when using a heat thermal fluid such as molten salts, large tanks containing the same. However, their cost is still very high and often require the use of large quantities of precious materials.

There is therefore the long-felt need for a process to produce pyrolysis oil from essentially plastic materials which use a renewable energy source, and that is able to tackle the intermittency and variability of said energy source while
5 producing a pyrolysis oil of constant quality.

SUMMARY OF THE INVENTION

The Applicant has surprisingly found a process to produce at least a pyrolysis oil from essentially plastic material using variable-intensity energy sources which comprises the steps of:

- 10 a) heating a heat transfer fluid to a temperature (THTF) comprised between 350°C and 700°C by means of a variable-intensity energy source;
- b) heating a pyrolysis reactor by means of the heated heat transfer fluid;
- 15 c) feeding the essentially plastic material, optionally already in the molten and/or preheated state, to the said pyrolysis reactor;
- d) bringing said material in said pyrolysis reactor to a temperature (TMPR) between 330°C and 650°C in the
20 substantial absence of oxygen and at a pressure of between atmospheric pressure and 20 bar(a) using said variable-intensity energy source;
- e) holding said material in said pyrolysis reactor at a temperature (TMPR) of between 330°C and 650°C for a time
25 sufficient to produce at least one effluent in the gaseous state in said pyrolysis reactor;
- f) keeping substantially constant the composition of the pyrolysis oil produced by dynamically adjusting the pressure in said pyrolysis reactor in relation to a

reference temperature (TREF), which is either the said temperature of said heated heat transfer fluid (THTF) or the said temperature of the material in said pyrolysis reactor (TMPR), at a value between atmospheric pressure and 20 bar(a);

g) partly or totally condensing said effluent in the gaseous state so as to form at least one liquid fluid quantitatively being at least 10% by mass with respect to the mass of essentially plastic material fed, and which comprise hydrocarbons that have a standard boiling point not below 25°C.

In other words, the invention stands in defining an interpolation equation of the temperature-pressure relationship, where the pressure is the pyrolysis reactor pressure (more precisely, its set point PMPR) and the temperature is the pyrolysis reactor temperature (more precisely, the above defined reference temperature TREF), said interpolation equation being configured for producing a pyrolysis oil of substantially constant composition and quality.

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

- Effectiveness with intermittent and variable-intensity energy sources, which are instead generally unsuitable for processes of pyrolysis of plastic materials;
- Constant quality pyrolysis oil product: even varying the intensity of the energy source, and even without thermal storage that keep the heat transfer fluid at constant temperature, the product quality is substantially

unaltered.

- Resilience to changes in process temperature.
- 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 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).
- Mixed plastic waste and Plasmix ready: Preferably the process is fed by mixed plastic 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, 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 plastic 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.

With reference to Figure 1, the present invention discloses and claims also a plant to produce at least a pyrolysis oil from essentially plastic materials which comprises:

- A) A 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 molten salts;
- B) A condenser (72) which receives the gaseous effluent of said pyrolysis reactor;
- C) A solar collector and receiver assembly (61, 62), the receiver comprising at least one inlet and one outlet for the molten salts, where said solar collector is able to deliver concentrated solar radiation to said solar receiver that in turns is configured to heat said molten salts;
- D) A first tank ("cold tank", 63) which is fluidically connected to the outlet for molten salts of the pyrolysis reactor (70) to receive and store the molten salts returning from the pyrolysis reactor (A) and it is fluidically connected to an inlet of the solar receiver (62);

E) A second tank ("hot tank", 64) which is fluidically connected to an outlet of the solar receiver (62) to receive and store the molten salts returning from the solar collector and receiver (SCA1) and it is fluidically connected to the inlet for molten salts of the pyrolysis reactor (70);

F) A controller (23) that adjusts, through a pressure manager (22), the pressure set point of the pyrolysis reactor (24) in relation to the reference temperature TREF, which is either the temperature THTF (21A) of the molten salts coming from the second tank ("hot tank", C2) or the temperature TMPR (21B) of the material in the first pyrolysis reactor (70).

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 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).

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 (1) necessarily includes the listed ingredients and (2) is open to unlisted ingredients that do not materially affect

the basic properties and innovative properties of the composition.

In the description of the present invention, unless otherwise specified, the act of maintaining a certain parameter
5 (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 falls within the indicated range, and/or by regulating the parameter by means of a feedback regulating system in which a
10 value of this parameter is set within the indicated range.

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

In the description of the present invention, the act of condensing, totally or partially, the gas exiting the pyrolysis reactor so as to form at least a liquid which comprises hydrocarbons having a standard boiling point not below 25°C does
20 not exclude that such liquid can comprise also hydrocarbons having boiling point below 25°C, and non-hydrocarbon compounds.

In the description of the present invention, by variable-intensity energy source, or, equivalently, by intermittent energy source, energy sources that cannot deliver constant power
25 because of their nature are meant, such as, for instance, solar energy, wind energy, tidal energy and so on.

In the description of the present invention, by essentially plastic material, a composition of one or more 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
5 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, by "pyrolysis vapors", the gaseous phase which is produced in the pyrolysis of
10 the essentially plastic material is meant, such as the effluent in the gaseous state of the pyrolysis reactor. This latter 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
15 essentially plastic material subjected to the pyrolysis or added or already present in the pyrolysis reactor (for instance, in the inerting gas), such as nitrogen, water or low boiling point plasticizers. The content of hydrocarbons in the pyrolysis vapors is typically more than 50 wt%.

20 In the description of the present invention, by "pyrolysis oil", the liquid formed by partly or totally condensing the pyrolysis vapors, which comprises hydrocarbons that have a standard boiling point not below 25°C, is meant. The content of hydrocarbons in the pyrolysis oil is typically more than 50 wt%.

25 In the description of the present invention, by pyrolysis residue or char, the product which is in the liquid, solid, or semi-liquid state in the pyrolysis reactor 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 vapors 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 vapors.

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 applied process conditions.

In the description of the present invention, by molten salts, a salt which is solid at ambient temperature and ambient pressure, i.e. 25°C and 1 bar, 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 mixture of salts (e.g. mixture of sodium and potassium nitrate).

In the description of the present invention, unless 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.

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.

By "C5-C12 wax fraction" the sum of the mass of the chemical compounds having from 5 to 12 carbon atoms (extremes included) in the wax with respect to the total mass of said wax product is meant.

5 By "C5-C12 light oil fraction" the sum of the mass of the chemical compounds having from 5 to 12 carbon atoms (extremes included) in the light oil with respect to the total mass of said wax product is meant.

By "C5-C12 yield" the "C5-C12 light oil fraction" multiplied by the "light oil fraction" plus the "C5-C12 wax fraction" multiplied by the "wax fraction" is meant.

The "C5-C12 yield" is therefore the ratio of the mass of compounds having from 5 to 12 carbon atoms in the pyrolysis oil product by the mass of the essentially plastic material fed to the pyrolysis reactor.

By "hydrocarbons" the compounds consisting of carbon and hydrogen atoms are meant. Therefore, compounds having heteroatoms (such as N, S, O) are excluded.

By "C5-C12 hydrocarbons wax fraction" the sum of the mass of hydrocarbons having from 5 to 12 carbon atoms (extremes included) in the wax with respect to the total mass of said wax product is meant.

By "C5-C12 hydrocarbons light oil fraction" the sum of the mass of hydrocarbons having from 5 to 12 carbon atoms (extremes included) in the light oil with respect to the total mass of said wax product is meant.

By "C5-C12 hydrocarbons yield" (or, equivalently, "C5-C12 hc yield") the "C5-C12 hydrocarbons light oil fraction" multiplied by the "light oil fraction" plus the "C5-C12

hydrocarbons wax fraction" multiplied by the "wax fraction" is meant. The "C5-C12 hydrocarbons yield" is therefore the ratio of the mass of hydrocarbons having from 5 to 12 carbon atoms in the pyrolysis oil product by the mass of the essentially plastic material fed to the pyrolysis reactor.

By "lhc fraction" the ratio of the C5-C12 hydrocarbons yield to the C5-C12 yield is meant. Therefore the "lhc fraction" is the fraction (percentage) of hydrocarbons in the C5-C12 cut.

Unless otherwise specified, in this document "part" and "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 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 and relative plant, illustrative of an embodiment of the present invention, characterized by the two heat transfer fluid reservoirs, one pyrolysis reactor, a solar collector assembly, and the pressure regulation system of said pyrolysis reactor.

Figure 2 shows a process scheme and relative plant, illustrative of an embodiment of the present invention, characterized by the same elements of Figure 1 and in addition some optional devices: a preheater, a second reactor, a char-feeder and a coker.

Figure 3 shows a process scheme and relative plant,

illustrative of a scheme of condensation of the pyrolysis vapors effluent of the pyrolysis reactor(s), characterized by the use of three condensers in series, the first condenser being cooled by the heat transfer fluid, the third condenser being a flooded
5 condenser.

Figure 4 shows a process scheme and relative plant, illustrative of a scheme of feeding the heat transfer fluid to several devices (the preheater, the pyrolysis reactor, the second pyrolysis reactor) in a semi-series way by means of a
10 weir.

Figure 5 shows graphically three different interpolation equations of the temperature-pressure relationship. From top to bottom, the represented interpolation equations are the linear interpolation, the monotonic non-increasing piecewise constant
15 function, the generalized logistic function.

DETAILED DESCRIPTION OF THE INVENTION

An embodiment of the present invention is shown in Figure 1. The scheme comprises:

- A pyrolysis reactor (70);
- 20 - A pyrolysis vapors lamination valve (81) which regulates the pressure in the reactor (70) by lamination of the pyrolysis vapors exiting the reactor;
- A condenser (72) which condensates the pyrolysis vapors;
- A separator (73) which separates the gaseous (non condensed)
25 phase from the liquid one;
- A solar collector (61) and receiver (62);
- A "cold" reservoir of the heat transfer fluid (63);
- A "hot" reservoir of the heat transfer fluid (64);
- Heat transfer fluid pumps (65), (66) which deliver the heat

transfer fluid to the heating system (solar receivers) and to the pyrolysis reactor (70);

- Optional bypasses (B1) and (B2);

- A temperature transmitter (21) which reads the temperature of the heat transfer fluid;

- A pressure transmitter (24) which reads the pressure of the pyrolysis reactor (70);

- A pressure controller (23) which adjusts the pressure of the pyrolysis reactor (70) by regulating the opening of the pyrolysis vapors lamination valve (81);

- A pressure manager (22) which sets the pressure set point PMPR of the pyrolysis reactor (70) in relation to the temperature TREF which is either the temperature THTF of the heat transfer fluid (21A) or the temperature TMPR of the material in the (first) pyrolysis reactor (70).

In relation to the plant to produce at least a pyrolysis oil from essentially plastic materials of the present invention:

- in the pyrolysis reactor (70), the outlet where at least one gaseous effluent is removed is fluidly connected to the condenser (72) which receives the gaseous effluent of said pyrolysis reactor [(A)-(B) connection];

- in the pyrolysis reactor (70), in the jacket and/or coil provided with at least one inlet and one outlet for molten salts, said at least one inlet is fluidly connected to said second tank ("hot tank", 64) which receives and stores the molten salts returning from the solar collector and receiver [(A)-(E) connection];

- in the pyrolysis reactor (70), in the jacket and/or coil provided with at least one inlet and one outlet for molten

salts, said at least one outlet is fluidly connected to said first tank ("cold tank", 63) which receives and stores the molten salts returning from the pyrolysis reactor (A) [(A)-(D) connection];

- 5 - in the solar collector and receiver assembly (61, 62), the inlet of the molten salts is fluidly connected to the first tank ("cold tank", 63) which receives and stores the molten salts returning from the pyrolysis reactor [(C)-(D) connection];
- 10 - in the solar collector and receiver assembly (61, 62), the outlet of the molten salts is fluidly connected to the second tank ("hot tank", 64) which receives and stores the molten salts returning from the solar collector and receiver [(C)-(E) connection];
- 15 - the pressure controller (23) that adjusts the pressure of the pyrolysis reactor (24) in relation to the reference temperature TREF is electronically connected with the temperature sensor of the temperature THTF (21A) of the molten salts coming from the second tank ("hot tank", C2)
- 20 or with the temperature sensor of the temperature TMPR 21B of the material in the first pyrolysis reactor (70) [(A)-(F) connection].

In the context of the present invention, a fluid connection may comprise devices that are sandwiched or anyway positioned in
25 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 (33) coming from the hot reservoir (64). The heat transfer fluid coming out of the first pyrolysis reactor (therefore at lower temperature) is brought to the cold reservoir (63).

The solid or semi-solid residuum (like char) is recovered (at 53).

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

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 optionally integrated in the condenser (72).

Optional bypasses (B1) and (B2) 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 solar collector (61) and receiver (62) heat up the heat transfer fluid (31) from the cold tank (63). From the solar receiver (62), the heat transfer fluid is brought to the hot reservoir (64).

25 A temperature transmitter (21) reads the temperature of the heat transfer fluid. According to another embodiment, such temperature transmitter can read directly the temperature of the non-gaseous phase inside the pyrolysis reactor (70).

The pressure transmitter (24) reads the pressure of the pyrolysis gases. Such transmitter can be placed inside the reactor, or in any other location where the pressure is substantially the same.

5 In Figure 1 the pressure transmitter (24) is located in the connection which brings the pyrolysis vapors (52) produced in the pyrolysis reactor (70) to the lamination valve (81). In this position, the reading of the pressure can be even more reliable and precise than the location inside the reactor. In
10 fact, inside the reactor there can be boiling conditions and, as a result of a sudden pressure release, foaming can occur. If the sensor is located inside the reactor, it is therefore more likely to be fouled.

The pressure transmitter (24) is connected to the pressure
15 controller (23) which adjusts the opening of the valve (81) so as to reach the pressure set point given by the pressure manager (22).

The pressure manager (22) sets the pressure set-point in relation to the temperature measured by transmitter (21).

20 Some embodiments of possible different relationships between said temperature and said pressure set-point are given in the following.

Preferably said essentially plastic material comprises compositions of different plastics. Still more preferably, said
25 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.

Alternatively, or in combination, said different plastic compositions include high carbon index polymers such as polyethylene (including LDPE, LLDPE, HDPE), polypropylene, polystyrene, elastomers and low carbon index polymers such as
5 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, even more preferably between 85
10 and 96.

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

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

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

20

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

25

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

where "weight of ALL atoms" corresponds to the weight of the

essentially plastic material.

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 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 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 retardant properties. Examples of said additives are hexabromocyclododecane, decabromodiphenyloxy, polybrominated diphenyl ethers, and bromine-containing polymers such as brominated styrene-butadiene copolymers or brominated polystyrene.

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 materials are also

recycled.

Preferably, said essentially plastic materials also contain halogenated components in an amount ranging from 0.01% to 10% by weight with respect to the weight of the essentially plastic material.

Preferably, said essentially plastic materials are obtained from a plastic material sorting process. Still more preferably said essentially plastic materials are the essentially plastic residual material, i.e. the essentially plastic 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 monoplasic) of certain plastics. Typically, in a selection process (sorting), it is possible to extract streams of substantially pure plastics (i.e. as a monoplasic) of the polyethylene, polypropylene and polyethylene terephthalate components. In this preferred selection, the essentially plastic 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 n.4502 of 05/18/2017).

Another embodiment of the present invention is shown in Figure 2. The scheme comprises the same elements of Figure 1 and in addition:

- A preheater of the essentially plastic material (74);
- A second pyrolysis reactor (71);
- A char-feeder (75), that is an element which is able to move the liquid, solid or semi-solid material comprised in the pyrolysis reactor to the coker (76);
- A coker (76), that is an element which is able to subject the liquid, solid and semi-solid material coming from the pyrolysis reactor to a heat treatment at high temperature;
- A coke collector (77).

10 The above-mentioned elements are optional and can be present individually or in any possible combination.

 Being already crammed, in Figure 2 the reference temperature TREF is the temperature of the heat transfer fluid THTF; however, the same embodiment represented in Figure 2 but
15 where TREF is the temperature of the material in the first pyrolysis reactor is part of the invention as well.

 In the embodiments where there is the second pyrolysis reactor, the pyrolysis reactor (70) is referred to as the first pyrolysis reactor, to avoid confusion. In any case, if not stated
20 otherwise (for instance, with "second pyrolysis reactor"), by pyrolysis reactor the (first) pyrolysis reactor (70) is meant.

 In particular, according to one embodiment, depicted in Figure 2, the essentially plastic material is preheated in the preheater (74) before being fed to the pyrolysis reactor (70).
25 If the heat transfer fluid is fed to the pyrolysis reactor and the preheater in series, as shown in Figure 2, preferably the same is sent to the pyrolysis reactor and then to the preheater.

 According to another embodiment, always depicted in Figure 2, the liquid, solid or semi-solid material of the pyrolysis

reactor is discharged by means of the char-feeder device (75).

According to another embodiment, always depicted in Figure 2, in a second pyrolysis reactor (71) the pyrolysis gas coming from the first pyrolysis reactor (70) is further heated to a higher temperature by means of the heat transfer fluid (37) coming from the hot reservoir (64). In the second reactor (71) the pyrolysis gases are therefore further pyrolyzed.

The second reactor (71) can either comprise at least a catalyst, preferably a solid catalyst, or no catalysts. When no catalysts are used, in said second pyrolysis reactor the gaseous effluent coming from the first pyrolysis reactor is heated at a temperature (TMSR) that is higher than the temperature of the material in the first pyrolysis reactor (temperature TMPR). When catalysts are used, the gaseous effluent coming from the first pyrolysis reactor is optionally heated or cooled to a temperature (TMSR) different from the temperature of the material in the first pyrolysis reactor (TMPR), before passing through the catalyst. Preferably, when the gaseous effluent coming from the first pyrolysis reactor is heated, the temperature difference between the temperature of the gaseous effluent after heating (TMSR) and the temperature of the material in the first pyrolysis reactor (TMPR) is at least 10°C, preferably between 30°C and 300°C, even more preferably between 60°C and 250°C. According to one embodiment, when the gaseous effluent coming from the first pyrolysis reactor is cooled and catalysts are used, the absolute value of the temperature difference between the gaseous effluent after cooling (TMSR) and the temperature of the material in the first pyrolysis reactor (TMPR) is between 10°C and 250°C, preferably between 30°C and 150°C.

Therefore, according to one embodiment of the present invention, in the process to produce at least a pyrolysis oil from essentially plastic material, the gaseous effluent of the pyrolysis reactor, before the condensation of step (g), is brought to a second pyrolysis reactor, where, if no catalysts are used, the gaseous stream is heated to a temperature (TMSR) that is higher than the temperature (TMPR) of the essentially plastic material in step (e); or, if catalysts are used, where the gaseous effluent of the pyrolysis reactor, before the condensation of step (g), is optionally heated or cooled to a temperature (TMSR) that is respectively higher or cooler than the temperature (TMPR) of the essentially plastic material in step (e), and then passed through the catalyst. Preferably, when the gaseous stream is heated to a temperature that is higher than the temperature (TMPR), the temperature at which the gaseous stream is brought is at least 10°C more than the temperature of the essentially plastic material in step e), 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 operated at a temperature that is higher than the temperature of the first pyrolysis reactor, if no catalysts are used in said second pyrolysis reactor, or about the same temperature or higher, if catalysts are used, with the additional condition that such temperature is between 400°C and 650°C, preferably between 440°C and 550°C, even more preferably between 460°C and 530°C.

Residence time of the pyrolysis vapors in said second pyrolysis reactor, computed dividing the volume occupied by vapors 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 gaseous state effluent is in relative
5 motion with respect to said solid catalyst in contact with said gaseous state effluent, and said relative 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.

10 Therefore, according to an embodiment of the present invention, in the process to produce at least a pyrolysis oil from essentially plastic material, the second reactor contains a catalyst, wherein said gaseous effluent of the pyrolysis reactor is put into contact with.

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

A separator (77), which can be integrated into the coker
25 device, allows the gaseous phase (53E) to be recycled back into the process (for instance, in the first pyrolysis reactor as depicted in Figure 2), while the non-gaseous 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 pyrolysis reactor to said coker device, allowing at the same time a physical separation between the two devices. An example of such device is a gear pump. Alternatively, the char-feeder device
5 (75) can be a valve, such as a rotary valve, gate valve or butterfly valve.

Advantageously, according to this embodiment, if the heat transfer fluid is fed in a series arrangement, the heat thermal fluid (37) coming from the hot reservoir is preferably delivered
10 first to said coker device (76) and then to the pyrolysis reactor (70). Advantageously, said char-feeder device (75) can be heated by the heat transfer fluid exiting the heating jacket of the pyrolysis reactor (70).

In the coker (76) said material is heated to a temperature
15 from 500°C to 1200°C, preferably from 600°C to 1000°C, even more preferably from 700°C to 900°C for a time of at least 5 minutes, preferably between 15 and 180 minutes, even more preferably between 30 and 120 minutes.

Therefore, according to one embodiment of the present
20 invention, the solid, semi-solid or liquid material in the pyrolysis reactor is withdrawn and heated to a temperature from 500°C to 1200°C, preferably from 600°C to 1000°C, even more preferably from 700°C to 900°C, for a time of at least 5 minutes, preferably between 15 and 180 minutes, even more preferably
25 between 30 and 120 minutes.

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

The coker can be heated by means of a heat transfer fluid, by means of electric resistance (Joule effect), or combinations thereof.

According to another embodiment of the present invention,
5 the condensation of the pyrolysis gas exiting the pyrolysis reactor(s) is split in more than one unit, such as two or more units, or three or more units. According to an embodiment, shown in Figure 3, it is split into three units (72A), (72B), (72C). More in detail, the pyrolysis gas (54) exiting the pyrolysis
10 reactor(s) passes through a first condenser (72A), at "high-temperature", and a first separator (73A), which separates first condensed liquid (56A) from first non-condensed vapors (55A). Said first non-condensed vapors (55A) are then passed through a second condenser (72B) at lower temperature, and a second
15 separator (73B), which separates second condensed liquid (56B) from second non-condensed vapors (55B). Said second non-condensed vapors (55B) are then passed through a third condenser (72C) at even lower temperature than the second condenser, and a third separator (73C), which separates third condensed liquid
20 (56C) from third non-condensed vapors (55C).

Therefore, according to an embodiment of the present invention, the condensation of step g) is carried out in more than one condensing unit in series.

Advantageously, according to this embodiment, the cooling
25 of the first condenser (72A) is carried out by means of the heat thermal fluid (33E) already used to heat the pyrolysis reactor, 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, it reduces the required heat duty of the solar collector and receiver.

Figure 3 shows also two additional modes for the control of the pressure according to the present invention.

5 In particular, the pressure controller (23), in order to modify the pressure of the pyrolysis reactor (70), can adjust the opening of a valve on the non-condensed gaseous stream (55). Alternatively or in combination (the latter being the configuration shown in Figure 3), when a flooded condenser is
10 used, in order to modify the pressure of the pyrolysis reactor (70), the pressure controller (23) can adjust the flooding of the condenser (72C), for instance by regulating the opening of a valve on the condensed liquid coming from said condenser (72C). In fact, in flooded condensers, the condensing power is
15 essentially proportional to (or at least a monotonous function of) the area of the condenser that is not covered by the condensate. This is due to the fact that the heat transfer coefficient is exceedingly higher for boiling/condensation ("latent") phenomena than for thermal conduction alone. By
20 flooding the condenser, the power of the same is therefore strongly reduced. As the density of the liquid phase is orders of magnitude higher than the density of the vapor phase, condensation reduces the pressure of a system; thus, it is possible to regulate the pressure by acting on the condensing
25 power.

In Figure 3 pressure control is carried out both by regulation of the condensing power (valve 81C) and by regulation of the flow of the incondensable effluent (valve 81B).

Therefore, according to an embodiment of the present

invention, the adjustment of the pressure in said pyrolysis reactor is carried out by regulating the pressure drop of the effluent of the pyrolysis reactor in the gaseous state before the condensation of step g).

5 According to another embodiment of the present invention, the regulation of the pressure drop on the effluent in the gaseous state is carried out by means of a throttling device, preferably a valve.

 When more than one device to control the pressure are used,
10 as shown in Figure 3, advantageously a so-called split-range control mode can be used.

 According to split-range control mode, the action is carried out on a single device at a time. The choice of the device is according to the "operation point" (OP) of the
15 controller. For instance, in the case of Figure 3, for OP values between 0 and 50, the valve 81B is kept at 0 (valve kept closed), while the valve regulating the level of the flooded condenser (valve 81C) is varied. In this way the pressure is varied by varying the power of the condenser. For OP values between 50 and
20 100, the valve (81C) is kept full open, progressively varying the opening of the valve (81B). In this way, the pressure of the pyrolysis reactor is regulated by varying the power of the condenser, but if the pressure keeps being in excess of the desired set-point, the condenser is kept at maximum power and
25 the pressure is adjusted by varying the opening of the valve 81B of the residual gas (the non-condensed stream). In relatively stationary conditions, the pyrolysis process generally produces some incondensable gases, so, if the adjustment is made in this mode, the OP value remains between 50 and 100, operating the

condenser at maximum power while modulating the opening of the valve on the residual gas.

All the other ancillary and miscellaneous devices and parts that link such devices (for instance, the connecting pipes) can be heated with the same heat transfer fluid used to heat the devices disclosed in the present invention (pyrolysis reactor(s), coker, etc.).

Preferably, the distribution of the heat transfer fluid to 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 hot reservoir (64) is first fed to the devices requiring higher temperature (such as the coker) and the pyrolysis reactor(s), and then to the other devices, such as the preheater (74) or the char-feeder device (75). More preferably, the order is: coker (76) (if present and if heated by heat transfer fluid), second pyrolysis reactor (71), 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 the heat transfer fluid, as depicted in Figure 3, such series includes also said first condenser, and preferably in said order the last element is said first condenser.

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

An embodiment of a semi-series configuration is depicted in Figure 4.

Figure 4 shows a weir device (78) which receives the heat transfer fluid coming from the hot reservoir (64) and delivers such fluid to the second pyrolysis reactor (71), 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 hot reservoir is sent. In such first chamber is located a first pump (66B) which delivers the heat transfer fluid to the first 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 second pyrolysis reactor (71), 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 incoming from the hot 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 pump (66B) delivers the heat transfer fluid to the first pyrolysis reactor (70) and collects its return. Similarly, another weir ensures that the pump (66B) which delivers the fluid to the reactor has enough NPSH and that no gas is entrained. The excess heat transfer fluid overflows from the weir, thus entering in the subsequent chamber. Similarly to the second chamber, in the third chamber another pump (66B) is located, which pump (66B)

delivers the heat transfer fluid to the preheater (74) and 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
5 includes another pump to deliver the heat transfer fluid to the cold reservoir (63). Start and stop of such pump can be handled 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
10 (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 hot reservoir), the weir device makes it possible to deliver a heat transfer fluid at higher temperature to the device which
15 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
20 configurations.

In another embodiment, such weir device can be located inside the hot reservoir itself, so that the pump delivering the heat transfer fluid to the weir device is not required any longer. In another embodiment, the cold and hot reservoirs can
25 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 should be understood that there are many different other customizations of the weir device, e.g. allowing more chambers
5 for managing more devices to be heated by the heat transfer fluid.

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

10 More precisely, according to this embodiment, the first device which receives the heat transfer fluid from the pumps (66) 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
15 into the device by gravitational force. Doing so, there is no need of 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
20 properly and to maintain in case of failure. Moreover, in this 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, the heat jacket being not in pressure, an accidental breakage of the heat jacket is much safer
25 as the spill from the breakage is reduced.

According to a preferred embodiment, both hot and cold heat transfer fluid reservoirs are located at ground level.

The cold and hot reservoirs optionally can comprise some mixing means, 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.

5 However, even without said mixing means, the flow of the heat transfer fluid from inlets to outlets and natural convection contribute to a certain degree of internal recirculation and mixing in the reservoirs.

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

 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
15 equivalent means where the heat transfer fluid can flow.

 Optionally, the heat transfer fluid flows also inside the 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
20 the pyrolysis reactor (70). A means to obtain such result is to use the same plastic 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 vapor and any other gases
25 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. 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
5 oxide, sodium hydroxide, sodium carbonate, potassium oxide, potassium hydroxide, potassium carbonate, sodium aluminosilicate.

The preheating temperature can be between 120°C and 360°C, preferably between 150°C and 260°C, more preferably between
10 170°C and 230°C, even more preferably between 180°C and 210°C, and optionally the plastic feed is partly or totally melted before feeding to the pyrolysis reactor.

The residence time in said preheating apparatus is preferably less than 10 minutes, more preferably less than 2
15 minutes, in particular less than one minute.

The first pyrolysis reactor (70) can be any reactor which 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
20 essentially plastic material can be operated both in batch mode, in continuous mode, and in semi-continuous mode. In the latter mode, the essentially plastic material is loaded continuously, the vapors generated are extracted continuously, but any solid residue is not continuously removed from the pyrolysis reactor.

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

Preferably, the reactor is operated in continuous or semi-

continuous mode, still more preferably in semi-continuous mode.

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

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

Among the stirred reactors, continuously stirred reactors (CSTR) and multizone reactors can be used. Plug flow reactors (PFR) can also be used, preferably stirred so as to facilitate
10 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
15 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.

According to a preferred embodiment, the reactor is a stirred reactor with a free surface.

20 According to a preferred embodiment, the reactor is substantially of cylindrical shape, with its axis being vertical.

The temperature of the material in the pyrolysis reactor can be measured by any method known in the art. For example, the
25 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. Multiple systems can be used simultaneously for improved reliability.

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

Preferably, the heat transfer fluid flows in a jacket. Optionally, the heat transfer fluid flows also inside the stirrer, so that an improved heating of the liquid mass is obtained.

Preferably, the heat transfer fluid are molten salts. Any molten salt can be used for the present invention.

The heat transfer fluid may be 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 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 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% 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).

5 Among low melting temperature alkaline metals, sodium and potassium are preferred; among (III)A, (IV)A and (V)A-group 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
10 Galinstan are preferred.

 According to one embodiment, the 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 nitrate or mixtures thereof.

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

 According to one embodiment, such nitrate/nitrite mixture
20 is the eutectic mixture of 53 wt% potassium nitrate, 40 wt% of sodium nitrite and 7 wt% of sodium nitrate; alternatively, 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.

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

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

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

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

Preferably, the heat transfer fluid has a low melting
20 temperature. More preferably, said melting temperature is at most 310°C, still more preferably at most 250°C, even more preferably at most 220°C. Preferably, this heat transfer fluid has a high decomposition temperature. More preferably, said decomposition temperature is at least 400°C, more preferably at
25 least 450°C, still more preferably at least 490°C, even more preferably at least 540°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
5 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.

10 The solar collector and receivers 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.
15 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.

Preferably, the solar collector is a parabolic trough or
20 linear Fresnel.

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
25 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". It is coated with a selective coating which maximize 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
5 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
10 in parallel, in series, or in combination of parallel and series. The combination of parallel and series is preferred.

The concentration factor 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
15 which 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.

The hot and cold reservoirs can be any container that can
20 be filled with a heat transfer fluid, such as vertical 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.

25 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 reservoir becomes too low.

According to an embodiment of the present invention, there

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
5 is a vertical vessel, preferably of essentially cylindrical 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
10 is observed. Fouling is in fact critical in pyrolysis reactors.

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 that is filled with the liquid and solid phase is continuously or semi-
15 continuously wiped (e.g., not necessarily the gaseous phase). Preferably, the 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,
20 or in some cases turbine stirrers.

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
25 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 stirrers actively run, but more than zero.

By the term "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 equipment are condensers comprising coils
5 inside which a heat transfer fluid flows, which is capable of removing heat from the fluid in the gaseous state being processed.

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

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

Alternatively, the condenser can consist of a distillation
20 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 vapors that are inside it. In this way, a better fractionation of the incoming vapors is also obtained, i.e. a better separation
25 between higher boiling components which are condensed and lower boiling components which remain in the vapor 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 vapors

operated by the column allows any solid particulate present in the incoming vapors to be separated and reunited in the liquid phase.

The condenser of the pyrolysis vapours can be a single
5 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.

When condensers are in series, each condenser receives the
10 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
15 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
20 liquid state, condensed in at least one condenser, is recycled to the 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
25 the heat transfer fluid as already described in Figure 3 (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. For this purpose, for example, a gas
5 heater can be used, which 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 an embodiment of the invention, C5-C12
10 compounds are also obtained in the pyrolysis oil. The yield of C5-C12 compounds in the pyrolysis oil is at least 18%, preferably at least 28%, more preferably between 38% and 85%. According to an embodiment of the invention, C5-C12 hydrocarbons are also obtained in the pyrolysis oil. The yield of C5-C12 hydrocarbons
15 in the pyrolysis oil is at least 15%, preferably at least 25%, more preferably at least 30%, even more preferably between 35% and 80%. According to an embodiment of the invention, the lhc fraction is at least 70%, preferably at least 85%, more preferably between 96% and 99.9%.

20 According to the invention, the fluid which is in the liquid state after condensing in said at least one condenser (that is, the pyrolysis oil) is quantitatively at least 10% by mass, preferably between 20% and 92%, more preferably between 30% and 85%, still more preferably between 40% and 75%, with
25 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, even more preferably between 80°C and 220°C.

It is possible that other liquid phases are formed (such as an aqueous phase rich in water), for instance due to the use of steam or to the presence of water in the essentially plastic material. These other liquid phases can be separated from the hydrocarbon rich phase by means of standard equipment, such as separators, or even by removing it from the bottom of the container of the condensed liquid (as the water phase is typically heavier than the organic phase comprising hydrocarbons).

In such situation, it is intended that the at least one fluid which is in the liquid state and comprises hydrocarbons having a standard boiling point not below 25°C is the organic phase comprising hydrocarbons.

Preferably, at least the first pyrolysis reactor is operated at a pressure that is atmospheric or supra-atmospheric pressure (that is, more than atmospheric pressure). According to one embodiment, the pressure is between 1.1 and 20 bara, preferably between 2 and 10 bara, and more preferably between 2.1 and 6 bara.

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

According to one embodiment, the residence time of the essentially plastic material in said first pyrolysis reactor is

at least 20 minutes, preferably from 1 hour to 15 hours, even more preferably from 2 hours to 8 hours. If the first pyrolysis reactor operates in batch mode, the residence time is computed as the period of time the essentially plastic material is at a temperature of at least 300°C. If the first pyrolysis reactor operates in continuous or semi-continuous mode, the residence time is computed as the ratio of the volume of the reactor not occupied by the gas phase alone and the volumetric flow of the essentially plastic material entering the reactor.

10 The heating of the essentially plastic material in the pyrolysis reactor is obtained by the flow of said heat transfer fluid in the reactor. As a result, when good stirring is ensured, the temperature of the liquid, solid and semi-solid mixture in the pyrolysis reactor approaches the temperature of the heat transfer fluid which is flowing in the reactor.

15 According to an alternative embodiment, the temperature 21 that is used to control the process pressure (manager 22, controller 23) is the temperature of the non-gaseous phase (the liquid, solid or semi-solid phase) in the pyrolysis reactor.

20 In fact, since the pyrolysis reactor is heated by the heat transfer fluid, the temperature of said non-gaseous phase in the pyrolysis reactor is closely related to the temperature of the heat transfer fluid.

25 Any technique known in the art can be used to maintain the pressure in the pyrolysis reactor at a defined value, wherein such 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 regulating the heat extracted from the condenser located

downstream of the reactor and in fluid connection with it. In this mode, the increase of the heat removed from the condenser results in greater vapor condensation. This condensation, bringing the evaporated material from the gaseous state to the 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 by regulating the flow of such gas by means of a valve. According to one embodiment, such gas is introduced in the 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 is not condensed (in case of more than one condenser is used in series, the gaseous stream of the last condenser).

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.

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 meaning of "substantial absence of oxygen" defined before. Advantageously, the pyrolysis process of the present invention produces a product particularly useful for use as 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.

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

Residence time of the pyrolysis vapors, computed dividing the volume occupied by vapors in the reactor and the volumetric flow rate, is at least 20 seconds, preferably between 30 seconds and 6 minutes, more preferably between 1 and 4 minutes.

Preferably, the second pyrolysis reactor is catalytic. This means that a catalyst is present inside said second pyrolysis reactor, preferably a solid catalyst, and that the pyrolysis vapors are brought into contact with said catalyst. 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 motion is at a velocity of at least 10 m/s, more preferably 20 to 300 m/s.

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

According to one embodiment, the process of the present invention, which produces at least a pyrolysis oil from essentially plastic material using variable-intensity energy sources, comprises the steps of:

a) heating a heat transfer fluid to a temperature (THTF)

comprised between 350°C and 700°C by means of a variable-intensity energy source;

b) heating a first pyrolysis reactor by means of the heated heat transfer fluid;

5 c) feeding the essentially plastic material, optionally already in the molten and/or preheated state, to the first pyrolysis reactor;

d) bringing said essentially plastic material in said first pyrolysis reactor to a temperature between 330°C and 650°C
10 in the substantial absence of oxygen and at a pressure of between atmospheric pressure and 20 bar(a) using said variable-intensity energy source;

e) holding said essentially plastic material in said first pyrolysis reactor at a temperature of between 330°C and
15 650°C for a time sufficient to produce at least one effluent in the gaseous state in said first pyrolysis reactor;

f) keeping the composition of the pyrolysis oil produced substantially constant by dynamically adjusting the
20 pressure in said first pyrolysis reactor in relation to the reference temperature (TREF), which is either the temperature of said heated heat transfer fluid (THTF) or to the temperature of the material in said first pyrolysis reactor (TMPR), at a value between atmospheric pressure
25 and 20 bar(a);

g) partly or totally condensing said effluent in the gaseous state so as to form at least one liquid fluid quantitatively being at least 10% by mass with respect to the mass of essentially plastic material fed, and which

comprises hydrocarbons that have a standard boiling point not below 25°C.

In step f), by "keeping the composition of the pyrolysis oil produced substantially constant by dynamically adjusting the pressure in said first pyrolysis reactor in relation to the reference temperature (TREF)", it is meant that the composition of the pyrolysis oil can vary within a certain tolerance. The tolerance is such that the skilled person knows it does not affect the function of the pyrolysis oil, i.e. to obtain the yield of C5-C12 compounds in the pyrolysis oil of at least 18%, and yield of C5-C12 hydrocarbons in the pyrolysis oil is at least 15%; and relative preferred values.

Moreover, by "dynamically adjusting" it is meant that the adjusting is not carried out once, but repeatedly from time to time. The frequency of such adjustment can be at least once per 8 hours, preferably at least once per hour, even more preferably once per minute.

According to one embodiment, the variable-intensity energy source is the solar source by concentrated solar power (CSP), the solar photovoltaic, the wind, the tidal and combinations thereof. Preferably, according to one embodiment, the variable-intensity energy-source is the solar photovoltaic, solar source by concentrated solar power (CSP), even more preferably the solar energy source by concentrated solar power (CSP).

According to one embodiment, additionally there is a second energy source which is of a different type from said variable-intensity energy source and where the heating of step (a) is carried out by means of both a variable-intensity energy source and said second energy source.

Preferably, said second energy source is an electric or thermal source from fossil, biomass (in particular biomethane or renewable natural gas) or nuclear fuels, and relative combinations.

5 According to one embodiment, the process to produce at least a pyrolysis oil from essentially plastic material according to the present invention, comprises the following additional step:

10 a2) storing the heat transfer fluid heated at a temperature (THTF) in a tank.

 According to one embodiment, the process disclosed in the present invention produces at least a pyrolysis oil from essentially plastic material, where the pressure adjustment of step (f) in relation to a reference temperature (TREF), which is
15 either the temperature of said heated heat transfer fluid (THTF) or to the temperature (TMPR) of the material in said pyrolysis reactor, is carried out by increasing the pressure when the temperature (TREF) decreases and by decreasing the pressure when the temperature (TREF) increases so that the resulting pressure-
20 temperature value corresponds to a pressure-temperature value of a predefined set of pressure-temperature values obtained according to the interpolation described below.

 It has to be understood that, according to another embodiment, the temperature used for the adjustment of step (f)
25 is the temperature of the liquid/solid/semisolid mass that is comprised in the pyrolysis reactor.

 Different schemes of regulation are possible. According to one embodiment of such control schemes, the pressure adjustment of step (f) in relation to the reference temperature (TREF),

which is either the temperature of said heated heat transfer fluid (THTF) or to the temperature of the material in said pyrolysis reactor (TMPR), is carried out by a method providing setting a lower temperature threshold (TTL) and an upper
5 temperature threshold (TTU), and, while the temperature (TREF) is within said lower temperature threshold (TTL) and upper temperature threshold (TTU), by increasing the pressure when the temperature (TREF) decreases, and vice-versa, wherein such an increase or decrease of the pressure is calculated preferably
10 according to an interpolation equation of the temperature-pressure relationship between TTL and TTU, the method further comprising keeping the pressure constant while the temperature (TREF) is above said upper temperature threshold or below said lower temperature threshold.

15 According to one embodiment, the interpolation equation of the temperature-pressure relationship between TTL and TTU is a linear interpolation. That means that, in the pressure (ordinates) vs temperature (abscissa) chart, the operating line is the line between point (TTL, PLU) and point (TTU, PLL); thus,
20 according to this the embodiment, the pressure set point (PMPR), for temperature TREF between TTL and TTU, is the ordinate value of said line, at a given abscissa value.

According to an alternative embodiment, the interpolation equation of the temperature-pressure relationship between TTL
25 and TTU is a monotonic non-increasing piecewise linear function passing by the (TTL, PLU) and (TTU, PLL) endpoints, in particular a monotonic non-increasing piecewise constant function, such as the monotonic non-increasing piecewise constant functions derived by a linear combination at least one Heaviside (step)

function, preferably from 2 to 10 Heaviside (step) functions.

According to an alternative embodiment, the interpolation equation of the temperature-pressure relationship between TTL and TTU is a generalized logistic function passing by the (TTL, PLU) and (TTU, PLL) endpoints, preferably a sigmoid function (also called "logistic function").

Preferably, the interpolation equation of the temperature-pressure relationship between TTL and TTU is the linear interpolation or the piecewise constant function or the generalized logistic function, more preferably the linear interpolation or the piecewise constant function, even more preferably the linear interpolation function.

Therefore, according to an embodiment of the present invention, the process of the present invention is characterized in that, when the temperature is between said lower (TTL) and upper (TTU) temperature threshold, the pressure is set to the value obtained by an interpolation equation of the temperature-pressure relationship, wherein preferably said interpolation equation is the linear interpolation or the piecewise constant function or the generalized logistic function.

The pressure is set by fixing the target pressure set value by the pressure manager (22) to the given value, so that the pressure controller (23) can regulate the pressure of the (first) pyrolysis reactor to the target value, as described before.

According to a possible sub-scheme of control, which can be used for any interpolation equation, when the temperature (TREF) is equal or below said lower temperature threshold (TTL) the pressure is set to an upper limit pressure (PLU), and when the temperature (TREF) is equal or above said upper temperature

threshold (TTU) the pressure is set to a lower limit pressure (PLL).

In this case, preferably, said lower limit pressure (PLL) is comprised between atmospheric pressure and 3 bar(a), more preferably between atmospheric pressure and 2.1 bar(a), even more preferably is atmospheric pressure, and said higher limit pressure (PLU) is 3.2 bar(a) or above, more preferably between 3.5 bar(a) and 10 bar(a), even more preferably between 4 bar(a) and 6 bar(a). In this case, preferably, the lower temperature threshold (TTL) is from 350°C to 500°C, more preferably from 380°C to 440°C, even more preferably from 400°C to 420°C, and the upper temperature threshold (TTU) is from 400°C to 700°C, more preferably from 420°C to 480°C, even more preferably from 440°C to 460°C, with the additional provision that the upper temperature threshold is in any case at least 10°C, preferably at least 20°C, even more preferably at least 40°C more than the lower temperature threshold.

The variability of the temperature in specific ranges is due to the fact that different plastic materials to be processed (e.g. different Plas mix compositions) require different process temperatures. For instance, process conditions such as in particular residence time being equal, LDPE requires higher process temperatures than PS polymers (see for instance Tuffi et al. Express Polymer Letters Vol.12, No.1 (2018) 82-99). The expert technician knows how to modify the temperature based on the variability of the feedstock (that is, there are data that highlight the degradation temperature of the various plastics), for instance by carrying out a thermogravimetric analysis (TGA) at the standard rate of 10°C/min on a sample of the essentially

plastic material feedstock and determining the temperature corresponding to 50% weight loss. Therefore he/she is also able to offset the range, with respect to that given above, to obtain similar results with other compositions of plastic materials, for instance taking the value at 50% weight loss in TGA for the upper threshold (TTU), and the same value less 40°C for the lower threshold (TTL).

Some schemes of regulation are shown in Figure 5. In this Figure, three different interpolation equations are shown graphically: from top to bottom, the linear relationship, the monotonic non-increasing piecewise constant function, and the generalized logistic function. For each case, a chart is provided where the pyrolysis temperature is in abscissa and pyrolysis pressure in ordinates. In all cases, outside the range of temperature between said lower temperature threshold (TTL) and said upper temperature threshold (TTU) the set point (set by the pressure manager 22) of the pyrolysis pressure (PMPR) is kept constant to the value at said endpoints (i.e., PMPR equal to PLU for temperature TREF not higher than TTL, and PMPR equal to PLL for temperature TREF not lower than TTU). When the temperature TREF is inside the range (TTL, TTU), the pressure set point PMPR is set according to the corresponding interpolation equation.

The linear interpolation is generally effective and shows to be stable, however it has the shortcoming that even in case of very small changes of the pyrolysis temperature, the pressure set point is always changing. This can be cumbersome for some pressure regulators which require the set point to be unchanged for some time. In such cases, a piecewise constant function can be more effective. Finally, the generalized logistic function is

able to remove the discontinuity in the first derivative at the endpoints (TTL, TTU), as the derivative of such function at endpoints is substantially zero. Therefore, such interpolation equation shows to be particularly stable for PID controls (23) 5 which have a significant derivative component.

According to one embodiment of the present invention, the step (f) comprising dynamically adjusting the pressure in relation to the temperature of said heated heat transfer fluid is carried out with a latency of at most 120 seconds, preferably 10 between 0.1 to 60 seconds.

By latency it is meant the time delay between the measurement of temperature and the definition of the set point of the pressure, and therefore it comprises the time required for temperature measurement, optional data filtering, evaluation 15 of the pressure set point and definition of the same.

Examples

Raw material

It was considered appropriate to use primarily virgin raw material, the composition of which is therefore known and 20 constant, thus also facilitating the repeatability of the experiment. By preparing suitable mixtures of the raw materials, it was therefore possible to evaluate the effect of different pyrolysis conditions cancelling the effect of the variability in the composition of the essentially plastic 25 material sources. Moreover, in this way it was possible to prepare a mixture that was representative of the average "Plas mix", that is the residue after sorting of recycled plastics material.

In fact, several Plas mix samples were collected and analyzed over time, from which an average composition of the same was determined and used in the preparation of the mixture used in the present Examples.

5 The used polymeric materials were the following:

Polymer	Abbrevi ation	Commercial name / Producer code	Producer
Low density polyethylene	LDPE	Riblene® FC20	Versalis
Low density linear polyethylene	LLDPE	Flexirene® CL10	Versalis
High density polyethylene	HDPE	Eraclene® BC82	Versalis
Polypropylene	PP	Isplen® PP040	Repsol
Polystyrene	PS	Edistir® N3782	Versalis
Polyethylene terephthalate	PET	Monflakes® R-PET	Montello
Cellulose	CELL	C6288	Sigma- Aldrich
Polyvinyl chloride	PVC	S3160	Vinnolit
Nylon 6	PA	181110	Sigma- Aldrich

The following table shows the atomic composition (percentages by weight) of the materials used.

10

		MATERIALS (in abbreviation)						
		PE	PP	PS	PET	CELL	PVC	PA
ATOM	H	14.3%	14.3%	7.7%	4.2%	6.2%	4.8%	17.7%
	C	85.7%	85.7%	92.3%	62.5%	44.4%	38.7%	58.1%
	N	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	11.3%
	O	0.0%	0.0%	0.0%	33.3%	49.4%	0.0%	12.9%
	Cl	0.0%	0.0%	0.0%	0.0%	0.0%	56.5%	0.0%

The used inorganic materials were the following:

Additive	Abbreviation	Code	Producer
Calcium carbonate (≥99%)	CaCO ₃	239216	Sigma-Aldrich
Sodium chloride (≥99%)	NaCl	S9888	Sigma-Aldrich
Titanium dioxide (≥99%)	TiO ₂	14021	Sigma-Aldrich
Silicon dioxide	SiO ₂	381276	Sigma-Aldrich
Aluminium (80wt.% in polyolefin carrier)	Al80	Mastersafe MP 10-20B	Eckart

5 **Preparation of the mixture**

Firstly, a master batch of inorganic additives (named MBINORG) was prepared by mixing and extruding the following composition in a twin-screw extruder:

Composition of master batch MBINORG	
Additive (by abbreviation)	Quantity (wt.%)
LDPE	46.65
LLDPE	26.66
Calcium carbonate (≥99%)	20.76
Sodium chloride (≥99%)	2.97
Titanium dioxide (≥99%)	1.48
Silicon dioxide	1.48
TOTAL	100.00

10

Then, the following mixture ("PYROMIX-1") has been prepared in dry-blend:

PYROMIX-1	
Additive (by abbreviation)	Quantity (wt.%)
LDPE	27.98
LLDPE	15.99
HDPE	3.03
PP	25.58
PS	6.80
PET	6.80
CELL	2.91
PVC	0.97
PA	1.46
Al80	0.30
MBINORG	8.18
TOTAL	100.00

The above composition was prepared to mimic the typical composition of an essentially plastic material, as found in the Plas mix. In fact, it is essentially the average composition of several Plas mix samples which were analyzed to evaluate the type of plastics and the different inorganic materials contained in it.

Pyrolysis apparatus used in the Examples

The pyrolysis apparatus used in the examples in the present invention ("A1") consisted of:

- a pyrolysis reactor, equipped with a flange for loading materials, a dip tube for entry of the inerting gas (nitrogen), a nozzle for the inlet of the essentially plastic material, a nozzle for the outlet of pyrolysis

vapours and openings (NT1, NT2, NT3) for measuring by means of thermocouples the temperature of the liquid/solid/semi-solid mass inside the reactor (3 points of measurement, for better accuracy), and one nozzle (NP1) for measurement of the pressure;

- a flow meter equipped with a fine adjustment valve for regulating the rate of inerting gas flow into the reactor;

- a pressure transducer located at the reactor top, which reads the pressure of the gases inside the reactor;

- three thermocouples to measure the actual temperature of the liquid/solid/semi-solid mass inside the reactor, and therefore located in the lower part of the reactor;

- an electric heating jacket with thermal insulation system;

- a reactor temperature regulating system that reads the temperature value of one of the three thermocouples and regulates the electric heating power in feedback, the control parameters of which have been suitably calibrated to ensure high thermal stability (temperature fluctuations below 5°C);

- a condenser for condensation of the vapours leaving the reactor, held at -10 °C by means of a cooling fluid made to flow from a refrigeration unit at a controlled temperature;

- a valve for regulating the flow of gas leaving the reactor located between said reactor and said condenser;

- a reactor pressure regulating system which reads the pressure value of said pressure transducer and acts through feedback on said regulating valve, so as to ensure high pressure stability (pressure oscillations lower than
5 50 mbar);

- an expandable flask hermetically connected to the upper outlet of said condenser intended to collect the gaseous fraction which is not condensed;

- a receiving container hermetically connected to
10 the lower outlet of said condenser intended to collect the condensed fraction and therefore in the liquid state, with vents connected to said upper outlet of the condenser;

- a valve for nitrogen inlet;

- an intercept valve between the outlet of the
15 liquid product leaving the condenser and the sealed connection with the receiving container;

- an intercept valve between the outlet of the gaseous product leaving the condenser and the sealed connection with the expandable flask.

20 The reactor is vertical and has a substantially cylindrical profile.

Pyrolysis examples (comparatives and according to the invention)

Examples were prepared using the dry-blended mixture of
25 polymers and inorganic compounds PYROMIX-1.

The following table shows the conditions for each Example.

Example number	[#]	1	2	3
Comparative/		Inv.	Comp.	Inv.

Invention	[-]			
T _{pyro} (Pyrolysis temperature)	[°C]	450	410	410
P _{pyro} (Pyrolysis pressure)	[bar(a)]	2.1	2.1	5.1

In the reactor of "Apparatus 1" described above the dry-blended mixture was charged. The occupied volume in the reactor was about 1/3 of the geometric volume.

5 The valve for regulating the flow of the pyrolysis vapours leaving the reactor was manually set to full opening.

Nitrogen was then injected from below through the dip tube, fully opening the fine adjustment valve of the flow meter.

The gases contained in the reactor were then removed over
10 a time equal to 24 hours, in order to ensure full elimination of oxygen.

The valves on the outlet of the gaseous and liquid products from the condenser were then closed. Immediately afterwards, the nitrogen supply was interrupted. The expandable flask for
15 collecting the gases produced and the receiving container for collecting the liquids produced were connected.

Then, the valves on the outlet of the gaseous and liquid products from the condenser were reopened.

The valve for regulating the flow of gas leaving the
20 reactor was set for automatic regulation at the value chosen for the test (P_{pyro}, as given in the table).

Nitrogen was then injected from below through the dip tube,

but setting a very low flow rate, selected so that the quantity of gas collected in the expandable balloon before its replacement did not exceed 30% of the maximum volume of the balloon.

The following program was loaded in the thermal regulation
5 system of the pyrolysis reactor:

1. first heating ramp: 4 degrees per minute, until the pyrolysis temperature T_{pyro} is reached;
2. holding the temperature T_{pyro} for 6 hours;
3. switching off the heating.

10 The reactor thermal regulation system was turned on.

After 12 hours from the end of the program, the reactor temperature was checked being below 60°C. Then, the nitrogen supply was interrupted, the intercept valves on the liquid and gaseous product outlets leaving the condenser were closed and
15 the reactor flange was opened.

A semi-solid material was found in the reactor (corresponding to the material that did not transform into pyrolysis vapours). This material, which is named "char", is carefully removed from the reactor and weighted.

20 The reactor inner walls were carefully cleaned so as to remove the fouling that eventually could have been formed.

The liquid contained in the liquid receiving container (the pyrolysis oil condensate) was weighed and then ultracentrifuged (Thermo Scientific ultracentrifuge model
25 Sorvall Evolution RC) at 25000 rpm for 45 minutes.

The material left on the bottom after ultracentrifugation (hereinafter described as the wax) and the supernatant (hereinafter described as the light oil) were then separated and weighed.

The fraction of light oil ("light oil fraction") was calculated by dividing the weight of light oil by the weight of the material initially fed into the reactor (the dry-blended mixture).

5 Similarly, the fraction of wax ("wax fraction") was calculated by dividing the weight of wax by the weight of the material initially fed into the reactor (the dry-blended mixture).

Similarly, the fraction of char ("char fraction") was
10 calculated by dividing the weight of the semi-solid material extracted from the reactor by the weight of the material initially fed into the reactor.

The mass of gas produced was calculated as the difference between the weight of the material initially fed into the reactor
15 and the sum of the weights of char and pyrolysis oil fractions (the latter being the sum of the light oil and wax). The fraction of non-condensed gas produced ("gas fraction") was calculated by dividing the mass of the gas fraction thus calculated by the weight of the material initially fed into the reactor.

20 METHOD OF GAS-CHROMATOGRAPHIC ANALYSIS OF LIGHT OIL SAMPLES

The light oil samples were characterised by gas chromatographic analysis. The compounds were first qualitatively identified by means of a coupled gas chromatography - mass
25 spectrometry (GC-MS) technique, while they were quantified by gas chromatography with a flame ionization detector (GC-FID).

Below are the instrumental parameters used for the GC-FID analyses:

- GC: Agilent HP 7890 B, fitted with Gerstel MPS

autosampler

- Column: HP-PONA Agilent Technologies J&W - 50 m - 0.2 mm - 0.5 μ m,
- Carrier (H₂): 1.1 mL/min constant flow
- 5 - Injector: 320°C, 255:1 split, 3 mm (Ultra Inert) liner with glass wool
- Detector: 360°C
- Oven: Column temperature program: 20°C 5 min, in 2°C/min up to 70°C for 5 min, in 2°C/min at 160°C for 5 min, in 10 2°C/min to 320°C for 30 min (Run time: 195 min).

Each sample was analysed as is by attributing an arbitrary response factor equal to one for all compounds; the concentrations obtained were then normalized to 100%.

The fractions obtained were analysed using the techniques 15 described above. About 130 chemical compounds were identified.

For each of these chemical compounds the number of atoms for each element (C, N, O, H) was computed. Therefore, it was possible to compute the mass fraction of C, N, O and H atoms by summing up the products of the masses of each chemical compound 20 by the mass fractions of each atom in the compound.

GAS-CHROMATOGRAPHIC ANALYSIS MODE ON WAX SAMPLES

This fraction is analysed in different ways to allow the identification of high molecular weight compounds as well.

In fact, these compounds could plausibly not be eluted and 25 analysed in the gas chromatographic analyses.

Before taking the sample for GPC analysis, the pyrolysis oils contained in Schott bottles were heated to 50°C to homogenize their contents (in some cases characterised by deposits and/or layers of waxy compounds at room or chilled

temperature). A few mg of sample in 1,2,4-trichlorobenzene (Baker) with added 10 μ L of n-heptane (internal marker) were dissolved with heating (one hour of dissolution at 150°C) in order to obtain a concentration of approximately 1.8 mg/mL.

5 The analyses were carried out on a chromatographic apparatus consisting of:

- High temperature Char Polymer GPC-IR
- bench of 3 TSK gel HT2 columns of dimension 13 μ m and pre-column
- 10 - IR5 high temperature infra-red detector that provides an absorbency signal proportional to the quantity of methyl and methylene groups.

 The adopted experimental conditions were as follows:

- eluent: 1,2,4 TAB stabilised with BHT
- 15 - flow: 1 mL/min
- temperature: pump at 25°C, injector at 150°C, columns at 150°C, detector at 150°C
- injection volume: 200 microlitres
- internal standard: n-heptane.

20 By "C5-C12 wax fraction" it is meant the sum of the mass of the chemical compounds having from 5 to 12 carbon atoms (extremes included) in the wax with respect to the total mass of said wax product.

 By "C5-C12 light oil fraction" it is meant the sum of the
25 mass of the chemical compounds having from 5 to 12 carbon atoms (extremes included) in the light oil with respect to the total mass of said wax product.

 By "C5-C12 yield" it is meant the "C5-C12 light oil fraction" multiplied by the "light oil fraction" plus the "C5-

C12 wax fraction" multiplied by the "wax fraction". The "C5-C12 yield" is therefore the ratio of the mass of compounds having from 5 to 12 carbon atoms in the pyrolysis oil product by the mass of the essentially plastic material fed to the pyrolysis reactor. This is the most relevant parameter in the results as the C5-C12 compounds are the most desired compounds for closed-loop recycle of plastics.

In the following table the C5-C12 yield, the C5-C12 hc yield and the lhc fraction are reported.

10

Example number	[#]	1	2	3
Comparative/ Invention	[-]	Inv.	Comp.	Inv.
T_pyro (Pyrolysis temperature)	[°C]	450	410	410
P_pyro (Pyrolysis pressure)	[bar(a)]	2.1	2.1	5.1
C5-C12 yield	[%]	41.9	28.9	39.4
C5-C12 hc yield	[%]	41.3	27.7	38.1
lhc fraction	[%]	98.6	95.8	96.7

These parameters are very relevant as C5-C12 compounds are very desired compounds for closed-loop recycle of plastics. Among such compounds, the hydrocarbons are the most desired compounds, as in most cases compounds comprising heteroatoms (such as sulphur, oxygen and nitrogen) have to be separated to prepare some high quality virgin plastics, such as polyethylene, polypropylene, polystyrene.

It can be seen that the yield in C5-C12 was very good in Example 1 (pyrolysis at 450°C at 2.1 bar(a)), but decreased

strongly when the pyrolysis temperature was reduced by 40°C at the same pressure (410°C at 2.1 bar(a)).

However, when the pressure was increased to 5.1 bar(a) (Example 3) it was possible to get almost the same yield in the
5 desired C5-C12 fraction, even though the temperature was the same as the temperature of Comparative Example 2 (410°C).

Similarly, the C5-C12 hydrocarbons yield was very good in Example 1 (41.3%), but decreased strongly (to 27.7%) when the pyrolysis temperature was reduced by 40°C at the same pressure.

10 However, when the pressure was increased to 5.1 bar(a) (Example 3) it was possible to get almost the same yield in the C5-C12 hydrocarbons (38.1%), even though the temperature was the same as the temperature of Comparative Example 2.

Finally, the *lhc* fraction, which is the ration of C5-C12
15 *hc* yield to the C5-C12 yield, is very high for the inventive Examples 1 and 3 (>96.5%). That means the C5-C12 compounds in the pyrolysis oil mostly consists of hydrocarbons, being the non-hydrocarbon compounds less than 5% of the total. Instead, Comparative Example 2 shows a significant lower percentage of
20 hydrocarbons (95.8%).

That means it is possible to compensate a reduction in the pyrolysis temperature due to reduction in the power delivered by said intermittent or variable-intensity energy source (for instance, when the sun is setting or some clouds reduces the
25 sunlight power) by increasing the process pressure.

CLAIMS

1. A process to produce at least a pyrolysis oil from essentially plastic material using variable-intensity energy sources which comprises the steps of:
- a. heating a heat transfer fluid to a temperature (THTF) comprised between 350°C and 700°C by means of a variable-intensity energy source;
 - b. heating a pyrolysis reactor by means of the heated heat transfer fluid;
 - c. feeding the essentially plastic material, optionally already in the molten and/or preheated state, to a pyrolysis reactor;
 - d. bringing said material in said pyrolysis reactor to a temperature (TMPR) between 330°C and 650°C in the substantial absence of oxygen and at a pressure of between atmospheric pressure and 20 bar(a) using said variable-intensity energy source;
 - e. holding said material in said pyrolysis reactor at a temperature (TMPR) of between 330°C and 650°C for a time sufficient to produce at least one effluent in the gaseous state in said pyrolysis reactor;
 - f. keeping the composition of the pyrolysis oil produced substantially constant by dynamically adjusting the pressure in said pyrolysis reactor in relation to a reference temperature (TREF), which is either the said temperature of said heated heat transfer fluid (THTF) or the said temperature of the material in said pyrolysis reactor (TMPR), at a value between atmospheric pressure and 20 bar(a);

g. partly or totally condensing said effluent in the gaseous state so as to form at least one liquid fluid quantitatively being at least 10% by mass with respect to the mass of essentially plastic material fed, and
5 which comprise hydrocarbons that have a standard boiling point not below 25°C.

2. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 1, where the pressure adjustment of step (f) in relation to the
10 reference temperature (TREF) is carried out by increasing the pressure when the temperature (TREF) decreases and by decreasing the pressure when the temperature (TREF) increases.

3. A process to produce at least a pyrolysis oil from
15 essentially plastic material according to claim 1, where the pressure adjustment of step (f) in relation to the reference temperature (TREF) is carried out by setting a lower temperature threshold (TTL) and an upper temperature threshold (TTU), and increasing the pressure when the
20 reference temperature (TREF) decreases and vice-versa, while the temperature (TREF) is within said lower temperature threshold (TTL) and upper temperature threshold (TTU), and keeping the pressure constant while the reference temperature (TREF) is above said upper
25 temperature threshold or below said lower temperature threshold.

4. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 3, where when the temperature (TREF) is equal or below said lower

temperature threshold (TTL) the pressure is set to a upper limit pressure (PLU), and when the temperature (TREF) is equal or above said upper temperature threshold (TTU) the pressure is set to a lower limit pressure (PLL).

- 5 5. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 4, wherein said lower limit pressure (PLL) is comprised between atmospheric pressure and 3 bar(a), more preferably between atmospheric pressure and 2.1 bar(a), and said higher limit
- 10 pressure (PLU) is 3.2 bar(a) or above, more preferably between 3.5 bar(a) and 10 bar(a), even more preferably between 4 bar(a) and 6 bar(a).
6. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim 3 to 5,
- 15 characterized in that, when the reference temperature (TREF) is between said lower (TTL) and upper (TTU) temperature threshold, the pressure is set to the value obtained by an interpolation equation of the temperature-pressure relationship, wherein preferably said
- 20 interpolation equation is the linear interpolation or the piecewise constant function or the generalized logistic function.
7. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim from 1
- 25 to 6, where the said variable-intensity energy source is the solar, the wind, the tidal and combinations thereof.
8. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 7, where the said variable-intensity energy source is the solar

energy, preferably by concentrated solar power (CSP) means.

9. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim from 1 to 8, comprising the following additional step:

5 a2. storing the heat transfer fluid heated at a temperature (THTF) in a tank;

10. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim from 1 to 9, where additionally there is a second energy source
10 which is of a different type from said variable-intensity energy source and where the heating of step (a) is carried out by means of both a variable-intensity energy source and said second energy source.

11. A process to produce at least a pyrolysis oil from
15 essentially plastic material according to claim 10, where said second energy source is an electric or thermal source from fossil, biomass (such as biomethane) or nuclear fuels, and relative combinations.

12. A process to produce at least a pyrolysis oil from
20 essentially plastic material according to any claim from 1 to 11, where the step (f) comprising dynamically adjusting the pressure in relation to the temperature of said heated heat transfer fluid is carried out with a latency of at most 120 seconds, preferably between 0.1 to 60 seconds.

25 13. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim from 1 to 12, where the heat transfer fluid are molten salts.

14. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 13, where

the molten salts are of group IA and IIA of the periodic table, preferably sodium nitrate, sodium nitrite, potassium nitrite, potassium nitrate, lithium nitrate, calcium nitrate and mixtures thereof.

5 15. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 14, where the molten salt is the mixture of 60.% sodium nitrate and 40.% of potassium nitrate; or the eutectic mixture of 53 wt.% potassium nitrate, 40 wt.% of sodium nitrite and 7wt.%
10 of sodium nitrate; or the eutectic mixture of 45.5 wt.% potassium nitrate and 54.5 wt.% of sodium nitrite.

16. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim from 1 to 15, where the gaseous effluent of the pyrolysis reactor,
15 before the condensation of step (g), is brought to a second pyrolysis reactor, wherein, if no catalysts are used, the gaseous stream is heated to a temperature (TMSR) that is higher than the temperature (TMPR) of the essentially plastic material in step (e); or wherein, if catalysts are
20 used, the gaseous effluent of the pyrolysis reactor, before the condensation of step (g), is optionally heated or cooled to a temperature (TMSR) that is respectively higher or cooler than the temperature (TMPR) of the essentially plastic material in step (e), and then passed through the
25 catalyst.

17. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 16, where the second reactor contains a catalyst where said gaseous effluent of the pyrolysis reactor is put into contact with.

18. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim 1 to 17, where the condensation of step (g) is carried out in more than one condensing unit in series.
- 5 19. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim 1 to 18, where the adjustment of the pressure in said pyrolysis reactor is carried out by regulating the pressure drop of the effluent of the pyrolysis reactor in the gaseous state
10 before the condensation of step (g).
20. A process to produce at least a pyrolysis oil from essentially plastic material according to claim 19, where the regulation of the pressure drop on the effluent in the gaseous state is carried out by means of a throttling
15 device, preferably a valve.
21. A process to produce at least a pyrolysis oil from essentially plastic material according to any claim 1 to 20, where the essentially plastic material is preheated preferably to a temperature in the range between 120° and
20 360°C, even more preferably between 150°C and 260°C, even more preferably between 170 and 230°C, even more preferably between 180 and 210°C, and optionally partly or totally melted before feeding to the pyrolysis reactor.
22. A process to produce at least a pyrolysis oil from
25 essentially plastic material according to any claim 1 to 21, where the solid, semi-solid or liquid material in the pyrolysis reactor is withdrawn and heated to a temperature from 500°C to 1200°C, preferably from 600°C to 1000°C, even more preferably from 700°C to 900°C for a time of at least

5 minutes, preferably between 15 and 180 minutes, even more preferably between 30 and 120 minutes.

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

- 5 a. A 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 molten salts;
- 10 b. A condenser (72) which receives the gaseous effluent of said pyrolysis reactor;
- c. A solar collector and receiver assembly (61,62), the receiver comprising at least one inlet and one outlet for the molten salts, where said solar collector is able to deliver concentrated solar radiation to said solar receiver that in turns is configured to heat said molten salts;
- 15 d. A first tank ("cold tank", 63) which is fluidically connected to the outlet for molten salts of said pyrolysis reactor (70) to receive and store the molten salts returning from the pyrolysis reactor (70) and it is fluidically connected to an inlet of said solar receiver (62);
- 20 e. A second tank ("hot tank", 64) which is fluidically connected to an outlet of said solar receiver (62) to receive and store the molten salts returning from the solar collector and receiver (SCA1) and it is fluidically connected to the inlet for molten salts of said pyrolysis reactor (70);
- 25

f. A controller (23) that adjusts, through a pressure manager (22), the pressure set point of the pyrolysis reactor (24) in relation to the reference temperature TREF, which is either the temperature THTF (21A) of the molten salts coming from the second tank ("hot tank", C2) or the temperature TMPR (21B) of the material in the first pyrolysis reactor (70).

10