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(54) **Title:** METHOD FOR THE PYROLYSIS OF RAW MATERIALS, IN PARTICULAR RAW MATERIALS DERIVING FROM TIRES OR BITUMEN AND PYROLYSIS EQUIPMENT OPERATING ACCORDING TO SAID METHOD

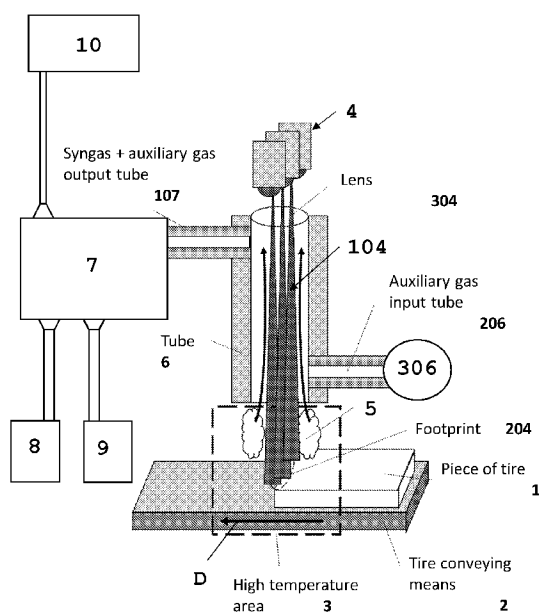


Fig. 1

(57) **Abstract:** A method for the pyrolysis of raw materials, in particular raw materials deriving from tires or bitumen, the method providing the steps of: - feeding to a reactor the material to be subjected to the pyrolysis process; heating said material in said reactor at the temperatures needed for establishing the pyrolysis process; - collecting the final products of the pyrolysis reaction; - separating one from another the gaseous, liquid and solid phases of the reaction products and storing, for further treatment, said reaction products separated one from another. According to the invention, the heating of the pyrolysis process to the activation temperature is obtained by irradiation of the raw material with laser radiation, - said laser radiation being concentrated or focused on a localized area of a pre-established surface area on the surface of the mass of raw material of the focusing area, being progressively moved along the entire surface of the mass of raw material by activating the pyrolytic reaction on all of said mass of raw material.

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Method for the pyrolysis of raw materials, in particular raw materials deriving from tires or bitumen and pyrolysis equipment operating according to said method.

Object of the present invention is a method for the pyrolysis of raw materials, in particular raw materials deriving from tires or bitumen, the method providing the steps of

Feeding to a reactor the material to be subjected to the pyrolysis process; heating the reactor where required;

heating said material in said reactor at the temperatures needed for establishing the pyrolysis process;

collecting the final products of the pyrolysis reaction;

separating one from another the gaseous, liquid and solid phases of the reaction products and storing, for further treatment, said reaction products separated one from another.

Currently the pyrolysis processes on masses of material, such as bio-masses, wastes, among which there are also materials constituted by rubber or bituminous materials, are carried out by heating the mass to be subjected to the pyrolysis reaction by

different techniques for transferring the thermal energy.

A widespread technique provides a carrier of thermal energy, which is pre-heated and thermally
5 contacted with the material of the mass to be subjected to the pyrolysis reaction. Some widespread embodiments of such a technique provide the mass of the starting material to be heated thanks to heat carriers consisting of spherical, spheroidal or
10 spherical-like bodies, which are subjected to heating in an oven to be brought to a pre-established working temperature. Subsequently said bodies are contacted with the mass to be treated in a reactor. In order to ensure an effective transfer of thermal energy from
15 the carriers to the mass, it is preferable that the material to be treated is chopped to pre-established granulometry such that the contact among the mass of the material and the carriers allows high transfer flows of thermal energy from said carriers to said
20 material to be obtained.

In this type of equipment, the treatment process provides

- the heating of the heat carrier, which normally is obtained by an oven;
- 25 - the transport of the heat carrier, within a transport circuit;
- the need to arrange specific inlets and outlets for the heat carrier in the reactor, which

has to work in the absence of oxygen and in vacuum conditions;

- the cleaning of the heat carrier getting dirty with the residues of the reaction ashes.

5 In the state of the art further alternative pyrolysis techniques exist, such as those using:

induction heating of a ferrous carrier that in turn heats the matter to be pyrolyzed;

microwave heating of the matter to be pyrolyzed;

10 heating of the matter to be pyrolyzed by a plasma torch;

heating by ablative effects, such as for example gasification by high speed bumps.

All of the known equipment despite being
15 functionally satisfactory, has improvement possibilities which can concern, for some limitations to a different extent, both the process steps and the needed structures and designs of the equipment.

According to a first aspect, the invention aims
20 to improve process efficiency, not only for what concerns triggering and maintaining the reaction, but also for what concerns simplifying the collecting and separating process of the various phases of the reaction products and, not the least, for what also
25 concerns simplifying the equipment itself needed to implement the process.

According to a further aspect, the invention aims to make the equipment much more compact,

allowing its stationary design and a mobile or transportable design thereof, for example integrable inside a container or the like.

Still according to an aspect, the invention
5 wants to overcome the limits of known processes and equipment regarding the reaction control, allowing precise control of the transfer of thermal energy and consequently of the reaction temperature to be exerted.

10 In order to satisfy one or more of the preceding aspects, the invention refers to a method for the pyrolysis of raw materials, in particular raw materials deriving from tires or bitumen, the method providing the steps of

15 - Feeding to a reactor the material to be subjected to the pyrolysis process;

- heating said material in said reactor at the temperatures needed for establishing the pyrolysis process;

20 - collecting the final products of the pyrolysis reaction;

- separating one from another the gaseous, liquid and solid phases of the reaction products and storing, for further treatment, said reaction
25 products separated one from another,

and wherein

- the heating of the pyrolysis process to the activation temperature is obtained by irradiation of

the raw material with laser radiation,

- said laser radiation being concentrated or focused on a localized area of a pre-established surface area on the surface of the mass of raw material of the focusing area, being progressively moved along the entire surface of the mass of raw material by activating the pyrolytic reaction on all of said mass of raw material.

According to an embodiment, the area on which the laser radiation is projected, is kept stationary in a reaction station and the mass of raw material is passed with a pre-established translation speed in said reaction station.

Still according to an embodiment, the reaction temperature is such to transform the mass of raw material into a mixture of ablation gas containing the reaction products and these are drawn by suctioning them from the reaction station in a drawing room open towards the reaction station and set at a pressure lower than that of the reaction station.

Still according to an embodiment provided in combination with one or more of the preceding embodiments, the separation of the reaction products having the different gaseous, liquid and solid phases, takes place by condensation of the mixture of ablation gas by means of a cooling step of said gas mixture at a pre-established temperature.

An embodiment variation can provide a step of pre-heating the raw material to an initial temperature lower than the reaction temperature by different factors.

5 The reaction temperature is in the order of magnitude from 420 to 950°C, depending on the type of material and anyway preferably about 600°C, whereas when a pre-heating is provided, the pre-heating temperature of the raw material can be in the order
10 of magnitude of about 45°C to 200°C, preferably about 150°C.

Still according to a possible embodiment variation, it is possible to feed an auxiliary gas in the drawing room, in the flow of the mixture of
15 ablation gas.

A possible embodiment variation provides for the raw material being in the form of whole pieces of products or objects, or else being preliminarily treated for example by destructuring processes, such
20 as dismemberment, separation of materials, delamination and/or cuts in smaller parts and/or shredding of the raw material to pre-established granulometry.

It is possible to use different types of lasers,
25 depending on energy requirements to heat the raw material to the activation temperature of the pyrolysis reaction.

Typically the energies needed to activate such a

reaction are in the order of magnitude of some hundreds Watt/cm² at most, on average about 100 W/cm² at most.

To supply these energies to the matter various
5 types of lasers are advantageous, among which the diode laser and in particular the laser of the VCSEL type and solid state laser. The wavelengths of the interesting radiation comprise lasers having wavelength variable between 600 and 1100 nm. Although
10 it is less efficient, another laser very much used in the industry that can be useful is the gas laser, and in particular CO₂ lasers emitting at about 10,000 nm.

An embodiment provides a method for producing gaseous, liquid and solid products obtained from the
15 treatment by pyrolysis of a mass of raw material constituted by tires of vehicles such as for example cars, agricultural vehicles, cargo vehicles or vehicles of different type.

Thanks to the use of the laser for heating to
20 the reaction activation temperature, the pyrolysis has lower emissions because the heat carrier requiring an oven for being heated is eliminated and thus the production of exhaust fumes from the oven is avoided.

25 The energy source is used directly without the aid of intermediate transformations and allows better yield indices. Furthermore, the direct heating allows a more controllable and controlled energy management.

The equipment is less complex as the part relating to the heating of the carriers and the part for the transfer of the carriers from the heating oven into the reactor, as well as the systems needed
5 for cleaning the carriers from the reaction scraps, are missing.

In principle, the laser heating does not require preventive treatment of the raw material, such as for example the latter to be shredded to a pre-
10 established granulometry. By providing a pre-established irradiation footprint and the translation thereof along a surface of the mass of raw material, it is also possible to treat whole parts without their breaking down into smaller parts.

15 The heating of the raw material by a laser also offers greater versatility as it can be used outside the reactor or inside it, but with lower volumetric impact. As it will be more clearly apparent below, an equipment design provides two distinct environments
20 between the gas feeding and the storage one, which environments are communicated with each other by a suction channel.

A further embodiment of the method provides the step of maintaining the temperature of the reaction
25 products constant at the value of the reaction temperature, since the ablation time until the separation step of the reaction products which have different phases.

This further step can be passive, i.e. for containing the dispersion of thermal energy, or else an active step supplying thermal energy to an extent which compensates the losses of thermal energy, or a
5 combination of these steps.

A further characteristic further provides for using the same laser radiation used for the heating or a different laser source but having lower power and higher precision, in order to carry out real time
10 measurements on the reaction products, that is during the reaction itself, and thus to allow having immediate feedback to adjust the irradiation energy.

According to a further aspect, object of the invention is a method for producing Syngas, TAR
15 liquid reaction products and CHAR solid reaction products, the method providing the steps of:

subjecting to heating a mass of raw material constituted by whole tires or parts of tires, or by tire material shredded to a pre-established
20 granulometry,

said heating being carried out by irradiation with laser radiation having pre-established power on a surface of the mass of raw material,

the thermal energy and/or the frequency of the
25 laser radiation being calibrated so that to generate heating to a gasification temperature for the pyrolysis of the raw material;

drawing the gaseous reaction products by suction

directly from the area wherein the reaction has been activated;

maintaining the temperature of the drawn gases until the treatment of separating the reaction products according to the various phases at their storage temperature, and

separating the reaction products according to the various phases by cooling condensation of the gaseous reaction products drawn from the area wherein the reaction has been activated.

The typical compositions of a tire are reported in the following table 1:

Material	Component name	Minimum content %	Maximum content %
Natural rubber	Rubber	14	29
Synthetic polymers	Isoprene; Styrene- Butadiene overall	22	27
Carbon black, soot	Grade N110 Grade N330 Grade N765 overall	21	28
Steel		10	16.5
Fabric		5.5	
Others		3	7.5

Material	Component name	Minimum content %	Maximum content %
Zinc oxide		1	
Sulfur		1	

The products obtained from the pyrolysis reaction are a gaseous part (Syngas), a liquid part (TAR) and a solid part (CHAR).

The following table 2 summarizes the distribution of the reaction products, their compositions and their Lower Heating Value (LHV) as a function of the reaction temperature.

T [°C]	Type	Moisture	Ashes	C [%w]	H [%w]	N [%w]	S [%w]	% w	LHV [MJ/Kg]
500	Syngas						3,3	14,9	25,8
	TAR			82,6	11,9	0,89	0,97	46,3	38,4
	CHAR	0	25,2	74,7	0,31	0,26	2,74	38,8	25,2
600	Syngas						2,19	18,2	24,9
	TAR			81,7	11,4	1,9	1,16	45,2	37,9
	CHAR	0	30,2	72,9	0,19	0,2	2,75	36,6	23,8
700	Syngas						1,62	24,7	36,7
	TAR			85,8	11,4	1,18	1,54	36,2	39,2
	CHAR	0	25,2	73,6	0,2	0,2	2,89	39,1	25,2

Object of the invention is also a piece of equipment for the implementation of the above mentioned pyrolysis method, which equipment comprises:

- a reaction station;
- feeders of a mass of raw material;
- a source transmitting thermal energy to the mass of raw material fed to the reaction station in order to induce a pyrolysis reaction in it;
- a drawing member to draw the reaction products from said reaction station;

a separator of the reaction products having different phases in the conditions, in particular at room temperature;

According to the present invention,

5 the source transmitting thermal energy to the mass of raw material is constituted by at least one laser source in combination with focusing/distributing means to focus/distribute the beam of the laser radiation on an irradiation surface
10 of a pre-established size and smaller than the surface exposed to said radiation of the mass of raw material.

In an embodiment, the laser source and/or the raw material are supported by handling structures
15 which generate a relative movement between the mass of raw material and the incidence area of the laser radiation, causing the movement of said incidence area along a surface exposed to the radiation of said mass of raw material.

20 An embodiment provides that the source(s) of laser radiation are stationary, whereas the mass of raw material is translated by a conveyor with respect to the incidence area of the laser radiation in the reaction station.

25 The incident energy on the mass of raw material in said distribution area of the laser radiation is determined to such an extent to cause an ablation of material through the gasification of the raw

material. The gasified reaction products comprise the products in the gaseous phase and those in the liquid phase and are removed by suction from the reaction station by the drawing member of the reaction products.

The reaction products in the solid phase, the so-called CHAR, are not suctioned but they are extracted from the reaction station by the transport system feeding the mass of raw material in the reaction station.

An embodiment provides that the separation of the reaction products according to their own phases at room temperature and/or storage conditions, i.e. at a temperature lower than the reaction temperature, is carried out by means of a condenser cooling the gas fed by the drawing member at the liquefaction or solidification temperature of the different reaction products, whereby at the storage conditions the products in gaseous, solid and liquid phases are separated and can be stored separately.

According to an improvement of the present equipment, it is possible to provide a system to maintain the temperature stable in combination with the drawing member.

A first variation can only provide passive means to limit the heat dispersion. A second embodiment variation can provide a unit for generating thermal energy compensating the heat losses to maintain the

temperature constant along the path of the reaction products through the drawing member from the reaction station to the separator.

A third embodiment variation can provide a
5 combination of said first and second variations.

According to a further characteristic, it is possible to provide one or more drawing members, one or more of the same being designed so that to draw the reaction products in the gaseous (syngas) and/or
10 solid (char) and/or liquid forms after the condensation step. Their design can take account of draw times, draw temperatures and draw modes.

According to an embodiment, downstream of a suction orifice of the reaction products in gasified
15 form from the reaction station, a feed branch of an auxiliary gas is provided.

Such an auxiliary gas also has the function of enriching the Syngas produced by the reaction in a following step.

20 When an inert fluid is selected as the auxiliary gas or fluid, said fluid also has the function of protecting the lens of the source of laser radiation.

The design of the equipment according to one or more of the characteristics described above, provided
25 in any combination thereof, allows having the following advantages:

- The ablation area is subjected to the depression condition for the suction of the gaseous

reaction products, without necessarily requiring the same extent of vacuum over all the feeding environment;

The area to be treated, that is the incidence
5 area of the laser radiation on which the radiation emitted by the laser is distributed, is not of many cm^2 (if compared to the treatment area of the equipment using heat carriers such as beads or the like, which at present is as big as the whole reactor
10 (15 square meters)), such a reaction area is very small in size. Thus the laser allows a local treatment of a very small area and the created gases are simultaneously transferred to the ablation.

- The heating to the reaction temperature of the
15 raw material is only carried out where needed, i.e. the part of rubber that is about to be treated.

- By carrying out the ablation, the suctioned
gas can easily be maintained at the reaction temperature also during the passage from the reaction
20 station to the separator. Here it is stored and cooled to extract the liquid part (oil) from the gas and possibly the solid part (char) that has come in the suction flow together with the gas.

Thanks to this design the separation area of
25 the products occurs in a different area than the reaction one.

The final products are only obtained by condensation, as all of the material related to the

gaseous phase and the liquid phase is brought to the reaction temperature (at 600 degrees) and then cooled to separate the reaction products in the gaseous phase and those in the liquid phase.

5 In the most widespread design of the state of the art with heat carriers such as beads or the like fed to a reactor together with the reacting raw material, when the beads are hot only gas is created instead, whereas as they pass through the reactor
10 they cool down and the reaction temperature with the rubber is lowered down to reactions at less than 450 degrees. In these thermal conditions, oil is immediately formed but remains mixed with the char, whereby it is necessary to separate CHAR from the
15 oil. This activity is more complex than that of separating the ash from a gas. As it appears from the foregoing, the design according to the invention allows a process up to the separator, wherein the temperature of the drawn reaction products can always
20 be maintained above the critical point of TAR. This critical point is depending on the composition of the raw material and on the specific application of the rubber or bitumen composition, is usually above 250. According to an embodiment variation, industrially,
25 for safety reasons, there is the attempt of maintaining the temperature around 450°C, i.e. at least above 250 degrees C and however the structure of the equipment allows a temperature control much

easier and precise than the methods and equipment according to the state of the art.

According to a further improvement, the equipment according to one or more of the preceding
5 exemplary embodiments or one or more of the preceding variations provides an inlet into the drawing member to feed an auxiliary gas and a feeder of said auxiliary gas connected to said inlet and to a tank or source of auxiliary gas.

10 Still according to an improvement that can be provided in combination with one or more of any of the preceding embodiments and/or embodiment variations, it is possible to provide a controlling system of the type and concentration of the reaction
15 products, which provides detectors of presence of said products and measurement sensors of the concentration of said products.

To carry out said measurements, an embodiment variation provides for using the same heating laser
20 radiation or laser instruments of lower power but higher precision, measurement sensors of the absorption spectrum of said radiation passed through the gas containing the reaction products being provided and of the numeric evaluation of the
25 absorption peaks of determined characteristic frequencies of different reaction products from which concentration values have to be extracted, at least related to one type of reaction product with respect

to other types.

According to a further characteristic, different types of sources are possible as sources of laser radiation, which can also vary depending on the type
5 of raw materials to be treated.

The types of diode lasers and solid state lasers are particularly suitable, also with reference to a specific application wherein the raw material is constituted by tires of vehicles, such as cars,
10 agricultural vehicles, cargo vehicles and others. In particular a laser type can consist of the so-called VCSEL (Vertical Cavity Surface Emitting Laser). A type of laser that is less suitable, but however compatible, consists of gas CO₂ lasers.

15 For what concerns the power of the preferred emitted radiation and radiation frequencies, the characteristics already explained above regarding the method apply.

Further improvements are object of the dependent
20 claims.

The characteristics described above and other characteristics, with the related advantages of the present invention, will be clearer from the following description of some exemplary embodiments depicted in
25 the attached drawings wherein:

Figure 1 shows a schematic view of an exemplary embodiment of a piece of equipment for the treatment of raw material, in particular raw material such as

waste and especially raw material constituted by vehicle tires.

Figure 2 shows a flow diagram of a treatment process of raw material implemented with the equipment of figure 1.

Figure 3 shows a table summarizing the composition of the molecules constituting the Syngas (CH_4 , H_2 , CO , CO_2 , etc.) obtained from the pyrolysis of vehicle tires and having a Lower Heating Value (LHV) and moisture as a function of the reaction temperature.

Figure 4 shows the composition of the Syngas in terms of elements, ashes and moisture as a function of the type of tire used: Car, Truck or OTR.

Figures 5 and 6 show the composition of the reaction products in the liquid phase (TAR) and in the solid phase (CHAR).

With reference to figure 1, the latter shows a schematic example based on which the possible variations will be depicted and will be clear to the technician of the art, if referred as differences or variations of the example depicted.

The depicted example is referring to a specific application wherein the raw material to be subjected to the pyrolysis reaction is constituted by vehicle tires or similar materials.

The raw material to be subjected to the pyrolysis reaction is denoted with 1 and is

transported by a conveyor 2 to a reaction station 3, wherein an area at high temperature is generated by the irradiation of the raw material with the laser radiation 104 generated by a laser source 4 or a combination of more than one laser source 4.

The radiation 104 is distributed on the raw material 1 so as to generate an incidence area of said radiation 104, also called footprint, wherein the radiation 104 is distributed so as to heat the raw material coincident with said footprint 204 to the expected reaction temperature. At this reaction temperature the pyrolysis reaction is activated and part of the material the raw material is constituted by, is gasified as depicted by 5.

In some configurations and for some laser types, a lens 304 or a device forming the radiation beam 104 can be provided and is depicted by 304.

The reaction products in the gaseous form 5 are separated from other materials remaining on the conveyor 2 which are brought, as the raw material is moved forward in the reaction station, to an unloading station and drawn for a further treatment, not specified because it is not an object of the present invention.

The gasified reaction products 5 are drawn in different ways. A preferred embodiment provides for the gas being suctioned thanks to a drawing tube 6, whose open end is provided as coincident with the

reaction station and wherein depressurization is generated with respect to the external environment and/or the reaction station.

Thus the reaction products under the gaseous form are transferred from the feeding duct to a separation chamber 7, wherein the reaction products having different phases such as the gaseous phase, so-called Syngas, the liquid phase so-called TAR essentially constituted by oils and the solid phase so-called CHAR, are separated one from another.

The separation among products having different phases is carried out thanks to a condensation process obtained by cooling the reaction products still at the reaction temperature to a lower temperature, in particular to room temperature or a typical storage or usage temperature of these products.

Thus the phase separation allows the separated collection and separated storage of each reaction product having gaseous, liquid and solid phases, as depicted by the tanks or warehouses 8, 9, and 10.

In order to avoid the cooling of the gas produced in the reaction station and thus a separation of the various phases already along the path of the drawing tube 6 and feeding ducts towards the separation chamber 7, along said path passive and/or active devices could be provided for preserving the temperature of the gas produced in the

reaction station.

Such passive devices can be constituted by a thermal insulation of the drawing tube 6 and feeding ducts 107 to the separation chamber 7. The active
5 devices can be sources feeding thermal energy and configured so as to bring a contribution of thermal energy substantially corresponding to the dissipated heat and thus to compensate the heat losses of the gas passing through the drawing tube 6 towards the
10 separation chamber 7.

Obviously the two types of devices can be present in combination. The specific selection of insulations and/or sources of thermal energy to maintain the gas temperature can fall on any known
15 type and depends on the specific structure of the equipment, the heat losses to be compensated and other considerations of opportunities dictated by the conditions of the specific application. Such alternatives are part of the base knowledge of the
20 technician of the art and their selection falls within the normal activities of equipment design.

According to a further characteristic, a feed branch 206 of an auxiliary gas opens into the drawing tube 6 from a tank 306 of said gas. This gas can
25 alternatively or in combination have different functions.

A first function is to enrich the Syngas so as to optimize the composition for its subsequent

exploitation.

A second function is to protect the lenses 304 of the laser sources 4. In this case the auxiliary gas is constituted by, or comprises, an inert
5 component.

A possible embodiment variation provides for insulating the reaction station from the environment, so that the reaction occurs in the absence of oxygen.

Also in this case, the technician of the art is
10 able to configure a chamber enclosing the reaction station and allowing the raw material to be fed and the residual material of the pyrolysis reaction to be unloaded, so as to avoid ambient air and thus oxygen to pass in said chamber, since in the state of the
15 art there are a number of solutions among which the technician of the art can choose depending on the raw material which is treated and other specificities of the different cases of use.

The depicted example shows a design wherein the
20 drawing tube 6 opens into the reaction station and the laser radiation 104 is transmitted through said drawing tube 6 substantially coaxially or parallel to the axis of the same.

Such a solution allows also the radiation to be
25 used as a source to maintain stable the temperature of the gas containing the reaction products during the path in the drawing tube 6.

Different alternatives are possible, one of

which provides the laser source 4, both in the form of unique source and in the form of a combination of laser sources such as an array of laser diodes, being provided outside the drawing tube 6 and the radiation
5 being transmitted to the footprint 204 on the raw material 1 passing through the reaction station from the outside of said tube.

In this case the optical axis of the radiation can be parallel to the axis of the drawing tube 6 or
10 else it can be inclined with respect to the axis of the tube.

When a delimitation of the reaction station is provided in a reaction chamber, the source 4 or the combination of sources 4 can be provided outside or
15 inside said reaction chamber.

Still according to an embodiment variation, instead of providing a conveyor 2 of the raw material to be pyrolyzed and instead of keeping stationary the footprint 204 generated by the laser radiation 104,
20 it is possible to provide for moving said footprint 204 only, for example by translating the laser sources so as to move the footprint 204 on the surface of the mass of raw material 1, or else it is also possible to provide a combination of reciprocal
25 movements of the raw material 1 and the footprint 2. Such a solution could for example provide a translation of the raw material 1 through the reaction station along a first direction, as depicted

by the arrow D in figure 1, whereas the footprint is moved along the surface of the mass of raw material 1 in a direction perpendicular to the feed direction of the material 1 depicted by the arrow D. In this case, 5 it could be a flow of raw material having width size, that is perpendicular to the feed direction, greater than the extent of the footprint 204 along said direction perpendicular to the feed direction of the mass of raw material 1.

10 The raw material 1 can be subjected to preventive mechanical machining reducing its dimensions and shape, such as for example the segmentation into parts and/or the separation of parts constituted by different materials, or else the 15 shredding to pre-established granulometry.

Depending on the physical conditions of the raw material, it is possible to use different types of conveyors, such as linear belts, rotary augers, or the like. Such conveyors are known in the state of 20 the art and the specific choice is a choice which is part of the design activities of the technician of the art and is based on the contingent conditions of the raw material.

For what concerns the drawing tube, this can be 25 made as in figure 1, or else it can be in the form of helical tube wrapping itself around the beam of laser radiation 104. In this case more than one coaxial helical tube can also be provided. Also in this case,

despite the laser radiation 104 is outside the drawing tube, it can interfere with the same at least in the peripheral area of the beam and can transfer thermal energy to the drawing tube to an extent
5 sufficient to compensate for the heat losses and thus the temperature losses of the drawn gas.

In combination with an embodiment wherein the footprint 204 of the laser radiation on the surface of the material 1 is translated along said surface,
10 it is also possible to provide for the moving of the drawing tube 6 along a path corresponding to that of said footprint 204.

For what concerns the type of lasers used, these can be selected depending on the raw material to be
15 treated and the desired reaction temperatures in combination with the qualitative composition of the raw material.

When, as in the present application, you want to treat a raw material constituted by vehicle tires, it
20 is substantially possible to provide three types of laser sources, which choice derives from the specific characteristics of this type of raw material.

A first relevant characteristic for the choice of the laser sources concerns the wavelength of the
25 radiation, which is related to the generated thermal energy and the absorption effect of such energy by the raw material and thus the efficiency of the heating action of the raw material at the desired

reaction temperature.

A first aspect of the specific raw material is that the material of which the vehicle tires are made of can be equated, to a first approximation, with a
5 black body for what concerns the absorption and dissipation behaviors. In fact this material absorbs well the radiation of any wavelength and the heat dissipation by irradiation is low.

By analyzing the absorption spectra of the main
10 components of a tire, it is possible to verify that the interest frequency range is from 400 nm (blue) to 2300 nm (medium infrared).

Based on these considerations, an embodiment provides for the possible wavelength being in the
15 range between 600 nm and 1100 nm.

Among the existing laser sources, there are diode lasers and solid state lasers.

Such sources, if taken with power of at least 1 KW, are able to generate the power needed to heat the
20 raw material to the expected reaction temperatures. This power is then translated on the material with a minimum of 100 W/cm².

A further embodiment is that with a wavelength around 10000 nm, covered by CO₂ gas laser that can
25 even deposit this power with sources lower than one KW/cm².

An embodiment provides the use of a laser source or combinations of laser sources of the diode type

and in particular of the type called VCSEL (Vertical Cavity Surface Emitting Laser).

With these sources it is possible to generate laser arrays that emit power even beyond 10 kW. The
5 lasers of this type have small dimensions in the order of mm, at most some centimeter and thus the laser array doesn't get to very big dimensions negatively affecting the design of the equipment.

Despite this type of sources has a non-optimal
10 laser beam, often a divergent one, they are extremely easy to be integrated in horizontal or vertical or customized arrays. That is so as to generate arrays having shapes ad lib, and which can be air or water cooled, or cooled by Peltier cooler systems.

15 A further type of lasers is that of the solid state lasers that however have a relatively high cost with respect to diode lasers.

Figure 2 shows an example of the main steps of the treatment method of a generic raw material to be
20 subjected to pyrolysis reaction in order to generate reaction products.

At step 200 I generates a beam of laser radiation having pre-established energy density and pre-established wavelength, for example according to
25 one or more of the variations described above and which laser beam is adapted to generate an incidence area of the radiation on a mass of raw material, in which air the energy of the radiation is

substantially distributed homogeneously.

Being laser beams, said area forms a footprint substantially corresponding to the cross-section of the beam, i.e. the projection of the beam on a plane
5 perpendicular to the optical axis propagating the radiation.

In this case the term substantially is referred to an approximation, as the beam of the radiation of a laser source or an array of laser sources is not
10 always perfectly parallel but can have a certain opening, even if minimal, but whose effect depends on the distance of the surface against which the beam is projected by the source or array of sources.

The beam is transmitted to the step 201 into a
15 reaction chamber wherein, at step 202, the mass of raw material is fed. The feed takes place along a relative movement path between the mass of raw material and the footprint of the radiation projected on the surface of the mass of raw material. This path
20 is selected and defined so as to allow the entire exposed surface of the mass of raw material to be subjected to the action of the laser radiation and thus the pyrolytic reaction to be triggered.

The described relative movement can occur
25 according to one or more of the variations described above with reference to figure 1.

Possibly, as depicted by 211, before feeding the raw material to the reaction chamber, the raw

material is mechanically treated, for example reduced to pieces of pre-established size or else, depending on the composition and structure, dismembered in different parts, some of which are not suitable to the pyrolysis treatment or are treated differently according to their chemical composition.

At step 203, the path and speed of the relative movement between the footprint, i.e. irradiation area and mass of raw material, are set so that all of the mass of raw material is progressively led to the reaction temperature and for the time needed to the completion of said reaction in the area hit by the laser radiation.

Step 204 provides the suction of the reaction products. Such a suction takes place according to one or more of the previously described modes and collects all the reaction products in gaseous form, whereas the reaction residues remain on the conveyor.

Step 204 can be combined with step 214, which is optional, wherein to the reaction products in gaseous form an auxiliary gas or fluid are added that can be of the type according to one or more of the previously described variations.

At step 205 the reaction products are fed to a separation chamber of said products according to the various phases they take in a pre-established environmental condition, such as for example the storage condition or the usage condition or else the

external environment condition.

At step 206 in the chamber said separation of the products in the single gaseous, liquid and solid phases takes place. Such separation takes place by
5 cooling the reaction gas and by mechanically drawing the reaction products in the gaseous, liquid and solid phases and by storing them in dedicated warehouses, as depicted at step 207 and 208.

Similarly to step 209, the reaction residues
10 remained on the conveyor are also themselves separately drawn and stored or sent to further treatment processes.

As already described before, the invention is also referring to a particular application for which
15 the method and the described equipment are particularly suitable. This specific application concerns the treatment of waste materials and in particular vehicle tires of any type.

As already previously described, the tires have
20 a complex structure containing materials adapted to take part to the pyrolytic reaction and others that remain excluded. The composition of the tire depends, to a first approximation, on the use, i.e. on the type of vehicle to which is intended to and, as
25 depicted in table 1, the main organic materials in the tires are constituted by natural rubber, i.e. caoutchouc and synthetic polymers. Furthermore, another component being in considerable amount is the

carbon black or soot. These three components form more than about half of the percentage of the raw material contained in the tires. The other components and their percent amounts are depicted in table 1.

5 Table 2 shows the composition of the generated reaction products and related to each of the three phases (liquid, solid and gaseous) depending on three different reaction temperatures.

With reference to the above mentioned
10 application, the method and the equipment are designed so as to generate reaction temperatures, in the mass of raw material constituted by tires, in the order of 500°C to 700°C and preferably in the order of not less than 600°C.

15 According to an advantageous characteristic, as the characteristics of the raw material are substantially corresponding to those of a black body, as already previously set forth, the choice of the electromagnetic radiation and thus of the sources and
20 power thereof is substantially limited to laser sources able to generate at least 100 W/cm² on the material to be pyrolyzed and with any wavelength.

A preferred frequency range essentially referring to the absorption spectrum of the main
25 components of the tire as set forth above, provides for the wavelength of the electromagnetic radiation being in the range between 400 nm and 2300 nm, preferably between 600 and 1100 nm.

The measurements of the compositions of the reaction products for different conditions are depicted in the tables of figures 3 to 6.

Figure 3 shows the composition of the Syngas, i.e. the gaseous component of the reaction products which is obtained at the different reaction temperatures.

The Lower Heating Value of the Syngas and the moisture in the Syngas at the different reaction temperatures are also depicted.

The table of figure 4 shows the composition of the Syngas obtained as a function of the type of tire treated.

The tables of figures 5 and 6 show the compositions of the liquid phase of the reaction products, which are substantially oils, and of the solid phase, which are substantially called TAR and CHAR.

From the tables depicted the effectiveness of the method according to the present invention and of the particular application to generate reaction products from the waste raw material having high energy value is evident.

Fig.1

Tubo di uscita Syngas + gas ausiliario = Syngas
+ auxiliary gas output tube

Lente = Lens

5 Tubo di ingresso gas ausiliario = auxiliary gas
input tube

Orma = Footprint

Pezzo di pneumatico = Piece of tire

Mezzo di trasporto del pneumatico = Tire
10 conveying means

Zona ad alta temperature = High temperature area

Tubo = Tube

Fig. 2

200 - Generating a beam of laser radiation
15 having a pre-established energy distribution on a
pre-established incidence area

201 - Transmitting said beam into a reaction
chamber

211 - In case, mechanically treating the raw
20 material

202 - Feeding the raw material to a reaction
chamber along a path crossing the beam of laser
radiation

203 - Setting the relative speed of movement
25 between mass of raw material and beam of laser
radiation so that all of the mass of raw material is
progressively heated to the pre-established reaction
temperature

204 - Suctioning the generated reaction products being in gaseous form

214 - In case, mixing an auxiliary gas

205 - Feeding the reaction products in a gaseous form to a phase separation chamber

206 - Separating the phases of the reaction products by cooling condensation of the gas

207 - Separating the phases of the reaction products by cooling condensation of the gas

208 - Storing the reaction products, having different gaseous, liquid and solid phases, separately from one another

209 - Unloading the reaction residues constituted by the mass of treated raw material from the reaction chamber.

Fig. 3

composition of the molecules constituting the Syngas (CH_4 , H_2 , CO , CO_2 , etc.) and having Lower Heating Value (LHV) and moisture as a function of the reaction temperature.

Fig. 4

composition of the Syngas in terms of elements, ashes and moisture as a function of the type of tire used: Car, Truck or OTR.

Fig. 5

Liquid Oil

Fig. 6

Solid

CLAIMS

1. Method for the pyrolysis of raw materials, in particular raw materials deriving from tires or bitumen, the method providing the steps of

5 - Feeding to a reactor the material to be subjected to the pyrolysis process;

 - heating said material in said reactor at the temperatures needed for establishing the pyrolysis process;

10 - collecting the final products of the pyrolysis reaction;

 - separating one from another the gaseous, liquid and solid phases of the reaction products and storing, for further treatment, said reaction products separated one from another,

 and wherein

 - the heating of the pyrolysis process to the activation temperature is obtained by irradiation of the raw material with laser radiation,

20 - said laser radiation being concentrated or focused on a localized area of a pre-established surface area on the surface of the mass of raw material of the focusing area, being progressively moved along the entire surface of the mass of raw material by activating the pyrolytic reaction on all

25 of said mass of raw material.

2. Method according to claim 1, wherein the reaction temperature is such to transform the mass of

raw material into a mixture of ablation gas containing the reaction products intended to assume a gas and/or liquid phase condition and these are drawn by suctioning them from the reaction station in a drawing room open towards the reaction station and set at a pressure lower than that of the reaction station.

3. Method according to claim 1 or 2, wherein the separation of the reaction products having the different gaseous, liquid and solid phases takes place by condensation of the mixture of ablation gas by means of a cooling step of said gas mixture at a pre-established temperature.

4. Method according to one or more of the preceding claims wherein the reaction temperature is in the order of magnitude from 420°C to 950°C, preferably about 600°C and optionally provides a pre-heating step of the raw material wherein the pre-heating temperature is in the order of magnitude from about 45°C to about 200°C, in particular 150°C.

5. Method according to one or more of the preceding claims wherein an auxiliary gas is fed into the drawing room, in the flow of the reaction gas mixture.

6. Method according to one or more of the preceding claims wherein the radiation is a laser radiation having power in the order of magnitude of at least hundreds of Watt/cm², on average in the

order of some kW/cm² and capable of transferring on the piece to be pyrolyzed at least 100 W/cm², optionally having wavelengths of the laser radiation that can range, in the diode and solid state lasers, from 600 to 1100 nm, or a frequency around 10000 nm, i.e. the CO₂ gas lasers.

7. Method according to one or more of the preceding claims wherein the mass of raw material to be treated by pyrolysis process is constituted by tires of vehicles such as for example cars, agricultural vehicles, cargo vehicles or vehicles of different type and/or bitumen and materials containing bitumen and waste or scraps, in particular of industrial type whose composition allows a pyrolysis reaction to be activated by using laser radiation according to one or more of the preceding claims.

8. Method according to one or more of the preceding claims wherein the step of maintaining the temperature of the reaction products constant at the value of the reaction temperature, since the ablation time until the separation step of the reaction products having different phases, is further provided.

9. Method according to one or more of the preceding claims wherein a further step of taking real time measurements on the reaction products, that is during the reaction itself, and generating

immediate feedback adjusting the irradiation energy, by using the laser radiation itself or a laser radiation of another source to determine the concentration of the reaction products in the gas generated by the pyrolytic reaction, are further provided.

10. Method for producing Syngas, TAR liquid reaction products and CHAR solid reaction products, the method providing the steps according to one or more of the preceding claims 1 to 9.

11. Equipment for the implementation of the method according to one or more of the preceding claims 1 to 10, which equipment comprises:

- a reaction station;
- 15 feeders of a mass of raw material;
- a source transmitting thermal energy to the mass of raw material fed to the reaction station in order to induce a pyrolysis reaction in it;
- a drawing member to draw the reaction products from said reaction station;
- 20 a separator of the reaction products having different phases in the conditions, in particular at room temperature;
- characterized in that,
- 25 the reaction station is provided in between the feeding area of raw material and the separation chamber of the reaction products and is functionally separated from said feeding area and said separation

chamber,

and the source transmitting thermal energy to the mass of raw material is constituted by at least one laser source optionally in combination with
5 focusing/distributing means to focus/distribute the beam of the laser radiation for generating a distribution of the electromagnetic energy on an irradiation surface of a pre-established size and smaller than the surface exposed to said radiation of
10 the mass of raw material.

12. Equipment according to claim 11, wherein the laser source and/or the raw material are supported by handling structures which generate a relative movement between the mass of raw material and the
15 incidence area of the laser radiation, causing the movement of said incidence area along a surface exposed to the radiation of said mass of raw material.

13. Equipment according to claim 11 or 12,
20 wherein the separation of the reaction products according to their own phases at room and/or storage temperature conditions, i.e. at a temperature lower than the reaction temperature, is carried out by means of a condenser cooling the gas fed by the
25 drawing member at the liquefaction or solidification temperature of the different reaction products, whereby at the storage conditions the products in gaseous, solid and liquid phases are separated and

they can be stored separately.

14. Equipment according to one or more of preceding claims 11 to 13 wherein at the drawing member, downstream of a suction orifice of the
5 reaction products in a gasified form from the reaction station, a feed branch of an auxiliary gas is provided.

15. Equipment according to one or more of preceding claims 11 to 14, wherein a controlling
10 system of the type and concentration of the reaction products, which provides detectors of presence of said products and measurement sensors of the concentration of said products, is provided.

16. Equipment according to one or more of
15 preceding claims 11 to 15, comprising a laser source or an array of laser sources, which are preferably selected from one of the following alternatives: diode laser, solid state laser and CO₂ laser.

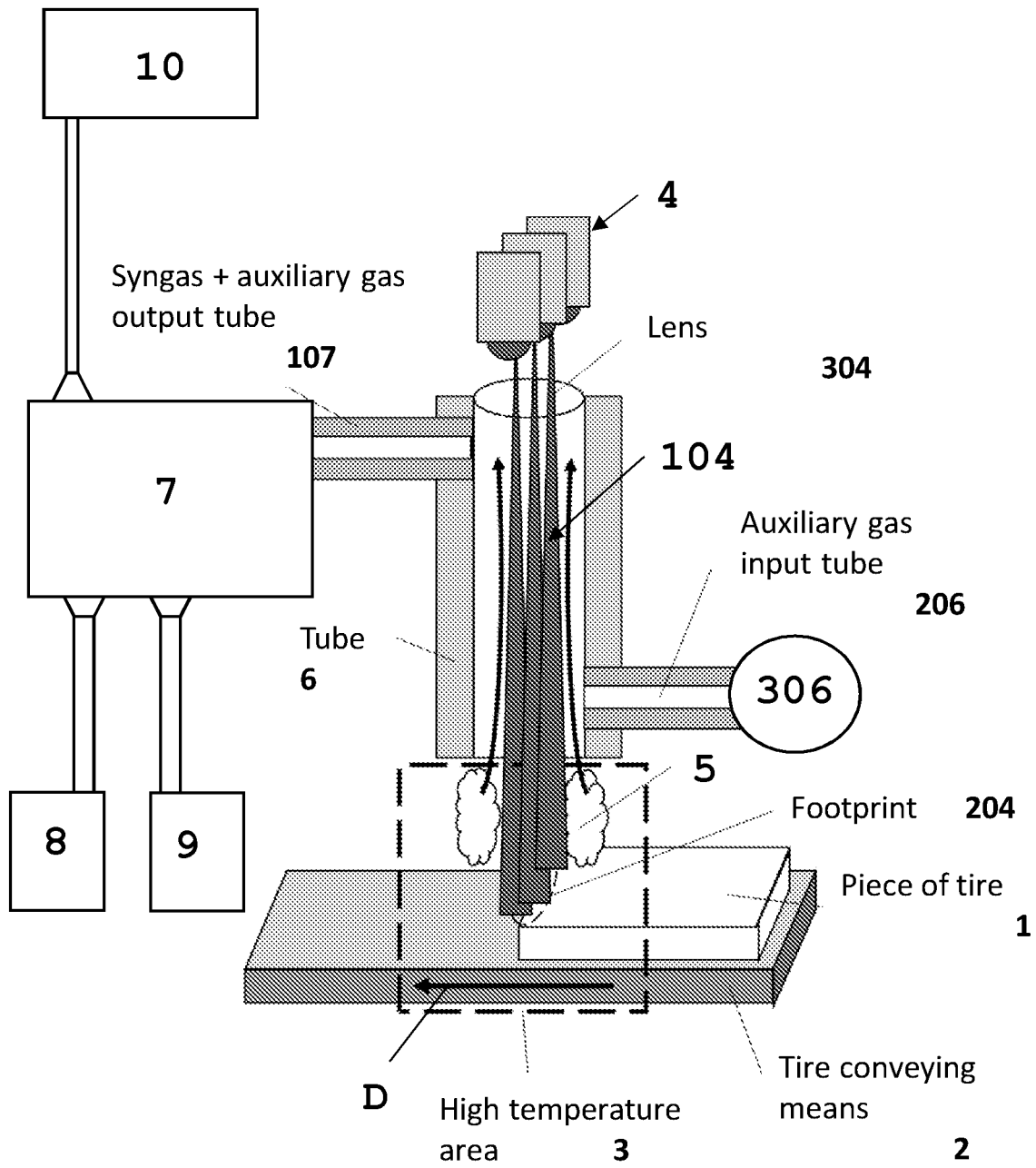


Fig. 1

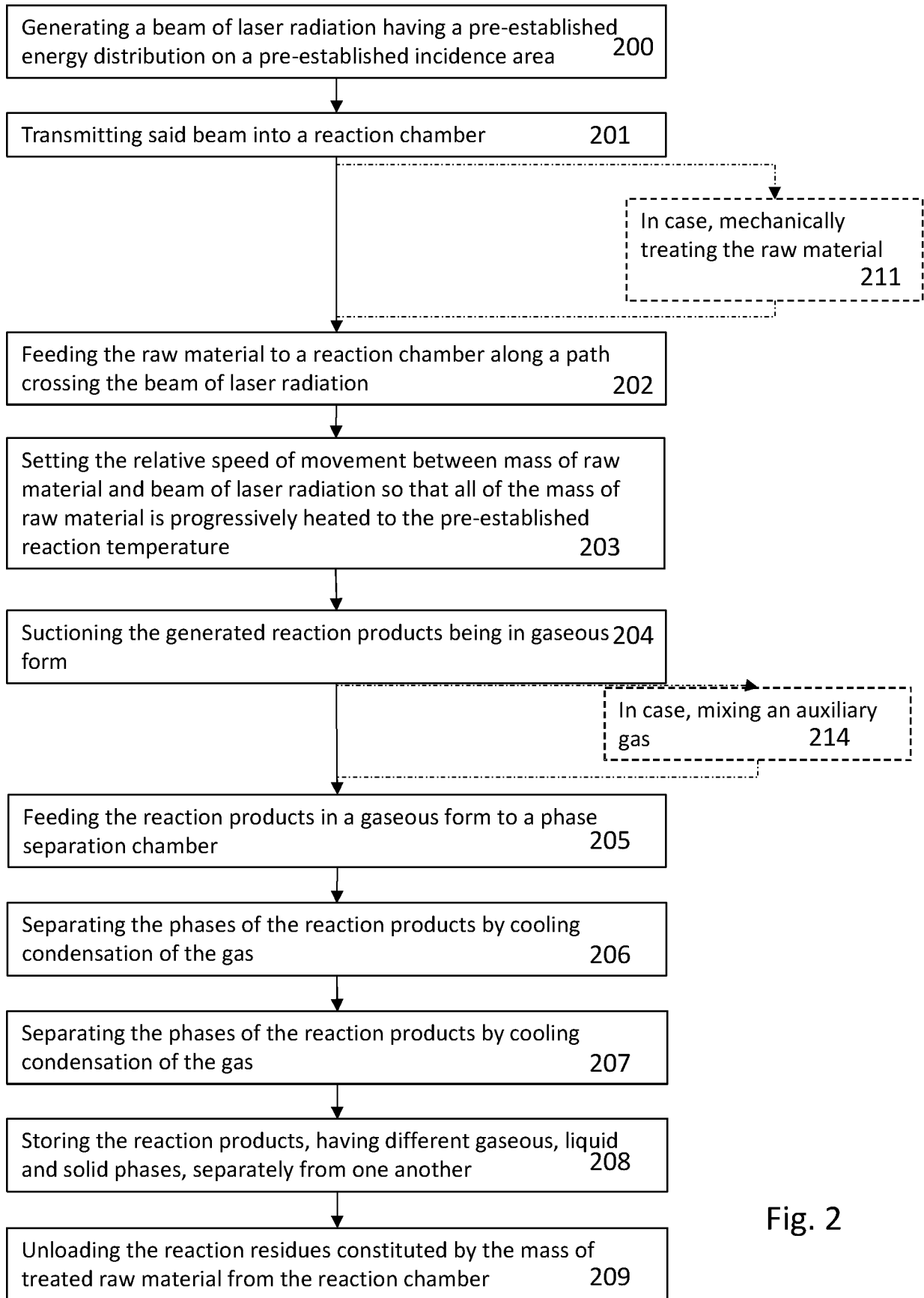


Fig. 2

T [°C]	CH ₄ [%v]	H ₂ [%v]	CO [%v]	CO ₂ [%v]	C ₂ H ₆ [%v]	C ₃ H ₈ [%v]	C ₄ H ₁₀ [%w]	S [%w]	LHV [MJ/Kg]	% w
500	39,1	23,7	21,6	12	1,7	1,5	0,5	3,36	25,80	14,9
600	31	27,1	30,9	7,9	2,4	0,6	0,2	2,20	24,90	18,2
700	28,8	52,5	16,5	1,8	0	0,3	0,1	1,62	36,70	24,7

composition of the molecules constituting the Syngas (CH₄, H₂, CO, CO₂, etc.) and having Lower Heating Value (LHV) and moisture as a function of the reaction temperature.

Fig. 3

Sample Name					
Parameter	Unit	Car	Truck	OTR	Typical(*)
LHV	[MJ/kg_dry basis]	33.8	36.7	34.18	33 - 35
C	%_dry basis	81.78	83.4	79.7	81.83
H	%_dry basis	7.2	7.8	7.2	7.1
N	%_dry basis	0.52	0.5	0.92	0.38
S	%_dry basis	1.94	1.99	1.82	1.53
Cl	%_dry basis	0.07	0.05	<0.03	<0.1
Ash	%_dry basis	10.11	5.1	9.3	7.1
Moisture	%_total	0.06	0.3	0.7	< 1.0

composition of the Syngas in terms of elements, ashes and moisture as a function of the type of tire used: Car, Truck or OTR.

Fig. 4

Parameter	UdM	min	max
Flash Point	°C	60	93
Pour Point ⁽¹⁾	°C	-	10
LHV	KJ/Kg	37000	39000
Water	% W	-	-
C	% W	81,8	85,8
H	% W	11,36	11,58
N	% W	1	1,7
S	% W	1,2	1,5

Liquid Oil (TAR)

Fig. 5

PARAMETER	UdM	MIN	MAX
LHV	kJ/kg	22000	25000
Moisture	% w	0	0
C	% w	65,49	74,76
H	% w	0,18	0,57
N	% w	0,2	0,37
S	% w	2,28	2,89
ASHES	% w	25,19	31,75
Ashes analysis:			
Al	mg/kg	4968	23323
B	mg/kg	12	63
Ba	mg/kg	42	413
Ca	mg/kg	23376	198659
Cd	mg/kg	9	35
Cl	mg/kg		
Co	mg/kg	0	416
Cr	mg/kg	29	50
Cu	mg/kg	83	257
Fe	mg/kg	2703	5861
Hg	mg/kg		
K	mg/kg	3859	5873
Li	mg/kg	0	0
Mg	mg/kg	1924	16133
Mn	mg/kg	41	108
Mo	mg/kg	3	8
Na	mg/kg	1987	6741
Ni	mg/kg	0	8
P	mg/kg	518	1390
Pb	mg/kg	124	864
Si	mg/kg	1474	7754
Ti	mg/kg	144	457
V	mg/kg	11	35
Zn	mg/kg	78756	156028
IT (Initial Deform. Temp.)	°C		1005

Solid (CHAR)

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/051182

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10B53/06 C10B19/00 C10B53/07
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10B C10L

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
6 May 2019	15/05/2019

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bertin, Séverine
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