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(54) Title: PYROLYSIS METHOD AND REACTOR FOR RECOVERING SILICA FROM POLYMER WASTE MATERIAL

(57) Abstract: The invention relates to a pyrolysis method and a pyrolysis reactor for recovering silica from a polymer waste material containing silica, particularly a rubber or plastics waste material containing silica, using thermal decomposition for separating silica from at least one non-silica component of the polymer waste material. The waste material is delivered to a pyrolytic chamber (1), and heated to a decomposition temperature of at least one non-silica component of the waste material by microwave radiation. The decomposition temperature is selected such that the at least one non-silica component comprises a higher microwave absorptivity than silica.

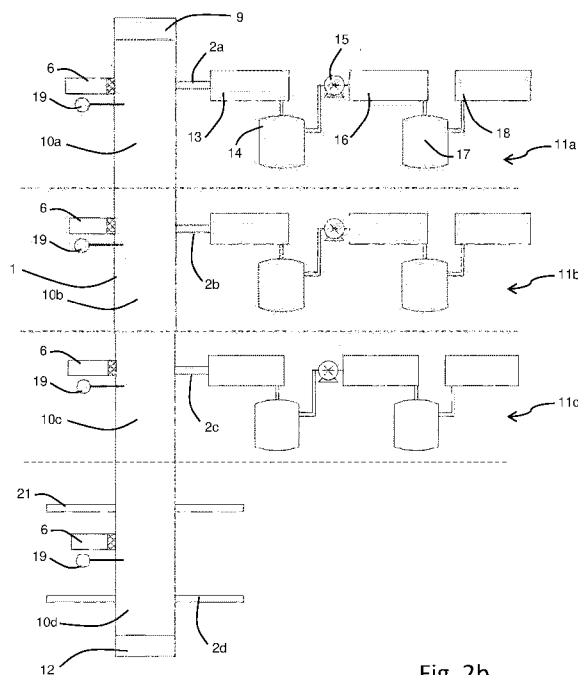


Fig. 2b

Pyrolysis method and reactor for recovering silica from polymer waste material

The invention relates to a pyrolysis method and a pyrolysis reactor for recovering silica from polymer waste materials containing silica. Particularly, the invention relates to the recovery of silica from silica containing rubber or rubber compositions or silica reinforced composite materials, especially from vehicle tires made of rubber compounds containing silica.

Recycling of polymeric waste material, particularly rubber and plastics waste material, poses an environmental challenge, due to an increasing volume of scrap from such materials being produced annually. Polymeric waste materials disposed in landfill remain in the environment for hundreds of years and contribute to the environmental pollution. Waste incineration may release toxic emissions, which require additional treatment. Therefore, waste management for polymeric waste materials is difficult and expensive.

For example, car tires are composite products of up to 14 different rubber compounds, textiles and steel, which are built to last but very difficult to recycle due to their complex construction. The most common rubbers used in the manufacture of tires are natural rubber (NR), cis-polybutadiene rubber (CBR), isobutylene-isoprene copolymer rubber (i.e., butyl rubber (BR)) and styrene-butadiene copolymer rubber (SBR). These synthetic rubber compounds comprised of cross-linked long-chain polymers with sulphur atoms, which make the elastomers chemically, stable and, therefore, limit their degradability. Furthermore, the low density and elasticity of the rubber make it difficult to

recycle and subsequently dispose of the material, as it cannot be compacted. In addition to the natural and synthetic rubber, the rubber fraction of tires usually contains carbon black, plasticizers, lubricants, antioxidants and inorganic materials such as calcium carbonate and silica, which add greater complexity to the sustainable waste management of the used tires. Furthermore, there are vast composition differences between different types of tires, for example between car tires (80% synthetic rubber, 20% natural rubber, mostly Silica filler in tread compound) and truck tires (80% natural rubber, 20% synthetic rubber, mostly carbon black in tread compound). Within one category of tires, there are additional differences from one manufacturer to the other.

For example rubber waste transformation is notoriously difficult to achieve in a way that: (1) improves the efficiency and sustainability of solid waste management operations and systems, (2) recovers reusable and recyclable materials, and (3) recovers conversion products and energy in the form of combustible biogas. When recycling waste rubber products the use of valuable raw materials should be maximized while at the same time consider environmental sustainability. Recycling of secondary raw materials is an important resource saving mechanism in the light of decreasing natural resources. In general polymeric waste materials form a significant source of raw materials for new production.

However, existing recycling solutions prove to be either ineffective, energy intensive or require a significant investment in resource and infrastructure. For rubber for example a grinding process is often used to create crumb rubber. Despite its apparent simplicity, it is a very difficult process, not only to determine the nature, magnitude

and direction of loads, but also to define and quantify the results of destruction. Multiple different types of elastic material, increases in temperature as well as occurring shear resistance can result in increased power consumption and intensive wear and tear. This in turn results in a low yield of marketable recycled material.

Cryogenic techniques may reduce energy consumption for grinding and separate reinforcing elements of products for the mechanical processing of rubber products and polymeric waste products in general. The main disadvantages of cryogenic processing methods are: High energy costs associated with the need to obtain a sufficient amount of a cryogenic liquid gas, and achieve and maintain a low temperature in a processing chamber. The large product sizes and low thermal conductivity of polymeric waste products lead to considerable process time. The cooling process as a whole and super cooling of the outer layers of material causes even greater increase in the total energy consumption while reducing the performance of the equipment. Therefore, in an overall life cycle assessment of the polymeric materials used in products and recycled at their end-of-life the requirement of sustainability mostly cannot be met by cryogenic recycling techniques.

Another known recycling method is vulcanization, which is a chemical process for converting for example rubber or related polymers into more durable materials by the addition of sulphur or other equivalent curatives or accelerators. At the same time devulcanization is the process by which the polymer attributes of vulcanization are reversed. The process of regeneration is associated with a significant amount of harmful emissions. Reclaimed polymer compounds consist of a gel fraction, which preserves the sparse network structure of

the vulcanization, and a sol fraction containing relatively short segments of branched chains. Since the network structure is maintained in regenerate vulcanization, the introduction of reclaimed polymers in a mixture to produce new polymer materials affects the strength properties of new materials. This results in a downcycling of the original material. In this regard, the regenerate is almost never used in the same industry, which works against a circular economy.

Common methods to recycle for example vehicle tires include crumbing the rubber, burning the tires in furnaces as tire derived fuel (TDF), or pyrolysis to decompose the tire into pyrolysis oil, carbon black and the steel used in the construction of the tire. Large industrial tires, such as those used by earth moving equipment, are difficult to recycle and are normally cut up into manageable sections before recycling by one of the aforementioned processes. There is significant wear on the equipment used to cut these tires.

Existing Pyrolysis methods use a maximum heat to decompose of rubber between 310-540°C which produces recovered Carbon Black (rCB) with a Carbonaceous Residue, called Char, of 7%-20%, as an unwanted by-product of the rubber pyrolysis. Recovered Carbon Black can for example be used as a substitute filler for Virgin Carbon Black (vCB) in the tire manufacturing process. However, tire recycling companies are struggling to produce recovered carbon black that is good enough to be re-used in tire manufacturing. Unfortunately, the rCB's performance in application is compromised due to the presence of Char. Furthermore, volatiles produced in current pyrolysis methods are combined in a single condensate resulting in a less valuable feedstock.

Finally, a reverse depolymerisation process is described for example in US 9649613 B2, wherein tires are loaded in succession into a microwave tunnel system with a conveyor. The tunnel system is provided with multiple small magnetrons, e.g. 35 rows of 3 magnetrons, each with 1.2kW. The process is operated under slight positive pressure to encourage the movement of pyrolysis gases. It is believed that microwave energy results in the severing of weaker molecular bonds in longer chain molecules to reduce those molecules to simpler forms, which causes the depolymerisation process. Again, in the overall life cycle assessment of a recycling material mostly such a depolymerisation process is energetically not sustainable.

For example, almost 1,5 billion metric tons of end-of-life tires are discarded globally each year; global sustainability objectives are pushing tire manufacturing companies to create circular economies.

It is an object of the present invention to provide a pyrolysis method and a pyrolysis reactor for thermal decomposition of polymer waste materials, particularly rubber and plastics waste materials, which allows for sustainable polymer waste management and efficient recovery of reusable and recyclable materials, and which improves the environmental impact over the life cycle of a polymer material product.

Particularly, it is an object of the present invention to provide a pyrolysis method and a pyrolysis reactor for efficiently recovering a rubber or plastics waste material containing silica as used in vehicle tires, that supports a circular economy model for tire manufacturing and supports the

use of recovered tire material, e. g. an alternative filler to recovered carbon black (rCB).

These and other objects, which will appear from the description below, are achieved by a pyrolysis method and a pyrolysis reactor as set forth in the appended independent claims. Preferred method details and embodiments are defined in the dependent claims.

The present invention provides a pyrolysis method and a pyrolysis reactor for recovering silica from a polymer waste material containing silica, particularly from a rubber or plastics waste material containing silica, using thermal decomposition for separating silica from at least one non-silica component of the polymer waste material. The waste material is delivered to a pyrolytic chamber, and is heated to a decomposition temperature of at least one non-silica component of the waste material by microwave radiation, wherein an exothermic depolymerisation reaction of the waste material occurs. The decomposition temperature is selected such that the at least one non-silica component comprises a higher microwave absorptivity at the selected temperature than silica. The heating with microwaves to remove non-silica components such as carbon material, rubber and volatiles leave the silica's structural and chemical integrity intact, as silica does not absorb the microwaves.

Thus, silica can be recovered from silica containing rubber composites or silica reinforced polymer composites by removing the carbon material, rubber, polymer and volatiles, and valuable volatile components can be extracted and collected.

For example, the decomposition temperature is selected from a range between 300°C and 900°C, wherein carbonaceous components of the polymer waste material have a high microwave absorptivity and silica has a low microwave absorptivity. Thus, carbonaceous components can be recovered from the waste material due to decomposition and the silica is separated from the carbonaceous components for further use.

In an advantageous variant of the inventive pyrolysis method an oxygenated environment and/or an inert environment and/or a negative pressure environment is applied in the pyrolytic chamber. Preferably, an inert environment and a negative pressure is applied in the pyrolytic chamber before the oxygenated environment is applied in the pyrolytic chamber.

Recovering silica from remaining solid residue by heating with microwaves and selecting the decomposition temperature as explained above, such an environment supports oxidizing and removing the carbonaceous material from the waste material to yield a silica-containing product.

An inert environment in the pyrolytic chamber is not interacting with the polymer waste material during decomposition and supports recovery of the material components.

Applying a negative pressure in the pyrolytic chamber allows for efficient removal or evacuation of pyrolysis gases. The evacuation of gases from the pyrolytic chamber is encouraged by drawing a partial vacuum in the off-gas lines. Preferably, a negative pressure of less than 0.4 bar absolute, more preferably between 0.1 and 0.3 bar is applied. Operating

the pyrolysis process according to the present invention under negative pressure rapidly evacuates the volatile components from the heated chamber or chamber zones, preventing secondary thermal breakdown of volatiles that may cause the deposition of carbonaceous residues (Char) on the carbon black mixed into the tire during manufacture and to be recovered, which helps retaining the properties of the rCB for reuse. In addition, the negative pressure lowers the boiling point of the organic components, further preventing secondary thermal breakdown thereof.

By applying an oxygenated environment the microwave heating process can become self-limiting as for example the microwave absorbing carbon material is oxidized. Thus, the microwave radiation to heat the waste material is selected such that carbonaceous components of the waste material are subjected to a self-limiting process with respect to the silica. This enables the production of high quality recovered Silica that can be used as fillers in the manufacturing of tires and silica-containing rubber products, thus creating a circular economy in industries such as tire manufacturing.

Preferably, the microwave radiation to heat the waste material to its decomposition temperature has a power density between 30kW and 700kW per cubic meter of the pyrolytic chamber. More preferably microwave radiation has a power density between 100kW and 500kW per cubic meter to ensure energy efficiency of the method and also thermal decomposition of the material. In general the microwave power selected for the pyrolysis process depends on the type of polymer waste material. For example, for tire rubber material a power density between 50kW and 500kW per cubic meter is recommended.

In a further variant of the pyrolysis method according to the invention the polymer waste material is subjected to a sequential thermal decomposition by successively applying differing target temperatures at the waste material, wherein the differing target temperatures correspond to a target decomposition temperature of at least one individual non-silica component of the waste material.

This variant of the pyrolysis method focuses on material recovery for a polymer waste material, particularly rubber waste material, which comprises a plurality of differing material components, like vehicle tires for example.

The waste material is subjected to a sequential thermal decomposition of said differing material components by successively applying differing target temperatures corresponding to a target decomposition temperature of at least one of the plurality of individual material component. Since differing material components can decompose at differing temperatures, a target temperatures equals to the decomposition temperature of a specific component. Of course, two or more differing components may have the same or very similar decomposition temperature, which results in the same target decomposition temperature for the two or more differing components.

The differing target temperatures can for example be applied in successive heating steps or in differing heat zones of a pyrolysis reactor. For the sequential thermal decomposition the temperature in each heating step or heat zone will be increased. So over the course of the sequential thermal decomposition the target decomposition temperature for each of the differing material components of the waste

material will be meat. However, silica is not affected by the microwave heating due to its low microwave absorptivity and will remain intact.

The method according to the present invention is based on the fact that during the decomposition of different types of rubber present in a raw material, SBR decomposes mainly at high temperatures, natural rubber (NR) at lower temperatures whilst BR can be decomposed at both higher and lower temperatures. Therefore during a first heating stage of the reaction at a first temperature, the main by-products formed were produced by the decomposition of NR and BR while the compounds formed during a second heating stage at a temperature higher than during the first heating stage, mainly liquid fraction, were produced by the thermal decomposition of SBR and in low-proportion BR.

During the sequential thermal decomposition process differing volatile products gained from the pyrolysis of one or more differing material components at one target decomposition temperature may be extracted from the pyrolytic chamber. Thus, the differing volatiles can be recovered separate from each other. In the case of successive heating steps, the differing volatile products can be extracted during each step. In the case of successive heat zones, the differing volatile products can be extracted at different locations in a pyrolysis reactor, which correspond to the heat zones.

According to one variant of a sequential decomposition process to pyrolyse for example rubber tires primarily microwave power is used in a partial vacuum to rapidly heat the rubber to different temperatures where depolymerisation starts for the different rubber components mixed into the tire

part, e.g. natural rubber, BR or SBR. The sequential decomposition of individual rubber components at different target temperatures together with the extraction of volatiles at the different target temperatures reduce the presence of Carbonaceous Residue (Char) on the Recovered Carbon Black (rCB) and allows the separation of the volatile fractions to be recovered.

The temperature of the pyrolysis reaction of the non-silica components is regulated within a range that allows the polymer to decompose to volatile components, but not so high that the functional properties of the silica is compromised by prolonged exposure to excessive temperatures. As mentioned before, reaction temperatures of between 300°C and 900°C are suitable for the pyrolysis process to occur. Temperatures at or below 650°C are favourable to the production of high quality recovered silica. The pyrolysis temperature is increased in steps and applied to the waste material, to allow volatile components associated with each polymer in the waste material, to be extracted, condensed and collected separately. In the case of passenger car tires the preferred temperatures are for example firstly 300°C - 350°C, then 400°C - 450°C and finally 500 - 550°C.

Advantageously, an oxygenated environment is applied in the pyrolytic chamber at least at the highest target decomposition temperature of the sequential thermal decomposition. Thus, recovering the silica from the remaining solid residue involves heating the solid residue with microwaves in an oxidizing atmosphere to oxidize and remove the carbonaceous materials, such as char or carbon black, to yield a silica-containing product.

Thus, preferably the pyrolytic chamber comprises subsequent heat zones that are each heated to successively higher target decomposition temperatures, and an oxygenated environment is applied in a last zone of the pyrolytic chamber for complete oxidization and removal of carbonaceous materials.

Preferably, the pyrolysis method is controlled by a process control system that allows for accurate and differential heating of the components of the polymer waste material during the successive differing heating steps or during transporting the waste material through successive heat zones.

In one variant of the pyrolysis method of a polymer waste material comprising a plurality of differing material components an initial mass of the silica and the differing non-silica components is determined before decomposition starts. Alternatively or additionally, after the thermal decomposition of differing material components of the polymer waste material a ratio of products resulting from the thermal decomposition of the silica and differing non-silica components is determined. The data of the initial component mass and/or the ratio of products is provided to the process control system to manage the pyrolysis process. Also, the temperature in the pyrolytic chamber may be monitored over time and/or at different zones in the chamber. For example, a power density of the microwave radiation and/or a residence time of products gained from the pyrolysis process are controlled according to a ratio of products resulting from the thermal decomposition of differing material components and/or a temperature applied in the pyrolytic chamber.

In the pyrolysis method the process to pyrolyse polymer waste material primarily uses microwave power to rapidly heat the non-silica components to temperatures where decomposition starts. Subsequent heating to higher temperatures may be achieved by a combination of microwaves and a further heating. Thus, the pyrolysis method advantageously may comprise a first heating step in which the waste material is heated to a first target decomposition temperature by microwave radiation as mentioned above, and a second heating step which is a subsequent step for heating the waste material to a second target temperature above said first decomposition temperature by microwave radiation in combination with an additional heat source. Additional heat sources may be conductive heating means, electrical heating means or any other suitable heating means.

Advantageously, at least portions of volatile products gained from the pyrolysis process are used as additional heat source for conductive heating of the waste material in the pyrolytic chamber. Thus, for example gases evaporated during the first heating step and the initial decomposition may be used for the second heating step.

The combination of microwaves and an additional heat source may improve the overall energy efficiency of the method. The temperatures used for the pyrolysis method depend on the type of the polymer waste material.

The two subsequent heating steps for example are helpful to optimize the decomposition process of different non-silica components of the polymer waste material. In the range of low-temperature pyrolysis, gas organic compounds are extracted from the waste material e.g. by dry distillation. For example

additives, oils and softening agent evaporate during the initial thermal decomposition. In the range of higher temperature pyrolysis for example natural rubber, styrene-butadiene rubber or poly-butadiene rubber may be regenerated during continued decomposition.

The pyrolysis method can be conducted in the fast pyrolysis regime, where volatile gases generated during pyrolysis are evacuated from the pyrolysis reactor in less than 4 seconds, preferably less than 2 seconds. The minimal contact time between pyrolysis gases and the hot environment in the reactor prevent further decomposition of the pyrolysis gases to solid compounds. This results in a large volatile yield, compared to slow pyrolysis where the carbon yield is higher. Using the volumetric heating properties of microwave power allows the polymeric waste material, particularly rubber, to be rapidly heated to the temperature range where an exothermic depolymerisation reaction occurs. Also, long exposure times to high temperatures can be avoided for the silica.

In general, the functional properties of silica recovered from silica reinforced rubber or other polymer composites, are determined by the processing temperature and duration - high processing temperatures or long exposure times result in inferior functional properties of the recovered Silica. Rapid processing and precise regulation of the process temperature is therefore required and the self-limiting nature of the microwave heating process is advantageous in achieving this.

The pyrolysis reactor according to invention comprises a pyrolytic chamber for accommodating the waste material and at least one heat source for heating the waste material to a

decomposition temperature of the waste material, wherein the at least one heat source includes a microwave radiation source. Advantageously, the pyrolytic chamber comprises an oxygen inlet and a gas outlet for applying an oxygenated environment at least in a zone of the pyrolytic chamber and extracting gas from the oxygenated environment. Further advantageously, at least a zone of the pyrolytic chamber comprises an inert environment or a negative pressure environment. That zone could be time period within the decomposition process or a heating zone along a length of the chamber. In case the zone is defined as a time period, preferably the inert environment or negative pressure environment is applied before the oxygenated environment is applied in the pyrolytic chamber.

In one variant of the pyrolysis reactor according to the invention the waste material is delivered through the pyrolytic chamber in a continuous motion by a conveyor. Thus, the waste material can be transported through subsequent heat zones along a length of the pyrolytic chamber that are each heated to successively higher target decomposition temperatures. Further, pyrolysis gases of the waste material may be evacuated from the pyrolytic chamber in intervals during the continuous motion of the waste material at differing exit ports in the pyrolytic chamber. The exit ports may correspond to the differing heat zones. This will allow for physical separation of different volatile non-silica products during the thermal decomposition of the polymer waste materials.

Furthermore, the pyrolysis reactor may provide different storage systems for different volatile products gained from the pyrolysis process. Each system can be connected to a

different heat zone. In case of successive heating steps within the same space of the chamber, like in a batch reactor, the reactor output may switch between different storage systems for each heating step.

Preferably, the pyrolysis reactor comprises a process control system as mentioned above. The process control system may be connected to at least one temperature sensor in the pyrolytic chamber and/or to a mass measuring device for determining a mass of differing material components of the waste material. Thus, the process control system can control a sequential thermal decomposition process for differing material components by successively applying differing target temperatures in the pyrolytic chamber.

Furthermore, the speed of the waste material conveyor can also be controlled by the process control system. Advantageously, the conveyor is designed as a weigh feeder system comprising a mass measuring device for determining a mass of differing material components of the waste material fed into the pyrolytic chamber. The data of the mass measuring device is also provided for controlling the pyrolysis method.

The reactor is sealed to the environment to prevent pyrolysis gases escaping or oxygen entering in an uncontrolled manner. The reactor may be purged with e.g. nitrogen prior to operation.

The pyrolytic chamber of the pyrolysis reactor may comprise an internal refractory lining made from a microwave transparent material. The refractory lining can contain the heat around the polymer waste material being pyrolysed. It also allows the microwave energy to disperse inside the

pyrolytic chamber for more uniform heating of the product. In an advantageous variant the refractory lining extends to only a part of the length of the pyrolytic chamber where microwave radiation is introduced. The remaining part of the pyrolytic chamber may have a double wall construction instead for providing an additional heat source for the reactor walls.

The pyrolysis reactor may comprise at least one waveguide feed comprising a plurality of radiation exits. The radiation exits preferably are diverted along a length of the pyrolytic chamber in a distance from each other.

In case of an elongated pyrolytic chamber of the pyrolysis reactor, a conveyor may be provided to feed polymer waste material into and through the pyrolytic chamber. Thus, the polymer waste material and its compounds respectively may be transferred along the length of the pyrolytic chamber from one end to an opposing end of the chamber. Further, the pyrolytic chamber may comprise several exit ports distanced from each other along a length of the pyrolytic chamber for evacuating pyrolysis gases of the waste material in intervals at differing exit ports.

Alternatively, the pyrolysis reactor may comprise a pyrolytic chamber in the form of a batch reactor, wherein sequential thermal decomposition is realized by successive heating steps within the same chamber space. For recovering polymer waste material from vehicle tires, the reactor may have a circular shape, or a ring shape having a hollow centre portion.

Preferred embodiments of the invention will be described in the accompanying drawings, which may explain the principles

of the invention but shall not limit the scope of the invention. The drawings illustrate:

Fig. 1: a schematic three-dimensional view of a pyrolytic chamber used for a pyrolysis method and a first embodiment of a pyrolysis reactor according to the invention;

Fig. 2a: a schematic diagram of a set up of a pyrolysis reactor for example as described for Figure 1;

Fig. 2b: a further schematic diagram of a set up of a pyrolysis reactor for example as described for Figure 1; and

Fig. 3a: a schematic view of a pyrolytic chamber of a second embodiment of a pyrolysis reactor according to the invention.

Fig. 3b: a schematic diagram of a condenser system according to the invention.

In the following, two embodiments of a pyrolysis reactor according to the present invention are described, which are suitable to for recovering silica from a polymer waste material containing silica, particularly a rubber or plastics waste material containing silica, using thermal decomposition for separating silica or silica products from at least one non-silica component of the polymer waste material according to the invention.

In both of the embodiments, the pyrolysis reactor for thermal decomposition of polymer waste materials comprises a pyrolytic chamber 1 for accommodating polymer waste material

and at least one heat source for heating the waste material to a decomposition temperature of non-silica components of the waste material. The at least one heat source includes a microwave radiation source.

The shown reactor embodiments may use microwaves in a partial vacuum or negative pressure, respectively, to sequentially pyrolyse polymer waste components. The process performed by the reactors aims to recover non-silica components, such as carbonaceous residue, polymer components and volatiles by pyrolysing different components at different target decomposition temperatures and extracting volatiles and other products gained in the process at different stages in the reactor.

The described reactor embodiments may be used particularly for the pyrolysis of rubber waste material, especially end-of-life vehicle tires, with the goal of full recovery of reusable and recyclable materials. In terms of composition of the fractions produced during the pyrolysis of vulcanized rubber, the composition of the different fractions is mainly a mixture of aromatic, cyclic and aliphatic hydrocarbons. The main aliphatic and naphthene compounds found in the liquid fraction of pyrolysis of SBR are pentenes, hexenes, 4-ethenylcyclohexene and other C8 and C9 aliphatic compounds. Additionally, the SBR's co-monomer, 1,3-butadiene, is decomposed producing reactive components such as 4-ethenylcyclohexene that participate in secondary and tertiary reactions during the pyrolysis. The amount of aliphatic compounds usually increases slowly with temperature. Thus, similar proportions of aliphatic compounds can be obtained at different temperatures. In contrast, the amount of aromatic compounds increases considerably with a rise of temperature.

The main aromatic compound in the liquid fraction is styrene followed by ethyl benzene, benzene, toluene and xylenes (BTX), and in a lower proportion, methylstyrenes. Benzothiazoles and thiophenes, used during vulcanization of the rubber, are also commonly found in the liquid fraction. For the gas fraction, the main products are 1,3-butadiene with a small percentage (lower than 0.5%) of methane, carbon monoxide, carbon dioxide, hydrogen sulphide, methane, ethane, propene, and n-Butane. The solid fraction, also referred to as pyrolytic char, contains mainly carbon black mixed into the tire during manufacture and, in a minor proportion, carbonized rubber polymer, non-volatile hydrocarbons and residual portions of rubber additives such as zinc, sulphur, clays and silica.

Studies have shown that regardless of the use of hydrogen during the pyrolysis, low temperatures (for example 450°C) result in the high production of carbonized rubber polymer. Similarly, the solid fraction decreases with an increase in temperature until about 550°C. Further increases in temperature may result in an increase of about 4% in the production of solids. In contrast, it was shown that high temperatures favour the production of the liquid fraction. Only about 10% of the initial material resulted in a liquid fraction for pyrolysis performed at external temperature of around 450°C. On the other hand, the highest amount of liquid fraction (about 37wt%) was obtained at 550°C with a constant hydrogen flow. Pyrolysis carried out at 600°C, with and without hydrogen, led to the higher production of the gas fraction and a reduction of the liquid fraction compared to samples obtained at 550°C. Studies using inert atmospheres have also reported an increase of the liquid fraction with temperature and a reduction or stabilization of the liquid yield at temperatures higher than 600°C.

The two embodiments mainly differ in the design of their pyrolytic chamber, while other features of the reactor and steps of the method are the same. Therefore, structural features of the reactor and explanations of method steps that are suitable for both embodiments shall be regarded as interchangeable between the two embodiments. Their repetition will be avoided to enhance clarity of the specification.

For example, for both embodiments it is advantageous to apply an inert environment or a negative pressure environment in the pyrolytic chamber for recovery of non-silica components and afterwards to apply an oxygenated environment in the pyrolytic chamber for recovering silica. Also, in addition to a microwave radiation source the pyrolysis reactor may include a conductive heating source, which serves as an additional heating. Some of the volatile products produced during the thermal decomposition of a polymer waste material, such as non-condensable gases may be used to heat walls of the pyrolytic chamber, assisting with the pyrolysis process by conductive heating by the chamber walls. Alternatively, electrical heating elements may also be used for this purpose. In the same way other features and steps apply to both of the embodiments.

Figures 1, 2a and 2b show an example of a pyrolytic chamber 1 of a pyrolytic reactor according to the present invention. The reactor may be in the form of a continuous flow retort with an elongated design. For example, it may comprise a conveyor to deliver polymer waste material to the pyrolytic chamber 1 and transfer the waste material and decomposed compounds thereof through the pyrolytic chamber 1.

For example, complete tires or tire pieces can intermittently be fed into the pyrolytic chamber 1 from a first end of the chamber. A first air lock system 9 with means for purging of oxygen can be provided at the first end. Similarly, tire pieces can be fed into the retort with a screw feeder.

Since microwave energy heats the bulk of the waste material directly, it is possible to obtain zones of product, each at a different temperature, in close proximity along the length of the reactor. That means the reactor is virtually divided into several successive heat zones for recovering the waste material. Successive heat zones 10a to 10c are indicated the reactor variant shown in Figures 2a and 2b.

This results in a compact system. The microwave power input can instantly be adjusted to regulate the temperature within a narrow temperature band, for optimum pyrolysis of each of the non-silica components for example in a rubber tire.

Pyrolysis gases are drawn off at intervals along the length of the pyrolytic chamber 1, wherein successive gas exit ports 2a to 2c are provided at points of increasing product temperature and the gases collected, corresponding to different components of rubber, will differ. In the variants of Figure 2a and 2b, off-gases are collected from exit ports 2a, 2b and 2c at three positions on the side of the chamber, that correspond to three different product target temperatures. This allows for physical separation of the different volatile products through individual condenser systems 11a to 11c associated to the exit ports.

A multivariate process control system, such as a programmable logic controller (PLC), is used to control the pyrolysis process according to the invention. The control system can for instance measure the mass of product entering the reactor through e.g. a weigh feeder system on an in-feed conveyor, as well as the temperature of the pyrolytic chamber or heat zones and off-gases at various places, and use this information to control the temperature of the reactor and the product, and regulate the microwave power to maximise production and minimise energy input.

Further, the mass flow of solid, liquid and gaseous pyrolysis products is measured with mass flow meters and load cells, to determine the ratios of products gained by the pyrolysis process. The PLC also monitors the temperature of the material, reaction vessel and volatiles exiting the reactor at the gas exit ports 2a - 2c, and at the various decomposition heat zones 10a - 10c along the length of the reactor. For example, temperature sensors 19 in form of thermocouples are used. Online and offline analysis of the pyrolysis products may also be used to provide inputs to the control system. Based on the data collected the process control system regulates the microwave power input into the reaction heat zones and the residence time of the material in the reactor. By regulating the microwave power in the different heat zones of the reactor the material is heated to predefined temperatures corresponding to target composition temperatures of differing material components to allow these components to decompose in each heat zone and the volatiles produced during the decomposition of that component, to be collected in a dedicated condenser and storage system. In subsequent heat zones the remaining material components are heated to successively higher target decomposition

temperatures, each time extracting the volatile components associated with the different material components and collecting it in separate condenser systems 11. This sequential decomposition of differing material components allows the different hydrocarbons produced to be collected separately, increasing the value of the hydrocarbon feedstock produced.

A slotted waveguide feed, as shown in Figure 1, comprising a plurality of slots 3 extending along the length of the pyrolytic chamber 1 may be used to distribute microwave radiation along the length of the pyrolytic chamber 1. Microwave radiation may be introduced at various places around the circumference of the chamber 1 and along the length of the chamber 1, to ensure uniform heating of the product. The slotted waveguide feed shown in Fig. 1 is designed in such a way that the slots 3 radiate a power profile such that more energy is emitted in the zone where the initial heating phase occurs and less towards the end of the process, where the material is substantially carbonised and an elevated temperature is maintained to ensure removal of the last traces of volatile material.

The pyrolytic chamber 1 may have an internal refractory lining 4 made from a microwave transparent material, such as alumina or mullite, to contain the heat around the tires being pyrolysed. It also allows the microwave energy to disperse inside the refractory material, along the periphery of the reactor, for more uniform heating of the product.

The refractory lining may extend to only that part of the length of the pyrolytic chamber where the microwave power is introduced, while the remainder of the chamber may have a

double wall construction to allow hot medium, like gases or heating oil, to circulate, providing conventional heating of the reactor walls to aid with the process. These may for instance be obtained by burning the non-condensable fraction of the volatiles collected.

Figures 2a and 2b show variations of the pyrolysis reactor and the pyrolysis method according to the first embodiment. At the first end of the pyrolytic chamber 1 polymer waste material containing silica is introduced by a conveyor and transported along the length of the pyrolytic chamber 1.

In the course of the successive thermal decomposition according to the pyrolysis method of the invention the pyrolytic chamber and the waste material respectively are first heated to the first target decomposition temperature of a first material component of the rubber in a first heat zone 10a by microwave radiation causing an exothermic depolymerisation reaction of the non-silica components of the waste material. The first target decomposition temperature may for example be around 350°C. First volatile products may be evacuated through a first exit port 2a.

Subsequently, the remaining non-silica components are heated in a subsequent second heat zone 10b to a second target decomposition temperature that is higher than the first target decomposition temperature. The second target decomposition temperature may for example be around 450°C. The second heat zone may be heated by microwave radiation alone or by a combination of microwave radiation and an additional heat source. During the additional heating second volatile

components may be evacuated via exit port 2b distanced from the exit port 2a along the length of the chamber 1.

Accordingly, in a successive third heat zone 10c a third even higher target decomposition temperature can be applied and third volatile products may be evacuated via exit port 2c further distanced from the exit port 2b along the length of the chamber. The third target decomposition temperature may for example be around 550°C.

Although the heat zones 10a - 10c are separated by dashed lines for illustrative reasons, the pyrolytic chamber 1 is designed as a continuous reactor and the subsequent heat zones merge into each other. Each of the heat zones has a heating port, preferably a microwave feed port 20, to heat each of the zones to the target decomposition temperature. Further, each of the heat zones may be provided with a temperature sensor 19, for example a thermocouple, to monitor the temperature and provide temperature data to a process control system (not shown).

After passing the exit ports 2a - 2c the respective recovered volatile products enter condenser systems 11a - 11c associated to the exit ports. In one embodiment such a condenser system comprises a first condenser 13 connected to a first collection vessel 14. A vacuum pump 15 is connected to the first condenser 13 and the first collection vessel 14 to provide a negative pressure as mentioned above. Thus, the first condenser 13 and the first collection vessel 14 define a low pressure side and collection portion. This portion is connected to an ambient or high pressure portion comprising a second condenser 16 connected to a second collection vessel 17. Further components of the volatile product are condensed

in the second condenser 16 and collected in the second collection vessel 17. A third collection vessel 18 gathers the non-condensable gases exiting from the pyrolytic chamber 1.

Each of the heat zones 10a - 10c connected to the condenser systems 11a - 11c comprises a first collector vessel 14, a second collector vessel 17 and a third collector vessel 1b, which together provide different storage systems for the differing non-silica components exiting the pyrolysis chamber 1 at the exit ports 2a - 2c. The recovered components can be extracted from the vessels for further use or appropriate disposal.

The pyrolysis reactor of Figures 1, 2a and 2b is designed such that successive gas exit ports 2a - 2b coincide with increasing decomposition temperature and the gases collected will differ, allowing physical separation of the different volatile components through the individual condenser systems 11a - 11c. Solid products are discharged through a second airlock system 12 or with a screw feeder.

Figure 2b shows a schematic of a continuous flow microwave reactor for the pyrolysis of tire pieces, fed into it with a screw feeder. In this case pyrolysis gases are collected at the three exit ports 2a - 2c on the side of the pyrolytic chamber 1, wherein three exit ports 2a - 2c correspond to three different heat zones 10a - 10c having different target decomposition temperatures. Preferentially, these temperatures are as described above.

Microwave power is introduced at various places around the circumference and along the length of the reactor by microwave feed ports 20, to ensure uniform heating of the polymer waste material. The slotted waveguide feed, extending along the length

of the chamber may be used and designed in such a way that the slots radiate a power profile, where more energy is emitted during the initial heating phase and less towards the end of the process, where the material is substantially carbonized and an elevated temperature is to be maintained to ensure removal of the last traces of volatile material. The maximum product temperature is regulated at a value that prevents thermal degradation of silica products contained in the solid fraction in the reactor.

Alternative to the internal refractory lining, the reactor may have a metallic inner wall to contain the microwaves, with refractory insulation on the outer surface to retain the heat and with thermally insulating and gas barrier windows in the microwave feed port apertures to retain heat and prevent pyrolysis gases from entering the microwave feed structure.

The microwave power input can instantly be adjusted to regulate the target decomposition temperature within a narrow temperature band, for optimum pyrolysis of each of the non-silica components in the waste material. To support the decomposition process an inert environment or a negative pressure environment can be applied in the three heat zones 10a - 10c pyrolytic chamber 1.

Operating the pyrolysis process in a negative pressure environment or under vacuum, respectively, rapidly evacuates the volatile components from the heated zone, preventing secondary thermal breakdown of the volatiles in the reactor, to yield high value volatile gases that are condensed and collected as valuable hydrocarbon oils. In addition, the negative pressure environment or vacuum lowers the boiling point of the organic components, further preventing secondary thermal breakdown thereof. A negative pressure environment of less than 0.3 bar absolute is employed, preferably between 0.1 and 0.3 bar.

The first condenser 13 and the first collection vessel 14 collect the hydrocarbons condensable at reduced pressure, while the second condenser 16 and the second collection vessel 17 after the vacuum pump 15, collects the hydrocarbon that are condensable at ambient or positive pressure. With suitable cooling mediums the condenser systems 11 can be cooled to ambient or lower temperatures to maximize the condensation of volatile components. Non-condensable gases are collected in the third collection vessel.

At the end of the pyrolysis stage steel components are separated from the carbon- and silica-containing solid component. The Silica containing material is then exposed to microwave power in a final stage of the Silica recovery process in a fourth heat zone 10d. This silica recovery heat zone 10d is provided with an oxygen inlet 21 and gas exit port 2d. Microwave energy is introduced through the microwave feed ports 20 in the reactor wall. Preferably, thermal insulation of the reactor walls is provided to limit heat loss. The oxidizing environment is introduced through the oxygen inlets 21 in the reactor wall to oxidize the carbonaceous material present in the oxidation stage of the pyrolysis method. The gas exit ports 2d are placed in a manner that encourages flow of the oxidizing medium through the bed of waste material. The movement of the material, coupled with the flow of oxygen gas through the waste material encourages exposure of the surfaces of the material for effective oxidation.

The multivariate process control system monitors the temperature of the waste material, e.g. vehicle tires, in the different decomposition heat zones 10, as well as the temperature of the volatiles exiting the chamber 1 at the gas exit ports 2a - 2c to regulate the microwave power input into the decomposition zones. By regulating the microwave power in the different heat

zones of the chamber the tires are heated to predefined temperatures to allow individual rubbers to decompose in each zone and the volatiles produced during the decomposition of that rubber, to be collected in a dedicated condenser and storage system 11. In subsequent heating zones the remaining tire material is heated to successively higher target temperatures, each time extracting the volatile components associated with the different rubbers and collecting them in separate condenser systems 11. This sequential pyrolysis allows the different hydrocarbons produced to be collected separately, increasing the value of the hydrocarbon feedstock produced. In the final, oxidation stage in heat zone 10d the microwave power is regulated to limit the temperature of the carbonaceous material mixed with silica, to the temperature range described above where the functional properties of the silica are not degraded. Finally, solid products are discharged through a second airlock system 12 or with the screw feeder at a second end of the pyrolytic chamber 1.

Figure 3 shows a schematic view of a pyrolytic chamber 1 of a second embodiment of a pyrolysis reactor according to the present invention. The reactor has the form of a batch reactor such as a pressure vessel that opens to accept a load of smaller tires. For example, the pyrolytic chamber 1 of the reactor is of circular shape and may be opened at the top of the circular chamber. In the shown embodiment the reactor is loaded with a single large tire 7 such as for example used by earth moving equipment. Microwave radiation is applied to the pyrolytic chamber 1 through feed port 6 on the side of the chamber. The reactor may be provided with pressure windows 22 to allow the chamber to be operated in an inert environment, a negative pressure environment or under vacuum. Electrical elements or burning off some of the pyrolysis products may provide heating of the chamber walls to assist with heating

and to prevent condensation inside the vessel. The chamber may also be in the shape of an annulus where a central portion is removed to reduce unoccupied volume in the pyrolytic chamber 1.

In the batch reactor the temperature of the waste material is increased in heating steps to a target decomposition temperature for each differing material component of the tire and the volatile to be collected and the condensate collected in a storage dedicated to that component, switching between condensate storages for each step of the sequential pyrolysis process. During the process the reactor wall temperature is also increased in heating steps to prevent re-condensation of the volatiles in the reactor. A temperature sensor may be connected to chamber 1 to report temperature within the chamber.

In each heating step volatile products are extracted from the pyrolytic chamber 1 through exit ports 2a and 2b on the side, top and bottom walls of the chamber to allow pyrolysis gases to be extracted and enter a condenser system 11, see figure 3b. The condenser system 11 may for example condense the pyrolysis gases into pyrolysis oils, A raised metallic mesh 8 may be fitted to the bottom of the reactor, with the waste material placed on top of it, to allow pyrolysis gases to exit the chamber through exit port 2b in the bottom wall and at the same time prevent the waste material from clogging the gas exhaust port 2b.

The condenser system 11 may be designed in the same manner as the condenser systems 11a - 11c described for the first embodiment. Thus, the condenser system 11 may include a first condenser 13, a first collection vessel 14, a vacuum pump 15, a second condenser 16, a second collection vessel 17

and a third collection vessel 18. Although only one condenser system is shown in Figure 3b, more such systems can be connected to the pyrolytic chamber 1 for different recovery products of different heating steps. As the processing temperature is increased to the sequential target temperatures for each of the volatiles to be collected, the condensate can be collected in a vessel dedicated to that component, switching the condensate stream from one condenser system 11 to the next, for each heating step of the sequential thermal decomposition process.

A first condenser 13 and the first collection vessel 14 collect the hydrocarbons condensable at reduced pressure. The second condenser 16 and the second collection vessel 17, after the vacuum pump 15, collect the hydrocarbon that is condensable at ambient or positive pressure. Remaining non-condensable gas is collected in the third collection vessel 18. With suitable cooling mediums the condensers can be cooled to ambient or lower temperatures to maximise the condensation of volatile components.

The pyrolysis method and the pyrolysis reactor according to the present invention are based on the fact that each of the material components present in a polymer waste material has different microwave absorption properties. Microwaves directly heat the organic compounds, sulphur and carbon black to different temperatures, depending on the mix of materials present at the time. Since the sulphur can be heated and sublimed by the microwave energy, it can be evaporated from the material and removed with the pyrolysis gases during the latter stages of the sequential pyrolysis. This results in a recycled carbon black product with lower ash content.

In contrast to that, the procedure for recovering the silica from the remaining solid residue in the last heating step, involves heating the solid residue with microwaves in an oxidizing atmosphere to oxidize and remove the carbonaceous materials, such as char or carbon black, from it to yield a Silica-containing product. In the temperature range of interest, 300-900°C, the carbonaceous components have a high microwave absorptivity and silica has a low microwave absorptivity, resulting in preferential microwave heating of the carbonaceous component with respect to the silica and advantageously a self-regulating process.

By conducting the pyrolysis process under an inert environment, negative pressure environment of vacuum the formation of secondary volatile breakdown products (such as carbonaceous residues) is limited, allowing high quality oils to be collected in the condenser. The temperatures selected for the sequential heating steps may be for instance around 350°C, 450°C and 550°C, in the case for a passenger car tire, to recover the volatile components associated with natural rubber, butadiene rubber and styrene-butadiene rubber, respectively. A carrying gas such as nitrogen may be introduced to gas inlet port 21, to assist with the removal of pyrolysis gases. Preferentially, the carrying gas is fed in at the top of the chamber and volatile components are extracted near the bottom of the chamber, to set up a laminar flow of gases that limit the time the volatile components are exposed to high temperature, limiting the formation of secondary pyrolysis products, like carbonaceous residues.

During the last heating step of the process, oxidizing gas is introduced through the gas inlet port 21 and the microwave power is regulated to keep the carbon-silica mixture at the oxidation temperature until the carbonaceous solids are oxidized.

Towards the end of the oxidation process the reduction in the amount of microwave absorptive material present causes the process to become self-regulating.

A sample of silica recovered by the pyrolysis method according to the present invention was sent to an accredited laboratory (Artis, UK) and a rubber test sample prepared using the recovered silica as a reinforcing material and compared to a sample reinforced with a commercial silica, Ultrasil U7000GR, which is commonly used for the reinforcement of car tire rubber.

The elemental analysis for the recovered Silica is shown in the table below. It indicates that the recovered silica has a high percentage of silica and a low carbon content proving the level of purity of the recovered silica. Therefore, higher modulus and lower energy loss could be of significant interest to rubber compounders to use recovered silica as a filler.

Element	Concentration (%)
Oxygen	45.9
Silicon	44.7
Zinc	7.4
Aluminium	0.5
Sulphur	0.6
Calcium	0.5
Potassium	0.4
Others	<0.4

List of Reference Numbers

- 1 pyrolytic chamber
- 2 exit ports
- 3 slots
- 4 lining
- 5 vibrating screen
- 6 feed port
- 7 rubber tire
- 8 metallic mesh
- 9 first air lock system
- 10 heat zones
- 11 condenser system
- 12 second air lock system
- 13 first condenser
- 14 first collection vessel
- 15 vacuum pump
- 16 second condenser
- 17 second collection vessel
- 18 third collection vessel
- 19 temperature sensor
- 20 heating port
- 21 gas inlet port
- 22 pressure window

Patent Claims

1. Pyrolysis method for recovering silica from a polymer waste material containing silica, particularly a rubber or plastics waste material containing silica, using thermal decomposition for separating silica from at least one non-silica component of the polymer waste material, wherein the waste material
 - is delivered to a pyrolytic chamber (1), and
 - is heated to a decomposition temperature of at least one non-silica component of the waste material by microwave radiation, wherein the decomposition temperature is selected such that the at least one non-silica component comprises a higher microwave absorptivity than silica.
2. Pyrolysis method according to claim 1, wherein an oxygenated environment and/or an inert or a negative pressure environment is applied in the pyrolytic chamber (1).
3. Pyrolysis method according to claim 2, wherein an inert environment or a negative pressure environment is applied in the pyrolytic chamber before the oxygenated environment is applied in the pyrolytic chamber (1).
4. Pyrolysis method according to any of the preceding claims, wherein the polymer waste material is subjected to a sequential thermal decomposition by successively applying differing target temperatures corresponding to a target decomposition temperature of at least one individual non-silica component of the waste material.

5. Pyrolysis method according to claim 4, wherein an oxygenated environment is applied in the pyrolytic chamber at the highest target decomposition temperature of the sequential thermal decomposition.
6. Pyrolysis method according to any of the preceding claims, wherein the decomposition temperature and target decomposition temperatures of individual non-silica components, respectively, are selected in the range of 300°C to 900 °C.
7. Pyrolysis method according to any of the preceding claims, wherein the decomposition temperature is selected such that carbonaceous non-silica components oxidize in the pyrolytic chamber.
8. Pyrolysis method according to any of the preceding claims, wherein the microwave radiation to heat the waste material to its decomposition temperature has a power density between 30kW and 700kW per cubic meter of the pyrolytic chamber, preferably between 100kW and 500kW per cubic meter.
9. Pyrolysis method according to claim 3, wherein the negative pressure environment is of less than 0.4 bar, preferably between 0.1 and 0.3 bar.
10. Pyrolysis method according to claim 4, wherein differing volatile products gained from the pyrolysis of one or more differing non-silica components of the waste material at one target decomposition temperature are extracted from the pyrolytic chamber.

11. Pyrolysis method according to any one of the preceding claims, wherein a mass of the silica and differing non-silica components is determined and/or a ratio of products resulting from the thermal decomposition is determined.
12. Pyrolysis method according to any one of the preceding claims, wherein a power density of the microwave radiation and/or a residence time of products gained from the pyrolysis process are controlled according to a ratio of products resulting from the thermal decomposition of differing material components and/or a temperature applied in the pyrolytic chamber.
13. Pyrolysis method according to claim 2, wherein the microwave radiation to heat the waste material is selected such that carbonaceous components of the waste material are subjected to a self-limiting process with respect to silica components.
14. Pyrolysis method according to any one of the preceding claim, wherein after the waste material was heated to a first target decomposition temperature in a first heating step, a subsequent second heating step for heating the waste material to a second target decomposition temperature above said first decomposition temperature is achieved by microwave radiation or by microwave radiation in combination with an additional heat source.
15. Pyrolysis method according to the preceding claim, wherein at last portions of volatile products gained from the pyrolysis process are used as additional heat source

for conductive heating of the waste material in the pyrolytic chamber (1).

16. Pyrolysis method according to any one of the preceding claim, wherein a fast pyrolysis process is used defined in that volatile gases are generated in less than 4 seconds, preferably less than 2 seconds, when the waste material is heated to its decomposition temperature by microwave radiation.
17. Pyrolysis method according to any one of the preceding claim, wherein the pyrolytic chamber (1) comprises subsequent heat zones (10a, 10b, 10c) that are each heated to successively higher target decomposition temperatures, and wherein an oxygenated environment is applied in a last zone of the pyrolytic chamber (1).
18. Pyrolysis method according to claim 17, wherein the waste material is delivered through the subsequent heat zones (10a, 10b, 10c) by a conveyor.
19. Pyrolysis method according to any one of the preceding claim, wherein the waste material is delivered through the pyrolytic chamber (1) in a continuous motion by a conveyor and pyrolysis gases of the waste material are evacuated from the pyrolytic chamber in intervals during the continuous motion of the waste material at differing exit ports (2a, 2b, 2c) in the pyrolytic chamber (1).
20. Pyrolysis reactor for recovering silica from a polymer waste material containing silica, particularly a rubber or plastics waste material containing silica, using thermal decomposition for separating silica from at least

one non-silica component of the polymer waste material, comprising a pyrolytic chamber (1) for accommodating the waste material and at least one heat source for heating the waste material to a decomposition temperature of the waste material, wherein the at least one heat source comprises a microwave radiation source.

21. Pyrolysis reactor according to claim 20, wherein the pyrolytic chamber (1) comprises an oxygen inlet (21) and a gas outlet (2a) for applying an oxygenated environment at least in a zone of the pyrolytic chamber and extracting gas from the oxygenated environment.
22. Pyrolysis reactor according to claim 20 or 21, wherein at least a zone of the pyrolytic chamber (1) comprises an inert environment or a negative pressure environment.

1/3

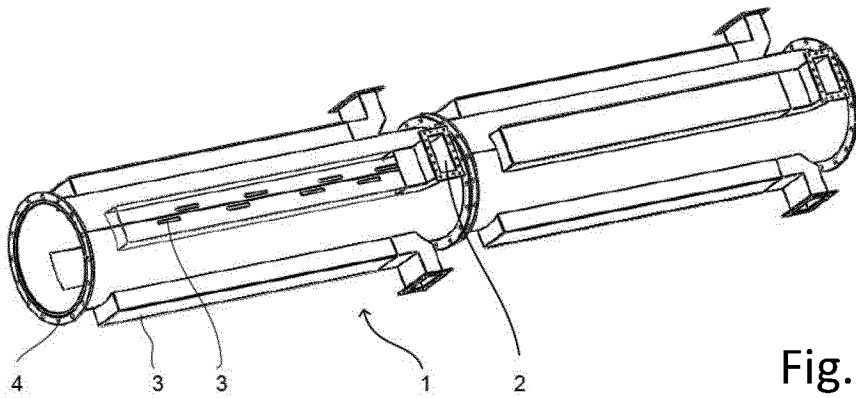


Fig. 1

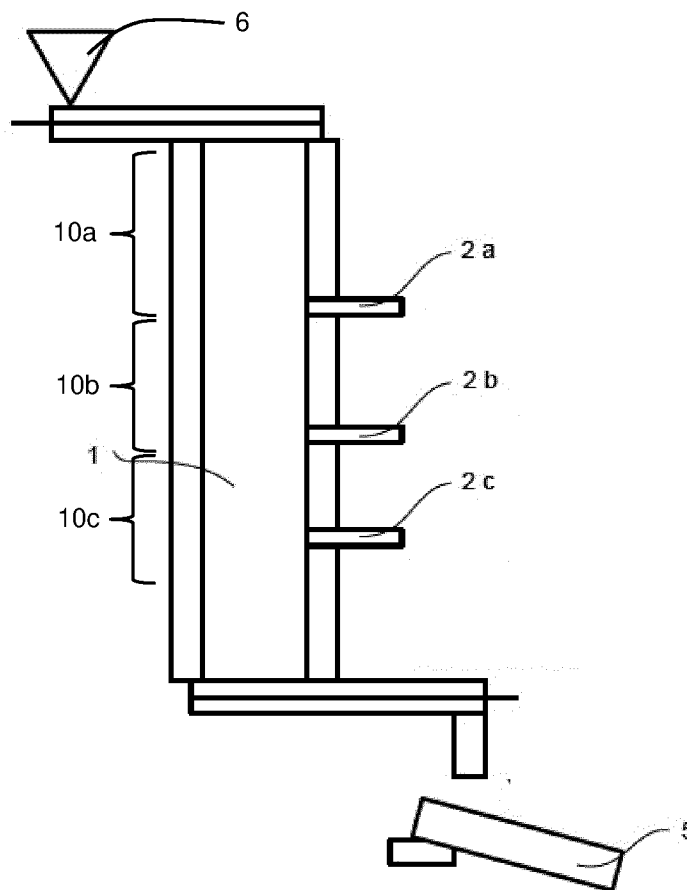


Fig. 2a

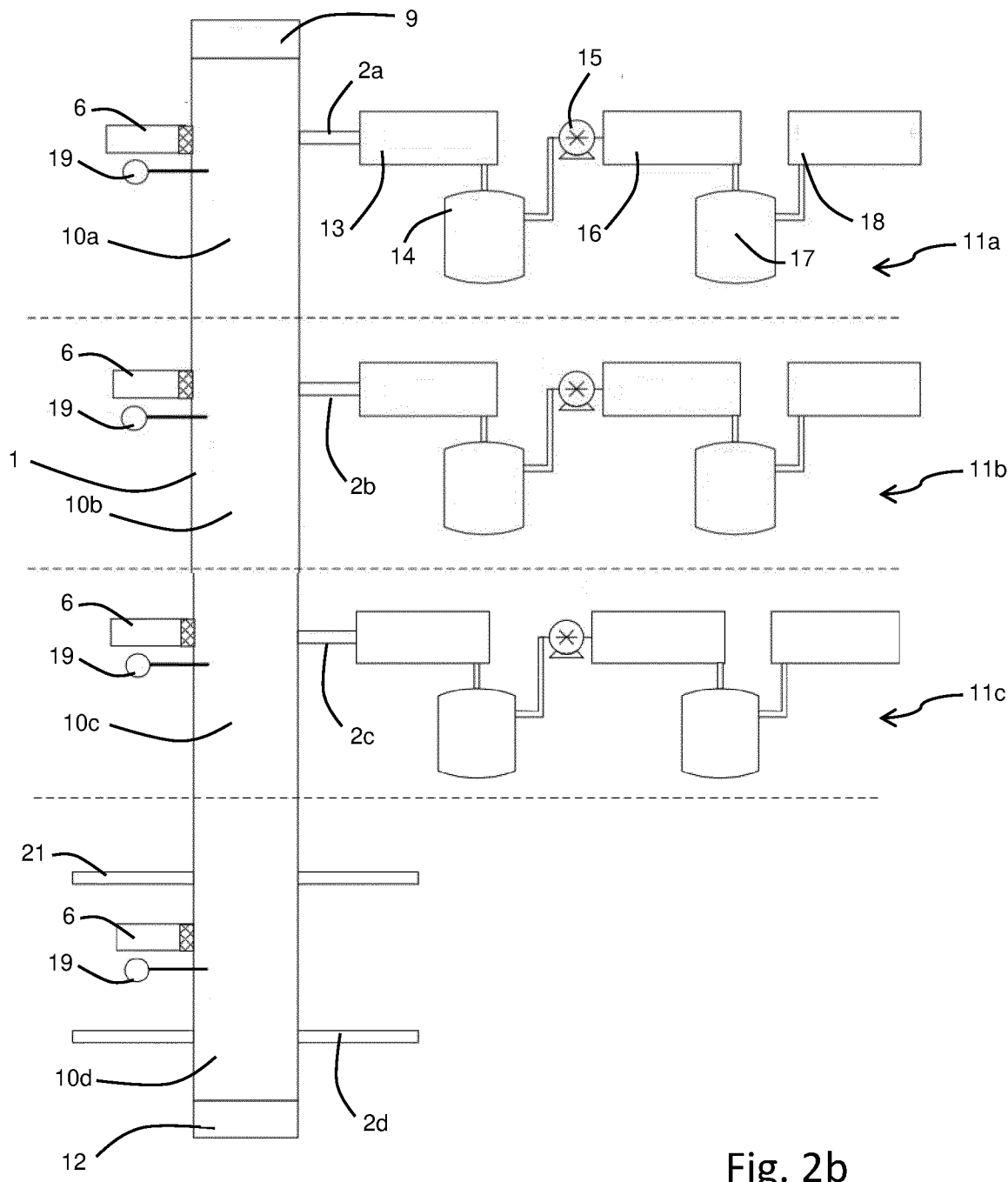


Fig. 2b

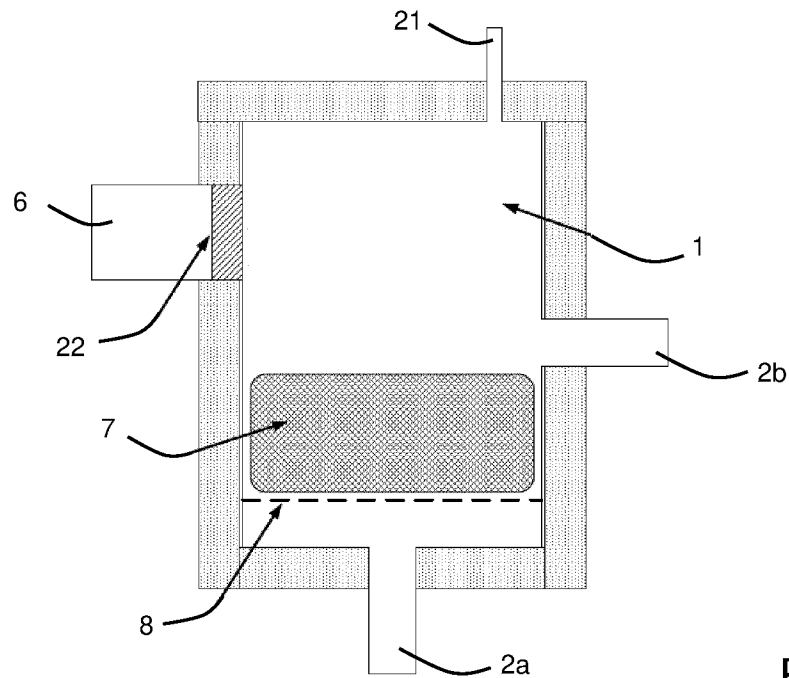


Fig. 3a

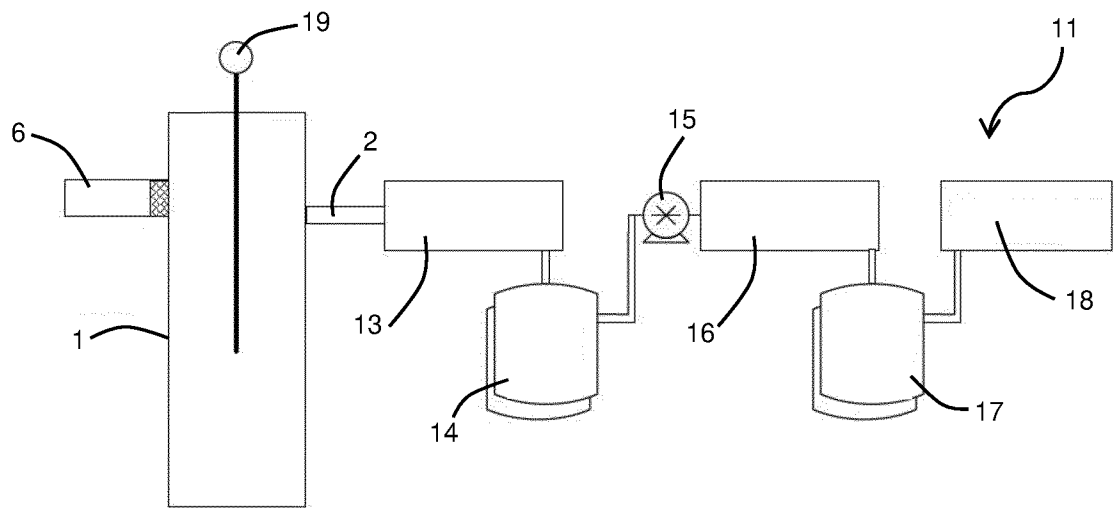


Fig. 3b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/057695

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10B53/07 C10B19/00
ADD. C01B33/12 C08K3/36

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 C08K C01B

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, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2015/159054 A1 (AVON POLYMER PROD LTD [GB]) 22 October 2015 (2015-10-22) claims 1-15 page 7, line 13 - page 10, line 19 examples	1-19
X	WO 01/03473 A1 (AMAT LTD [GB]; SKEELS PETER RYAN [GB]; BELL JAMES RICHARD [GB]) 11 January 2001 (2001-01-11) figures 1A-4	20-22
Y	claims 1-32 page 10, lines 12-28 page 9, lines 25-27	1-19
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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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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 May 2020

Date of mailing of the international search report

02/06/2020

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/057695

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	figure 1 table 1 2. Experimental section -----	1-19

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